Ab Initio Study of Complexes with Two Cations as N−H Donors to F$^-$: Structures and Spin−Spin Coupling Constants across N−H−F Hydrogen Bonds

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A systematic ab initio study has been carried out to determine the MP2/6-31+G(d,p) structures and EOM-CCSD coupling constants across N−H−F−H−N hydrogen bonds for a series of complexes $F(H_3NH)_2^+$, $F(HNNH_2)_2^+$, $F(H_2CNH_2)_2^+$, $F(HCNH)_2^+$, and $F(FCNH)_2^+$. These complexes have hydrogen bonds with two equivalent N−H donors to F$^-$. As the basicity of the nitrogen donor decreases, the N−H distance increases and the N−H−F−H−N arrangement changes from linear to bent. As these changes occur and the hydrogen bonds between the ion pairs acquire increased proton-shared character, $^{2h}J_{F-N}$ increases in absolute value and $^{1h}J_{H-F}$ changes sign. $F(H_3NH)_2^+$ complexes were also optimized as a function of the N−H distance. As this distance increases and the N−H···F hydrogen bonds change from ion-pair to proton-shared to traditional F−H···N hydrogen bonds, $^{2h}J_{F-N}$ initially increases and then decreases in absolute value, $^{1}J_{N-H}$ decreases in absolute value, and $^{1h}J_{H-F}$ changes sign. The signs and magnitudes of these coupling constants computed for $F(H_3NH)_2^+$ at short N−H distances are in agreement with the experimental signs and magnitudes determined for the F(collidineH)$_2^+$ complex in solution. However, even when the N−H and F−H distances are taken from the optimized structure of F(collidineH)$_2^+$, $^{2h}J_{F-N}$ and $^{1h}J_{H-F}$ are still too large relative to experiment. When the distances extracted from the experimental NMR data are used, there is excellent agreement between computed and experimental coupling constants. This suggests that the N−H−F hydrogen bonds in the isolated gas-phase F(collidineH)$_2^+$ complex have too much proton-shared character relative to those that exist in solution.

Introduction

In recent studies Limbach and co-workers[1−6] have investigated one- and two-bond spin−spin coupling constants across F−H−N hydrogen bonds in 1:1, 2:1, 3:1, and 3:2 FH:collidine complexes, the latter corresponding to an ion-pair complex (collidineH:F:Hcollidine)$^+$:(FHF)$^-$. These investigators measured F−N, F−H, and H−N coupling constants associated with this cation and, from their NMR data, proposed a structure for the cationic complex in which collidinium ions are hydrogen-bond donors to F$^-$.[6] To our knowledge, this is the first time that coupling constants for such a complex have been reported. It is also the case that there are no ab initio studies of coupling constants in corresponding complexes with two N−H−F hydrogen bonds.

In the present study we have optimized the structures of a group of cationic complexes with N−H−F−H−N hydrogen bonds in which the N atoms are sp ($HCNH^+$ and $FCNH^+$), sp^2 ($HNNH_2^+$, $H_2CNH_2^+$, pyridineH$^+$, and collidineH$^+$), and sp^3 (NH_4^+ and $HCN:NH_4^+$) hybridized and have computed two-bond $^{19}F-^{15}N$ ($^{2h}J_{F-N}$) and one-bond $^{15}N-^{1}H$ ($^{1}J_{N-H}$) and $^{1}H-^{19}F$ ($^{1h}J_{H-F}$) coupling constants across the N−H−F hydrogen bonds for these complexes except those containing aromatic rings. In addition, we have examined the dependence of the structures and coupling constants of the complexes $(H_3N-H-F-H-NH_3)^+$ and $(HCN-H-F-H-NCH)^+$ on the N−H distance. In this paper we report the results of this study and compare computed coupling constants with corresponding experimental values.

Methods

The structures of the cationic complexes $F(FCNH)_2^+$, $F(HCNH)_2^+$, $F(HNNH_2)_2^+$, $F(H_2CNH_2)_2^+$, $F(NH_4)_2^+$, $F(HCN:NH_4)_2^+$, F(pyridineH)$_2^+$, and F(collidineH)$_2^+$ were optimized at second-order Møller−Plesset perturbation theory (MP2)[7−10] with the 6-31+G(d,p) basis set.[11−14] During these optimizations, the two N−H donor cations were constrained to be equivalent. Vibrational frequencies were computed for all complexes except F(collidineH)$_2^+$ to ascertain whether they correspond to equilibrium structures on their potential energy surfaces. To examine the effects of varying the N−H distance on the structures of such complexes, $F(NH_4)_2^+$ and $F(HCNH)_2^+$ were also optimized at a set of fixed N−H distances, beginning with an N−H distance of 1.00 Å and incrementing this distance in steps of 0.10 Å.

Spin−spin coupling constants were computed for the complexes $F(FCNH)_2^+$, $F(HCNH)_2^+$, $F(HNNH_2)_2^+$, $F(H_2CNH_2)_2^+$, $F(NH_4)_2^+$, and $F(HCN:NH_4)_2^+$ by the equation-of-motion coupled cluster singles and doubles (EOM-CCSD)[15−18] method in the CI (configuration interaction)-like approximation with the qzp basis set of Ahlrichs and co-workers[19] on C, N, and F atoms, qz2p on the hydrogen-bonded H atoms, and the cc-pVDZ basis of Dunning and co-workers[20,21] on other hydrogens. In addition, spin−spin coupling constants were computed for the $F(NH_4)_2^+$ and $F(HCNH)_2^+$ complexes as a function of the N−H

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TABLE 1: Selected Structural Parameters for Optimized Cationic Complexes with N−H−F−H−N Hydrogen Bonds[a]

	complex	symmetry	*R*(N−F)	*R*(N−H)	*R*(F−H)	∠N−F−N
1	$(FCNH:F:HNCF)^+$	C_{2v}	2.390	1.279	1.112	132
2	$(HCNH:F:HNCH)^+$	C_{2v}	2.388	1.259	1.130	135
3	$(HNNH_2:F:H_2NCH_2)^+$	C_{2v}	2.427	1.132	1.303	163
4	$(H_2CNH_2:F:H_2NCH_2)^+$	C_{2v}	2.441	1.114	1.329	163
4	$(H_2CNH_2:F:H_2NCH_2)^+$	C_{2h}	2.441	1.113	1.328	180
5	$(H_3NH:F:HNH_3)^+$	D_{3d}	2.454	1.116	1.338	180
6	$(HCN:H_3NH:F:HNH_3:NCH)^+$ [b]	C_{2v}	2.467	1.105	1.362	180
7	$(pyridineH:F:Hpyridine)^+$	D_{2h}	2.458	1.103	1.355	180[c]
7	$(pyridineH:F:Hpyridine)^+$	D_{2d}	2.457	1.102	1.355	180[c]
8	$(collidineH:F:Hcollidine)^+$	C_{2v}	2.483	1.093	1.390	180[c]
8	$(collidineH:F:Hcollidine)^+$	C_1	2.482	1.093	1.389	180[c]

[a] Distances are given in angstroms; angles are given in degrees. [b] NH_4^+ is also a proton donor to HCN, forming an N−H−N hydrogen bond. [c] Geometry-constrained structures. The D_{2d} structure of $(pyridineH:F:Hpyridine)^+$ is an equilibrium structure on the potential surface.

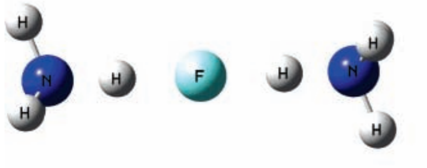
distance. In the nonrelativistic approximation, spin−spin coupling constants are a sum of four contributions: the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin−dipole (SD) terms.[22] All electrons were correlated for the EOM-CCSD calculations, and all terms were evaluated for these complexes with the one exception noted below. Optimizations were carried out with the Gaussian 03 software package,[23] and coupling constants were calculated with ACES II.[24] These calculations were done on the Cray X1 or the Itanium cluster at the Ohio Supercomputer Center.

Results and Discussion

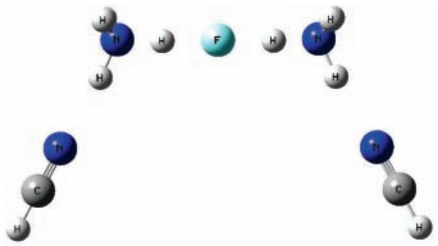
Structures. The symmetries, N−F, F−H, and F−N distances, and the N−F−N angles for the optimized structures of the complexes $F(FCNH)_2^+$, $F(HCNH)_2^+$, $F(HNNH_2)_2^+$, $F(H_2CNH_2)_2^+$, $F(NH_4)_2^+$, $F(HCN:NH_4)_2^+$, $F(pyridineH)_2^+$, and $F(collidineH)_2^+$ are reported in Table 1, and selected complexes are illustrated in Chart 1. With respect to the hybridization of the nitrogen, complexes 1−6 are listed in Table 1 in the order sp, sp^2, sp^3. When the nitrogen base is NH_3 with an sp^3-hybridized N atom, the hydrogen-bonded H atom is essentially covalently bonded to N, and the complex $F(NH_4)_2^+$ (structure 1 in Chart 1) can be described as having two NH_4^+ cations acting as proton donors to F^-. The N−F−N angle in this complex is 180°, giving a complex that has D_{3d} symmetry with hydrogen-bonded N−H−F−H−N atoms collinear, as illustrated in Chart 1. With respect to complexes 1−5, the N−F and F−H distances are longest in $F(NH_4)_2^+$, which suggests that as the basicity of the nitrogen increases, the proton-shared character of the N−H−F hydrogen bonds decreases.

$F(HCN:NH_4)_2^+$ (complex 6, structure 2 in Chart 1) is one in which NH_4^+ is also a proton donor to NCH, forming an N−H−N hydrogen bond. The formation of a second hydrogen bond by NH_4^+ results in a lengthening of the F−N and F−H distances relative to $F(NH_4)_2^+$. Thus, the F−H−N hydrogen bonds have even greater ion-pair character in $F(HCN:NH_4)_2^+$,

CHART 1



1. $[H_3N\text{-}H\ldots F\ldots H\text{-}NH_3]^+$

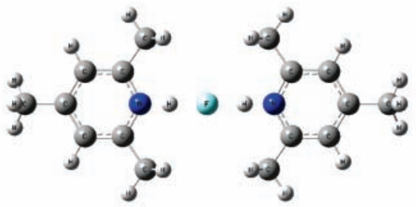


2. $[HCN\ldots H_3N\text{-}H\ldots F\ldots H\text{-}NH_3\ldots NCH]^+$

3. $[HNN(H)\text{-}H\ldots F\ldots H\text{-}N(H)NH]^+$

4. $[H_2CN(H)\text{-}H\ldots F\ldots H\text{-}N(H)CH_2]^+$

5. $[HCN\text{-}H\ldots F\ldots H\text{-}NCH]^+$


6. $[collidineH\ldots F\ldots Hcollidine]^+$

and the N−F−N angle remains linear. The effects of such structural changes on coupling constants will be discussed below.

The optimized planar structures of $F(HNNH_2)_2^+$ and $F(H_2CNH_2)_2^+$, illustrated as structures 3 and 4, respectively, in Chart 1, have C_{2v} symmetry with one very low imaginary frequency corresponding to an out-of-plane twist of the two cations. As judged by their gas-phase proton affinities,[25] N_2H_2 is a weaker base (PA = 192 kcal/mol) than H_2CNH and NH_3, which have similar proton affinities (203.8 and 204.0 kcal/mol, respectively). However, in hydrogen-bonded complexes with HF, the MP2/6-31+G(d,p) electronic binding energies of FH:N(H)NH and FH:N(H)CH_2 (9.5 and 13.0 kcal/mol, respectively) are less than that of FH:NH_3 (14.4 kcal/mol). The structures of the $F(HNNH_2)_2^+$ and $F(H_2CNH_2)_2^+$ complexes are similar to that of $F(NH_4)_2^+$, although the N−F and F−H distances are slightly shorter in these complexes, which are also slightly bent with N−F−N angles of 163°. Thus, the ion-pair character of the N−H−F hydrogen bonds decreases in the order $F(NH_4)_2^+ > F(H_2CNH_2)_2^+ > F(HNNH_2)_2^+$. The C_{2h} structure of $F(H_2CNH_2)_2^+$, which by symmetry must have a linear N−F−N arrangement, has also been optimized and found to be only 0.1 kcal/mol less stable than the C_{2v} structure.

The weakest nitrogen bases are HCN and FCN with sp-hybridized N atoms. The optimized C_{2v} structures of $F(HCNH)_2^+$ (structure 5 in Chart 1) and $F(FCNH)_2^+$ have one imaginary frequency corresponding to a distortion of the complex, which makes the two HCN (or FCN) molecules nonequivalent. Analysis of these frequencies suggests that the hydrogen-bonding scheme at equilibrium is $XCN{-}H^+{\cdots}F{-}H{\cdots}NCH$, that is, $XCNH^+$ is a proton donor to FH, which is a proton donor to NCH. However, for the purpose of this study, it is the C_{2v} structures of these two complexes that are of interest for comparisons of coupling constants. The shortest F−N and F−H distances are found in these two complexes, indicating that the F−H−N hydrogen bonds have the most proton-shared character. As the two H atoms approach F, the N−F−N angle bends to 132° and 135° in $F(FCNH)_2^+$ and $F(HCNH)_2^+$, respectively. Not surprisingly, the N−H−F hydrogen bonds in $F(FCNH)_2^+$ have greater proton-shared character (less ion-pair character) than those in $F(HCNH)_2^+$. In both complexes, the N−H−F hydrogen bonds remain essentially linear. It is interesting to note that the MP2/6-31+G(d,p) equilibrium structure of the anionic complex $(F{-}H{\cdots}F{\cdots}H{-}F)^-$ is also bent with an F−F−F angle of 131° and linear $F{-}H{\cdots}F$ hydrogen bonds.

Since the proton affinity of pyridine (222 kcal/mol) is greater than that of NH_3 (204 kcal/mol),[25] the $F(\text{pyridineH})_2^+$ complex should have a linear N−F−N arrangement. The $F(\text{pyridineH})_2^+$ complex in which the two rings are perpendicular (D_{2d} symmetry) has been optimized and is found to be slightly more stable by 0.1 kcal/mol than the optimized complex of D_{2h} symmetry in which the rings are coplanar. Vibrational frequencies computed for the D_{2d} complex confirm that it is an equilibrium structure on the potential surface with a linear N−H−F−H−N arrangement. Although the experimental proton affinity of collidine is not available,[25] its computed electronic MP2/6-31+G(d,p) proton affinity without zero-point and thermal corrections (240 kcal/mol) is greater than the computed electronic proton affinity of pyridine (230 kcal/mol) at the same level of theory. Thus, $F(\text{collidineH})_2^+$ complexes should also have a linear N−H−F−H−N arrangement. A complex with the rings coplanar (C_{2v} symmetry, structure 6 in Chart 1) has been optimized, as has a second perpendicular structure of C_1 symmetry generated from the C_{2v} structure by a 90° rotation of one ring about the N−N axis. The structure with the rings perpendicular is again slightly more stable by 0.1 kcal/mol than the coplanar arrangement. Although vibrational frequencies have not been computed for $F(\text{collidineH})_2^+$, the short N−H and long N−F and F−H distances are consistent with the high proton affinity of collidine and a linear N−H−F−H−N arrangement. In complexes with this arrangement, the N−F and F−H distances increase in the order $F(NH_4)_2^+ < F(\text{pyridineH})_2^+ < F(\text{collidineH})_2^+$, and the N−H distances change accordingly, indicating that the ion-pair character of the N−H−F hydrogen bonds increases in the same order.

TABLE 2: Fermi-Contact Terms and Total Spin−Spin Coupling Constants for Complexes with N−H−F−H−N Hydrogen Bonds[a]

$(X{-}F{-}X)^+$, where X =	F−N		N−H		F−H	
	FC	*J*	FC	*J*	FC	*J*
$FCNH^+$	−196.8	−196.7	−50.3	−50.4	194.4	210.0
$HCNH^+$	−184.5	−185.3	−52.6	−53.0	159.0	170.7
$HNNH_2^+$	−122.4	−125.6	−73.7	−75.0	−68.2	−73.1
$H_2CNH_2^+$ C_{2v}	−114.6	−115.1	−75.1	−76.0	−69.5	−74.7
$H_2CNH_2^+$ C_{2h}	−116.5	−117.0	−75.5	−76.4	−69.9	−74.8
NH_4^+	−95.4	−93.3	−59.6	−60.2	−75.3	−79.1
$HCN{:}H_3NH^+$	−88.3		−60.8		−81.0	

[a] See Table 1 for the corresponding structures. Both Fermi-contact terms (FC) and coupling constants (*J*) are given in hertz.

At this point it should be noted that all of these complexes have very large binding energies, not because they are hydrogen-bonded but because they are ion-pair complexes, each having two cations interacting with the same anion. For example, the complex $F(NH_4)_2^+$ has an electronic stabilization energy of 205 kcal/mol relative to two NH_4^+ cations and F^-. However, an accurate estimate of the binding energies of these complexes requires a higher level of correlation and a larger basis set than used for the MP2/6-31+G(d,p) optimizations. Moreover, not all of the complexes listed in Table 1 correspond to equilibrium structures on their potential surfaces. Interest in these complexes arises from their structures and the effects of structural changes on coupling constants. Thus, the calculation of accurate binding energies and enthalpies for these complexes is beyond the scope of this project.

Coupling Constants. The computed one-bond N−H ($^1J_{N-H}$) and H−F ($^{1h}J_{H-F}$), and two-bond N−F ($^{2h}J_{N-F}$) coupling constants and the corresponding Fermi-contact terms for the complexes $F(FCNH)_2^+$, $F(HCNH)_2^+$, $F(HNNH_2)_2^+$, $F(H_2CNH_2)_2^+$ (C_{2v} and C_{2h}), and $F(NH_4)_2^+$ are given in Table 2. For these complexes, the Fermi-contact terms for F−N and N−H coupling are good approximations to $^{2h}J_{N-F}$ and $^1J_{N-H}$, respectively, but the FC term is not a good approximation to $^{1h}J_{F-H}$.[26,27] Since the calculation of all terms for $F(HCN{:}NH_4)_2^+$ is not feasible, only the Fermi-contact terms for F−N, F−H, and N−H coupling are listed in Table 2 for comparison purposes.

As indicated above, the complexes $F(FCNH)_2^+$, $F(HCNH)_2^+$, $F(HNNH_2)_2^+$, $F(H_2CNH_2)_2^+$, $F(NH_4)_2^+$, and $F(HCN{:}NH_4)_2^+$ are listed in order of increasing ion-pair (decreasing proton-shared) character of the N−H−F hydrogen bonds. Consistent with the decreasing proton-shared character of the N−H−F hydrogen bonds is the decrease in the absolute value of $^{2h}J_{N-F}$, from −196.7 Hz in $F(FCNH)_2^+$ to −93.3 Hz in $F(NH_4)_2^+$. Although only the Fermi-contact terms have been computed for $F(HCN{:}NH_4)_2^+$, the value of the FC term of −88.3 Hz for F−N coupling is less than the absolute value of the FC term for $F(NH_4)_2^+$. These results reinforce previous observations that two-bond spin−spin coupling constants are greatest when the hydrogen bonds are quasi-symmetric proton-shared[28] and dramatically illustrate that the ion-pair character of the N−H−F hydrogen bonds increases in the series $F(FCNH)_2^+ < F(HCNH)_2^+ < F(HNCNH_2)_2^+ < F(H_2CNH_2)_2^+ < F(NH_4)_2^+ < F(HCN{:}NH_4)_2^+$. Since the magnetogyric ratio of ^{15}N (γ_N) is negative while that of ^{19}F (γ_F) is positive, the reduced coupling constants $^{2h}K_{N-F}$

$$^{2h}K_{N-F} \propto {}^{2h}J_{N-F}/\gamma_N\gamma_F$$

are always positive, consistent with previous findings.[29]

As is evident from Table 2, N−H coupling constants ($^1J_{N-H}$) are negative. This is consistent with the generalization that $^1K_{X-H}$ is always positive for X−H proton donors in hydrogen-bonded complexes,[30] given that γ_H for ^1H is positive and γ_N for ^{15}N is negative. As will be discussed in detail below, the magnitude of this coupling constant decreases for a given proton donor as the N−H distance increases and the hydrogen bond acquires increased proton-shared character. However, the value of this coupling constant also depends on the nature of the N−H donor, so no simple relationship between $^1J_{N-H}$ and the N−H distance is evident from Table 2. However, a relationship between ratios of X−H coupling constants and X−H distances for complexes and corresponding monomers has been demonstrated previously.[30]

Another interesting feature of the data reported in Table 2 is the change of sign of the F−H coupling constants in this series of complexes. For a traditional X−H···Y hydrogen bond, it has been established that $^{1h}K_{H-Y}$ is negative.[31] Ion-pair hydrogen bonds are similar to traditional hydrogen bonds, with the roles of X and Y reversed ($Y{-}H^{+}\cdots{}^{-}X$). Thus, in an ion-pair hydrogen bond the $Y{-}H^+$ distance is elongated relative to this distance in the corresponding isolated cation, the Y−H infrared stretch is shifted to lower frequency relative to the cation, and the reduced X−H coupling constant is negative. Since γ_F and γ_H are positive, $^{1h}K_{H-F}$ and $^{1h}J_{H-F}$ have the same signs. In the complexes $F(HCN{:}NH_4)_2^+$ and $F(NH_4)_2^+$, which have the greatest ion-pair character, the FC terms for H−F coupling are negative, with values of −81.0 and −75.3 Hz, respectively. $^{1h}J_{H-F}$ for $F(NH_4)_2^+$ is −79 Hz, slightly more negative than the values of −73 Hz for $F(HNNH_2)_2^+$ and −75 Hz for the two isomers of $F(H_2CNH_2)_2^+$, which is indicative of the increased proton-shared character of the hydrogen bonds in $F(H_2CNH_2)_2^+$ and $F(HNNH_2)_2^+$. When the proton donors are sp-hybridized nitrogens and the proton-shared character of the N−H−F hydrogen bond is greatest, $^{1h}J_{H-F}$ is positive with values of +171 and +210 Hz in $F(HCNH)_2^+$ and $F(FCNH)_2^+$, respectively. These observations are consistent with a previous theoretical study[31] and with experimental studies which demonstrated that sign changes of one-bond coupling constants accompany the proton-transfer process.[1−6,32] Insight into the signs of these coupling constants can be gained by considering the nuclear magnetic resonance triplet wave function model (NMRTWM) and the nodal properties of excited-state triplet wave functions.[33]

To further investigate structural and coupling constant changes in cationic complexes with two N−H−F hydrogen bonds as a function of the N−H distance and therefore hydrogen-bond type, the N−H distance in $F(NH_4)_2^+$ was set to 1.00 Å and then incremented to 1.80 Å in steps of 0.10 Å. At each distance, the complex was fully optimized, subject to the constraint of C_{2v} symmetry. The optimized F−N and F−H distances and the N−F−N angles for these complexes are reported in Table 3. At relatively short N−H distances from 1.00 to 1.15 Å, a range that includes the equilibrium structure, the F−N distance varies by less than 0.01 Å, from 2.451 to 2.458 Å, but the F−H distance decreases dramatically from 1.452 to 1.308 Å. However, in this range the N−H−F−H−N arrangement remains linear, and these complexes have D_{3d} symmetry.

TABLE 3: Distances and Angles for $(H_3NH{:}F{:}HNH_3)^+$ Complexes as a Function of the N−H Distance[a]

R(N−H)[b]	R(F−N)	R(F−H)	∠N−F−N
1.00	2.452	1.452	180
1.051	2.451	1.400	180
1.10	2.453	1.353	180
1.116[c]	2.454	1.338	180
1.15	2.458	1.308	180
1.20	2.466	1.267	172
1.30	2.490	1.192	151
1.40	2.530	1.133	138
1.50	2.587	1.091	131
1.60	2.657	1.060	127
1.70	2.735	1.038	124
1.80	2.819	1.022	122

[a] Complexes optimized with C_{2v} symmetry. Distances are given in angstroms; angles are given in degrees. [b] Fixed value of the N−H distance. [c] Equilibrium structure of D_{3d} symmetry.

TABLE 4: Fermi-Contact Terms and Total Coupling Constants for $(H_3NH{:}F{:}HNH_3)^+$ Complexes as a Function of the N−H Distance[a]

	F−N		N−H		F−H	
R(N−H)	FC	J	FC	J	FC	J
1.00	−72.7	−70.6	−71.0	−72.0	−70.5	−77.6
1.051	−82.4	−80.3	−66.2	−67.1	−76.8	−83.0
1.10	−92.1	−90.0	−61.2	−61.9	−76.9	−81.4
1.116[b]	−95.3	−93.2	−59.6	−60.2	−75.3	−79.2
1.15	−102.0	−99.9	−56.0	−56.5	−69.1	−71.1
1.20	−110.8	−108.8	−50.6	−51.0	−52.0	−50.8
1.30	−119.7	−118.1	−38.9	−39.1	11.2	19.5
1.40	−119.1	−117.9	−28.3	−28.5	96.6	113.1
1.50	−112.9	−112.1	−20.5	−20.7	180.7	205.6
1.60	−104.1	−103.8	−15.1	−15.3	253.4	286.3
1.70	−94.7	−94.6	−11.4	−11.6	312.4	352.4
1.80	−85.3	−85.4	−8.9	−9.1	359.6	405.6
1.093[c]	−84.5	−82.5	−63.2	−63.9	−75.4	−80.1
1.08[d]	−70.1	−68.2	−65.7	−66.5	−69.4	−73.9
exptl[e]		−64		−75		−71

[a] See Table 3 for the corresponding structures. N−H distances are given in angstroms. Both Fermi-contact terms (FC) and coupling constants (*J*) are given in hertz. [b] Equilibrium structure. [c] Computed for $(H_3NH{:}F{:}HNH_3)^+$ at the optimized geometry of the (collidineH:F:Hcollidine)$^+$ complex with N−H and F−H distances of 1.093 and 1.389 Å, respectively. [d] Coupling constants for $(H_3NH{:}F{:}HNH_3)^+$ computed at the N−H and F−H distances for (collidineH:F:Hcollidine)$^+$ given in ref 6. [e] Reference 6.

As the N−H distance further increases, the complexes bend and the symmetry changes to C_{2v}, with the degree of bending increasing as the N−H distance increases. At the same time, the F−N distance increases dramatically from 2.466 to 2.819 Å, and the F−H distance decreases from 1.267 to 1.022 Å. Thus, this artificial way of transferring the proton from N to F eventually results in hydrogen-bonded complexes stabilized by traditional F−H···N hydrogen bonds.

Coupling constants $^{2h}J_{F-N}$, $^1J_{N-H}$, and $^{1h}J_{H-F}$ for the $F(NH_4)_2^+$ complexes listed in Table 3 are reported in Table 4, and a plot of these coupling constants versus the N−H distance is shown in Figure 1. The variation in coupling constants with changing hydrogen-bond type is not unexpected. These changes are similar to those computed for $FH{:}NH_3$ and FH:pyridine[34] and observed experimentally for FH:collidine complexes as a function of temperature and solvent ordering.[1−6,32] However, in the gas phase, $FH{:}NH_3$ and FH:pyridine are stabilized by

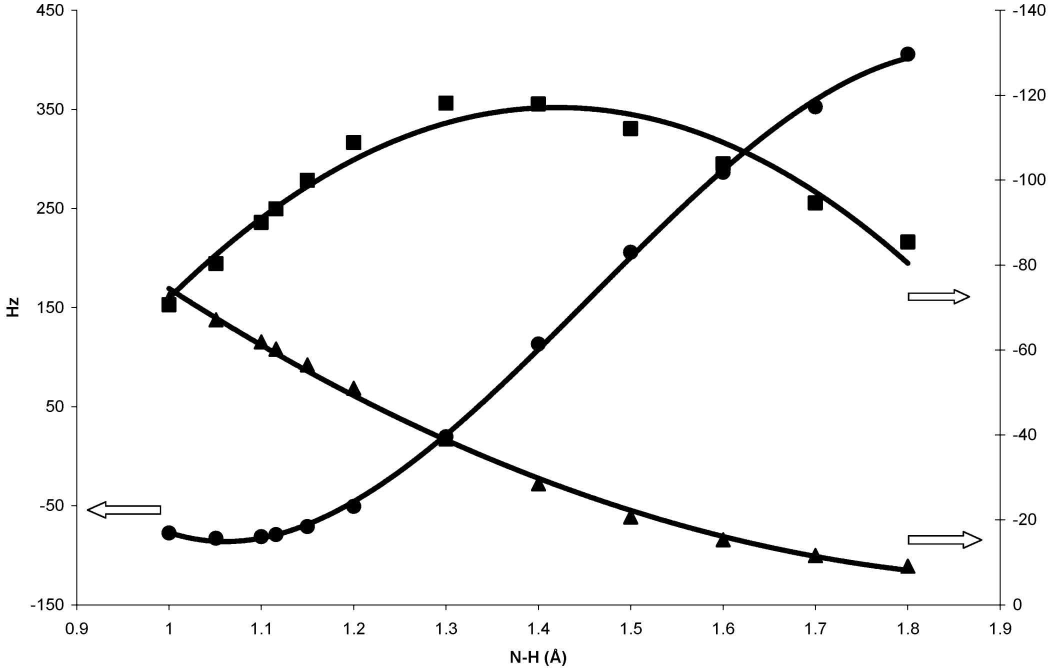


Figure 1. ${}^{2h}J_{F-N}$ (■),${}^{1}J_{N-H}$ (▲), and ${}^{1h}J_{H-F}$ (●) for complexes $(H_3N-H-F-H-NH_3)^+$ as a function of the N−H distance.

traditional F−H···N hydrogen bonds, and proton transfer and changes in hydrogen-bond type occur as the proton is transferred from F to N. In contrast, the gas-phase structure of $F(NH_4)_2{}^+$ is stabilized by traditional $N-H^+\cdots F^-$ hydrogen bonds, and proton transfer from N to F occurs as the N−H distance increases. As this distance increases, ${}^{2h}J_{N-F}$ increases in absolute value, has a maximum in the region in which the N−H−F hydrogen bonds are quasi-symmetric proton-shared hydrogen bonds, and then decreases as the proton is transferred to F and the hydrogen bonds become traditional F−H···N hydrogen bonds. At short N−H distances, the increase in ${}^{2h}J_{N-F}$ is due to an increase in the proton-shared character of the N−H−F hydrogen bonds and not to changes in the F−N distances. ${}^{1}J_{N-H}$ decreases in absolute value as the N−H bond lengthens, approaching zero at long N−H distances. ${}^{1h}J_{H-F}$ becomes slightly more negative as the N−H bond lengthens from 1.00 Å but then decreases dramatically in absolute value and changes sign when the N−H distance is between 1.25 and 1.30 Å, the region of the quasi-symmetric proton-shared hydrogen bonds. Subsequently it becomes large and positive as F−H becomes the proton donor to N. At an N−H distance of 1.80 Å, the F−H distance is 1.022 Å and ${}^{1}J_{F-H}$ is 406 Hz. This coupling constant is still smaller than the computed value of 495 Hz for the HF monomer at its optimized MP2/6-31+G(d,p) distance of 0.926 Å. A similar variation of ${}^{2h}J_{N-F}$, ${}^{1}J_{N-H}$, and ${}^{1h}J_{H-F}$ occurs for $F(HCNH)_2{}^+$ as a function of the N−H distance.

Comparisons with Experimental Data. The computed coupling constants may be compared with the experimental values of ${}^{2h}J_{N-F}$, ${}^{1}J_{N-H}$, and ${}^{1h}J_{H-F}$ for $F(\text{collidineH})_2{}^+$, which are also reported in Table 4.[6] Although the calculations were performed on $F(NH_4)_2{}^+$ complexes and not on $F(\text{collidineH})_2{}^+$, both the signs and magnitudes of ${}^{2h}J_{N-F}$, ${}^{1}J_{N-H}$, and ${}^{1h}J_{H-F}$ computed for complexes with short N−H distances are consistent with the signs and magnitudes of the experimental coupling constants. Negative values of ${}^{1h}J_{H-F}$ at short N−H distances indicate the existence of traditional $N-H^+\cdots F^-$ hydrogen bonds and support the conclusion of ref 6 that, in solution, two equivalent collidinium ions are proton donors to F^-. Moreover, the computed equilibrium structures of both $F(NH_4)_2{}^+$ and $F(\text{collidineH})_2{}^+$ have the hydrogen-bonded H atoms already covalently bonded to the nitrogens. This is consistent with the experimental observation that coupling constants for $F(\text{collidineH})_2{}^+$ exhibit little change as a function of temperature and solvent ordering.[6] The computed structures of $F(NH_4)_2{}^+$, $F(\text{pyridineH})_2{}^+$, and $F(\text{collidineH})_2{}^+$ suggest that $F(\text{collidineH})_2{}^+$ has a linear or nearly linear N−H−F−H−N arrangement and most probably does not have the bent geometry illustrated in ref 6.

Also reported in Table 4 are computed coupling constants for $F(NH_4)_2{}^+$ at the computed equilibrium geometry of $F(\text{collidineH})_2{}^+$, which has N−H and F−N distances of 1.093 and 2.482 Å, respectively. The computed values of ${}^{2h}J_{N-F}$, ${}^{1}J_{N-H}$, and ${}^{1h}J_{H-F}$ are similar to those computed for an optimized $F(NH_4)_2{}^+$ complex with the N−H distance fixed at 1.10 Å. It is interesting to note that over a range of N−H distances from 1.051 to 1.116 Å, ${}^{1}J_{N-H}$ varies only from −67 to −60 Hz. These values of ${}^{1}J_{N-H}$ are less (in an absolute sense) than the experimental value of −75 Hz for $F(\text{collidinium})_2{}^+$. The dependence of N−H coupling constants on the nature of the N atom is known experimentally,[35] and is also evident from ${}^{1}J_{N-H}$ values computed for ammonium (−75 Hz) and pyridinium (−92 Hz). At the geometry of $F(\text{collidineH})_2{}^+$, ${}^{2h}J_{N-F}$ has a value of −83 Hz, compared to the experimental value of −64 Hz, while ${}^{1h}J_{H-F}$ has a value of −80 Hz, slightly greater than the experimental value of −71 Hz. These differences suggest that the computed gas-phase F−N distance of 2.482 Å for $F(\text{collidineH})_2{}^+$ may be too short relative to the F−N distance in solution. That is, the hydrogen bonds in the $F(\text{collidineH})_2{}^+$ complex that exists in solution have less proton-shared character than those in the isolated gas-phase complex.[36]

On the basis of the experimental values of ${}^{2h}J_{N-F}$, ${}^{1}J_{N-H}$, and ${}^{1h}J_{H-F}$, Limbach and co-workers[6] have estimated that the N−H and F−H distances for $F(\text{collidineH})_2{}^+$ in solution are 1.08 and 1.46 Å, respectively. With these distances held fixed, the optimized structure of $F(NH_4)_2{}^+$ has a linear N−H−F−H−N arrangement and a longer F−N distance of 2.54 Å. The computed value of ${}^{1}J_{N-H}$ for $F(NH_4)_2{}^+$ at this geometry is −67 Hz, consistently less than the experimental value of −75 Hz. However, the longer F−H and F−N distances give the N−H···F hydrogen bonds less proton-shared character. As a result, the absolute values of $^{2h}J_{N-F}$ and $^{1h}J_{H-F}$ are reduced (−68 and −74 Hz, respectively) and are in excellent agreement with the experimental values of −64 and −71 Hz, respectively.

Conclusions

A systematic ab initio study has been carried out to determine the structures and coupling constants across N−H−F−H−N hydrogen bonds for a series of complexes $F(H_3NH)_2^+$, $F(HNNH_2)_2^+$, $F(H_2CNH_2)_2^+$, $F(HCNH)_2^+$, and $F(FCNH)_2^+$. The results of this study support the following statements.

1. As the hybridization of the N−H donor nitrogen in these complexes changes from sp^3 to sp^2 to sp and its basicity decreases, the N−H distance increases, the N−F−N arrangement changes from linear to bent, and the ion-pair hydrogen bonds acquire increased proton-shared character.

2. The computed values of the two-bond ($^{2h}J_{N-F}$) and one-bond ($^{1}J_{N-H}$ and $^{1h}J_{H-F}$) coupling constants for these complexes reflect the structural changes that occur with changing hydrogen-bond type. As the nitrogen hybridization changes from sp^3 to sp^2 to sp, the absolute value of $^{2h}J_{N-F}$ increases and $^{1h}J_{H-F}$ changes sign.

3. The optimized structure of $F(NH_4)_2^+$ has a linear N−H−F−H−N arrangement of the hydrogen-bonded atoms. This arrangement is also found for the equilibrium structure of $F(pyridineH)_2^+$ and would therefore be expected for $F(collidineH)_2^+$, since collidine is an even stronger nitrogen base.

4. Systematic changes in $^{2h}J_{N-F}$, $^{1}J_{N-H}$, and $^{1h}J_{H-F}$ accompany changes in the N−H distance in the complex $F(NH_4)_2^+$. As this distance increases, the ion-pair N−H−F hydrogen bonds become proton-shared and then traditional F−H···N hydrogen bonds. During this process, $^{2h}J_{N-F}$ first increases and then decreases in absolute value, $^{1}J_{N-H}$ decreases, and $^{1h}J_{H-F}$ changes sign.

5. The signs and magnitudes of $^{2h}J_{N-F}$, $^{1}J_{N-H}$, and $^{1h}J_{H-F}$ computed for $F(NH_4)_2^+$ at short N−H distances are in agreement with the experimental signs and magnitudes of these coupling constants for the $F(collidineH)_2^+$ complex. However, even when these coupling constants are computed at the optimized geometry of $F(collidineH)_2^+$, $^{2h}J_{N-F}$ and $^{1h}J_{H-F}$ are still too large relative to experiment, suggesting that the hydrogen bonds in the isolated gas-phase structure of $F(collidineH)_2^+$ have too much proton-shared character relative to the hydrogen bonds that exist in solution. Excellent agreement between experimental and computed coupling constants is found when these coupling constants are computed for $F(NH_4)_2^+$ with the N−H and F−H distances estimated from the experimental NMR data. The experimental geometry has a longer N−F distance and results in N−H−F hydrogen bonds that have decreased proton-shared character.

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Supporting Information Available: Complete refs 23 and 24. This material is available free of charge via the Internet at http://pubs.acs.org.

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