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Two-Bond $^{15}N-^{19}F$ Spin−Spin Coupling Constants ($^{2h}J_{N-F}$) across $N-H^+$...F Hydrogen Bonds

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Two-bond $^{15}N-^{19}F$ NMR spin−spin coupling constants ($^{2h}J_{N-F}$) have been computed using equation-of-motion coupled cluster singles and doubles theory (EOM-CCSD) for a variety of cationic complexes stabilized by traditional $N-H^+\cdots F$ hydrogen bonds. The proton donors include protonated sp bases derived from HCN, protonated sp^2 aromatic rings and imines, and protonated sp^3 bases derived from NH_3, with FH as the proton acceptor. $^{2h}J_{N-F}$ is determined solely by the Fermi-contact term, which is distance dependent. The absolute values of N−F coupling constants for cationic complexes are significantly greater than the F−N coupling constants for neutral complexes stabilized by traditional $F-H\cdots N$ hydrogen bonds over a range of N−F distances. This may be attributed to the greater proton-shared character of hydrogen bonds in cationic complexes. Moreover, at a given distance, values of $^{2h}J_{N-F}$ for complexes with sp and sp^2 nitrogens as proton donors are considerably greater than $^{2h}J_{N-F}$ values for complexes with sp^3 nitrogens as donors. When the cationic complexes are grouped according to the hybridization of the nitrogen, good correlations are found between $^{2h}J_{N-F}$ and the N−F distance. Small perturbations of the $N-H^+\cdots F$ hydrogen bond from linearity are associated with only small decreases in $^{2h}J_{N-F}$.

Introduction

In the preceding paper in this issue,[1] we presented computed $^{19}F-^{15}N$ spin−spin coupling constants ($^{2h}J_{F-N}$) for a set of neutral complexes stabilized by traditional $F-H\cdots N$ hydrogen bonds. In this paper, we present computed $^{15}N-^{19}F$ coupling constants for a set of complexes in which the nitrogen has been protonated and the resulting cationic complexes are stabilized by traditional $N-H^+\cdots F$ hydrogen bonds. The following questions will be addressed in this study.

1. Can N−F coupling constants across $N-H^+\cdots F$ hydrogen bonds be approximated by the Fermi-contact term?
2. How does $^{2h}J_{N-F}$ vary with hydrogen bond distances and with the linearity of the hydrogen bond?
3. Can a single curve be constructed from coupling constants computed at optimized distances for a group of complexes with $N-H^+\cdots F$ hydrogen bonds, and can that curve be used to predict intermolecular distances from experimentally measured N−F coupling constants?
4. How do two-bond N−F coupling constants across hydrogen bonds in cationic complexes stabilized by $N-H^+\cdots F$ hydrogen bonds compare with those in neutral complexes stabilized by $F-H\cdots N$ hydrogen bonds?

Methods

Two-bond $^{15}N-^{19}F$ spin−spin coupling constants have been evaluated for 18 cationic complexes stabilized by $N-H^+\cdots F$ hydrogen bonds in which sp, sp^2, and sp^3 hybridized nitrogens are $N-H^+$ donors to FH. The proton donors include protonated sp bases derived from HCN (HCN, LiCN, CH_3CN, FCN, and NCCN), protonated sp^2 aromatic (pyridine, 4-Li-pyridine, 1,4-diazine (pyrazine), 1,3,5-triazine, and 1,2,4,6-tetrazine) and imine [$H_2C{=}NH$, F(H)C=NH, and $H_2C{=}NF$] bases, and protonated sp^3 bases derived from NH_3 [NH_3, NFH_2, NF_2H, NF_3, and $NH_2(CH_3)$]. The structures of all of these complexes were optimized under the constraint that the proton donor $N-H_{(d)}{}^+$ group and the proton acceptor $F-H_{(a)}$ molecule be collinear. These will be referred to as optimized linear complexes, with $H_{(d)}-N-F$ and $N-F-H_{(a)}$ angles fixed at 0 and 180°, respectively. The linearity constraint was imposed so that computed N−F coupling constants could be compared for complexes with similar structures. However, the linear complexes are not equilibrium structures on their potential surfaces. For comparison purposes, the structures of a subset of complexes were fully optimized. All structure optimizations were carried out at second-order many-body perturbation theory [MBPT(2) = MP2][2−5] with the 6-31+G(d,p) basis set.[6−9] Electronic binding energies for all complexes were computed as the difference between the total energy of the complex and the sum of the energies of the isolated monomers. No counterpoise corrections for basis-set superposition errors have been made.[10]

$^{15}N-^{19}F$ spin−spin coupling constants ($^{2h}J_{N-F}$) were obtained from equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations in the CI-like approximation[11−14] using the Ahlrichs[15] qzp basis on non-hydrogen atoms, qz2p on the hydrogen-bonded hydrogen, and Dunning's cc-pVDZ[16,17] basis set on all other hydrogens. $^{2h}J_{N-F}$ was evaluated as the sum of the paramagnetic spin−orbit (PSO), diamagnetic spin−

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TABLE 1: Structural Parameters [Bond Length (Å) and Angles (deg)] and Binding Energies (kcal/mol) for Selected Complexes with N−H$^+$···F Hydrogen Bonds

complex	N−F	N−H^a	<H$_{(d)}$−N−F^a	<N−F−H$_{(a)}$	Δ*E*
pyridinium:FH					
opt^b	2.880	1.021	4.8	162.1	−10.5
C_{2v}^{c}	2.882	1.021	0.0	180.0	−10.5
H_3NH^+:FH					
opt^b	2.813	1.029	9.6	163.2	−12.6
C_{3v}^{c}	2.835	1.028	0.0	180.0	−12.5
$H_2C{=}NH_2^+$:FH					
opt^b	2.771	1.021	25.9	163.1	−12.2
C_s^{c}	2.838	1.023	0.0	180.0	−11.8
LiCNH$^+$:FH					
opt^b	2.768	1.019	3.9	146.6	−10.5
$C_{\infty v}$^{c}	2.795	1.016	0.0	180.0	−10.3
FH_2NH^+:FH					
opt^b	2.736	1.038	7.7	151.6	−14.8
C_s^{c}	2.762	1.036	0.0	180.0	−14.5
F_2HNH^+:FH					
opt^b	2.656	1.053	5.3	145.1	−17.2
C_s^{c}	2.687	1.046	0.0	180.0	−16.6
HCNH$^+$:FH					
opt^b	2.603	1.046	4.2	140.6	−15.4
$C_{\infty v}$^{c}	2.647	1.035	0.0	180.0	−14.8
FCNH$^+$:FH					
opt^b	2.580	1.050	4.3	138.9	−16.4
$C_{\infty v}$^{c}	2.632	1.036	0.0	180.0	−15.6
NCCNH$^+$:FH					
opt^b	2.578	1.053	4.1	138.9	−16.8
$C_{\infty v}$^{c}	2.627	1.039	0.0	180.0	−15.9
F_3NH^+:FH					
opt^b	2.575	1.078	5.7	141.6	−19.9
C_{3v}^{c}	2.612	1.063	0.0	180.0	−19.1

[a] Monomer N−H distances (Å): NH_4^+, 1.023; NFH_3^+, 1.029; $NF_2H_2^+$, 1.036; NF_3H^+, 1.045; pyridinium, 1.017; $H_2C{=}NH_2^+$, 1.018; LiCNH$^+$, 1.008; HCNH$^+$, 1.017; FCNH$^+$, 1.016; NCCNH$^+$, 1.018. [b] Fully optimized structure. All of these complexes have C_s symmetry. [c] Optimized linear structure with ∠H$_{(d)}$−N−F and ∠N−F−H$_{(a)}$ constrained at 0.0° and 180.0°, respectively.

orbit (DSO), Fermi-contact (FC), and spin−dipole (SD) terms whenever feasible; otherwise, it was approximated by the Fermi-contact term. Structure optimizations were carried out using the Gaussian 98 suite of programs,[18] and coupling constants were evaluated using ACES II.[19] These calculations were carried out on the Cray SV1 computer at the Ohio Supercomputer Center. Electronic features of the hydrogen bond were analyzed by evaluting electron densities at hydrogen bond critical points by means of the atoms in molecules (AIM) theory.[20] This analysis was done at MP2/6-31+G(d,p) using the computing facilities at the Universidad Autónoma de Madrid.

Results and Discussion

Table 1 presents the symmetries, N−F and N−H distances, values of the hydrogen-bonding angle that measures the nonlinearity of the hydrogen bond (<H$_{(d)}$−N−F), values of the angle which describes the orientation of the proton-acceptor FH molecule (<N−F−H$_{(a)}$), and binding energies for selected optimized linear and fully optimized complexes stabilized by traditional N−H$^+$···F hydrogen bonds. The listing in Table 1 is in order of decreasing N−F distance in the fully optimized structure, which is not the same as the order of increasing binding energy. From a structural viewpoint, the hydrogen bonds in the fully optimized structures except for $H_2C{=}NH_2^+$:FH deviate only slightly from linearity, with <H$_{(d)}$−N−F ranging from 4 to 10°. In the fully optimized $H_2C{=}NH_2^+$:FH complex, the deviation from linearity is much greater at 26° and arises from a secondary interaction between the adjacent imine C−H and the proton acceptor F. (Even though the fully optimized and linear structures of $H_2C{=}NH_2^+$:FH are significantly different, three linear complexes with protonated imines as proton donors have been included in this study, so that the sp^2 N−H$^+$ donors would not be limited to aromatic nitrogens.) The N−F−H$_{(a)}$ angle, which describes the orientation of the proton-acceptor FH, exhibits a greater range of values, from 139° in FCNH$^+$:FH and NCCNH$^+$:FH to 163° in H_3NH^+:FH. The optimized value of this angle is a compromise between two competing factors which influence stabilization. The first is the preference for a lone pair of electrons on the proton-acceptor atom to be directed toward the hydrogen-bonded proton (the directed lone pair). Ideally, for a linear hydrogen bond with HF as the proton acceptor, this angle should be about 109°, the tetrahedral value. (The computed MP2/6-31+G(d,p) value of the corresponding angle in $(HF)_2$ is 115°; the experimental value is about 108°.[21]) The second factor arises from an electrostatic interaction that is particularly strong in cationic complexes and tends to produce a head-to-tail alignment of the bond dipole moment of the proton donor N−H$^+$ with the dipole moment of FH. This interaction is favored when the N−F−H$_{(a)}$ angle is 180°. It is apparent from Table 1 that the optimized values of this angle lie between these two values. The linear complexes have longer N−F and shorter N−H distances than the corresponding fully optimized complexes, differences consistent with their smaller binding energies. However, the binding energies of corresponding complexes differ by less than 1 kcal/mol.

TABLE 2: N−F Distances (Å) and Two-Bond Spin−Spin Coupling Constants ($^{2h}J_{N-F}$) and Components^a of $^{2h}J_{N-F}$ (Hz) for Selected Equilibrium and Linear Complexes with N−H$^+$···F Hydrogen Bonds

complex	F−N	PSO	DSO	FC	SD	$^{2h}J_{N-F}$
H_3NH^+:FH						
equil	2.813	0.6	0.0	−28.6	-0.2	−28.2
linear	2.835	0.5	0.0	−28.7	-0.2	−28.4
LiCNH$^+$:FH						
equil	2.768	0.5	−0.1	−47.2	−0.2	−47.0
linear	2.795	0.4	−0.1	−47.1	−0.1	−46.9
HCNH$^+$:FH						
equil	2.603	0.5	−0.1	−95.5	−0.4	−95.5
linear	2.647	0.4	−0.1	−94.5	−0.2	−94.3
FCNH$^+$:FH						
equil	2.580	0.6	−0.1	−111.3	−0.3	−111.1
linear	2.632	0.5	−0.1	−109.1	−0.1	−108.8

[a] PSO = paramagnetic spin−orbit; DSO = diamagnetic spin−orbit; FC = Fermi-contact; SD = spin−dipole.

Table 2 presents a comparison of the two-bond N−F spin−spin coupling constants for the equilibrium and linear structures of H_3NH^+:FH, LiCNH$^+$:FH, HCNH$^+$:FH, and FCNH$^+$:FH. Values of $^{2h}J_{N-F}$ for the fully optimized and linear forms of H_3NH^+:FH and LiCNH$^+$:FH are essentially identical, while the equilibrium structures of HCNH$^+$:FH and FCNH$^+$:FH have N−F coupling constants that are 1.2 and 2.3 Hz greater (in an absolute sense) than those of the linear structures. Given the large absolute values of the coupling constants, these differences are relatively small and reflect the shorter N−F distances in the equilibrium structures. A plot of $^{2h}J_{N-F}$ as a function of the linearity of the hydrogen bond for HCNH$^+$:FH is shown in Figure 1. To obtain the data for this plot, HCNH$^+$ was rotated about an axis through N perpendicular to the N−F line, keeping the N−F distance and all other coordinates fixed. $^{2h}J_{N-F}$ was then computed for different values of the H$_d$−N−F angle. It is evident from Figure 1 that perturbations that slightly distort the hydrogen bond from linearity lead to only small decreases in $^{2h}J_{N-F}$. However, $^{2h}J_{N-F}$ decreases rapidly as the linearity of the hydrogen bond is destroyed.

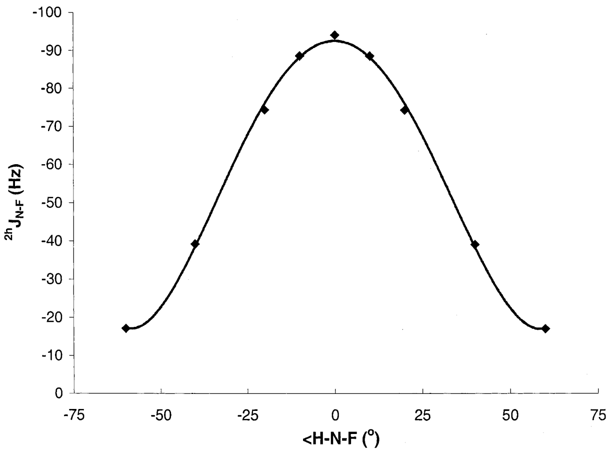

Figure 1. $^{2h}J_{N-F}$ as a function of the nonlinearity of the hydrogen bond for HCNH$^+$:FH. An angle of 0° corresponds to a linear N−H$^+$···F bond.

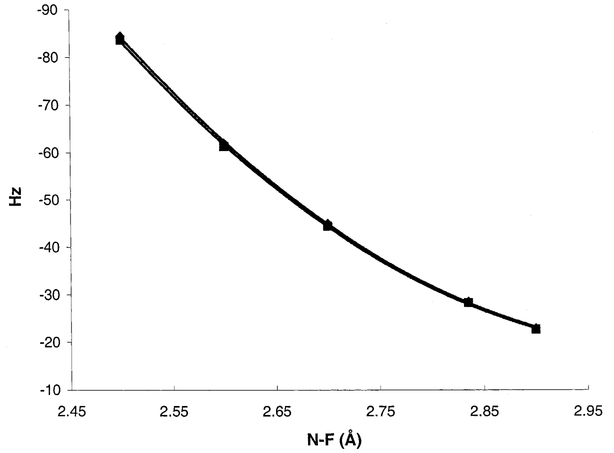

Figure 2. $^{2h}J_{N-F}$ and the Fermi-contact term versus the N−F distance for linear H$_3$NH$^+$:FH: ■, $^{2h}J_{N-F}$; ◆, FC.

Figure 2 shows the distance dependence of the total coupling constant ($^{2h}J_{N-F}$) and the Fermi-contact term for H$_3$NH$^+$:FH. The two curves are essentially superimposable. Among the complexes H$_3$NH$^+$:FH, FH$_2$NH$^+$:FH, LiCNH$^+$:FH, and HCNH$^+$:FH, the largest difference between the Fermi-contact term and $^{2h}J_{N-F}$ is found for H$_3$NH$^+$:FH at short N−F distances, but this difference is less than 1 Hz at an N−F distance of 2.50 Å. At the optimized distances of the five complexes, the difference between FC and $^{2h}J_{N-F}$ is 0.3 Hz or less. Therefore, the Fermi-contact term is a good approximation to $^{2h}J_{N-F}$ for linear complexes with N−H$^+$···F hydrogen bonds over a range of N−F distances.

Figure 3 illustrates the distance dependence of $^{2h}J_{N-F}$ for three complexes in which an sp hybridized nitrogen is the N−H$^+$ donor and for two complexes that have sp^3 nitrogens as N−H$^+$ donors. It is apparent from this figure that $^{2h}J_{N-F}$ varies with both the hybridization of the nitrogen and the nature of the substituent. At all distances, $^{2h}J_{N-F}$ is greater for complexes with sp N−H$^+$ donors than for complexes with sp^3 donors. The differences are largest at short N−F distances but are still appreciable even at a distance of 2.90 Å. These curves are very different from those that illustrate the distance dependence of $^{2h}J_{N-N}$ for complexes stabilized by N−H−N and N−H$^+$−N hydrogen bonds.[22−23]

Table 3 presents values of $^{2h}J_{N-F}$ for 18 linear complexes stabilized by N−H$^+$···F hydrogen bonds. The listing is again in order of decreasing N−F distance and indicates the overall tendency for the absolute value of $^{2h}J_{N-F}$ to decrease as the N−F distance increases. This is also evident from Figure 4, which presents a graphical representation of the variation of $^{2h}J_{N-F}$ with the N−F distance. The best-fit quadratic curve shown has a correlation coefficient of 0.97, evidence of scatter in the data. Also shown for comparison is a plot of $^{2h}J_{N-F}$ for the set of neutral complexes stabilized by traditional F−H···N hydrogen bonds.[1] There are three observations that are immediately evident from this figure.

1. The variation of $^{2h}J_{N-F}$ in these complexes is very large, ranging from about 20 to 110 Hz.

2. $^{2h}J_{N-F}$ is significantly greater for cationic complexes over the entire range of N−F distances.

3. A single curve cannot be constructed to relate $^{2h}J_{N-F}$ to the N−F distance using data encompassing both neutral and charged complexes. This is in marked contrast to the behavior of N−N and C−N coupling constants across hydrogen bonds in neutral and charged complexes. A single curve relates $^{2h}J_{N-N}$ to the N−N distance in neutral and cationic complexes,[23] and a single curve relates $^{2h}J_{C-N}$ to the C−N distance across C−H···N, C−H$^+$···N, C−H···$^-$N, and N−H$^+$···C hydrogen bonds.[24]

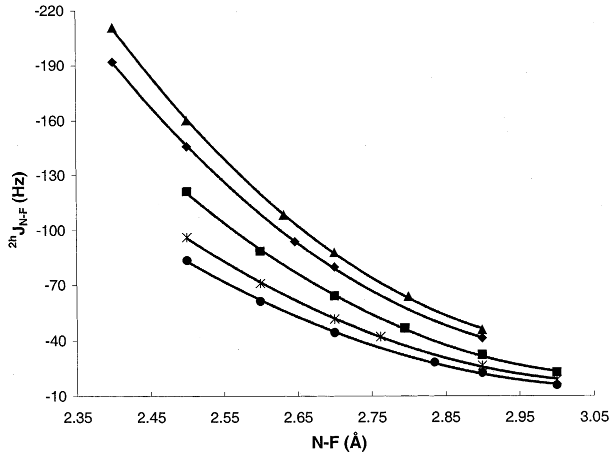

Figure 3. $^{2h}J_{N-F}$ versus the N−F distance for five complexes with linear N−H$^+$···F hydrogen bonds: ▲, FCNH$^+$:FH; ◆, HCNH$^+$:FH; ■, LiCNH$^+$:FH; ∗, FH$_2$NH$^+$:FH; ●, H$_3$NH$^+$:FH.

TABLE 3: Equilibrium Distances (Å) and Two-Bond Spin−Spin Coupling Constants ($^{2h}J_{N-F}$) and Components[a] of $^{2h}J_{N-F}$ (Hz) for Linear Complexes with N−H$^+$···F Hydrogen Bonds

complex	F−N	PSO	DSO	FC	SD	$^{2h}J_{N-F}$
4-Li-pyridinium:FH	2.933			−21.7		−21.7[b]
pyridinium:FH	2.882			−26.9		−26.9[b]
(CH$_3$)H$_2$NH$^+$:FH	2.872			−23.8		−23.8[b]
1,4-diazinium:FH	2.855			−30.1		−30.1[b]
H$_2$C=NH$_2$$^+$:FH	2.838			−33.5		−33.5[b]
H$_3$NH$^+$:FH	2.835	0.5	0.0	−28.7	−0.2	−28.4
1,3,5-triazinium:FH	2.834			−32.2		−32.2[b]
(F)HC=NH$_2$$^+$:FH	2.814			−36.9		−36.9[b]
LiCNH$^+$:FH	2.795	0.4	−0.1	−47.1	-0.1	−46.9
1,2,4,6-tetrazinium:FH	2.785			−49.7		−49.7[b]
FH$_2$NH$^+$:FH	2.762	0.3	−0.1	−42.3	-0.3	−42.4
H$_2$C=N(F)H$^+$:FH	2.748			−56.4		−56.4[b]
(CH$_3$)CNH$^+$:FH	2.696			-78.7		−78.7[b]
F$_2$HNH$^+$:FH	2.687	0.0	−0.1	−64.1	−0.5	−64.7
HCNH$^+$:FH	2.647	0.4	−0.1	−94.5	−0.2	−94.3
FCNH$^+$:FH	2.632	0.5	−0.1	−109.1	−0.1	−108.8
NCCNH$^+$:FH	2.627	0.4	−0.1	−105.4	−0.2	−105.3
F$_3$NH$^+$:FH	2.612			−102.3		−102.3[b]

[a] See Table 2 for definitions. [b] Estimated from the Fermi-contact term.

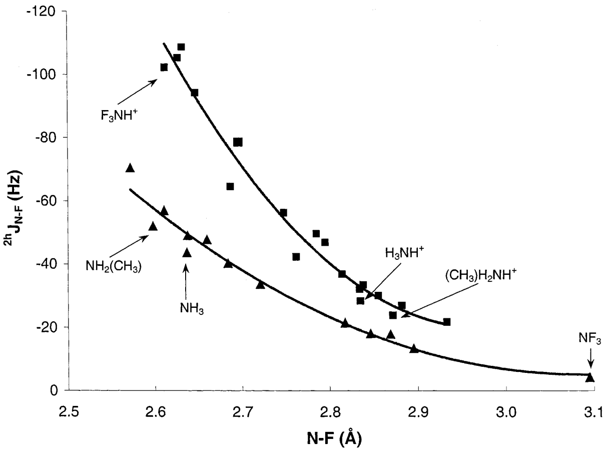

Figure 4. $^{2h}J_{N-F}$ versus the N−F distance for linear complexes with $N-H^+\cdots F$ hydrogen bonds. The corresponding curve from ref 1 for complexes with $F-H\cdots N$ hydrogen bonds is shown: ■, cations; ▲, neutrals.

Interesting relationships can be found between $^{2h}J_{F-N}$ values for a complex with a particular base and the corresponding cationic complex with the protonated base. It is well-known that the conjugate acid of a strong base is a weak acid, while the conjugate acid of a weak base is strong. This relationship is evident from the coupling constants for complexes with conjugate acid−base pairs. For example, the weak base NF_3 is a weak proton acceptor for hydrogen bonding in the neutral complex $FH:NF_3$. This complex has a long F−N distance and a small coupling constant. The conjugate acid F_3NH^+ is a strong proton donor, and it forms the complex $F_3NH^+:FH$, which has a short N−F distance and a very large coupling constant. Conversely, $(CH_3)NH_2$ and NH_3 are strong proton acceptors that form neutral complexes with HF that have short F−N distances and large coupling constants, whereas $(CH_3)NH_3^+$ and NH_4^+ are weak proton donors in complexes with long N−F distances and small coupling constants. These three sets of complexes are labeled in Figure 4. The complexes formed from NH_2F and its conjugate acid have similar N−F distances, in which case the cationic complex has the larger coupling constant. The bases with sp hybridized nitrogens tend to be weak proton acceptors, with the result that the complexes FH:NCCN, FH:NCF, and FH:NCH have longer F−N distances and smaller coupling constants than the corresponding complexes formed with the conjugate acids as proton donors. The complex FH:NCLi, which has the strongest of the sp bases as the proton acceptor, has a short F−N distance, but the F−N coupling constant for this complex is similar to that for the cationic complex $LiCNH^+$:FH formed from the conjugate acid, which has a longer N−F distance. The set of sp^2 aromatic nitrogen bases investigated in ref 1 (4-Li-pyridine, pyridine, 1,4-diazine, and 1,3,5-triazine) are strong bases, with the result that the neutral complexes with these bases have shorter F−N distances and greater F−N coupling constants than the corresponding cationic complexes.

TABLE 4: $^{2h}J_{N-F}$ Values (Hz) and Differences between F−H and N−H Distances (Å) for Neutral and Cationic Complexes with Similar F−N Distances (Å)

complex	R(N−F)	$\lvert R(N-H) - R(F-H)\rvert$	$^{2h}J_{N-F}$
FH:NCH	2.817	0.941	−21.5
$(F)HC{=}NH_2^+$:FH	2.814	0.767	−36.9
FH:1,3,5-triazine	2.684	0.778	−40.3
F_2HNH^+:FH	2.687	0.595	−64.7
$FH:NH_3$	2.637	0.711	−43.7
$FCNH^+$:FH	2.632	0.560	−108.8

TABLE 5: Differences between N−H and F−H Distances (Å) in Neutral and Charged Complexes with Similar N−F Coupling Constants (Hz)

complex	$\lvert R(N-H) - R(F-H)\rvert$	$^{2h}J_{F-N}$
FH:pyridine	0.678	−57.0
$H_2C{=}N(F)H^+$:FH	0.683	−56.4
FH:1,4-diazine	0.718	−49.1
1,2,4,6-tetrazinium:FH	0.721	−49.7
FH:NCLi	0.750	−47.8
$LiCNH^+$:FH	0.763	−46.9
$FH:NH_2F$	0.824	−33.7
$H_2C{=}NH_2^+$:FH	0.792	−33.5
FH:NCH	0.941	−21.5
4-Li-pyridinium:FH	0.899	−21.7

As evident from the above comparisons and from Figure 4, $^{2h}J_{N-F}$ is significantly greater in cationic complexes than in neutral complexes with the same F−N distance. Why is this? It has been demonstrated previously that complexes with proton-shared hydrogen bonds have larger coupling constants than complexes with traditional or ion-pair hydrogen bonds.[25,26] Does this imply that, at the same F−N distance, cationic complexes have greater proton-shared character than neutral complexes? One way to measure the degree of proton-sharing is to examine the difference between F−H and N−H distances in a pair of neutral and cationic complexes that have similar F−N distances. (This comparison is not strictly valid, since the van der Waals radii for N and F are different. However, the radii are similar enough at 1.55 and 1.47 Å, respectively, to warrant such a comparison.) Table 4 presents data for three sets of neutral and cationic complexes that have similar N−F distances. It is evident from these data that the absolute value of the difference between F−H and N−H distances is smaller in the cationic complexes, and these complexes have significantly larger coupling constants. Perhaps an even more compelling argument can be made from the data reported in Table 5, which lists absolute values of the difference between F−H and N−H distances for pairs of neutral and cationic complexes that have similar coupling constants. It is evident from this table that when the degree of proton sharing is approximately the same (as measured by the difference between F−H and N−H distances in the pair), then the coupling constants for the pair are very similar. Even though the hydrogen bonds in these complexes are traditional hydrogen bonds, they have a similar degree of proton-shared character. As a result, the N−F coupling constants for the pair are similar, irrespective of whether the complex is neutral or charged.

As noted above, there is scatter in the data for the cationic complexes shown in Figure 4. Some insight into the origin of this scatter may be gained by grouping the proton donors according to the hybridization of the nitrogen. Figure 5 presents three plots that illustrate the variation of $^{2h}J_{N-F}$ with the N−F distance for complexes with sp, sp^2, and sp^3 hybridized nitrogens. The correlation coefficients for these curves are 0.99, 0.98, and 1.00, respectively. Although the correlation coefficient is lowest for complexes with sp^2 hybridized nitrogens as proton donors, the proton donors encompass nitrogens in distinctly different (aromatic versus nonaromatic) chemical environments. In view of this difference, the correlation is quite good. These curves illustrate the dependence of $^{2h}J_{N-F}$ on the hybridization of the nitrogen, indicating that, at the same N−F distance, complexes with sp^3 $N-H^+$ donors have smaller N−F coupling constants than complexes with sp and sp^2 $N-H^+$ donors. The latter complexes have similar values of coupling constants at the same N−F distance. In fact, a single quadratic curve with a correlation coefficient of 0.99 relates $^{2h}J_{N-F}$ to the optimized N−F distances for these two sets of complexes.

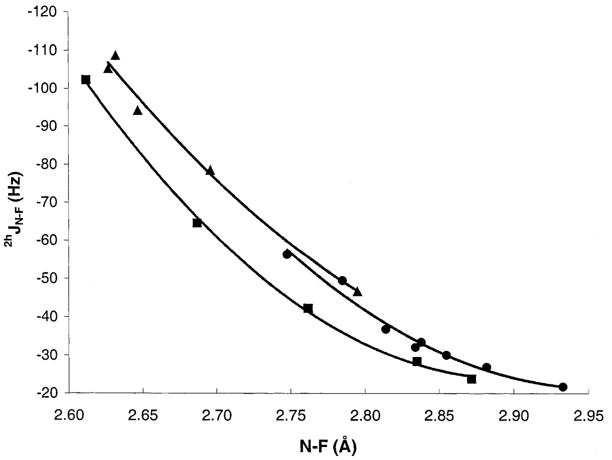

Figure 5. $^{2h}J_{N-F}$ versus the N−F distance for complexes with sp, sp^2, and sp^3 hybridized nitrogens as the N−H$^+$ donor group: ▲, sp; ●, sp^2; ■, sp^3.

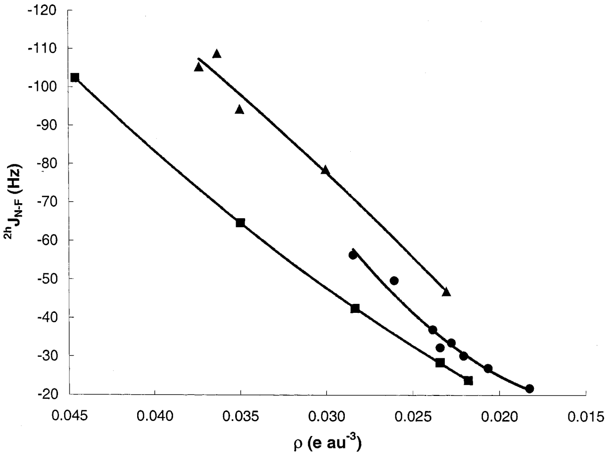

Figure 6. $^{2h}J_{N-F}$ versus the charge density at the hydrogen bond critical point for complexes with sp, sp^2, and sp^3 hybridized nitrogens as the N−H$^+$ donor group: ▲, sp; ●, sp^2; ■, sp^3.

It was observed previously for the neutral complexes stabilized by F−H···N hydrogen bonds that $^{2h}J_{N-F}$ correlates with the charge density at the hydrogen bond critical point if the complexes are grouped according to the hybridization of the proton-acceptor nitrogen.[1] A similar correlation exists for the cationic complexes, as evident from Figure 6. With the same grouping, $^{2h}J_{N-F}$ also correlates with the charge density at the hydrogen bond critical point. This correlation is important insofar as it relates an NMR property of a set of hydrogen-bonded complexes to the electronic characteristics of the hydrogen bond.

Conclusions

The results of EOM-CCSD calculations carried out to determine ^{15}N−^{19}F spin−spin coupling constants ($^{2h}J_{N-F}$) for complexes stabilized by traditional N−H$^+$···F hydrogen bonds support the following answers to the questions raised in the Introduction.

1. ^{15}N−^{19}F spin−spin coupling constants in complexes stabilized by traditional N−H$^+$···F hydrogen bonds can be approximated by the Fermi-contact term.

2. The Fermi-contact term and, therefore, the total $^{2h}J_{N-F}$ are strongly dependent on the N−F distance but only slightly dependent on small variations of the hydrogen bond from linearity.

3. $^{2h}J_{N-F}$ values for cationic complexes stabilized by traditional N−H$^+$···F hydrogen bonds are significantly greater than $^{2h}J_{F-N}$ values for neutral complexes stabilized by traditional F−H···N hydrogen bonds over the entire range of N−F distances in these complexes.

4. At a given N−F distance, a cationic complex has a greater coupling constant than a neutral complex, due at least in part to the greater proton-shared character of the hydrogen bond in the cationic complex. When the proton-shared character is the same (as measured by the difference between the F−H and N−H distances) in a neutral and a cationic complex, then the coupling constants in these two complexes are similar.

5. A quadratic curve can be drawn that relates $^{2h}J_{N-F}$ to the N−F distance in cationic complexes. However, there is scatter in the data points arising from the sensitivity of $^{2h}J_{N-F}$ to the hybridization of the nitrogen of the N−H$^+$ donor. Over a large range of N−F distances, $^{2h}J_{N-F}$ at a given N−F distance is significantly greater for complexes with sp and sp^2 nitrogens compared to those with sp^3 nitrogens. If the complexes are grouped according to the hybridization of the nitrogen, good correlations are found between $^{2h}J_{N-F}$ and the N−F distance. With the same grouping, good correlations also exist between $^{2h}J_{N-F}$ and the charge density at the hydrogen bond critical point.

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