J. Phys. Chem. A **2008,** *112,* 7925–7929

Spin−Spin Coupling across Intermolecular F−Cl···N Halogen Bonds

Janet E. Del Bene,*,† Ibon Alkorta,‡ and José Elguero‡

Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, Instituto de Química Médica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

Received: May 9, 2008; Revised Manuscript Received: June 7, 2008

Ab initio EOM-CCSD calculations have been performed to determine one- and two-bond spin−spin coupling constants ^{1}J(F−Cl), ^{1X}J(Cl−N), and ^{2X}J(F−N) across F−Cl···N halogen bonds in complexes with F−Cl as the Lewis acid and N_2, FCN, HCN, $(CH_3)CN$, LiCN, *Z*-HNNH, H_2CNH, NH_2F, NH_3, cyclic-$NH(CH_2)_2$, and $NH_2(CH_3)$ as Lewis bases. The structures of these complexes were optimized at MP2 with the aug′-cc-pVTZ basis set. The absolute value of ^{2X}J(F−N) increases in these complexes as the F−N distance decreases, a behavior similar to that of ^{2h}J(F−N) for complexes stabilized by F−H···N hydrogen bonds. ^{1X}J(Cl−N) also tends to increase in absolute value with decreasing F−N distance. ^{1}J(F−Cl) is always positive, decreases upon complex formation as the F−Cl distance increases, and appears to be sensitive to the hybridization of the nitrogen base. The relatively large differences in the values of these coupling constants in the various complexes and their variation along the chlorine-transfer coordinate for F−Cl···NH_3 suggest that they should be amenable to experimental investigation.

Introduction

Although halogen bonds (X-bonds) have been known for over a half-century, there has been a resurgence of interest in halogen bonds over the past decade.[1–23] In his recent article,[23] Legon reviewed the gas-phase structures and binding energies of complexes with intermolecular halogen bonds and compared them with corresponding properties of complexes with hydrogen bonds. This work prompted us to extend our recent studies of coupling constants across F−H···N hydrogen bonds[24–27] to an investigation of one- and two-bond spin−spin coupling constants across F−Cl···N halogen bonds. Although the number of papers dealing with halogen bonds is very large, there are no reports of coupling constants across intermolecular halogen bonds.

In the present paper, ab initio spin−spin coupling constants are reported for complexes with FCl as the Lewis acid and N_2, FCN, HCN, $(CH_3)CN$, LiCN, Z-N_2H_2 (diimide), H_2CNH, NH_2F, NH_3, cyclic-$NH(CH_2)_2$ (aziridine), and $NH_2(CH_3)$ (methylamine) as the Lewis bases. By analogy with the nomenclature used for coupling constants across X−H···Y hydrogen bonds [^{1h}J(H−Y) and ^{2h}J(X−Y)], we propose ^{1X}J(Cl−N) and ^{2X}J(F−N) to designate coupling across F−Cl···N halogen bonds. Systematic variations in these coupling constants are noted, and their characteristics compared with coupling constants for corresponding complexes stabilized by hydrogen bonds. Variations in coupling constants along the chlorine-transfer coordinate for F−Cl···NH_3 are compared with variations of the corresponding coupling constants across the proton-transfer coordinate for F−H···NH_3.

Methods

The structures of all complexes were optimized at second-order Møller−Plesset perturbation theory (MP2)[28–31] with the aug′-cc-pVTZ basis set, where aug′ implies that the aug-cc-pVTZ basis was used on all atoms except H, in which case the cc-pVTZ basis was employed.[32,33] Vibrational frequencies were computed to ensure that the stationary points found correspond to equilibrium structures on the potential surfaces. Structure optimizations were carried out using Gaussian 03.[34]

Structures were also optimized along the chlorine-transfer coordinate for F−Cl···NH_3. The first point at a Cl−N distance of 2.235 Å corresponds to the equilibrium structure of F−Cl···NH_3. The final point has the Cl−N distance fixed at 1.736 Å, the value for the isolated optimized ion H_3NCl^+. The remaining points correspond to fully optimized structures at fixed Cl−N distances of 2.13, 2.03, 1.93, and 1.83 Å.

One- and two-bond coupling constants ^{1}J(F−Cl), ^{1X}J(Cl−N), and ^{2X}J(F−N) were computed using the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD)[35–38] method in the CI (configuration interaction)-like approximation with all electrons correlated. These calculations were carried out with the Ahlrichs[39] qzp basis set on ^{13}C, ^{15}N, and ^{19}F, the qz2p basis on ^{35}Cl, the “hybrid” basis set on ^{7}Li,[40] and the cc-pVDZ basis set on ^{1}H.[32,33] In the Ramsey approximation, the total coupling constant is a sum of four terms: the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin-dipole (SD).[41] Except for F−Cl···$N(CH_3)_3$, all terms were computed for all of the complexes formed from FCl and the nitrogen bases. Although the structure of F−Cl···$N(CH_3)_3$ was optimized, the size and low computational symmetry of this complex limited the evaluation of coupling constants to the FC terms. Coupling constants were computed using ACES II.[42] All calculations were performed on the Itanium cluster at the Ohio Supercomputer Center.

Results and Discussion

Structures and Binding Energies. The computed structures and binding energies for complexes with halogen bonds are given in Table 1 along with the corresponding experimental Cl−N distances reported by Legon.[23,43] The complexes with sp hybridized N bases are listed first in order of increasing protonation energy (proton affinity[44]). These are followed by the two sp^2 hybridized bases and then the set of complexes with

---

* Corresponding author. E-mail: jedelbene@ysu.edu.
† Youngstown State University.
‡ CSIC.

10.1021/jp804119r CCC: $40.75

TABLE 1: F−N and Cl−N Distances (R, Å) and Binding Energies ($-\Delta E_e$, kcal/mol) for Complexes Stabilized by F−Cl···N Halogen Bonds, Base Protonation Energies (PE) and Experimental Proton Affinities (PA, kcal/mol)

complex	R(Cl−N) computed	R(Cl−N) exptl[a]	R(F−N)	$-\Delta E_e$	PE (PA)[b]
F−Cl···N_2	2.802	2.921[c]	4.444	2.3	121.2 (118)
F−Cl···NCF	2.578		4.231	5.3	168.8 (151)
F−Cl···NCH	2.541	2.693	4.197	5.8	173.8 (170.4)
F−Cl···$NCCH_3$	2.473	2.561[d]	4.135	7.1	189.7 (186.2)
F−Cl···NCLi	2.263		3.960	11.8	227.0
F−Cl···N_2H_2(Z)	2.231		3.928	9.1	195.1 (192.0)
F−Cl···N(H)CH_2	2.159		3.880	15.9	213.1 (203.8)
F−Cl···NH_2F	2.288		3.976	8.3	189.2
F−Cl···NH_3	2.235	2.371	3.949	11.7	210.6 (204.0)
F−Cl···N(H)$(CH_2)_2$	2.100		3.843	15.9	222.4 (214.9)
F−Cl···$NH_2(CH_3)$	2.116		3.869	16.5	221.9 (216.4)
F−Cl···$N(CH_3)_3$	2.042	2.090	3.834	23.9	233.8 (226.8)

[a] Experimental structural data from ref 23 except where noted. [b] Computed protonation energies; experimental proton affinities from ref 44. [c] Reference 43a. [d] Reference 43b.

the sp^3 hybridized N bases, again listed in order of increasing protonation energy (proton affinity), although the protonation energies and proton affinities of N(H)$(CH_2)_2$ and NH_2CH_3 are very similar, and these two measures of basicity are reversed for these two bases. Increasing base strength correlates with increasing binding energies of these complexes.

A comparison of the computed and experimental Cl−N distances indicates that the computed values underestimate the experimental. There are two factors which account for this difference, one related to the computed values and the other to the experimental values. The computed distances are R_e distances, whereas the experimental are R_o. Taking zero-point motion into account would lead to a lengthening of the equilibrium values of the Cl−N distance. On the other hand, the experimental distances were determined under the assumption of rigid monomer geometries. Optimization of the complexes FCl:NH_3 and FCl:$N(CH_3)_3$ under this same constraint leads to longer Cl−N distances of 2.335 and 2.143 Å, respectively. Nevertheless, from the perspective of the present investigation, the computed Cl−N distances are reasonable, and the decrease in the Cl−N distance observed experimentally upon methyl substitution in HCN and NH_3 is reproduced by the calculations.

The binding energies of complexes stabilized by F−Cl···N halogen bonds vary considerably, ranging from 2.3 kcal/mol for the complex with N_2, the weakest nitrogen base, to 23.9 kcal/mol for the complex with the strongest base, $N(CH_3)_3$. As noted previously by Legon,[23] these are comparable to the binding energies of corresponding hydrogen-bonded complexes. This is illustrated in Figure 1, which presents a plot of the binding energies for complexes with F−Cl···N halogen bonds versus the binding energies for corresponding complexes with F−H···N hydrogen bonds, both computed at MP2/aug′-cc-pVTZ. Figure 2 illustrates the relationship between the Cl···N and H···N distances in corresponding halogen-bonded and hydrogen-bonded complexes. Since the ground-state properties of complexes with halogen bonds have been discussed previously by others, no further discussion will be provided here except to relate the structures of these complexes to spin−spin coupling constants.

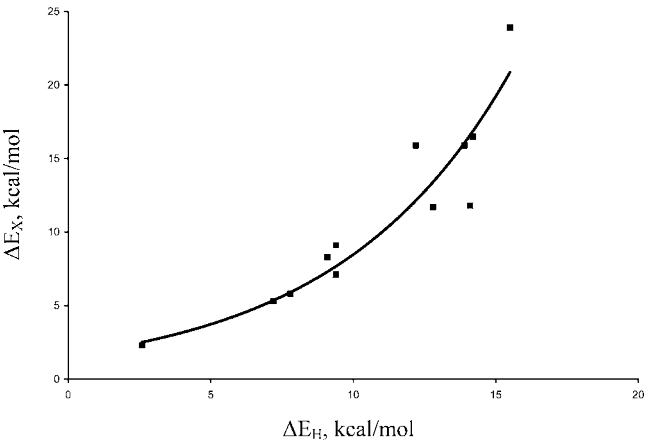

Figure 1. Binding energies (ΔE_X) for complexes with F−Cl···N halogen bonds vs binding energies (ΔE_H) for complexes with F−H···N hydrogen bonds. $\Delta E_X = 1.646\ e^{0.164\Delta E_H}$; $R^2 = 0.936$.

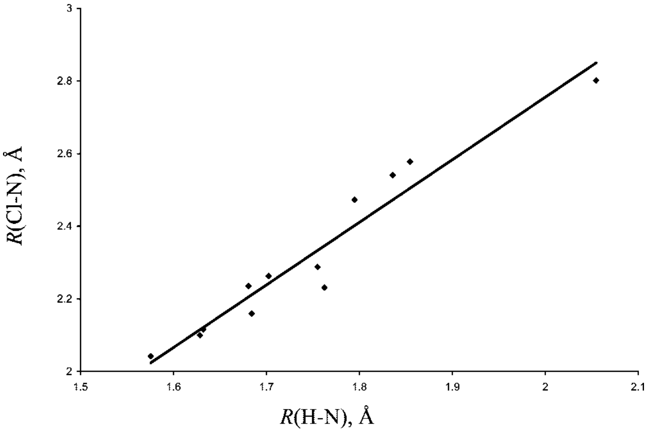

Figure 2. Cl···N distances R(Cl−N) in complexes with F−Cl···N halogen bonds vs H···N distances R(H−N) in complexes with F−H···N hydrogen bonds. $R(\text{Cl−N}) = 1.725\ R(\text{H−N}) - 0.695$; $R^2 = 0.936$.

TABLE 2: Spin−Spin Coupling Constants ^1J(F−Cl), ^{1X}J(Cl−N), and ^{2X}J(F−N) (Hz) across F−Cl···N Halogen Bonds

complex	^1J(F−Cl)[a]	^{1X}J(Cl−N)[b]	^{2X}J(F−N)
F−Cl···N_2	772.3	−13.9	−1.0
F−Cl···NCF	759.4	−32.1	−9.1
F−Cl···NCH	753.0	−32.7	−12.0
F−Cl···$NCCH_3$	747.5	−39.0	−18.3
F−Cl···NCLi	726.5	−51.6	−49.6
F−Cl···N(H)CH_2	679.6	−55.4	−73.0
F−Cl···N_2H_2(Z)	684.3	−57.0	−64.0
F−Cl···NH_2F	692.9	−54.3	−44.4
F−Cl···NH_3	693.6	−51.1	−48.6
F−Cl···N(H)$(CH_2)_2$	666.2	−58.6	−87.2
F−Cl···$NH_2(CH_3)$	663.5	−49.0	−70.8

[a] For F−Cl: R = 1.638 Å; ^1J(F−Cl) = 798.0 Hz. [b] For H_3NCl^+: R(Cl−N) = 1.736 Å; ^1J(Cl−N) = +8.5 Hz.

Spin−spin Coupling Constants for Complexes. *Components of J.* Spin−spin coupling constants for complexes of FCl with the nitrogen bases N_2, FCN, HCN, (CH_3)CN, LiCN, Z-HNNH, H_2CNH, NH_2F, NH_3, cyclic-NH$(CH_2)_2$, and $NH_2(CH_3)$ are reported in Table 2. Total coupling constants ^1J(F−Cl), ^{1X}J(Cl−N), and ^{2X}J(F−N) and the components of J are given for these complexes and the monomers FCl and H_3NCl^+ in Table S1 of the supporting data. From Table S1, it can be seen that ^{2X}J(F−N) is dominated by a negative FC term, due to a near cancelation of a positive PSO term with a negative SD term in the complexes with the sp nitrogen bases. With one exception (Z-N_2H_2), these terms have opposite signs in com-

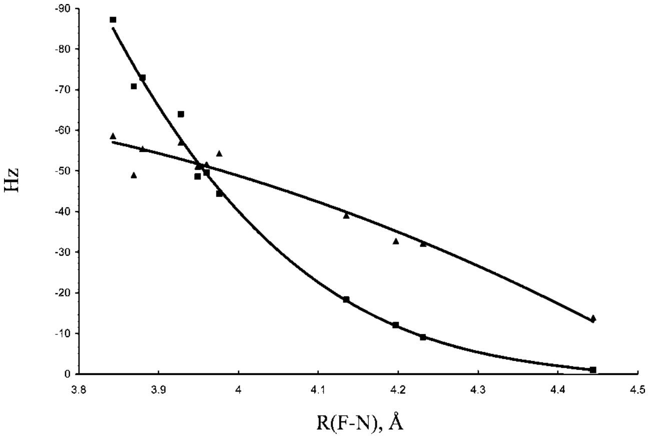

Figure 3. ^{2X}J(F−N) (■) and ^{1X}J(Cl−N) (▲) vs the F−N distance for complexes with F−Cl···N hlaogen bonds.

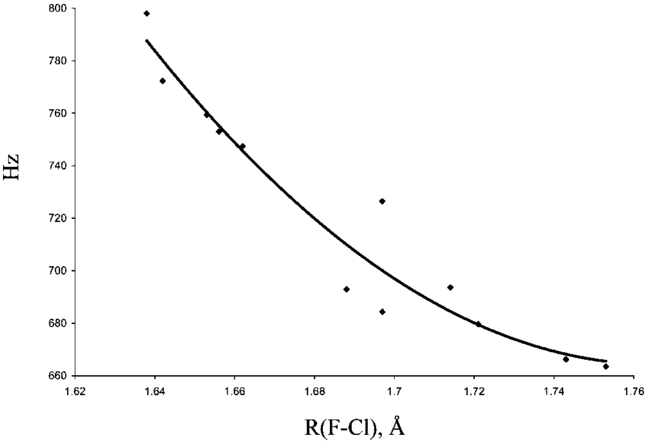

Figure 4. ^{1}J(F−Cl) vs the F−Cl distance for complexes with F−Cl···N halogen bonds.

plexes with the sp^2 and sp^3 bases, and although there is only a partial cancelation, the FC term still dominates.

^{1X}J(Cl−N) is negative in all complexes, ranging from −13 to −59 Hz. It is dominated by a negative FC term. It is interesting to note the difference between ^{1X}J(Cl−N) in the complexes relative to ^{1}J(Cl−N) for the isolated ion H_3NCl^+. In the ion the FC term has a positive value of 21.7 Hz and the PSO and SD terms have larger negative values compared to the complexes. Nevertheless, the FC term dominates and ^{1X}J(Cl−N) is +8.5 Hz in the isolated ion.

In contrast, the FC term does not dominate ^{1}J(F−Cl). For the isolated FCl monomer, the PSO and SD terms make large positive contributions of 642 and 255 Hz, respectively, while the FC term is relatively small and negative at −99 Hz. The FC term varies considerably in the complexes. It is large and negative for F−H...N_2, but decreases in absolute value and becomes positive in the complex with the strongest sp base, LiCN. It is positive for the complexes with the sp^2 bases. The FC term is only −2 Hz for F−Cl···NH_2F but then increases in the complexes with the sp^3 bases, having its largest value of 143 Hz for F−Cl···$N(CH_3)_3$. However, it is still the positive PSO and SD terms that dominate. Thus, ^{1}J(F−Cl) in the complexes is sensitive to the hybridization of the nitrogen and the strength of the base.

Coupling Constants across F−Cl···N Halogen Bonds. Table 2 lists the total coupling constants ^{1}J(F−Cl), ^{1X}J(Cl−N), and ^{2X}J(F−N) for the complexes of F−Cl with N_2, FCN, HCN, $(CH_3)CN$, LiCN, *Z*-HNNH, H_2CNH, NH_2F, NH_3, cyclic-$NH(CH_2)_2$, and $NH_2(CH_3)$. Figure 3 provides plots of the variation of ^{2X}J(F−N) and ^{1X}J(Cl−N) with the F−N distance. As evident from this figure, ^{2X}J(F−N) increases in absolute value as the F−N distance decreases. The equation of the third-order trendline shown in Figure 3 is

$$^{2X}J(\mathrm{F{-}N}) = 303.5R(\mathrm{F{-}N})^3 - 4060R(\mathrm{F{-}N})^2 + 1813R(\mathrm{F{-}N}) - 2701 \quad (1)$$

with a correlation coefficient of 0.990. [A second-order curve also fits the data well with a correlation coefficient of 0.988, but it has its extremum at R(F−N) = 4.38Å.] The increase in the absolute value of ^{2X}J(F−N) with decreasing F−N distance is similar to the increase in ^{2h}J(F−N) with decreasing distance for complexes with F−H···N hydrogen bonds.[25] All of the two-bond coupling constants ^{2X}J(F−N) across F−Cl···N halogen bonds are negative. Since the magnetogyric ratio of ^{19}F is positive whereas that of ^{15}N is negative, the reduced two-bond coupling constants ^{2X}K(F−N) are positive. Thus, reduced two-bond coupling constants across both hydrogen bonds[45] and halogen bonds are positive.

Also shown in Figure 3 is the variation of ^{1X}J(Cl−N) with the F−N distance. The equation of the trendline is

$$^{1X}J(\mathrm{Cl{-}N}) = 46.97R(\mathrm{F{-}N})^2 - 315.9R(\mathrm{F{-}N}) + 463.1 \quad (2)$$

with a correlation coefficient of 0.953. It is interesting to note the difference between the curvature of the trendline for ^{1X}J(Cl−N) and that for ^{2X}J(F−N). While it may have been anticipated that ^{1X}J(Cl−N) should be better correlated with the Cl−N distance, such is not the case. A plot of ^{1X}J(Cl−N) versus the Cl−N distance has a curvature similar to that shown in Figure 3, with a lower correlation coefficient of 0.946.

^{1}J(F−Cl) in the monomer is 798 Hz, and decreases in the complexes as it ranges from 772 Hz in FCl:N_2 to 664 Hz in FCl:$NH_2(CH_3)$. In this respect, ^{1}J(F−Cl) resembles ^{1}J(F−H) for complexes with F−H···N hydrogen bonds. The variation of ^{1}J(F−Cl) with the F−Cl distance is shown in Figure 4. The equation of the trendline is

$$^{1}J(\mathrm{F{-}Cl}) = 7543R(\mathrm{F{-}Cl})^2 - 2664R(\mathrm{F{-}Cl}) + 2419 \quad (3)$$

with a correlation coefficient of only 0.934. ^{1}J(F−Cl) appears to be sensitive to the hybridization of the nitrogen base. For example, the F−Cl distances in the complexes of F−Cl with LiCN and *Z*-N_2H_2 are identical at 1.697 Å, but ^{1}J(F−Cl) is 727 Hz in the former and 684 Hz in the latter. The smaller decrease in ^{1}J(F−Cl) upon complexation with LiCN resembles the smaller decreases observed for the sp-hybridized bases. Moreover, in Figure 4 there are four points which lie in the F−Cl distance interval from 1.688 to 1.714 Å. The one with the largest coupling constant belongs to the sp base LiCN, while the remaining three belong to sp^2 (Z-N_2H_2), and sp^3 bases (NH_2F and NH_3). As measured by its protonation energy, LiCN is a stronger base than any of the sp^2 and sp^3 hybridized bases, except for $N(CH_3)_3$. Nevertheless, the decrease in ^{1}J(F−Cl) for the F−Cl···NCLi complex is much less than would be expected from the F−Cl distance and the base strength of NCLi. Thus, the point for this complex lies far from the trendline shown in Figure 4.

Coupling Constants across the Chlorine-Transfer Coordinate. In a previous study, changes in one- and two-bond spin−spin coupling constants along the proton-transfer coordinate were characterized for FH:NH_3 and FH:pyridine complexes.[24] As the proton is transferred from F to N, ^{1}J(F−H)

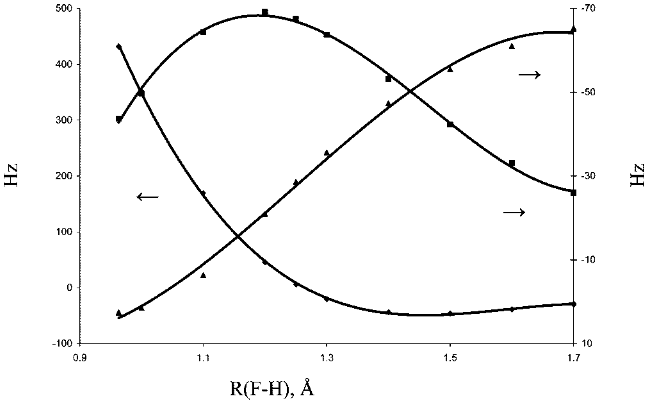

Figure 5. ^{2h}J(F−N) (■), ^{1h}J(H−N) (▲), and ^{1}J(F−H) (♦) vs the F−H distance across the proton-transfer coordinate in F−H···NH$_3$.

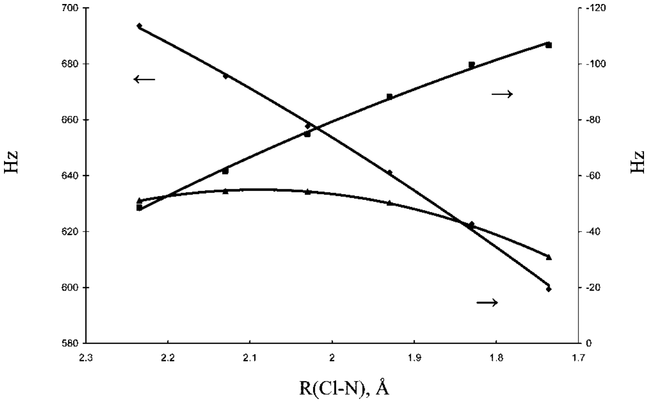

Figure 6. ^{2X}J(F−N) (■), ^{1X}J(Cl−N) (▲), and ^{1}J(F−Cl) (♦) vs the Cl−N distance across the Cl-transfer coordinate in F−Cl···NH$_3$.

decreases and changes sign as the F−H distance increases, and ^{1h}J(H−N) increases in absolute value as the N−H distance decreases, asymptotically approaching its value for the corresponding isolated protonated base. Along this same coordinate, ^{2h}J(F−N) initially increases in absolute value with decreasing F−N distance, reaches a maximum when the F−N distance is shortest and the hydrogen bond becomes quasi-symmetric proton-shared, and then decreases as the F−N distance increases and an ion-pair complex is formed. A plot illustrating the changes in ^{1}J(F−H), ^{1h}J(H−N), and ^{2h}J(F−N) across the proton-transfer coordinate for FH···NH$_3$ as a function of the F−H distance is given in Figure 5. The computed variations in these coupling constants are consistent with experimental data for changes in spin−spin coupling constants for FH:collidine as a function of temperature.[46,47] Subsequently, both ^{2h}J(X−Y) and the sign of ^{1h}J(H−Y) for X−H···Y hydrogen bonds have been shown to be NMR fingerprints of hydrogen bond type.[48]

How do the corresponding distances and coupling constants change across the chlorine-transfer coordinate for F−Cl···NH$_3$? As chlorine transfer occurs, the F−Cl distance exhibits only a relatively small change, increasing from 1.714 Å in the equilibrium structure to 1.843 Å in the ion-pair. Simultaneously, the F−N distance decreases continuously from 3.949 Å at equilibrium to 3.579 Å in the ion-pair. There is no contraction and then expansion of the F−N distance accompanying chlorine transfer as there is in proton transfer.

Figure 6 shows the variation of ^{1}J(F−Cl), ^{1X}J(Cl−N), and ^{2X}J(F−N) along the chlorine-transfer coordinate. ^{1}J(F−Cl) decreases from 694 to 599 Hz as the F−Cl distance increases, a change similar to the variation of ^{1}J(F−H) for proton transfer in FH···NH$_3$. It is here that the similarity ends. Along the proton-transfer coordinate, ^{1}J(F−H) is dominated by the FC term, which decreases and changes sign. Along the Cl-transfer coordinate, the FC term dominates ^{1}J(F−Cl) at equilibium and then decreases but does not change sign as Cl approaches N. Moreover, along this coordinate, the positive PSO and SD terms increase and are the dominant terms in the ion-pair complex. There is no sign change in ^{1}J(F−Cl) along the chlorine-transfer coordinate. The second one-bond coupling constant, ^{1X}J(Cl−N), initially increases slightly in absolute value from −51 to −54 Hz and then decreases to −31 Hz in the ion-pair as the Cl−N distance decreases. However, the value of ^{1}J(Cl−N) in the ion-pair complex F$^-$:$^+$ClNH$_3$ at a Cl−N distance of 1.736 Å does not approach the value of ^{1}J(Cl−N) for the isolated ion H$_3$NCl$^+$, which is +9 Hz. This may be attributed to the close proximity of F$^-$ to Cl in the ion-pair and its influence on the chlorine and nitrogen electron distributions in both the ground state and the excited electronic states which couple to it. An MP2 ground-state density analysis indicates a large alternation of charge [F (−0.41e), Cl (+0.25e), N (−0.49e)] in the ion-pair complex. In the isolated ion the chlorine bears a positive charge of +0.32e, but N is essentially uncharged (−0.04e). Finally, as the F−N distance continuously decreases along the chlorine-transfer coordinate, the two-bond spin−spin coupling constant ^{2X}J(F−N) continuously increases in absolute value from −49 to −107 Hz. This curve has no extremum value indicative of a “chlorine-shared” halogen bond. The ^{1X}J(Cl−N) and ^{2X}J(F−N) curves are quite different from the corresponding curves for ^{1h}J(H−N) and ^{2h}J(F−N) across the proton-transfer coordinate. Nevertheless, the changes in ^{1}J(F−Cl), ^{1X}J(Cl−N), and ^{2X}J(F−N) are large, and should be amenable to experimental study.

Conclusions

Ab initio EOM-CCSD calculations have been performed to determine one- and two-bond spin−spin coupling constants ^{1}J(F−Cl), ^{1X}J(Cl−N), and ^{2X}J(F−N) across F−Cl···N halogen bonds in complexes with F−Cl as the Lewis acid and N$_2$, FCN, HCN, (CH$_3$)CN, LiCN, *Z*-HNNH, H$_2$CNH, NH$_2$F, NH$_3$, cyclic NH(CH$_2$)$_2$, and NH$_2$(CH$_3$) as Lewis bases. The following statements are supported by these calculations.

(1) ^{2X}J(F−N) increases in absolute value in these complexes as the F−N distance decreases, a behavior similar to that of ^{2h}J(F−N) for complexes stabilized by F−H···N hydrogen bonds. In addition, the reduced two-bond coupling constants ^{2X}K(F−N) are positive, as are the reduced two-bond coupling constants ^{2h}K(X−Y) across X−H···Y hydrogen bonds.

(2) The absolute value of ^{1X}J(Cl−N) also increases with decreasing F−N distance, and has a slightly better correlation with this distance than with the Cl−N distance.

(3) ^{1}J(F−Cl) is always positive, decreases upon complex formation, and appears to be sensitive to the strength and hybridization of the nitrogen base.

(4) Along the chlorine-transfer coordinate in F−Cl···NH$_3$, ^{1}J(F−Cl) decreases but remains positive, ^{2X}J(F−N) continuously increases in absolute value, and ^{1X}J(Cl−N) initially increases in absolute value and then decreases but remains negative. Its value in the ion-pair complex does not approach the value of ^{1}J(Cl−N) for isolated H$_3$NCl$^+$.

(5) The relatively large variations in the one- and two-bond coupling constants across F−Cl···N halogen bonds in the various complexes and their variation along the chlorine-transfer coordinate for F−Cl···NH$_3$ suggest that they should be amenable to experimental investigation.

Acknowledgment. Thanks are due to the Ohio Supercomputer Center for continuing support of this research. This work was carried out with financial support from the Ministerio de Educación y Ciencia (Project No. CTQ2007-61901/BQU) and Comunidad Autónoma de Madrid (Project MADRISOLAR, ref S-0505/PPQ/0225).

Supporting Information Available: Coupling constants *J* and the components of *J* for all complexes investigated in this study. Also included are the full citations for refs 34 and 42. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Alkorta, I.; Rozas, I.; Elguero, J. *J. Phys. Chem. A* **1998**, *102*, 9278.

(2) Ouvard, C.; Le Questel, J.-Y.; Berthelot, M.; Laurence, C. *Acta. Crystallogr. Sect. B* **2003**, *B59*, 512.

(3) Karpfen, A. *Theor. Chem. Acc.* **2003**, *110*, 1.

(4) Auffinger, P.; Hays, F. A.; Westhof, E.; Ho, P. S. *Proc. Natl. Acad. Sci.* **2004**, *101*, 16789.

(5) Glaser, R.; Chen, N.; Wu, H.; Knotts, N.; Kaupp, M. *J. Am. Chem. Soc.* **2004**, *126*, 4412.

(6) Wang, W.; Wong, N.-B.; Zheng, W.; Tian, A. *J. Phys. Chem. A* **2004**, *108*, 1799.

(7) Berski, S.; Ciunik, Z.; Drabent, K.; Latajka, Z.; Panek, J. *J. Phys. Chem. B* **2004**, *108*, 12327.

(8) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. *Acc. Chem. Res.* **2005**, *38*, 386.

(9) Zou, J.-W.; Jiang, Y.-J.; Guo, M.; Hu, G.-X.; Zhang, B.; Liu, H.-C.; Yu, Q.-S. *Chem. Eur. J.* **2005**, *11*, 740.

(10) Zou, J.-W.; Lu, Y.-X.; Yu, Q.-S.; Zhang, H.-X.; Jiang, Y.-J. *Chin. J. Chem.* **2006**, *24*, 1709.

(11) Grabowski, S. J.; Bilewicz, E. *Chem. Phys. Lett.* **2006**, *427*, 51.

(12) Aakeröy, C. B.; Desper, J.; Helfrich, B. A.; Metrangolo, P.; Pilati, T.; Resnati, G.; Stevenazzi, A. *Chem. Commun.* **2007**, 4236.

(13) Lu, Y.-X.; Zou, J.-W.; Yu, Q.-S.; Jiang, Y.-J.; Zhao, W.-N. *Chem. Phys. Lett.* **2007**, *449*, 6.

(14) Lu, Y.-X.; Zou, J.-W.; Wang, Y.-H.; Yu, Q.-S. *Int. J. Quantum Chem.* **2007**, *107*, 1479.

(15) Aakeröy, C. B.; Fasulo, M.; Schultheiss, N.; Desper, J.; Moore, C. *J. Am. Chem. Soc.* **2007**, *129*, 13772.

(16) Riley, K. E.; Merz, K. M., Jr *J. Phys. Chem. A* **2007**, *111*, 1688.

(17) Alkorta, I.; Solimannejad, M.; Provasi, P.; Elguero, J. *J. Phys. Chem. A* **2007**, *111*, 7154.

(18) Lu, Y.-X.; Zou, J.-W.; Wang, Y.-H.; Jiang, Y.-J.; Yu, Q.-S. *J. Phys. Chem. A* **2007**, *111*, 10781.

(19) Palusiak, M.; Grabowski, S. J. *Struc. Chem.* **2007**, *18*, 859.

(20) Voth, A. R.; Hays, F. A.; Ho, P. S. *Proc. Natl. Acad. Sci.* **2007**, *104*, 6188.

(21) Wang, Y.; Li, L.; Lu, Y.; Zoub, J. *J. Chem. Phys.* **2007**, *20*, 531.

(22) Wang, W.; Hobza, P. *J. Phys. Chem. A* **2008**, *112*, 4114.

(23) Legon, A. C. *Struc. Bond* **2008**, *126*, 17, and references therein (from Metrangolo, P.; Resnati, G. *Halogen Bonding: Fundamentals and Applications*; Springer: Berlin, 2008).

(24) Del Bene, J. E.; Bartlett, R. J.; Elguero, J. *Magn. Reson. Chem.* **2002**, *40*, 767.

(25) Del Bene, J. E.; Perera, S. A.; Bartlett, R. J.; Yáñez, M.; Mó, O.; Elguero, J.; Alkorta, I. *J. Phys. Chem. A* **2003**, *107*, 3121.

(26) Del Bene, J. E.; Elguero, J. *J. Phys. Chem. A.* **2005**, *109*, 10759.

(27) Del Bene, J. E.; Elguero, J. *J. Phys. Chem. A.* **2006**, *110*, 1128.

(28) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1976**, *10*, 1.

(29) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(30) Bartlett, R.J.; Silver, D. M. *J. Chem. Phys.* **1975**, *62*, 3258.

(31) Bartlett, R.J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561.

(32) Dunning, T. H. Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(33) Woon, D. E.; Dunning, T.H. Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(34) Frisch, M. J., et al. *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004.

(35) Perera, S. A.; Sekino, H.; Bartlett, R.J. *J. Chem. Phys.* **1994**, *101*, 2186.

(36) Perera, S. A.; Nooijen, M.; Bartlett, R.J. *J. Chem. Phys.* **1996**, *104*, 3290.

(37) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 8476.

(38) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 7849.

(39) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(40) Del Bene, J. E.; Elguero, J.; Alkorta, I.; Yañez, M.; Mó, O. *J. Phys. Chem. A.* **2006**, *110*, 9959.

(41) Kirpekar, S.; Jensen, H. J. Aa.; Oddershede, J. *Chem. Phys.* **1994**, *188*, 171.

(42) Stanton, J. F. et al. *ACE II a program product of the Quantum Theory Project*; University of Florida: Gainesville, FL.

(43) (a) Cooke, S. A.; Cotti, G.; Hinds, K.; Holloway, J. H.; Legon, A. C.; Lister, D. G. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2671. (b) Page, M. D.; Waclawik, E. R.; Holloway, J. H.; Legon, A. C. *J. Mol. Struct.* **1999**, *509*, 55.

(44) Linstrom, P. J., Mallard, W. G., Eds.; In *NIST Chemistry Webbook*; NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg, MD, 2003. (http://webbook.nist.gov.).

(45) Del Bene, J. E.; Elguero, J. *Magn. Reson. Chem.* **2004**, *42*, 421.

(46) Shenderovich, I. G.; Burtsev, A. P.; Denisov, G. S.; Golubev, N. S.; Limbach, H.-H. *Magn. Reson. Chem.* **2001**, *39*, S91.

(47) Golubev, N. S.; Shenderovich, I. G.; Smirnov, S. N.; Denisov, G. S.; Limbach, H.-H. *Chem. Eur. J.* **1999**, *5*, 492.

(48) Del Bene, J. E.; Elguero, J. In *Computational Chemistry: Review of Current Trends*; Leszczynski, J., Ed.; World Scientific Publishing Co. Pte. LTD.: Singapore, 2006; Vol. 10, pp 229−264.

JP804119R