

# Interpreting $^{2\text{h}}J(\text{F},\text{N})$ , $^{1\text{h}}J(\text{H},\text{N})$ and $^1J(\text{F},\text{H})$ in the hydrogen-bonded FH–collidine complex<sup>†</sup>

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*Ab initio* EOM-CCSD calculations were performed to determine  $^{19}\text{F}, ^1\text{H}$ ,  $^{19}\text{F}, ^{15}\text{N}$  and  $^1\text{H}, ^{15}\text{N}$  spin–spin coupling constants in model complexes FH–NH<sub>3</sub> and FH–pyridine as a function of the F–H and F–N distances. The absolute value of  $^1J(\text{F},\text{H})$  decreases and that of  $^{1\text{h}}J(\text{H},\text{N})$  increases rapidly along the proton-transfer coordinate, even in the region of the proton-shared F–H–N hydrogen bond. In contrast,  $^{2\text{h}}J(\text{F},\text{N})$  remains essentially constant in this region. These results are consistent with the recently reported experimental NMR spectra of FH–collidine which show that  $^{1\text{h}}J(\text{H},\text{N})$  increases and  $^1J(\text{F},\text{H})$  decreases, while  $^{2\text{h}}J(\text{F},\text{N})$  remains constant as the temperature of the solution decreases. They suggest that the FH–collidine complex is stabilized by a proton-shared hydrogen bond over the range of experimental temperatures investigated, being on the traditional side of quasi-symmetric at high temperatures, and on the ion-pair side at low temperatures. Copyright © 2002 John Wiley & Sons, Ltd.

**KEYWORDS:** NMR;  $^1\text{H}$  NMR;  $^{15}\text{N}$  NMR;  $^{19}\text{F}$  NMR; spin–spin coupling; hydrogen bonds; FH–collidine complex

## INTRODUCTION

In recent papers, Limbach and co-workers reported NMR spin–spin coupling constants for the hydrogen-bonded FH–collidine (FH–2,4,6-trimethylpyridine) complex in solution as a function of temperature.<sup>1,2</sup> They observed that whereas the one-bond  $^{19}\text{F}, ^1\text{H}$  [ $^1J(\text{F},\text{H})$ ] and  $^1\text{H}, ^{15}\text{N}$  [ $^{1\text{h}}J(\text{H},\text{N})$ ] coupling constants changed over the range of temperatures investigated, the two-bond  $^{15}\text{F}, ^{19}\text{N}$  [ $^{2\text{h}}J(\text{F},\text{N})$ ] coupling constant across the F–H–N hydrogen bond was constant to within 5 Hz. They suggested that as a function of temperature and therefore changing dielectric constant of the solvent, the hydrogen-bonded proton moved from its position closer to the F atom at higher temperature, through a quasi-symmetric hydrogen bond, to a position closer to the N atom at lower temperature. They described these changes in terms of changing hydrogen-bond type, from traditional, to proton-shared, to zwitterion pair. Such a change would be consistent with their previous experimental observations,<sup>3–5</sup> and with computed data which suggest that an electric field can lead to proton transfer, a change in hydrogen bond type and changes in NMR spin–spin coupling constants across hydrogen bonds.<sup>6–20</sup> However, the proton transfer process

is usually associated with a change in the distance between the hydrogen-bonded atoms. If the hydrogen-bonding F–N distance were changing, it would be expected that  $^{2\text{h}}J(\text{F},\text{N})$ , which is distance dependent, should also change with temperature, but this was not observed experimentally. In this work, we examined  $^{2\text{h}}J(\text{F},\text{N})$ ,  $^{1\text{h}}J(\text{H},\text{N})$  and  $^1J(\text{F},\text{H})$  in two model systems, FH–NH<sub>3</sub> and FH–pyridine, to investigate these properties further and gain insight into the proton transfer process that gives rise to the temperature-dependent NMR spectra of FH–collidine.

## METHODS

The equilibrium structures of the complexes FH–NH<sub>3</sub>, FH–pyridine and FH–collidine were fully optimized at second-order many-body perturbation theory [MPBT(2)]<sup>21–24</sup> with the 6–31+G(d,p) basis set.<sup>25–28</sup> To mimic structural changes that accompany proton transfer and changing hydrogen bond type, the F–H distance in FH–NH<sub>3</sub> was set to 1.00 Å and then varied in increments of 0.10 Å to 1.70 Å. A structure with the F–H distance set to 1.25 Å was also included. For FH–pyridine, the F–H distance was varied between 1.10 and 1.50 Å. At each fixed F–H distance, the structures of these two complexes were fully optimized.

Equation-of-motion coupled cluster singles and doubles calculations (EOM-CCSD) employing the CI-like approximation<sup>29–32</sup> and the Ahlrichs basis set (qzp on C, N and F and qz2p on the hydrogen-bonded proton)<sup>33</sup> and the Dunning cc-pVDZ basis set<sup>34,35</sup> on all other hydrogens were performed to evaluate  $^{19}\text{F}, ^1\text{H}$ ,  $^{19}\text{F}, ^{15}\text{N}$  and  $^1\text{H}, ^{15}\text{N}$  spin–spin coupling constants for all of the optimized structures of

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FH-NH<sub>3</sub> and FH-pyridine. Because of the larger size and lower symmetry of FH-collidine, EOM-CCSD calculations on this complex are not feasible. Structure optimizations were done using Gaussian 98<sup>36</sup> and coupling constants were evaluated using ACES II.<sup>37</sup> All of the calculations were performed on the SV1 computer at the Ohio Supercomputer Center.

## RESULTS AND DISCUSSION

The F—H and F—N distances in the equilibrium structures of FH-NH<sub>3</sub>, FH-pyridine and FH-collidine are reported in Table 1. From these data, it is apparent that although these three complexes have equilibrium structures with traditional F—H...N hydrogen bonds, the proton-shared character of the hydrogen bond increases in the order FH-NH<sub>3</sub> < FH-pyridine < FH-collidine. As is evident from Table 1, this change parallels the order of increasing gas-phase basicity of these nitrogen bases.<sup>38</sup>

The optimized F—N distances for fixed F—H distances in FH-NH<sub>3</sub> and FH-pyridine are reported in Tables 2 and 3, respectively. From these data, it can be seen that as the F—H distance increases, the F—N distance initially decreases, is a minimum for complexes with proton-shared hydrogen bonds and then increases as the hydrogen bond assumes ion-pair character.

Table 2 also lists the computed coupling constants <sup>2h</sup>J(F,N), <sup>1h</sup>J(H,N) and <sup>1</sup>J(F,H) for FH-NH<sub>3</sub> that have been evaluated as the sum of the paramagnetic spin-orbit (PSO), diamagnetic spin-orbit (DSO), Fermi-contact (FC) and spin-dipole (SD) terms. Figure 1 presents plots of these three coupling constants and of the corresponding Fermi-contact terms as a function of the F—H distance. The following generalizations are based on these data.

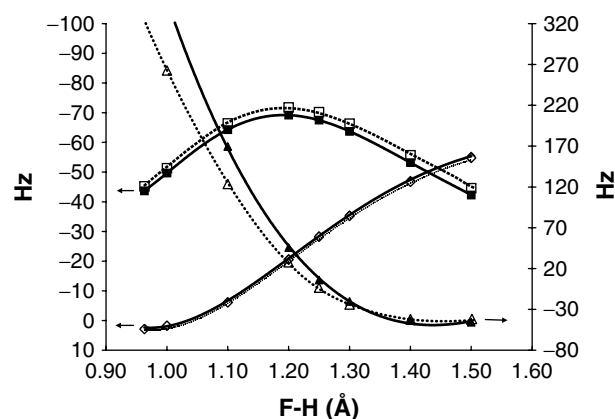
1. The variation in the Fermi-contact term as a function of F—H distance determines the distance dependence of <sup>2h</sup>J(F,N), <sup>1h</sup>J(H,N) and <sup>1</sup>J(F,H).
2. <sup>2h</sup>J(F,N) can be approximated by the Fermi-contact term. The absolute value of this term initially increases as the F—N distance decreases, exhibits a maximum value for structures which have proton-shared hydrogen bonds with short F—N distances and then decreases as the F—N distance increases and the hydrogen bond assumes greater ion-pair character.

**Table 1.** Equilibrium F—H and F—N distances (Å) and gas-phase basicities [kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ)] for FH-NH<sub>3</sub>, FH-pyridine and FH-collidine

Complex	F—H	F—N	Gas-phase basicity
FH-NH <sub>3</sub>	0.963	2.637	195.7 <sup>a</sup>
FH-pyridine	0.967	2.611	214.7 <sup>a</sup>
FH-collidine	0.974	2.593	227.8 <sup>b</sup>

<sup>a</sup> Ref. 38.

<sup>b</sup> The gas-phase basicity of collidine is not known experimentally. The value given is based on additivity considerations using the basicities of 4-picoline and 2,6-lutidine reported in Ref. 38.



**Figure 1.** Total <sup>19</sup>F,<sup>15</sup>N, <sup>1</sup>H,<sup>15</sup>N and <sup>19</sup>F,<sup>1</sup>H spin-spin coupling constants and the corresponding Fermi contact (FC) terms for FH-NH<sub>3</sub> as a function of F—H distance. ■, <sup>2h</sup>J(F,N); ◆, <sup>1h</sup>J(H,N); ▲, <sup>1</sup>J(F,H); □, F,N FC term; ◇, H,N FC term; △, F—H FC term. The filled symbol ◆ for total J and the open symbol ◇ for the Fermi contact term for H,N coupling are essentially superimposed.

3. <sup>1h</sup>J(H,N) can also be approximated by the Fermi-contact term over the range of F—H (and therefore H—N) distances considered. The value of <sup>1h</sup>J(H,N) at equilibrium is small but positive, but it increases (in an absolute sense) as the H—N distance decreases.
4. Although <sup>1</sup>J(F,H) is dominated by the Fermi-contact term, the PSO term makes a significant contribution to the total coupling constant, particularly at short F—H distances. However, both the Fermi-contact term and <sup>1</sup>J(F,H) show a similar distance dependence, decreasing with increasing F—H distance.
5. The largest (absolute) value of <sup>2h</sup>J(F,N) occurs at an F—H distance of 1.20 Å when the F—N distance is shortest and the hydrogen bond approaches a quasi-symmetric proton-shared hydrogen bond. However, in the range of F—H distances from 1.10 to 1.30 Å, the F—N distance varies by only 0.034 Å and <sup>2h</sup>J(F,N) varies by 5.5 Hz. In this same interval, <sup>1</sup>J(F,H) decreases from 169.5 to -20.3 Hz, and <sup>1h</sup>J(H,N) increases from -6.4 to -35.6 Hz.

Since evaluating all of the terms which contribute to the total spin-spin coupling constants for FH-pyridine is not computationally feasible, only the Fermi contact term has been computed using the EOM-CCSD formalism. The computed values for the optimized FH-pyridine complexes as a function of the F—H distance are reported in Table 3 and plotted in Fig. 2. The following generalizations are based on these data.

1. At a given F—H distance, the F—N distance in FH-pyridine is shorter than the F—N distance in FH-NH<sub>3</sub>. The shorter F—N distances and the dependence exhibited by F,N spin-spin coupling constants on the bonding at the nitrogen in complexes with F—H...N hydrogen bonds (J. E. Del Bene, to be published) produce larger values of the F,N spin-spin coupling constant for FH-pyridine than FH-NH<sub>3</sub>.
2. Although the F,H coupling constant at short F—H distances cannot be approximated by the Fermi contact

**Table 2.** F,H, F,N and H,N spin-spin coupling constants [ $^1J(\text{F,H})$ ,  $^{2h}J(\text{F,N})$ ,  $^{1h}J(\text{H,N})$ , Hz] and components of  $J^a$  for FH-NH<sub>3</sub> as a function of F-N and F-H distances (Å)

Coupling constant	Bond		PSO	DSO	Fermi	SD	Total $J$
	F—H	F—N					
$^1J(\text{F,H})$	0.963	2.637	108.8	1.3	325.5	-4.1	431.5
	1.00	2.605	93.3	1.4	262.7	-6.5	350.9
	1.10	2.532	53.5	1.9	123.5	-9.4	169.5
	1.20	2.498	23.9	2.4	27.6	-8.3	45.6
	1.25	2.498	13.9	2.6	-3.5	-7.1	5.9
	1.30	2.509	6.9	2.7	-24.1	-5.8	-20.3
	1.40	2.552	-1.2	2.9	-42.1	-3.5	-43.9
	1.50	2.614	-4.3	2.9	-42.5	-1.8	-45.7
	1.60	2.690	-5.1	2.8	-35.9	-0.6	-38.8
	1.70	2.772	-4.7	2.7	-27.8	0.3	-29.5
$^{2h}J(\text{F,N})$	F—H	F—N					
	0.963	2.637	2.8	0.0	-45.2	-1.3	-43.7
	1.00	2.605	3.2	0.0	-51.3	-1.6	-49.7
	1.10	2.532	4.2	0.0	-66.4	-2.1	-64.3
	1.20	2.498	4.8	0.0	-71.8	-2.2	-69.2
	1.25	2.498	4.9	0.0	-70.2	-2.2	-67.5
	1.30	2.509	4.8	0.0	-66.3	-2.2	-63.7
	1.40	2.552	4.6	0.0	-55.7	-2.1	-53.2
	1.50	2.614	4.2	0.0	-44.6	-1.9	-42.3
	1.60	2.690	3.8	0.0	-35.1	-1.8	-33.1
1.70	2.772	3.3	0.0	-27.7	-1.6	-26.0	
$^{1h}J(\text{H,N})$	F—H	H—N					
	0.963	1.674	0.5	-0.5	2.9	-0.3	2.6
	1.00	1.605	0.5	-0.5	1.8	-0.3	1.5
	1.10	1.432	0.4	-0.4	-6.1	-0.3	-6.4
	1.20	1.298	0.3	-0.4	-20.5	-0.3	-20.9
	1.25	1.238	0.2	-0.4	-28.2	-0.2	-28.6
	1.30	1.209	0.1	-0.3	-35.2	-0.2	-35.6
	1.40	1.152	-0.1	-0.3	-46.7	-0.2	-47.3
	1.50	1.114	-0.3	-0.2	-54.8	-0.1	-55.4
	1.60	1.090	-0.4	-0.2	-60.3	-0.1	-61.0
1.70	1.072	-0.6	-0.2	-64.3	-0.1	-65.2	

<sup>a</sup> PSO = paramagnetic spin-orbit; DSO = diamagnetic spin-orbit; Fermi = Fermi contact; SD = spin dipole.

term, the distance dependence of the Fermi contact terms for F,N, F,H and H,N coupling in FH-pyridine is similar to the distance dependence of these terms and the corresponding total spin-spin coupling constants for FH-NH<sub>3</sub>.

- The region of the proton-shared hydrogen bond extends from an F—H distance of 1.10 to 1.30 Å. In this interval, the F—N distance varies by only 0.019 Å, and the F,N spin-spin coupling constant changes by 7.9 Hz, exhibiting a maximum value of -90.0 Hz when the F—H distance is 1.20 Å and the F—N distance is 2.480 Å. The FH-pyridine complex at this geometry has a hydrogen bond which approaches a quasi-symmetric proton-shared hydrogen bond. In this same interval, the F—H Fermi contact term decreases from 121.4 to -28.4 Hz, and the absolute value of the H—N Fermi contact term increases from -11.7

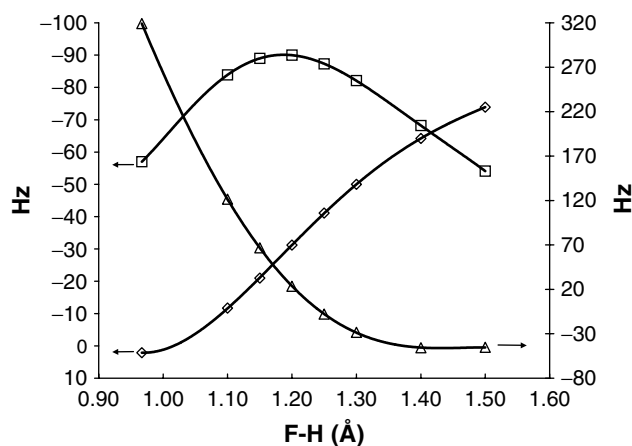
to -50.0 Hz. Thus, in the region with a proton-shared hydrogen bond, large changes in the F—H distance (and therefore the H—N distance) occur while the F—N distance remains nearly constant. As a result, the one-bond F,H and H,N coupling constants change dramatically, whereas the two-bond F,N coupling constant shows little variation.

Based on our computed results, we offer the following analysis of the FH-collidine complex and its NMR spectra.

- In the gas phase, FH-collidine is stabilized by a hydrogen bond that has greater proton-shared character than that of FH-pyridine, as reflected in its longer F—H and shorter F—N distances at equilibrium. However, it is anticipated that the F—H distance is longer and the F—N distance shorter in the ground vibrational state of

**Table 3.** Fermi contact term contributions to F,H, F,N and H,N spin–spin coupling constants for FH–pyridine as a function of F–N and F–H distances (Å)

F–H	F–N	Fermi contact contribution to ${}^{2h}J(\text{F,N})$	Fermi contact contribution to ${}^1J(\text{F,H})$	Fermi contact contribution to ${}^{1h}J(\text{H,N})$
0.967	2.611	–57.0	319.1	2.1
1.10	2.509	–83.9	121.4	–11.7
1.15	2.489	–89.0	66.7	–21.0
1.20	2.480	–90.0	23.5	–31.2
1.25	2.484	–87.3	–7.8	–41.1
1.30	2.494	–82.1	–28.4	–50.0
1.40	2.540	–68.2	–45.7	–64.2
1.50	2.605	–54.1	–45.3	–73.9

**Figure 2.** Fermi contact contributions to the total  ${}^{19}\text{F}$ ,  ${}^{15}\text{N}$ ,  ${}^1\text{H}$ ,  ${}^{15}\text{N}$  and  ${}^{19}\text{F}$ ,  ${}^1\text{H}$  spin–spin coupling constants for FH–pyridine as a function of the F–H distance. □, F,N; ◇, H,N; △, F,H.

this complex.<sup>11,17</sup> Thus, even at the highest temperature at which the experimental measurements were made in Ref. 1, this complex has a hydrogen bond which is proton-shared, although it is probably on the traditional side of a quasi-symmetric proton-shared hydrogen bond.

- In the experiments reported in Ref. 1, it was suggested that as the temperature is decreased, the proton moves away from the F atom and closer to the N atom. We agree with this statement, but emphasize that the hydrogen bond remains a proton-shared hydrogen bond as the proton moves, and the F–N distance is essentially constant. At the highest temperatures the hydrogen bond is on the traditional side of quasi-symmetric, and at the lowest temperatures on the ion-pair side. As a result, the two-bond F,N spin–spin coupling constant is essentially unchanged, whereas the F,H and H,N coupling constants change dramatically with temperature.
- Shenderovich *et al.*<sup>1</sup> characterized the quasi-symmetric hydrogen-bonded FH–collidine complex by the following NMR parameters:  ${}^{2h}J(\text{F,N}) = -96$  Hz,  ${}^1J(\text{F,H}) = 30$  Hz and  ${}^{1h}J(\text{H,N}) = -50$  Hz. These data are consistent with

the data for FH–pyridine in the proton-shared region from an F–H distance of 1.10 to 1.30 Å, as shown graphically in Fig. 2. We would expect the experimental F,H coupling constant to be greater than the values of the Fermi contact term in this region that are shown in this figure and reported in Table 3, and similar to  ${}^1J(\text{F,H})$  values for FH–NH<sub>3</sub>. Hence the computed NMR spin–spin coupling constants for the FH–pyridine model complex are consistent with those measured experimentally for FH–collidine, and provide insight into the variation of  ${}^{2h}J(\text{F,N})$ ,  ${}^{1h}J(\text{H,N})$  and  ${}^1J(\text{F,H})$  as a function of temperature.

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