NMR Spectra of Cis and Trans 1,2Difluoroethylene in the Gas Phase

George W. Flynn, Michiko Matsushima, John D. Baldeschwieler, and Norman C. Craig

---

NMR Spectra of *Cis* and *Trans* 1,2-Difluoroethylene in the Gas Phase

GEORGE W. FLYNN,* MICHIKO MATSUSHIMA, AND JOHN D. BALDESCHWIELER†

Department of Chemistry, Harvard University, Cambridge, Massachusetts

AND

NORMAN C. CRAIG

Department of Chemistry, Oberlin College, Oberlin, Ohio

(Received 2 November 1962)

The proton NMR spectra of *cis* and *trans* 1,2-difluoroethylene in the gas phase include a number of peaks of significantly different relative widths. The sharp peaks in the proton spectra can be associated with transitions between states with the largest singlet fluorine spin character if the spin–rotation interaction is assumed to provide the dominant fluorine relaxation mechanism. A comparison of the spectra in the gas and liquid phases then removes the usual ambiguity in the relative sign of $J_{AA'}$ and $J_{XX'}$ in these $AA'XX'$ systems. In both *cis* CHFCHF and *trans* CHFCHF, J_{HH} and J_{FF} are opposite in sign.
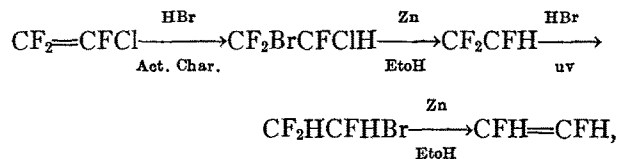
INTRODUCTION

THE proton NMR spectrum of CH_2CF_2 in the gas phase includes 10 peaks with a significant variety of relative widths.[1] If it is assumed that a spin–rotation interaction provides the dominant fluorine relaxation mechanism, and that the antisymmetric components of the spin–rotation interaction can be neglected, the relative widths of the proton transitions in CH_2CF_2 can be readily calculated. The relative linewidths obtained in this way are in rough agreement with the relative linewidths observed in the proton spectrum of gaseous CH_2CF_2, and thus lead to an identification of the origin of the transitions in this $AA'XX'$ system.[1] As a consequence, the analysis of the relative linewidths observed in the proton spectrum of gaseous CH_2CF_2 removes the usual ambiguity in the relative sign of J_{HH} and J_{FF}.

The analysis of the spectra of the remaining difluoroethylenes in the gas phase is reported in this paper. Since both *cis* and *trans* 1,2-difluoroethylene are simple examples of $AA'XX'$ systems, the analysis is analogous to that described for CH_2CF_2. However, the structures of the three difluoroethylenes are sufficiently different that a comparison of the relative signs of J_{HH} and J_{FF} is of considerable interest. The spectrum of *cis* 1,2-difluoroethylene in the liquid phase has been assigned by Coyle, Stafford, and Stone.[2] However, the spectrum of *trans* CHFCHF has not been reported. The detailed analysis of the proton and fluorine spectra of *trans* CHFCHF in the liquid phase is given in this paper. The coupling constants obtained for this compound are compared with the coupling constants observed in a variety of fluoro-olefins.

EXPERIMENTAL

Cis and *trans* 1,2-difluoroethylene were prepared in a four-step synthesis from chlorotrifluoroethylene.[3,4] The sequence of reactions was

$$CF_2=CFCl \xrightarrow[\text{Act. Char.}]{HBr} CF_2BrCFClH \xrightarrow[\text{EtoH}]{Zn} CF_2CFH \xrightarrow[\text{uv}]{HBr}$$

$$CF_2HCFHBr \xrightarrow[\text{EtoH}]{Zn} CFH=CFH,$$

with an over-all yield of 10%. Pure samples of the *cis* isomer (bp $-26.0°C$) and the *trans* isomer (bp $-53.1°C$) were obtained by gas chromatographic fractionation on a 4-m dibutylphthalate–firebrick column at 0°C. The purity of each isomer, as determined by gas chromatography, was greater than 99.7%.

Proton and fluorine NMR spectra of the liquid and gaseous difluoroethylenes were obtained at 40.0 Mc/sec with a Varian Associates V-4300 NMR spectrometer and 12-in. magnet. The frequencies reported for the liquid- and gas-phase spectra are the average values obtained from ten measurements of each line, and the error given is the standard deviation of these measurements. Liquid and gaseous samples were studied in 5-mm-o.d. NMR tubing. The pressures given for the gaseous samples are only the approximate values calculated from ideal gas considerations.

RESULTS

1. Analysis of Liquid-Phase Spectra

The proton NMR spectrum of a mixture of *cis* and *trans* 1,2-difluoroethylene is shown in Fig. 1. As ex-

* National Science Foundation Predoctoral Fellow, 1961–1963.
† Alfred P. Sloan Foundation Fellow.
[1] G. W. Flynn and J. D. Baldeschwieler, J. Chem. Phys. **38**, 226 (1963).
[2] T. D. Coyle, S. L. Stafford, and F. G. A. Stone, J. Chem. Soc. **1961**, 743.

[3] R. N. Haszeldine and B. R. Steele, J. Chem. Soc. **1957**, 2800.
[4] N. C. Craig and E. A. Entemann, J. Am. Chem. Soc. **83**, 3047 (1961).

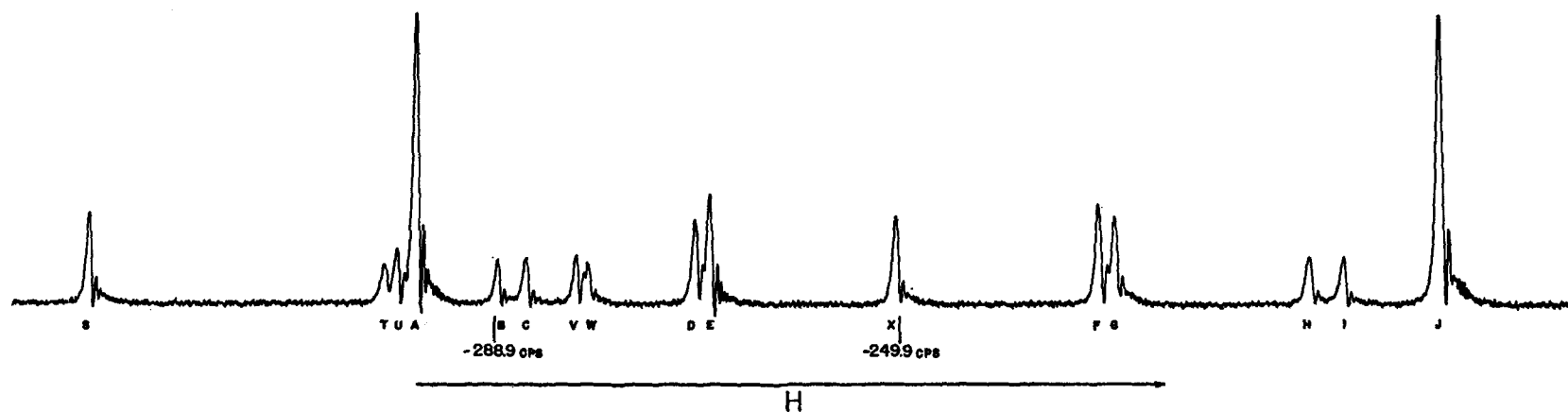FIG. 1. Proton NMR spectrum of a mixture of *cis* and *trans* CHFCHF in CCl₃F at 40.0 Mc/sec. Lines *a* through *j* are assigned to the *cis* isomer while lines *s* through *x* are assigned to the *trans* isomer.
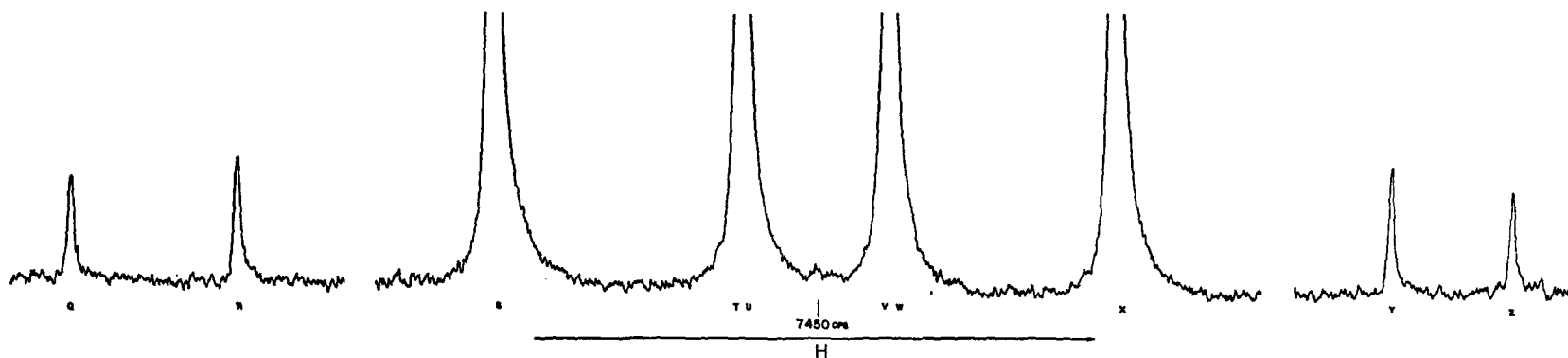

FIG. 2. F¹⁹ NMR spectrum of *trans* CHFCHF at 40.0 Mc/sec with a high rf power level showing lines *q*, *r*, *y*, and *z*.

TABLE I. Transition frequencies, relative intensities, and relative linewidths for eight assignments of the proton spectrum of *cis* CHFCHF.[a]

Line	Observed frequency, cps	Assignment of transitions				Relative intensity	Relative width
		$\lvert K \rvert = 20.7$		$\lvert M \rvert = 16.6$			
		1	2	3	4		
a, j	46.5 ± 0.1	1, 6, 7, 12	...	...	...	2.000	2.000
b, i	38.5 ± 0.4	3, 9	3, 9	2, 8	2, 8	0.319	2.637
c, h	35.7 ± 0.3	5, 11	4, 10	5, 11	4, 10	0.351	1.298
d, g	19.1 ± 0.1	4, 10	5, 11	4, 10	5, 11	0.649	0.702
e, f	17.8 ± 0.1	2, 8	2, 8	3, 9	3, 9	0.682	3.363
		$\lvert K \rvert = 16.6$		$\lvert M \rvert = 20.7$			
		5	6	7	8		
a, j	46.5 ± 0.1	1, 6, 7, 12	...	...	...	2.000	2.000
b, i	38.5 ± 0.4	4, 10	5, 11	5, 11	4, 10	0.319	1.363
c, h	35.7 ± 0.3	3, 9	3, 9	2, 8	2, 8	0.351	2.702
d, g	19.1 ± 0.1	2, 8	2, 8	3, 9	3, 9	0.649	3.298
e, f	17.8 ± 0.1	5, 11	4, 10	4, 10	5, 11	0.682	0.637

[a] The numbers under the Assignments 1 to 8 refer to the transitions given in Table II of reference 1.

pected in general for $AA'XX'$ systems,[5] the spectrum of the mixture of isomers at 40.0 Mc/sec consists of two symmetrical groupings of 10 lines. These groups are centered at -249.9 and -288.9 cps with respect to the Si(CH$_3$)$_4$ internal standard. The 10 lines symmetrically related about -249.9 cps are labeled as a through j, while the lines centered at -288.9 cps are labeled as q through z. The weak lines q, r, y, and z of the group centered at -288.9 cps are not shown in Fig. 1, since these are most readily observed at higher rf power levels. The measured spacings of the lines relative to each center are listed in Tables I and II. From the results of Coyle, Stafford, and Stone,[2] it is immediately apparent that lines a through j centered at -249.9 cps belong to the *cis* isomer, while lines q through z centered at -288.9 cps belong to the *trans* isomer.

The F^{19} NMR spectrum of the mixture of isomers at 40.0 Mc/sec consists of two well-separated groups of 10 lines centered at 6600 and 7450 cps from the CCl$_3$F internal reference. The spectrum centered at 6600 cps is identical to the proton spectrum of the *cis* isomer, while the group centered at 7450 cps is identical to the proton spectrum of the *trans* isomer. The F^{19} spectrum of the *trans* isomer at a high rf power level showing lines q, r, y, and z is given in Fig. 2.
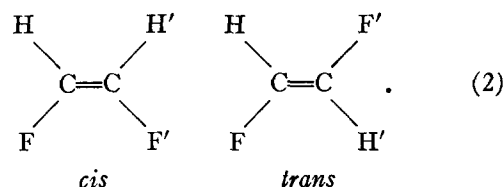
The frequencies and relative intensities of the allowed transitions in the A part of an $AA'XX'$ spectrum are given in Table II of reference 1 where the following constants have been introduced:

$$K = J_{HH'} + J_{FF'}, \qquad L = J_{HF} - J_{HF'},$$
$$M = J_{HH'} - J_{FF'}, \qquad N = J_{HF} + J_{HF'}, \qquad (1)$$
$$\cos\theta_s = K/(K^2 + L^2)^{\frac{1}{2}}, \quad \cos\theta_a = M/(M^2 + L^2)^{\frac{1}{2}};$$

and the nuclei have been designated as

$$
\begin{array}{cc}
\text{H} \quad\quad \text{H}' & \text{H} \quad\quad \text{F}' \\
\diagdown \;/ & \diagdown \;/ \\
\text{C}=\text{C} & \text{C}=\text{C} \\
/ \;\diagdown & / \;\diagdown \\
\text{F} \quad\quad \text{F}' & \text{F} \quad\quad \text{H}' \\
cis & trans
\end{array}
\qquad (2)
$$

The frequencies are given relative to the center of the A spectrum.

As has been previously noted,[1] an $AA'XX'$ spectrum is invariant to change in sign of K, L, M, or N. Thus, only $\lvert K \rvert$, $\lvert L \rvert$, $\lvert M \rvert$, and $\lvert N \rvert$ can be obtained from a spectral assignment. If it is assumed that the most intense lines in an $AA'XX'$ spectrum can be assigned to the transitions at $\pm 1/2N$, the spectrum can be assigned in eight independent ways.

For *cis* CHFCHF, a and j are the most intense lines. These are accordingly assigned to transitions 1, 6, 7, and 12 which occur at $\pm 1/2N$. The eight possible as-

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959), p. 140.

TABLE II. Transition frequencies, relative intensities, and relative linewidths for eight assignments of the proton spectrum of *trans* CHFCHF.[a]

Line	Observed frequency, cps	Assignment of transitions				Relative intensity	Relative width
		$\|K\| = 134.3$		$\|M\| = 115.3$			
		1	2	3	4		
q, z	142.9±0.7	3, 9	3, 9	2, 8	2, 8	0.057	2.114
r, y	125.1±0.7	4, 10	5, 11	5, 11	4, 10	0.073	1.855
s, x	39.4±0.5	1, 6, 7, 12	⋯	⋯	⋯	2.000	2.000
t, w	9.8±0.2	5, 11	4, 10	4, 10	5, 11	0.928	0.145
u, v	8.6±0.2	2, 8	2, 8	3, 9	3, 9	0.943	3.886
		$\|K\| = 115.3$		$\|M\| = 134.3$			
		5	6	7	8		
q, z	142.9±0.7	4, 10	5, 11	5, 11	4, 10	0.057	1.886
r, y	125.1±0.7	3, 9	3, 9	2, 8	2, 8	0.073	2.145
s, x	39.4±0.5	1, 6, 7, 12	⋯	⋯	⋯	2.000	2.000
t, w	9.8±0.2	2, 8	2, 8	3, 9	3, 9	0.928	3.855
u, v	8.6±0.2	5, 11	4, 10	4, 10	5, 11	0.943	0.114

[a] The numbers under the Assignments 1 to 8 refer to the transitions given in Table II of reference 1.

signments of the spectrum of *cis* CHFCHF then yield the two sets of constants:

(I) $\quad |K| = 20.7, |M| = 16.6, |L| = 52.3, |N| = 93.0;$

(II) $\quad |K| = 16.6, |M| = 20.7, |L| = 52.3, |N| = 93.0.$

$$(3)$$

These two sets of constants show that it is not possible to distinguish $|K|$ and $|M|$. The relative sign of $J_{HH'}$ and $J_{FF'}$ therefore can not be determined. Since only $|K|$, $|L|$, $|M|$, and $|N|$ can be obtained from the assignment, it is not possible to distinguish $J_{HH'}$ from $J_{FF'}$, or J_{HF} from $J_{HF'}$. However, definite values for $|L|$ and $|N|$ can be obtained. It is thus possible to find the relative sign of J_{HF} and $J_{HF'}$. The coupling constants for *cis* CHFCHF obtained from Eq. (3) are:

$$J_{HF}(gem) = +72.7 \text{ or } +20.4,$$

$$J_{HF'}(trans) = +20.4 \text{ or } +72.7,$$

$$J_{HH'}(cis) = \pm\pm2.0 \text{ or } \pm\pm18.7,$$

$$J_{FF'}(cis) = \pm\mp18.7 \text{ or } \pm\mp2.0, \qquad (4)$$

where J_{HF} and $J_{HF'}$ have been arbitrarily given with a positive sign to indicate that they are of the same sign. These results are in agreement with the coupling constants reported by Coyle, Stafford, and Stone.[2]

For *trans* CHFCHF, assignment of the most intense lines, *s* and *x* at ±39.4 cps, to transitions 1, 6, 7, and 12 at ±1/2 N yields the two sets of constants:

(I) $\quad |K| = 134.3, |M| = 115.3,$

$$|L| = 69.9, |N| = 78.8;$$

(II) $\quad |K| = 115.3, |M| = 134.3,$

$$|L| = 69.9, |N| = 78.8. \qquad (5)$$

It is again not possible to distinguish $|K|$ and $|M|$ since both sets of Assignments (I) and (II) are in agreement with the observed spectrum of the liquid. Thus the relative sign of $J_{HH'}$ and $J_{FF'}$ can not be obtained. It is also not possible to distinguish $J_{FF'}$ from $J_{HH'}$, and J_{HF} from $J_{HF'}$ as for the *cis* isomer. It is, however, possible to obtain the relative sign of J_{HF} and $J_{HF'}$ since definite values of $|L|$ and $|N|$ are obtained from the possible assignments. The coupling constants for *trans* CHFCHF obtained from Eq. (5) are:

$$J_{HF}(gem) = +74.3 \quad \text{or } +4.4,$$

$$J_{HF'}(cis) = +4.4 \quad \text{or } +74.3,$$

$$J_{HH'}(trans) = \pm\pm9.5 \quad \text{or } \pm\pm124.8,$$

$$J_{FF'}(trans) = \pm\mp124.8 \text{ or } \pm\mp9.5, \qquad (6)$$

where again J_{HF} and $J_{HF'}$ have been arbitrarily given the positive sign.

2. Analysis of Gas-Phase Spectra

If it is assumed that the F^{19} spin–rotation interaction provides the dominant fluorine relaxation mechanism for *cis* and *trans* CHFCHF in the gas phase, the relative widths of the proton resonances can be readily calculated.[1] The relative widths of the proton transitions are given in Table II of reference 1. When the relative widths of the proton transitions are considered, one set of four of the eight possible assignments of each of the $AA'XX'$ spectra is no longer identical to the remaining set of four assignments. The eight possible assignments of the spectrum of *cis* CHF-CHF are given in Table I, where the numbers under the assignments refer to the transitions numbered as in Table II of reference 1. The frequencies and intensities of the transitions calculated with these eight assignments are identical. However, it is apparent that the relative widths calculated for Assignments 1 through 4 are different from the relative widths calculated for Assignments 5 through 8. Assignments 1 through 4 correspond to the choice of $|K| = 20.7$ and $|M| = 16.6$, while Assignments 5 through 8 correspond to $|K| = 16.6$ and $|M| = 20.7$.

The proton spectrum of gaseous *cis* CHFCHF at 10.1 atm is shown in Fig. 3. The sharpest features in the spectrum of the gas occur at $\pm 18.9 \pm 0.3$ cps. This value unfortunately falls between the spacings of Lines d, g and e, f obtained from the spectrum of the liquid. However, the qualitative appearance of each of the innermost features in the spectrum of the gas is consistent with the overlap of two resonances of different relative width, with the sharper lines corresponding to Lines e and f, and the broader lines to d and g. The gas-phase spectrum of *cis* CHFCHF thus appears to be in agreement with the relative linewidths calculated for Assignments 5 through 8 in Table I. The second set of constants in Eq. (3), with $|K| = 16.6$ and $|M| = 20.7$ can thus be selected, indicating that $J_{HH'}$ and $J_{FF'}$ must be opposite in sign.[6]

The eight possible assignments of the spectrum of *trans* CHFCHF are given in Table II. Again, if the
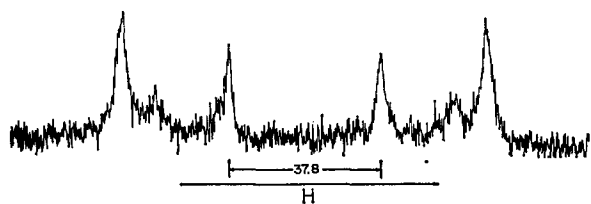

Fig. 3. Proton NMR spectrum of *cis* CHFCHF at 10.1 atm at 40.0 Mc/sec.

[6] This result has been confirmed by nuclear Overhauser effect measurements; K. Kuhlmann and J. D. Baldeschwieler (unpublished results).
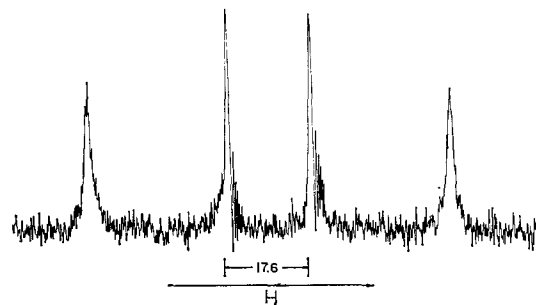

Fig. 4. Proton NMR spectrum of *trans* CHFCHF at 18.8 atm at 40.0 Mc/sec.

relative linewidths are considered, Assignments 1 through 4 are no longer identical to Assignments 5 through 8. The proton spectrum of gaseous *trans* CHF-CHF at 18.8 atm is shown in Fig. 4. The sharpest features in the spectrum of this gas are at $\pm 8.8 \pm 0.1$ cps. These lines clearly correspond to the innermost lines of the liquid spectrum, consistent with Assignments 5 through 8. The second set of constants given by Eq. (5), with $|K| = 115.3$ and $|M| = 134.3$, is consistent with the observed spectrum, indicating that for this molecule, $J_{HH'}$ is again opposite in sign to $J_{FF'}$.

DISCUSSION

The ambiguities in the magnitudes of the coupling constants given in Eqs. (4) and (6) are readily resolved by a comparison of the coupling constants observed in a variety of fluoro-olefins. The coupling constants observed for *cis* and *trans* CHFCHF are compared with the coupling constants for eight other fluoro-olefins in Table III. The values of $J_{HF}(gem)$ observed for four of these compounds fall between 72 and 89.9 cps. Thus the values of $J_{HF}(gem)$ equal to 72.7 and 74.3 cps for *cis* and *trans* CHFCHF can be chosen immediately. This choice then fixes $J_{HF}(trans) = 20.4$ cps for *cis* CHFCHF, and $J_{HF}(cis) = 4.4$ cps for *trans* CHFCHF. The magnitudes of $J_{FF}(trans)$ fall between 115 and 124 cps. Thus the choice of $J_{FF}(trans) = 124.8$ cps for *trans* CHFCHF is immediate, fixing J_{HH} $(trans) = 9.5$ cps. The values of $J_{FF}(cis)$ fall between 33 and 58 cps, while the values of $J_{HH}(cis)$ are 4.7 and 4.5 cps in Table III. The choice of $J_{FF}(cis) = 18.7$ cps and $J_{HH}(cis) = 2.0$ cps appears to be the most reasonable for *cis* CHFCHF, although the magnitudes of both these coupling constants are considerably less than those observed for other fluoro-olefins.

The assignment of the gas phase spectra of *cis* and *trans* CHFCHF removes the ambiguity in the relative sign of $J_{HH'}$ and $J_{FF'}$. However, the signs of $J_{HH'}$ or $J_{FF'}$ relative to J_{HF} or $J_{HF'}$ have not been obtained. Thus if $J_{HF}(gem)$ is assumed to be positive, the signs of the coupling constants in *cis* and *trans* CHFCHF determined by analysis of the liquid and gas phase spectra are as indicated in Table III. The relative signs of the

TABLE III. Coupling constants for some fluoro-olefins.

	cis CHFCHF	trans CHFCHF	CH$_2$CF$_2$[a]	CHFCF$_2$[b]	CHFCH$_2$[c]	cis CHFCHCH$_3$[d]	trans CHFCHCH$_3$[d]	CF$_2$CFCl[b]	CF$_2$CFBr[e,f]	CF$_2$CFCF$_3$[g,h]
J_{HH} (gem)			∓4.8		−3.2					
J_{HH} (cis)	∓2.0				+4.7	+4.5				
J_{HH} (trans)		±9.5			+12.8		+11.1			
J_{FF} (gem)			±36.4	±87				+78[i]	+75[i]	+60.0[i]
J_{FF} (cis)	±18.7			±33				+58	+57	+40.3
J_{FF} (trans)		∓124.8		∓119				−115	−124	−120.2
J_{HF} (gem)	+72.7[i]	+74.3[i]		+72[i]	+84.7[i]	+89.9[i]	+84.8[i]			
J_{HF} (cis)		+4.4	+0.7	−3	+20.1		+19.9			
J_{HF} (trans)	+20.4		+33.9[i]	+12	+52.4	+41.8				

[a] See reference 1.
[b] See references 8 and 11.
[c] See reference 7.
[d] See references 9 and 10.
[e] D. D. Elleman and S. L. Manatt, J. Chem. Phys. 36, 1945 (1962).
[f] See reference 11.
[g] See reference 8.
[h] J. D. Swalen and C. A. Reilly, J. Chem. Phys. 34, 2122 (1961).
[i] Sign arbitrarily assumed to be positive. Other signs are relative to this.

coupling constants for the other fluoro-olefins given in Table III have been obtained by double resonance and complete spectral analysis at low fields. By a comparison of the signs across the various rows of Table III, it is possible to check the consistency of all these relative sign determinations and to suggest the probable sign where ambiguities remain.

As a starting point for the comparison of the signs of these coupling constants, it is convenient to assume that the sign of $J_{HF}(gem)$ is the same for the six compounds where it is observed. This sign is arbitrarily chosen as positive. This leads to the choice of J_{HH} (*trans*) = +12.8 for CHFCH$_2$.[7] Since J_{HH}(*trans*) changes little in magnitude for the three compounds where it is observed, it is reasonable to choose J_{HH}(*trans*) = +9.5 cps for *trans* CHFCHF. This fixes J_{FF}(*trans*) as −124.8 cps for *trans* CHFCHF. This then leads to the choice of the negative sign for J_{FF}(*trans*) in the five compounds where it is observed. This removes the ambiguity in relative sign of the F–F and H–F coupling constants in CHFCF$_2$.[8] The values of J_{FF}(*cis*) and J_{FF} (*gem*) are then most reasonably all chosen to be positive. This fixes $J_{HH}(gem)$ as −4.8 cps for CH$_2$CF$_2$, in good agreement with $J_{HH}(gem)$ = −3.2 cps for CHFCH$_2$.[7] $J_{HH}(cis)$ also must be negative for *cis* CHFCHF, in contrast with the values for CHFCH$_2$ and CHFCH-CH$_3$.[9,10] The most probable choice of sign where ambiguities exist in Table III is indicated by the upper sign in each case. Thus from Table III it can be concluded that $J_{HH}(cis)$ is opposite in sign to the other coupling

constants in *cis* CHFCHF, while J_{FF}(*trans*) is opposite in sign to the other coupling constants in *trans* CHFCHF.

The only apparent inconsistencies in the signs of the coupling constants given in Table III are the negative signs for $J_{HF}(cis)$ in CHFCF$_2$,[8] and for $J_{HH}(cis)$ in *cis* CHFCHF. The magnitude of $J_{HF}(cis)$ varies greatly for the five compounds where it is observed. For CH$_2$-CF$_2$, $J_{HF}(cis)$ is only +0.7 cps. Since both $J_{HF}(cis)$ and J_{HF}(*trans*) seem to decrease as the number of substituted fluorine increases, a reversal in sign of J_{HF} (*cis*) between CH$_2$CF$_2$ and CHFCF$_2$ does not seem to be unreasonable. The negative value for $J_{HH}(cis)$ in *cis* CHFCHF is more surprising. However, J_{HH}(*trans*) appears to decrease with an increase in the number of substituted fluorine nuclei. Thus a large decrease in J_{HH} (*cis*) with an increase in the number of substituted fluorine nuclei is consistent with the behavior of J_{HH} (*trans*), $J_{HF}(cis)$ and J_{HF}(*trans*).

The magnitudes of the proton–proton coupling constants, J_{FF}(*trans*) and $J_{HF}(gem)$, fall within narrow ranges for these fluoro-olefins, while $J_{FF}(gem)$, J_{FF} (*cis*),$J_{HF}(cis)$, and J_{HF}(*trans*) vary widely. These features have been previously noted,[7,11] and their detailed explanation awaits further theoretical development.

ACKNOWLEDGMENTS

[7] C. N. Banwell and N. Sheppard, Proc. Roy. Soc. (London) **A263**, 136 (1961).

[8] D. F. Evans, Mol. Phys. **5**, 183 (1962).

[9] R. A. Beaudet and J. D. Baldeschwieler, J. Mol. Spectry. **9**, 30 (1962).

[10] M. Y. DeWolf and J. D. Baldeschwieler (unpublished results).

[11] H. M. McConnell, C. A. Reilly, and A. D. McLean, J. Chem. Phys. **24**, 479 (1956).