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The NMR Spectra of Oriented 1,1-Difluoroethylene, and Tetrafluoroethylene

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Abstract—An analysis of the NMR spectra of 1,1-difluoroethylene and tetrafluoroethylene in a nematic solvent is given. The results are compared with previous findings on ethylene itself. The geometrical structures of the fluorine substituted molecules, as determined from NMR data neglecting the anisotropy of the electron coupled spin–spin interaction, deviate considerably from structural data obtained by other methods. It is concluded that there is a strong anisotropy in the electron coupled interactions between the ^{19}F nuclei.

Introduction

The use of pure nematic liquid crystals or eutectic mixtures as anisotropic solvents to obtain high resolution NMR spectra of partially oriented molecules has become a standard technique by now.[1–7] We have used this method to study the spectra of 1, 1-difluoroethylene and tetrafluoroethylene. With the first molecule the comparison of the NMR determined ratio of the proton-proton and fluorine-fluorine distances with the corresponding value obtained by microwave spectroscopy[8] gives a deviation of 11%. In tetrafluoroethylene the difference of the ratio of the two sides of the rectangle formed by the fluorines amounts to 4% between

NMR and electron diffraction measurements. With ethylene the corresponding ratio differs less than 1% when comparing NMR and Raman data.

Experimental

The proton and fluorine spectra were recorded with a Varian DP 60 spectrometer operating at 56.4 MHz and 34 °C. The spectra were calibrated using the 2kHz sidebands of the baseline stabilizer. The average of several up- and down-field traces was taken to determine the experimental line positions. The statistical measuring error was approximately ± 1 Hz. The average full line width at half height was 9 Hz in the ^{19}F- and 12 Hz in the ^{1}H-spectrum.

The gases used were Matheson lecture bottle grade. An amount equal to 20 mole % in the nematic solvent at room temperature was condensed by liquid nitrogen into the sample tube. In the case of tetrafluoroethylene about 2 mole % of isopropyl mercaptan was added to prevent rapid polymerization.

All spectra were taken at 34 °C in a mixture of 60 mole % 0-carbobutoxy-*p*-oxybenzoic acid *p*-ethoxyphenyl ester and 40 mole % *p*-capronyloxy-*p'*-ethoxy-azobenzene.

Results

(a) *1,1-Difluoroethylene:* The ^{19}F- and ^{1}H-spectrum of difluoroethylene together with the corresponding theoretical spectrum is shown in Fig. 1. The two spectra were taken with the same sample at the same temperature. To analyze the spectrum we have chosen the following procedure. With a computer program similar to that of Snyder and Kornegay[9] which uses molecular dimensions, motional constants, chemical shifts, and scalar coupling constants as input parameters a spectrum was simulated which reproduced the number of lines, their frequencies and intensities roughly. In a second step known J values and the approximate direct coupling constants of the first calculation were introduced into a modified version of LAOCOON3[11] to get a

better fit with the observed spectrum by iteration. A number of calculations were carried out with various signs of the indirect and direct coupling constants. A good fit with the observed spectrum could only be obtained with equal signs (we used negative signs) for all direct and the geminal proton-proton scalar coupling constants. All other scalar couplings were taken with the opposite sign. The experimental and calculated line positions are reproduced in Tables 1 and 2. The root mean square error between the observed and calculated spectrum was 1.6 Hz, if one tried to get a good fit for both the ^{1}H and ^{19}F spectra at the same time. This error was reduced to 1.4 Hz trying to reproduce the proton spectrum only.

(b) *Tetrafluoroethylene:* The determination of the spectrum of tetrafluoroethylene, Figure 2, caused some experimental difficulties, partially due to the low solubility of the gas in the nematic

TABLE 1 Proton NMR spectrum of 1,1-Difluoroethylene

Line Pair	Experimental Position‡	Calculated Position‡	Calculated Rel. Intensity	Error ($\triangle\nu$)
a	658.9	658.1	2.0	+0.8
b	433.2	434.3	1.0	−1.1
c	420.7	421.2	2.0	−0.5
d	345.5	343.7	1.3	+1.8
e	282.1	283.9	0.7	−1.8
f	170.6	168.6	1.0	+2.0

‡ Distance from symmetry center in Hz.

TABLE 2 Fluorine NMR spectrum of 1,1-Difluoroethylene

Line Pair	Experimental Position‡	Calculated Position‡	Calculated Rel. Intensity	Error ($\triangle\nu$)
g	638.2	639.44	2.00	1.24
h	440.8	439.86	2.00	−0.94
i	387.2	386.84	1.05	−0.36
j	327.6	325.07	1.28	−2.53
k	299.5	302.59	0.72	3.09
l	215.3	216.00	0.95	0.71

‡ Distance from symmetry center in Hz.

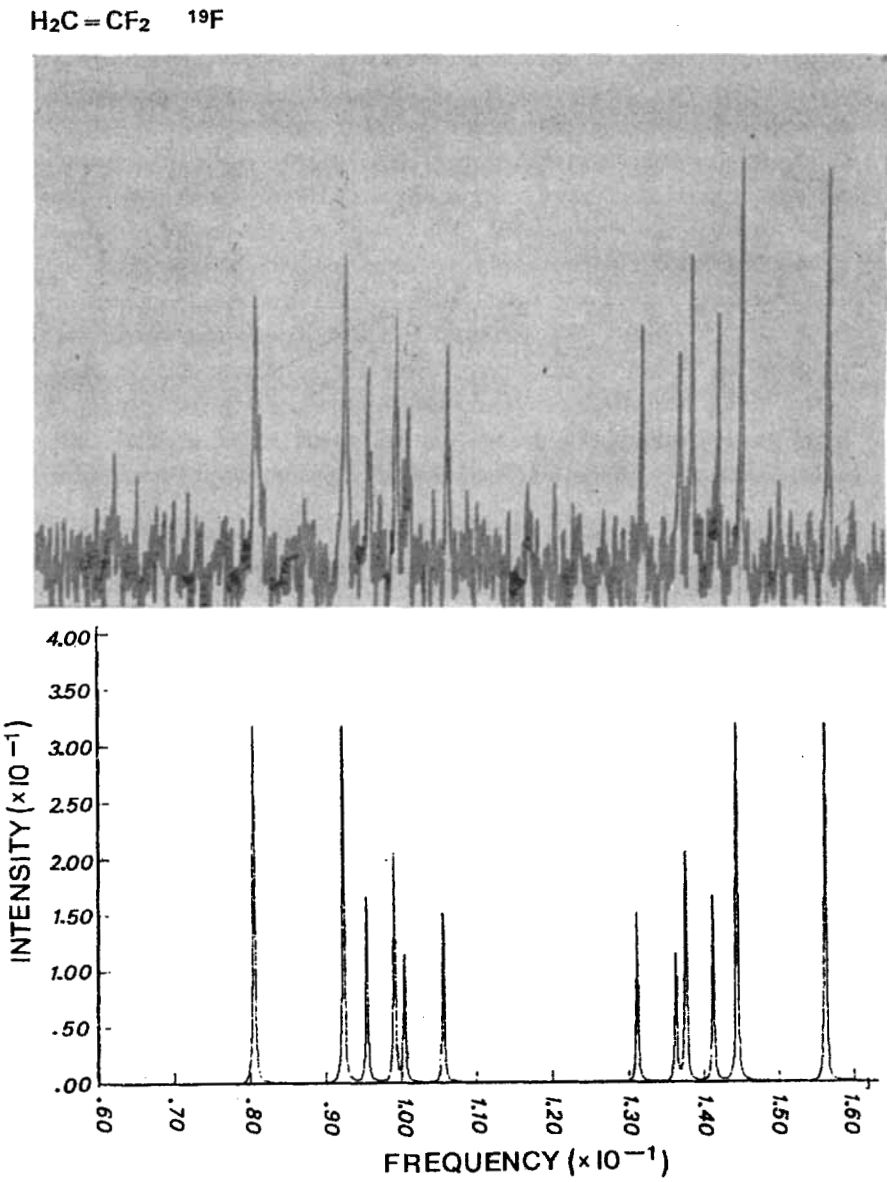
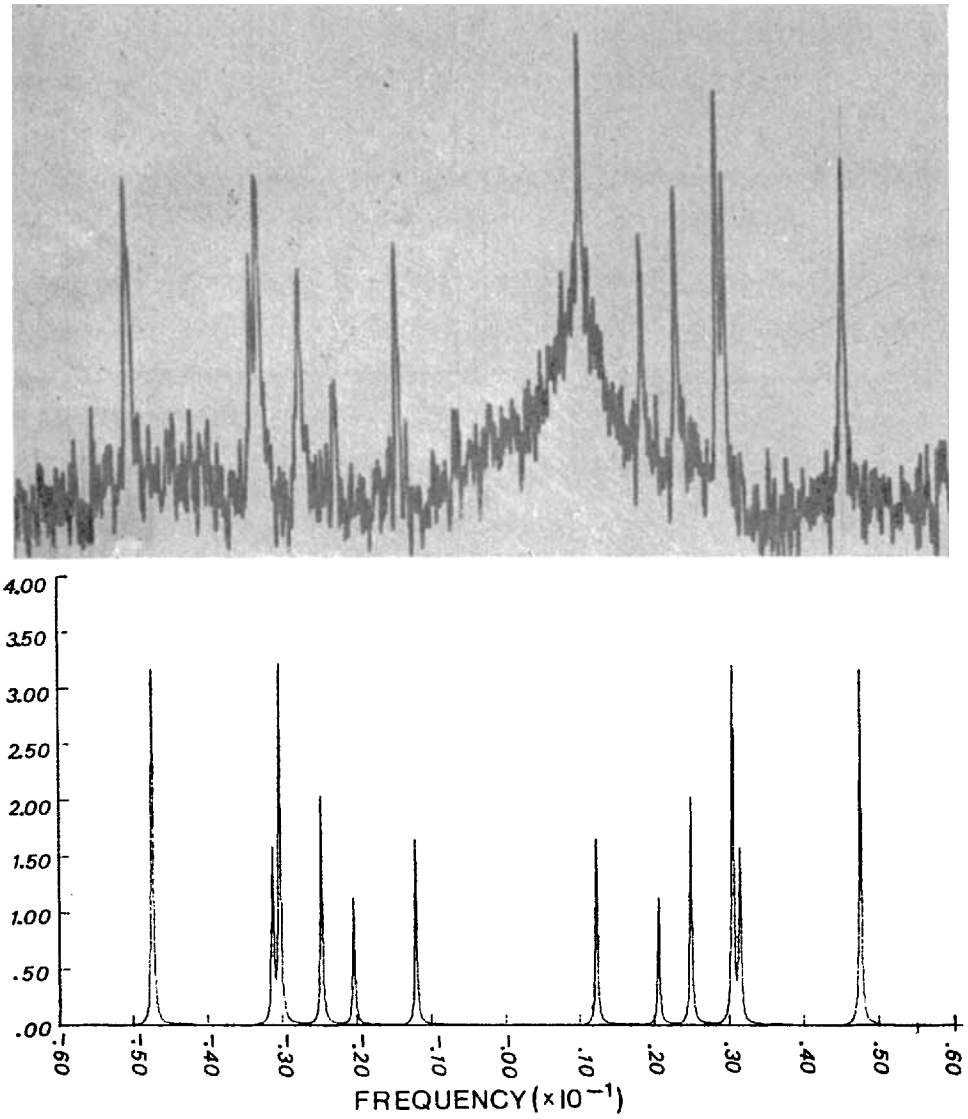
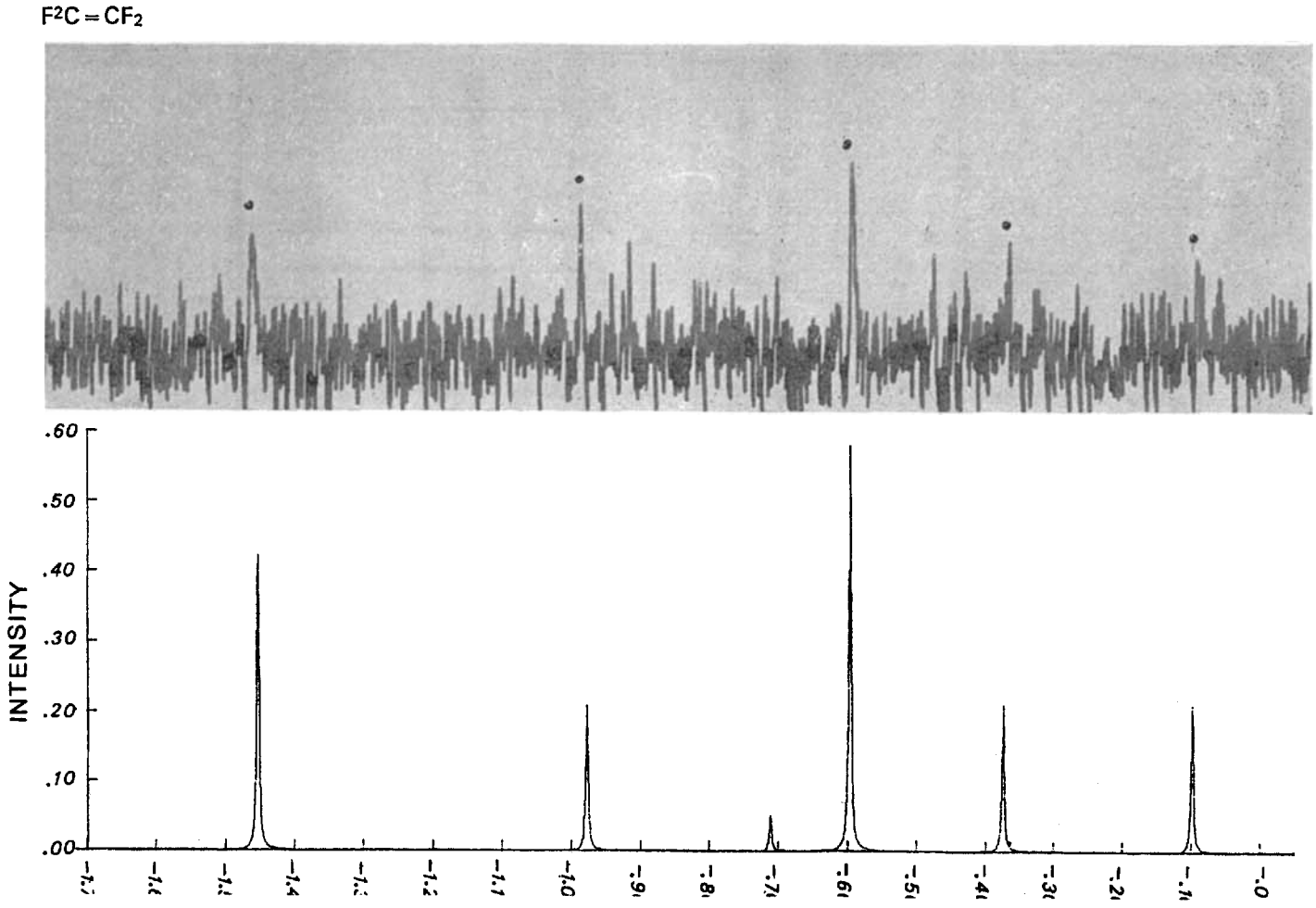


Figure 1. Experimental and calculated ^{1}H and ^{19}F spectra of 1,1-difluoroethylene.





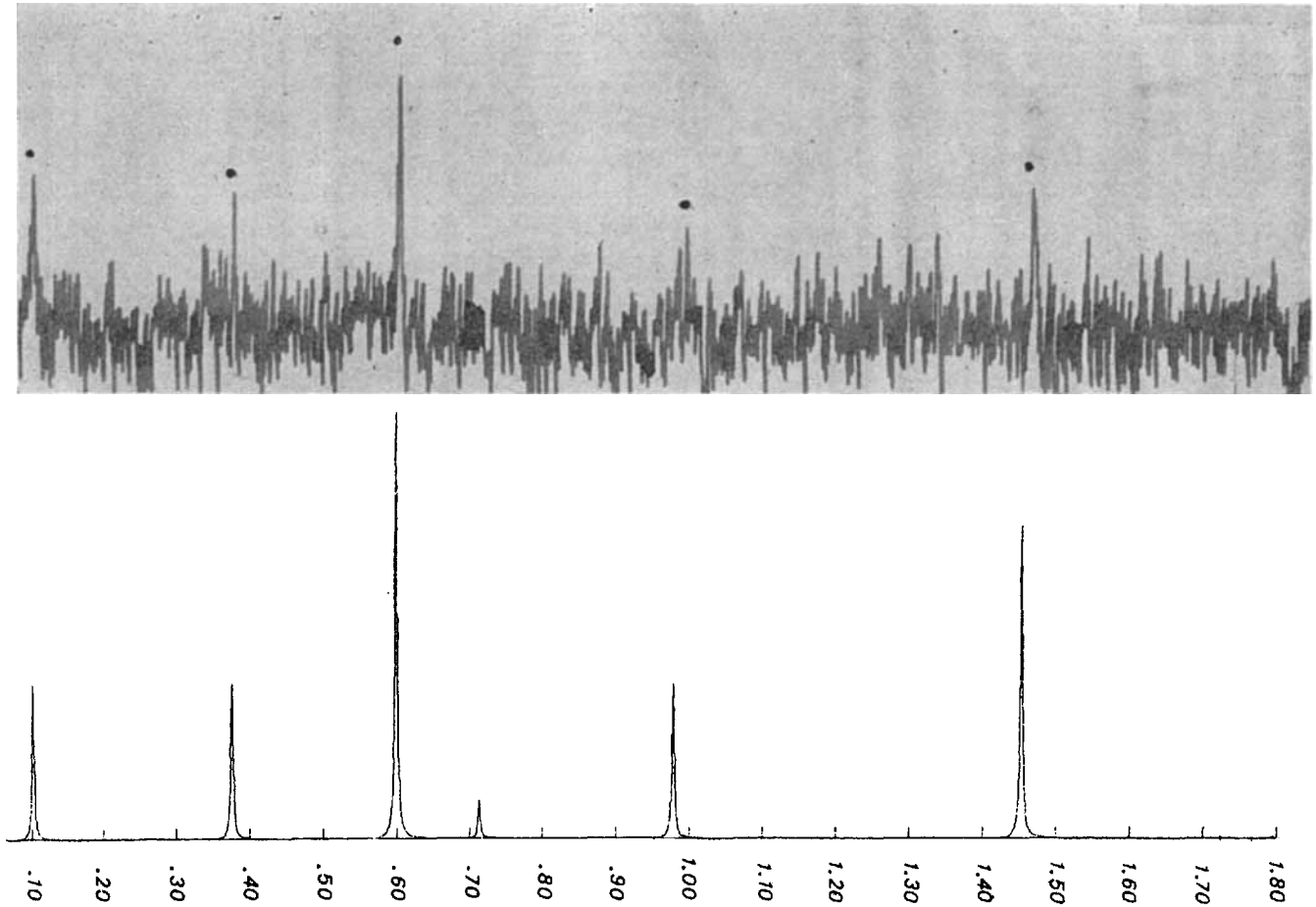


Figure 2. Experimental and calculated spectra of tetrafluoroethylene.

phase but mainly due to the rapid polymerization of the monomer at elevated temperatures which were necessary for safety reasons and equilibration purposes during the preparation. The symmetrical spectrum consists of twelve lines like that of ethylene. Only four lines are influenced by the scalar coupling constants.[3] Since the values of the latter are unknown we have used those of trifluorochloroethylene[12] for their calculation. These values are given in brackets in Table 3. The anisotropic coupling constants B_{pq}* for ethylene and the two fluorine derivatives are compared in Table 4. The probable errors are about 0.5 Hz for ethylene and tetrafluoroethylene and 0.5 Hz in the case of 1, 1-difluoroethylene. We number the magnetic nuclei proceeding clockwise and starting with the first proton of a methylene group or, in the case of, tetrafluoroethylene with the first ^{19}F of a methylene group. The

TABLE 3 Fluorine NMR spectrum of Tetrafluoroethylene

Line Pair	Experimental Position‡	Calculated Position‡	Calculated Rel. Intensity	Error ($\Delta\nu$)
f	2465	2464.7	4.0	+0.3
e	1658	1658.2	2.0	−0.2
d	?	(1208.0)	(0.5)	(–)
c	1005	(1013.7)	(5.5)	(−8.7)
b	636	636.2	2.0	−0.2
a	170	170.2	2.0	−0.2

‡ Distance from symmetry center in Hz.

TABLE 4 Anisotropic coupling constants of Ethylene, 1,1-Difluoroethylene and Tetrafluoroethylene

	Ethylene	1, 1-Difluoroethylene	Tetrafluoroethylene
B_{12}	615.0	−79.0	−609.5
B_{13}	−114.5	−136.2	−268.8
B_{14}	−511.2	−420.7	−764.8
B_{34}	615.0	−66.5	−609.5

* For a definition see for instance ref. 13.

assignment of the coupling constants to the interacting nuclear pair is uncertain for tetrafluoroethylene. Our assignment gives the best results for the geometrical structure but another assignment is possible that gives comparable results.

Discussion

1,1-Difluoroethylene and tetrafluoroethylene as well as ethylene itself are planar molecules belonging to the point group C_{2v} and D_{2h} respectively. Their orientation in the nematic host phase is completely described by two orientation parameters, for instance S_{zz} and S_{xx} (z-axis parallel to double bond, x-axis normal to double bond in molecular plane). With all molecules S_{xx} is equal to S_{12}, the degree of order of the 1, 2 axis which connects the protons or fluorines of a methylene group. We assume that the molecular planes align parallel to the magnetic field and S_{yy} is negative.

The S-values are given in Table 5. It can be seen that the

TABLE 5 Orientation Parameters and Ratios of Various Interproton and Fluorine Distances in Ethylene, 1,1-Difluoroethylene, and Tetrafluoroethylene. (For the calculation of the S-values the Raman, microwave, or electron diffraction results were used.)

		Ethylene	1,1-Difluoroethylene	Tetrafluoroethylene
S_{zz}		0.0635	0.0637	0.1475
S_{xx}		−0.0328	0.0046	0.0614
S_{yy}		−0.0306	−0.0682	−0.2089
$\frac{r_{34}}{r_{12}}$	NMR	1	1.017	1
	Other Methods		1.131	
$\frac{r_{14}}{r_{12}}$	NMR	1.318	1.301	1.193
	Other Methods	1.327	1.380	1.242

fluorine substitutions influence the orientation strongly. S_{yy} changes from -0.03 in ethylene to -0.22 in tetrafluoroethylene. It shows that the alignment increases with the number of fluorine substitutions. The S-values of tetrafluoroethylene are doubtful because of the uncertainty in the assignment and because the electron coupled interactions are neglected.

Due to the lower symmetry of 1,1-difluoroethylene one can derive four different anisotropic coupling constants from the spectrum which allow to express the ratio of the three independent distances between the protons and fluorine atoms by the following equations:[13,14]

$$\frac{r_{34}}{r_{12}} = \left(\frac{\gamma_F^2}{\gamma_H^2}\frac{B_{12}}{B_{34}}\right)^{1/3} = -\left(\frac{r_{14}}{r_{12}}\right)^2 + \left(\frac{r_{13}}{r_{12}}\right)^2 \tag{1}$$

$$\left(\frac{r_{34}}{r_{12}} + \left[\frac{r_{14}}{r_{12}}\right]^2\right)^{5/2} = \frac{B_{14}}{B_{13}}\left(\frac{r_{14}}{r_{12}}\right)^5 + \frac{\gamma_F}{\gamma_H}\frac{B_{12}}{B_{13}}\frac{r_{34}}{r_{12}} \tag{2}$$

The results are included in Table 5 and compared with the available Raman, microwave[8] or electron diffraction[15] data. The deviation found with ethylene is typical for data that do not involve fluorine couplings. It can be understood as an influence predominantly of zero point vibrations. These vibrations are as a rule stronger for lighter nuclei and we should therefore expect somewhat better results with fluorine couplings. But it is evident that the deviations found with the fluoroethylenes exceed strongly the usual error limits due to vibrations. We suppose that this is caused by a contribution of the electron coupled spin-spin interaction to the fluorine-fluorine coupling constants.‡ Neglecting of the relatively small indirect contribution to the proton-proton coupling B_{12} in 1,1-difluoroethylene, one finds for direct and indirect contribution to the coupling between the fluorines

‡ We get $r_{14}/r_{12} = 1.375$ for 1,1-difluoroethylene when $r_{34}/r_{12} = 1.131$ is used in Eq. (2). Only in B_{34} is, therefore, a noticeable indirect contribution.

$$B_{34}^{\mathrm{dir}} = \frac{\gamma_F^2}{\gamma_H^2} B_{12} \frac{r_{12}^3}{r_{34}^3} = 48 \text{ Hz}$$

$$B_{34}^{\mathrm{indir}} = B_{34} - B_{34}^{dir} = 78 \text{ Hz}. \qquad (3)$$

We can introduce a tensor (J_{ik}) for the indirect coupling which may be so defined that the scalar coupling constant is one third of its trace. This tensor is for symmetry reasons diagonal in our molecular coordinate system. It can be shown that[2]

$$S_{xx} J_{xx} + S_{yy} J_{yy} + S_{zz} J_{zz} = 3B_{34}^{\mathrm{indir}} \qquad (4)$$

Dividing by S_{zz} and using the S-values of Table 5 and B_{34}^{indir} from Eq. (3) gives

$$-0.07\, J_{xx} - 0.93\, J_{zz} + J_{yy} = 796 \text{ Hz}.$$

The corresponding scalar coupling is only 37 Hz. The difference between the principal elements is much larger than their average value.

B_{34}^{dir} assumes its maximum value of 10630 Hz for $S_{xx} = 1$. It is proportional to S_{xx}. Indirect couplings behave differently and that can explain why their contributions amount to more than 25% in the observed coupling constant. The observed value of S_{xx} is indeed very small against the other two S-values.

Unfortunately the data do not suffice to evaluate the individual components of (J_{ik}). Measurements with largely differing S-values would be necessary. There also remains a considerable uncertainty in these considerations since the influence of the vibrations is neglected. But it seems certain that there is a strong anisotropy in indirect fluorine couplings. Similar conclusions have also been obtained previously with the couplings in fluorobenzenes.[16–19]

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