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Microwave Spectra of *cis*- and *trans*-1-Chloro-1,2-difluoroethylene

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The microwave spectra of the ^{35}Cl and ^{37}Cl isotope species of *cis*- and *trans*-HFC=CFCl have been studied in the 8—50 GHz region. The rotational constants and the Cl quadrupole coupling constants in MHz are obtained and listed. The quadrupole coupling constants and the structures obtained for *cis*- and *trans*-HFC=CFCl are consistent with the results of other haloethylenes.

	cis-HFC=CF^{35}Cl	*cis*-HFC=CF^{37}Cl	*trans*-HFC=CF^{35}Cl	*trans*-HFC=CF^{37}Cl
A	9 126.182(10)	9 091.714(18)	5 336.381(8)	5 232.441(10)
B	2 461.037(5)	2 397.536(9)	3 516.721(9)	3 469.251(15)
C	1 936.689(4)	1 895.643(14)	2 117.416(5)	2 083.794(9)
χ_{aa}	−67.67(20)	−53.62(30)	9.78(10)	4.72(20)
χ_{bb}	30.05(20)	23.83(50)	−45.41(10)	−32.54(20)
χ_{cc}	37.62(20)	29.79(50)	35.63(10)	27.82(20)

The microwave spectra and Cl nuclear quadrupole coupling constants have been measured for several substituted ethylenes.[1-6] Substitutional change in the quadrupole coupling constants along the carbon-chlorine bond shows that the numerical values of the coupling constant increase as the number of substituted halogen atoms increases and that fluorine has a greater effect than chlorine.

On the other hand, complete structures for several haloethylenes have been determined by microwave spectroscopy.[1,7-9] The halogen substitution effect on the structure shows that the carbon-carbon double bond and carbon-halogen bond lengths decrease as the number of substituted halogen atoms increases and that fluorine has a greater effect than chlorione.

The present work was initiated to see if the nuclear quadrupole coupling constant and the molecular structure in *cis*- and *trans*-1-chloro-1,2-difluoroethylene are consistent with previous results on haloethylenes.

Experimental

The sample of HFC=CFCl was prepared by two different methods. The first method of preparation utilized an elimination reaction of hydrogen chloride as follows:

$$HFClC\text{-}CHFCl \xrightarrow[(EtOH)]{KOH} HFC{=}CFCl + HCl.$$

Because of competing side reactions the over-all yield was low. The doublet peak of *cis*- and *trans*-HFC=CFCl and some other peaks were observed by a vapor-phase chromatograph.

The second method of preparation was by photochemical reaction of hydrogen bromide with 1,2-dichloro-1,2-difluoroethylene followed by dehalogenation of the adduct as detailed by Birchall *et al.*[10]

$$FClC{=}CFCl + HBr \xrightarrow{h\nu} HFClC\text{-}CFClBr$$

$$HFClC\text{-}CFClBr + Zn \longrightarrow HFC{=}CFCl + ZnClBr$$

The product was shown to be a *cis-trans* mixture of almost equal amount by gas chromatography (resolved easily at room temperature on a 3 m column of Silicone DC-200(20%) and steric acid(5%) on celite). The infrared spectrum was identical to that of Birchall *et al.*[10] Separation of *cis-trans* isomers has been performed by gas chromatography at about −30 °C, the former and the latter peaks on the run were identified as *trans*- and *cis*-isomer, respectively.

The microwave spectrum was investigated in the frequency region from 8 to 50 GHz by using a conventional 100 kHz Stark modulation spectrometer. All measurements were made at the temperature of Dry Ice. The frequency measurements were performed automatically under the control of a microcomputer.[11] The microwave frequency measured by a counter YHP 5340A is processed by a microcomputer YHP 9825A. When a microwave frequency coincides with the marker frequency, the computer triggers a relay actuator YHP 59306A, which actuates a marker pen on the recorder.

Results and Disscusion

Microwave Spectra. A preliminary estimate of the molecular structure for *cis*-HFC=CFCl and *trans*-HFC=CFCl indicate that the dipole moments would lie along the b axis for the *cis*-isomer and between the a and b axes for the *trans*-isomer; spectra exhibiting b-type and both a- and b-type selection rules should be observed, respectively. Nearly all of the Q- and R-branch transitions were predicted to be multiplets due to the coupling of the over-all rotation angular momentum and the nuclear spin angular momentum for both isomers in the ^{35}Cl and ^{37}Cl isotopic species. Each Q-branch transition exhibits a characteristic quartet pattern ($\Delta F = \pm 1$ transitions being weak), and the splitting between the first and second components

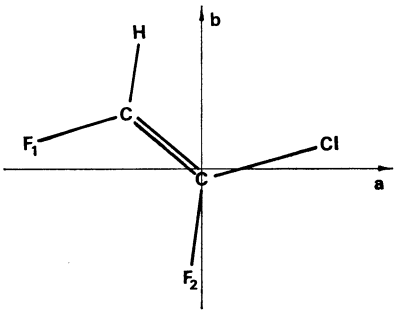

Fig. 1. Molecular structure of *cis*-HFC=CFCl.

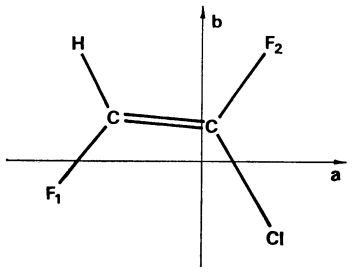

Fig. 2. Molecular structure of *trans*-HFC=CFCl.

equals that of the third and fourth components. The ratio $(\nu_C-\nu_B)/(\nu_D-\nu_A)$ (where ν_i is the frequency of the ith component of the quartet) depends only on Casimir's function. This ratio could be used to determine the J level for transitions exhibiting the characteristic Q-branch quadrupole splitting pattern.

The spectrum of *cis*-HFC=CFCl was found to be broad and moderately strong. A search was made for Q-branch transitions for the ^{35}Cl isotope in the 33—50 GHz region. Assignment was obtained by plotting $(A-C)/2$ *vs.* κ for the various Q-branch transitions. This information together with assumption of planarity, $I_c-I_a-I_b\approx 0$, give the approximate rotational constants. The measurements of R-branch transitions gave the complete assignments which were confirmed by their hyperfine structures. The final values of the rotational constants were fitted by using a least squares criterion to the rotational Hamiltonian involving a centrifugal distortion effect. In this case, when the planarity conditions are applied, only four centrifugal distortion coefficients are independent, *e.g.* τ_{aaaa}, τ_{bbbb}, τ_{aabb}, and τ_{abab}. The results are listed in Table 1. The experimental and calculated frequencies are given in Table 2. The assignment for *cis*-HFC=CF^{37}Cl was made in a manner similar to the ^{35}Cl species. The rotational constants and centrifugal distortion coefficients are listed in Table 1, and the experimental and calculated values of the transition frequency are given in Table 2.

The spectrum of *trans*-HFC=CFCl was found to be sharper and a little weaker than that of the *cis*-isomer. A search was made for Q-branch transitions for the ^{35}Cl isotope in the 8—18 GHz region and an assignment was obtained in the same way as for *cis*-HFC=CFCl. The rotational constants and centrifugal distortion coefficients are listed in Table 3, and the experimental and calculated frequencies are given in Table 4, together with the corresponding values for *trans*-HFC=CF^{37}Cl.

Nuclear Quadrupole Coupling. The Cl nuclear quadrupole interaction in 1-chloro-1,2-difluoroethylene is given by[12]

$$E_Q/h = 2\chi_{J_\tau}\cdot Y(I,J,F)/J(J+1),$$

where $Y(I,J,F)$ is Casimir's function. χ_{J_τ} is the quadrupole coupling constant (or splitting factor) for the rotational level which is given by first-order theory in terms of the diagonal elements in the χ_{J_τ} tensor in the principal inertial axis system as

$$\chi_{J_\tau} = \langle \boldsymbol{P}_a^2\rangle\chi_{aa} + \langle \boldsymbol{P}_b^2\rangle\chi_{bb} + \langle \boldsymbol{P}_c^2\rangle\chi_{cc},$$

where $\boldsymbol{P}_a^2$, $\boldsymbol{P}_b^2$, and $\boldsymbol{P}_c^2$ are the squares of the rotational angular momentum in the principal inertial-axis system. The values of $\langle \boldsymbol{P}_a^2\rangle$, $\langle \boldsymbol{P}_b^2\rangle$, and $\langle \boldsymbol{P}_c^2\rangle$ used in this work were calculated on HITAC M-200H computers at the Institute for Molecular Science and at Tokyo University.

Table 1. Rotational constants and centrifugal distortion coefficients for *cis*-1-chloro-1,2-difluroethylene[a]

	cis-HFC=CF^{35}Cl	*cis*-HFC=CF^{37}Cl
A	9 126.182(10) MHz	9 091.714(18) MHz
B	2 461.037(5)	2 397.536(9)
C	1 936.689(4)	1 895.643(14)
τ_{aaaa}	−0.0891(31)	−0.0915(61)
τ_{bbbb}	−0.00086(30)	−0.00006(77)
τ_{aabb}	0.0098(27)	0.0153(81)
τ_{abab}	−0.0097(19)	−0.0143(60)
I_a	55.376 u·Å^2	55.586 u·Å^2
I_b	205.351	210.790
I_c	260.948	266.599
Δ[b]	0.221	0.223

a) Standard deviations for last figures in parentheses.
b) $\Delta = I_c-I_a-I_b$.

The χ_{aa} and χ_{bb} components of quadrupole coupling tensor were determined from the transitions with relatively large hyperfine splitting. The χ_{cc} element was then determined from the Laplace equation $\chi_{aa}+\chi_{bb}+\chi_{cc}=0$. The results are listed in Table 5. From the observed splittings and the tabulated values of the Casimir's functions, the values ν_0 for an unperturbed transitions are easily calculated and are listed in Table 2 and Table 4. Using the results in Table 5, the quadrupole splitting in all measured transitions in both *cis*- and *trans*-HFC=CFCl was computed and compared with the experimental values. These values are also listed in Tables 2 and 4.

The diagonalized χ tensors for *cis*- and *trans*-HFC=CFCl were calculated by using the molecular structures obtained later with the assumption that the z axis coincides with the C–Cl internuclear line. θ_{az}, the angle between the a and z axes, for *cis*-HFC=CF^{35}Cl is 16.03°. It is very insensitive to the structural parameters because the C–Cl bond lies almost along a-axis. The result for *cis*-HFC=CF^{35}Cl is listed in Table 5 together with that of *cis*-HFC=CF^{37}Cl. In the same way, the diagonal χ tensor for *trans*-HFC=CF^{35}Cl was calculated, with $\theta_{az}=59.29°$, and listed in Table 5 together with the corresponding values of ^{37}Cl species. The values of $\chi_{zz}=-76.46$ MHz and $\chi_{zz}=-75.57$ MHz for *cis*- and *trans*-HFC=CF^{35}Cl, respectively, are consistent with those of other haloethylenes such as, placed in order of increasing number of substituted halogen atoms, −70.16, −70.7, −77.9, −73.42, −73.7, −77.40, and −89.14(−73.7) MHz for H_2C=CHCl,[1] *cis*-HClC=CHCl,[7] H_2C=CCl_2,[7] H_2C=CFCl,[5] *cis*-HFC=CHCl,[4] F_2C=CHCl,[6] and F_2C=CFCl,[5] respectively.

Molecular Structure. In order to determine the molecular structure the bond lengths were estimated by assuming a systematic shortening caused by halogen substitution which is well established in the r_s struc-

TABLE 2. OBSERVED AND CALCULATED SPECTRA OF *cis*-HFC=CFCl (MHz)

Transition	F[a]	*cis*-HFC=CF^{35}Cl				*cis*-HFC=CF^{37}Cl			
		ν(exptl)[d]	ν_0(exptl)	($\nu-\nu_0$) (exptl)	ν(calcd) $-\nu_0$(exptl)	ν(exptl)[d]	ν_0(exptl)	($\nu-\nu_0$) (exptl)	ν(calcd) $-\nu_0$(exptl)
$0_{00}\rightarrow 1_{11}$	3/2[c]	11 055.34	11 662.82	−7.48	−7.48	10 981.33	10 987.33	−6.00	−5.95
	3/2	11 061.32		−1.50	−1.47	10 986.21		−1.12	−1.18
	3/2[b]	11 068.81		5.99	6.04	10 992.08		4.75	4.91
$1_{01}\rightarrow 2_{12}$	1/2	14 919.32	14 936.21	−16.89	−16.90	14 765.39	14 778.62	−13.23	−13.40
	5/2[b]	14 926.09		−10.12	−10.09	e)			−8.00
	1/2[b]	14 928.63		−7.58	−7.48	e)			−5.96
	5/2	14 935.56		−0.68	−0.68	14 778.00		−0.62	−0.54
	3/2	14 943.10		6.89	6.84	14 784.01		5.39	5.41
	3/2[b]	14 949.67		13.46	13.55	14 789.23		10.61	10.73
$2_{20}\rightarrow 3_{31}$	7/2	e)	47 816.62		−2.19	47 591.25	47 592.93	−1.68	−1.67
	1/2	47 816.61		−0.01	0.05	47 593.00		0.07	0.10
	5/2	47 818.71		2.09	2.02	47 594.72		1.79	1.66
	3/2	47 820.98		4.36	4.25	47 596.27		3.34	3.43
$2_{21}\rightarrow 3_{30}$	7/2					47 619.44	47 621.17	−1.73	−1.82
	1/2					47 621.21		0.04	−0.07
	5/2					47 622.95		1.78	1.59
	3/2					47 624.62		3.45	3.39
$3_{12}\rightarrow 4_{23}$	3/2	36 790.92	36 795.46	−4.54	−4.62	36 494.74	36 498.45	−3.71	−3.73
	9/2	36 794.03		−1.43	−1.51	36 497.22		−1.23	−1.26
	5/2	36 795.86		0.40	0.36	36 498.69		0.24	0.22
	7/2	36 798.97		3.51	3.46	36 501.11		2.66	2.69
$3_{13}\rightarrow 4_{22}$	3/2	40 373.88	40 380.10	−6.22	−6.16	39 906.13	39 911.02	−4.83	−4.85
	9/2	40 377.95		−2.15	−2.11	39 909.25		−1.77	−1.64
	5/2	40 380·95		0.85	0.87	39 911.72		0.70	0.71
	7/2	40 385.03		4.93	4.92	39 914.92		3.90	3.92
$4_{22}\rightarrow 4_{31}$	5/2					34 410.14	34 417.52	−7.38	−7.14
	11/2					34 413.89		−3.63	−3.64
	7/2					34 420.47		2.95	2.83
	9/2					34 423.80		6.28	6.32
$4_{23}\rightarrow 4_{32}$	5/2	34 723.65	34 732.74	−9.09	−9.09	34 806.14	34 814.43	−7.29	−7.20
	11/2	34 728.10		−4.64	−4.63	34 809.69		−3.74	−3.67
	7/2	34 736.36		3.62	3.64	34 816.30		2.87	2.88
	9/2	34 740.86		8.12	8.10	34 819.85		6.42	6.42
$4_{14}\rightarrow 5_{05}$	7/2	16 748.62	16 749.96	−1.34	−1.33				
	9/2	16 749.20		−0.76	−0.79				
	5/2	16 750.39		0.43	0.47				
	11/2	16 751.00		1.04	1.02				
$4_{13}\rightarrow 5_{24}$	5/2	40 138.28	40 141.11	−2.83	−2.88				
	11/2	40 140.13		−0.98	−1.01				
	7/2	40 141.60		0.49	0.43				
	9/2	40 143.33		2.22	2.28				
$4_{14}\rightarrow 5_{23}$	5/2	46 379.97	46 384.35	−4.38	−4.33				
	11/2	46 382.60		−1.75	−1.75				
	7/2	46 385.46		1.11	1.09				
	9/2	46 388.08		3.73	3.67				
$5_{23}\rightarrow 5_{32}$	7/2	33 906.87	33 912.42	−5.55	−5.57	34 055.91	34 060.35	−4.44	−4.38
	13/2	33 909.20		−3.22	−3.23	34 057.80		−2.55	−2.53
	9/2	33 915.17		2.75	2.72	34 062.48		2.13	2.19
	11/2	33 917.56		5.14	5.06	34 064.42		4.07	4.04
$5_{24}\rightarrow 5_{33}$	7/2	34 884.56	34 890.20	−5.64	−5.63	34 953.27	34 957.73	−4.46	−4.46
	13/2	34 886.88		−3.32	−3.23	34 955.12		−2.61	−2.56
	9/2	34 892.95		2.75	2.89	34 959.87		2.14	2.29
	11/2	34 895.53		5.33	5.29	34 961.89		4.16	4.19

TABLE 2. (Continued)

Transition	F[a]	*cis*-HFC=CF^{35}Cl				*cis*-HFC=CF^{37}Cl			
		ν(exptl)[d]	ν_0(exptl)	$(\nu-\nu_0)$ (exptl)	ν(calcd) $-\nu_0$(exptl)	ν(exptl)[d]	ν_0(exptl)	$(\nu-\nu_0)$ (exptl)	ν(calcd) $-\nu_0$(exptl)
$5_{14}\rightarrow6_{25}$	7/2	43 234.12	43 235.97	−1.85	−1.90	42 828.29	42 829.82	−1.53	−1.44
	13/2	43 235.31		−0.66	−0.72	42 829.27		−0.55	−0.51
	9/2	43 236.36		0.39	0.31	42 830.08		0.26	0.32
	11/2	43 237.45		1.48	1.49	42 831.05		1.23	1.25
$6_{06}\rightarrow6_{15}$	9/2	13 896.60	13 898.14	−1.54	−1.52				
	15/2	13 897.14		−1.00	−0.95				
	11/2	13 899.04		0.90	0.88				
	13/2	13 899.61		1.47	1.45				
$6_{15}\rightarrow6_{24}$	9/2	17 498.39	17 500.33	−1.94	−1.89	17 603.56	17 605.10	−1.54	−1.48
	15/2	17 499.10		−1.23	−1.16	17 604.10		−1.00	−0.90
	11/2	17 501.46		1.13	1.17	17 606.00		0.90	0.94
	13/2	17 502.14		1.81	1.89	17 606.55		1.45	1.51
$6_{25}\rightarrow6_{34}$	9/2	35 155.19	35 159.08	−3.89	−3.88	35 201.55	35 204.59	−3.04	−3.13
	15/2	35 156.60		−2.48	−2.43	35 202.61		−1.98	−1.98
	11/2	35 161.29		2.21	2.35	35 206.33		1.74	1.73
	13/2	35 162.78		3.70	3.71	35 207.50		2.91	2.87
$6_{25}\rightarrow7_{16}$	13/2, 11/2	16 614.72	16 616.24	−1.52	−1.63, −1.40				
	15/2, 9/2	16 617.73		1.49	1.43, 1.66				
$6_{15}\rightarrow7_{26}$	9/2	46 097.50	46 098.74	−1.24	−1.19				
	15/2	46 098.30		−0.44	−0.40				
	11/2	46 098.96		0.22	0.31				
	13/2	46 099.81		1.07	1.10				
$7_{07}\rightarrow7_{16}$	11/2	16 695.79	16 697.12	−1.33	−1.38				
	17/2	16 696.18		−0.94	−0.94				
	13/2	16 697.95		0.83	0.78				
	15/2	16 698.42		1.30	1.22				
$7_{16}\rightarrow7_{25}$	11/2	17 309.90	17.311.27	−1.37	−1.37				
	17/2	17 310.29		−0.98	−0.91				
	13/2	17 312.21		0.94	0.89				
	15/2	17 312.53		1.26	1.35				
$7_{26}\rightarrow7_{35}$	11/2	35 571.34	35 574.25	−2.91	−2.88	35 584.16	35 586.41	−2.25	−2.33
	17/2	35 572.35		−1.90	−1.94	35 584.87		−1.54	−1.58
	13/2	35 576.05		1.80	1.77	35 587.87		1.46	1.36
	15/2	35 577.00		2.75	2.72	35 588.54		2.13	2.11
$8_{17}\rightarrow8_{26}$	13/2	17 528.37	17 529.44	−1.07	−1.04				
	19/2	17 528.67		−0.77	−0.72				
	15/2	17 530.15		0.71	0.74				
	17/2	17 530.47		1.03	1.06				
$8_{27}\rightarrow8_{36}$	13/2	36 167.88	36 170.10	−2.22	−2.23				
	19/2	36 168.54		−1.56	−1.57				
	15/2	36 171.57		1.47	1.45				
	17/2	36 172.27		2.17	2.11				
$9_{36}\rightarrow9_{45}$	15/2, 21/2					47 647.53	47 649.19	−1.66	−1.74, −1.25
	17/2					47 650.46		1.27	1.32
	19/2					47 651.00		1.81	1.81
$10_{37}\rightarrow10_{46}$	17/2, 23/2					47 068.91	47 070.16	−1.25	−1.47, −1.12
	19/2, 21/2					47 071.36		1.20	1.00, 1.36

a) $\Delta F=\Delta J$. b) $\Delta F=\Delta J-1$. c) $\Delta F=\Delta J-2$. d) ±0.1 MHz. e) Overlaps with other line.

TABLE 4. OBSERVED AND CALCULATED SPECTRA OF *trans*-HFC=CFCl (MHz)

Transition	F[a]	*trans*-HFC=CF^{35}Cl				*trans*-HFC=CF^{37}Cl			
		ν(exptl)[c]	ν_0(exptl)	$(\nu-\nu_0)$ (exptl)	ν(calcd) $-\nu_0$(exptl)	ν(exptl)[c]	ν_0(exptl)	$(\nu-\nu_0)$ (exptl)	ν(calcd) $-\nu_0$(exptl)
$1_{10}\rightarrow 2_{21}$	3/2	18 117.64	18 126.55	−8.91	−8.91	17 774.71	17 781.09	−6.38	−6.41
	3/2[b]	18 119.42		−7.13	−7.17	17 775.46		−5.63	−5.58
	5/2[b]	18 126.61		0.06	0.00	d)			0.55
	5/2	18 129.01		2.46	2.44	17 782.75		1.66	1.70
	1/2	18 135.45		8.90	8.87	17 788.12		7.03	6.98
	1/2[b]	18 137.93		11.38	11.31	17 789.27		8.18	8.09
$2_{12}\rightarrow 3_{03}$	1/2	14 117.88	14 120.75	−2.87	−2.89	13 916.66	13 918.68	−2.02	−1.98
	3/2	14 119.16		−1.57	−1.51	13 917.43		−1.25	−1.23
	7/2	14 120.75		0.00	−0.04	13 918.77		0.09	0.09
	5/2	14 122.13		1.38	1.35	13 919.53		0.85	0.84
$2_{12}\rightarrow 3_{13}$	1/2	14 503.60	14 505.53	−1.93	−1.89	14 280.72	14 282.30	−1.58	−1.55
	3/2	14 504.38		−1.15	−1.14	14 281.51		−0.79	−0.83
	5/2	14 505.45		−0.08	−0.03	14 282.14		−0.16	−0.16
	7/2	14 507.17		0.64	0.71	14.282.88		0.58	0.56
$2_{02}\rightarrow 3_{03}$	5/2	15 090.78	15 093.71	−2.93	−2.95	14 849.18	14 851.31	−2.13	−2.18
	3/2	15 092.19		−1.52	−1.49	14 850.03		−1.28	−1.27
	7/2	15 095.37		1.66	1.71	14 852.68		1.37	1.25
	1/2	15 096.86		3.15	3.17	14 853.42		2.11	2.16
$2_{02}\rightarrow 3_{13}$	5/2	15 474.26	15 478.61	−4.35	−4.45	15 211.71	15 214.85	−3.14	−3.09
	3/2	15 476.83		−1.78	−1.99	15 213.34		−1.51	−1.50
	7/2	15 480.88		2.27	2.34	15 216.57		1.72	1.81
	1/2	15 483.34		4.73	4.80	15 218.22		3.37	3.40
$2_{21}\rightarrow 3_{22}$	1/2	16 899.89	16 902.36	−2.47	−2.44	16 657.88	16 659.09	−1.21	−1.14
	7/2	16 901.71		−0.65	−0.69	16 658.75		−0.34	−0.32
	3/2	16 902.36		0.00	0.01	16 659.18		0.09	0.01
	5/2	16 904.09		1.73	1.76	16 659.90		0.81	0.83
$4_{23}\rightarrow 4_{32}$	5/2	14 133.43	14 135.04	−1.61	−1.63				
	11/2	14 134.15		−0.89	−0.83				
	7/2	14 135.74		0.70	0.65				
	9/2	14 136.46		1.42	1.45				
$4_{14}\rightarrow 4_{23}$	5/2	15 191.93	15 199.41	−1.48	−7.46				
	11/2	15 195.64		−3.77	−3.79				
	7/2	15 202.37		2.96	3.02				
	9/2	15 206.09		6.68	6.68				
$4_{31}\rightarrow 4_{40}$	9/2	16 079.65	16 084.44	−4.79	−4.89				
	7/2	16 082.30		−2.14	−2.17				
	11/2	16 087.20		2.76	2.86				
	5/2	16 089.80		5.36	5.57				
$4_{32}\rightarrow 4_{41}$	9/2	16 987.10	16 989.63	−2.53	−2.56				
	7/2	16 988.49		−1.14	−1.16				
	11/2	16 991.07		1.44	1.44				
	5/2	16 992.46		2.83	2.84				
$5_{32}\rightarrow 5_{41}$	11/2	14 577.04	14 581.66	−4.62	−4.66				
	9/2	14 579.15		−2.51	−2.53				
	13/2	14 584.57		2.91	2.88				
	7/2	14 586.65		4.99	5.01				
$5_{33}\rightarrow 5_{42}$	11/2	17 343.26	17 344.04	−0.78	−0.82	16 912.60	16 912.79	−0.19	−0.26
	9/2	17 343.59		−0.45	−0.45				−0.11
	13/2	17 344.57		0.53	0.51	16 913.00		0.21	0.26
	7/2	17 344.87		0.83	0.89				0.40
$6_{15}\rightarrow 6_{24}$	9/2	15 901.45	15 908.40	−6.95	−6.94	15 744.69	15 749.87	−5.18	−5.14
	15/2	15 904.04		−4.36	−4.36	15 746.62		−3.25	−3.22
	11/2	15 912.36		3.96	4.00	15 752.82		−2.95	2.98
	13/2	15 914.96		6.56	6.58	15 754.75		4.88	4.90

TABLE 4. (Continued)

Transition	F[a]	*trans*-HFC=CF^{35}Cl				*trans*-HFC=CF^{37}Cl			
		ν(exptl)[c]	ν_0(exptl)	$(\nu-\nu_0)$ (exptl)	ν(calcd) $-\nu_0$(exptl)	ν(exptl)[c]	ν_0(exptl)	$(\nu-\nu_0)$ (exptl)	ν(calcd) $-\nu_0$(exptl)
$6_{34}\rightarrow6_{43}$	9/2					17 910.25	17 910.75	−0.50	−0.75
	15/2								−0.50
	11/2					17 911.20		0.45	0.32
	13/2								0.57
$7_{43}\rightarrow7_{52}$	15/2					17 844.61	17 847.10	−2.49	−2.52
	13/2					17 845.47		−1.63	−1.66
	17/2					17 848.84		1.74	1.71
	11/2					17 849.70		2.60	2.57
$8_{44}\rightarrow8_{53}$	17/2	16 198.71	16 201.63	−2.92	−2.96	15 641.33	15 643.29	−1.96	−1.95
	15/2	16 199.55		−2.08	−2.05	15 641.88		−1.41	−1.34
	19/2	16 203.80		2.17	2.12	15 644.74		1.45	1.47
	13/2	16 204.64		3.01	3.03	15 645.35		2.06	2.08
$8_{36}\rightarrow8_{35}$	13/2	17 655.05	17 660.99	−5.94	−6.01	17 577.82	17 582.23	−4.41	−4.34
	19/2	17 656·80		−4.19	−4.24	17 579.19		−3.04	−3.04
	15/2	17 664.97		3.98	3.93	17 585.12		2.89	2.93
	17/2	17 666.71		5.72	5.71	17 586.48		4.25	4.23
$8_{26}\rightarrow8_{35}$	13/2					18 209.48	18 213.36	−3.88	−3.87
	19/2					18 210.59		−2.77	−2.73
	15/2					18 215.82		2.45	2.51
	17/2					18 216.98		3.62	3.36
$9_{45}\rightarrow9_{54}$	19/2	14 683.19	14 684.45	−1.26	−1.25	14 244.30	14 244.99	−0.69	−0.72
	17/2	14 683.55		−0.90	−0.89				−0.51
	21/2	14 685.39		0.94	0.97	14 245.70		0.71	0.60
	15/2	14 685.73		1.28	1.32				0.81
$9_{36}\rightarrow9_{45}$	15/2	15 684.13	15 687.45	−3.32	−3.29	15 558.84	15 561.40	−2.56	−2.51
	21/2	15 685.05		−2.40	−2.39	15 559.55		−1.85	−1.83
	17/2	15 689.78		2.33	−2.36	15 563.17		1.77	1.79
	19/2	15 690.66		3.21	3.26	15 563.88		2.48	2.48
$10_{46}\rightarrow10_{55}$	17/2	15 024.89	15 025.56	−0.67	−0.75	14 744.10	14 744.71	−0.61	−0.74
	23/2				−0.56				−0.56
	19/2	15 026.21		0.65	0.57	14 745.30		0.59	0.49
	21/2				0.76				0.67
$11_{57}\rightarrow11_{56}$	19/2	14 001.67	14 006.30	−4.63	−4.64				
	25/2	14 002.75		−3.55	−3.57				
	21/2	14 009.78		3.48	3.48				
	23/2	14 010.82		4.52	4.54				
$11_{56}\rightarrow11_{65}$	23/2	17 600.72	17 602.11	−1.39	−1.40	17 028.20	17 028.99	−0.79	−0.90
	21/2	17 600.98		−1.13	−1.06				−0.69
	25/2	17 603.25		1.14	1.17	17 029.80		0.81	0.69
	19/2	17 603.55		1.44	1.51				0.90
$11_{47}\rightarrow11_{56}$	19/2	17 748.64	17 751.17	−2.53	−2.53	17 612.91	17 614.89	−1.98	−1.96
	25/2	17 749.22		−1.95	−1.95	17 613.39		−1.50	−1.51
	21/2	17 753.05		1.88	1.90	17 616.36		1.47	1.47
	23/2	17 753.65		2.48	2.48	17 616.82		1.93	1.92
$12_{57}\rightarrow12_{66}$	21/2	17 405.20	17 405.47	−0.27	−0.35	17 041.70	17 042.04	−0.34	−0.37
	27/2				−0.29				−0.29
	23/2	17 405.73		0.26	0.18	17 042.36		0.32	0.30
	25/2				0.25				0.38
$13_{68}\rightarrow13_{67}$	23/2	14 696.33	14 700.41	−4.08	−4.15				
	29/2	14 697.15		−3.26	−3.32				
	25/2	14 703.61		3.20	3.24				
	27/2	14 704.42		4.01	4.08				

a) $\Delta F=\Delta J$. b) $\Delta F=\Delta J-1$. c) ±0.1 MHz. d) Overlaps with other line.

Table 3. Rotational constants and centrifugal distortion coefficients for *trans*-1-chloro-1,2-difluoroethylene[a]

	trans-HFC=CF^{35}Cl	*trans*-HFC=CF^{37}Cl
A	5 336.381 (8) MHz	5 232.441 (10) MHz
B	3 516.721 (9)	3 469.251 (15)
C	2 117.416 (5)	2 083.794 (9)
τ_{aaaa}	−0.0122 (13)	−0.0139 (14)
τ_{bbbb}	−0.0082 (14)	−0.0091 (26)
τ_{aabb}	0.0146 (55)	0.0144 (99)
τ_{abab}	−0.0095 (21)	−0.0085 (37)
I_a	94.704 u·Å^2	96.585 u·Å^2
I_b	143.707	145.673
I_c	238.676	242.527
Δ[b]	0.265	0.269

a) Standard deviations for last figures in parentheses.
b) $\Delta = I_c - I_a - I_b$.

tures of haloethylenes. The C–Cl bond lengths of 1.726, 1.717, and 1.718 Å determined for H_2C=CHCl,[1] HCl=CHCl,[7] and H_2C=CCl_2,[7] respectively, show a systematic shortening and suggest about 1.710 Å for the C–Cl bond in HFC=CFCl. Similarly, the C–F bond lenghts of 1.349, 1.335, and 1.323 Å for H_2C=CHF,[8] HFC=CHF,[9] and H_2C=CF_2,[9] respectively, suggest about 1.328 and 1.322 Å for the C–F and C–F′ bonds in HFC=CF′Cl, respectively. The C=C bond lengths of 1.332, 1.320, 1.338, 1.329, 1.324, and 1.315 Å for H_2C=CHCl,[1] HClC=CHCl,[7] H_2C=CCl_2,[7] H_2C=CHF,[8] HFC=CHF,[9] and H_2C=CF_2,[9] respectively, present a more confused situation. The C=C bond lengths in H_2C=CCl_2 and H_2C=CF_2, however, seem to have a large effect from zero point vibration because a carbon atom in either molecules lies very close to the center of mass.[7] From the rest of the molecules, the estimation of about 1.318 Å was made for the C=C bond length in HFC=CFCl.

Table 5. Quadrupole coupling constants for *cis*- and *trans*-1-chloro-1,2-difluoroethylene (MHz)

	cis-HFC=CFCl		*trans*-HFC=CFCl	
	^{35}Cl	^{37}Cl	^{35}Cl	^{37}Cl
	Principal-axis system			
χ_{aa}	−67.67 (20)	−53.62 (30)	9.78 (10)	4.72 (20)
χ_{bb}	30.05 (20)	23.83 (50)	−45.41 (10)	−32.54 (20)
χ_{cc}	37.62 (20)	29.79 (50)	35.63 (10)	27.82 (20)
	C–Cl bond-axis system[a]			
χ_{zz}	−76.46	−60.19	−75.57	−59.68
χ_{xx}	38.84	30.40	39.94	31.86
χ_{yy}	37.62	29.79	35.63	27.82
η_{bond}[b]	−0.0160	−0.0101	−0.0570	−0.0677

a) Z is coincident with the C–Cl bond axis and x is in the plane of the molecule. b) $\eta_{bond} = (\chi_{xx} - \chi_{yy})/\chi_{zz}$.

Table 6. Plausible structural parameters of *cis*-HFC=CFCl

r(C–H)	1.080 Å
r(C–F_1)	1.328
r(C=C)	1.318
r(C–Cl)	1.710
r(C–F_2)	1.322
∠H–C=C	122.1°
∠F_1–C=C	121.9
∠C=C–Cl	123.4
∠C=C–F_2	123.3
Calculated moments of inertia	
^{35}Cl I_a	55.396 u·Å^2
I_b	205.383
I_c	260.779
^{37}Cl I_a	55.622
I_b	210.784
I_c	266.406

Table 7. Plausible structural parameters of *trans*-HFC=CFCl

	Set I	Set II	Set III
r(C–H)	1.080 Å	1.080 Å	1.080 Å
r(C–F_1)	1.328	1.324	1.323
r(C=C)	1.318	1.319	1.316
r(C–F_2)	1.322	1.322	1.320
r(C–Cl)	1.710	1.712	1.712
∠H–C=C	119.7°	120.0°	120.0°
∠F_1–C=C	123.9	123.3	122.9
∠C=C–F_2	122.7	122.1	120.8
∠C=C–Cl	122.9	123.5	124.5
θ_{az}	62.36	61.16	59.27
	Calculated Moments of inertia		
^{35}Cl I_a	94.639 u·Å^2	94.685 u·Å^2	94.671 u·Å^2
I_b	143.820	143.746	143.740
I_c	238.460	238.432	238.410
^{37}Cl I_a	96.625	96.616	96.510
I_b	145.655	145.663	145.791
I_c	242.280	142.278	242.301

By assuming the bond lengths estimated above, the bond angles in *cis*-HFC=CFCl were fitted so as to give the observed moments of inertia of both Cl isotopic species. The result is shown in Table 6 together with the calculated moments of inertia. The structural parameters obtained are consistent with those of other haloethylenes.

The same treatment was made for *trans*-HFC=CFCl. The θ_{az}, however, was found to be very sensitive to the structural parameters and a small deviation in θ_{az} gives an unlealistic value for the diagonal χ tensor. Therefore, three sets of structural parameters which have various θ_{az} were tentatively calculated, as shown in Table 7, by keeping the bond lengths close to the estimated values. The parameters of Set I and Set II, however, lead to $\chi_{zz}=-66.26$ MHz and $\chi_{zz}=-69.43$ MHz, respectively, and besides $\chi_{xx}<\chi_{yy}$, which does not seem possible. On the other hand, Set III gives reasonable values for the χ tensor as discussed before and is very probable for the structure of *trans*-HFC=CFCl.

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References

1) D. Kivelson, E. B. Wilson, and D. R. Lide, *J. Chem. Phys.*, **32**, 205 (1960).
2) W. H. Flygare and J. A. Howe, *J. Chem. Phys.*, **36**, 440 (1962).
3) S. Sekino and T. Nishikawa., *J. Phys. Soc. Jpn.*, **12**, 43 (1957).
4) J. A. Howe, *J. Chem. Phys.*, **34**, 1247 (1961).
5) R. G. Stone and W. H. Flygare, *J. Mol. Spectrosc.*, **32**, 233 (1969); Krishnaji & Suresh Chandra, *Indian J. Pure Appl. Phys.*, **8**, 634 (1970).
6) R. G. Stone and W. H. Flygare, *J. Chem. Phys.*, **49**, 1943 (1968).
7) H. Takeo, M. Sugie, and C. Matsumura, to be published.
8) D. R. Lide and D. Christensen, *Spectrochim. Acta*, **17**, 665 (1961).
9) V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963).
10) J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, **1961**, 2204.
11) T. Ogata, *Reports of Faculty of Liberal Arts, Shizuoka University*, **16**, 13 (1980).
12) W. Gordy and R. L. Cook, "Microwave Molecular Spectra," ed by W. West, Interscience Publishers, New York, N. Y. (1970).