

## Vibrational Assignments and Thermodynamic Functions for *cis*- and *trans*-1,2-Difluoro-1-chloroethylenes

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Complete assignments of the vibrational fundamentals of *cis*- and *trans*-CFCl=CFH and CFCl=CFD have been obtained from infrared and Raman spectra. For *cis*-CFCl=CFH the fundamentals are: (a') 3137, 1716, 1326, 1159, 1112, 854, 480, 361, and 224 cm<sup>-1</sup>; (a'') 776, 523, and 255 cm<sup>-1</sup>. For *trans*-CFCl=CFH the fundamentals are: (a') 3120, 1708, 1290, 1196, 1150, 696, 578, 397, and 200 cm<sup>-1</sup>; (a'') 776, 467, and 310 cm<sup>-1</sup>. For the *cis*-to-*trans* reaction at 591°K, the equilibrium constant is 0.932 ± 0.022. From a rigid rotor, harmonic-oscillator treatment  $\Delta S_{591}^{\circ} = -0.12 \pm 0.26$  cal/mol °K, and  $\Delta E_0^{\circ}$  (electronic) = 80 ± 260 cal/mol with the *cis* isomer having the lower energy. Also,  $\Delta H_{591}^{\circ} = 10 \pm 160$  cal/mol.

This investigation of the *cis* and *trans* isomers of 1,2-difluoro-1-chloroethylene was undertaken as part of a study of nonbonded interactions in the *cis*-*trans* isomers of chlorofluoroethylenes. From thermodynamic and spectroscopic data the *cis* isomers of NF=NF, CFH=CFH, CFH=CClH, and CClH=CClH have been shown to have 3–0.6 kcal less electronic energy than the corresponding *trans* isomers.<sup>2</sup> This energy difference has been attributed to a nonbonded force acting between *cis* halogen atoms. CFCl=CFH was chosen as a convenient example of a trihaloethylene. In this system we expected all of the vibrational fundamentals to be accessible above 200 cm<sup>-1</sup> in the infrared and side reactions to be unimportant in the iodine catalyzed *cis*-*trans* isomerization.

The present paper is concerned with obtaining a complete assignment for the vibrational fundamentals of the 1,2-difluoro-1-chloroethylenes and with extracting the electronic energy difference between the *cis* and *trans* isomers. To reinforce the vibrational assignment, *cis*- and *trans*-CFCl=CFD are included in the spectroscopic study. Apparently no previous report of the vibrational spectra of these ethylenes is in the literature. However, Nielsen, Liang, and Smith have assigned all of the fundamentals of the gem isomer, 1,1-difluoro-2-chloroethylene,<sup>3</sup> and we have assigned several closely related molecules.<sup>2</sup> No thermodynamic data appear to be available.

### Experimental Section

**Syntheses.** CBrClFCClFH was prepared in 35% yield by reaction of CFCICFCI with hydrogen bromide on charcoal at 215°. This reaction was carried out by metering the gaseous reactants, each at a rate of about 2.5 l. (NTP)/hr, into a hot tube packed with the activated charcoal (Barneby-Cheney SV2). The ethane was collected and worked up as described before, and a fraction boiling between 93 and 97° was collected.

Dehalogenation of the CBrClFCClFH with zinc dust

in refluxing ethanol gave a 95% yield of *cis*- and *trans*-CFCICFH along with some CF<sub>2</sub>CClH and CF<sub>2</sub>CH<sub>2</sub>. (The CF<sub>2</sub>CClH is traceable to the CCl<sub>2</sub>CF<sub>2</sub> present in the starting olefin.)

*cis*- and *trans*-CClFCCFD were prepared by exchanging the crude olefin mixture at 80–90° with deuterium oxide saturated with calcium oxide. This exchange reaction involved two liquid phases sealed in standard-wall Pyrex tube. To prevent explosion of the tube, it was placed in a rocking bomb and pressurized to 225 psi; 2–3 days was taken for each exchange step.

Separation and purification of the *cis* and *trans* olefins were achieved by gas chromatography. Two passes at 0° through an 8-m column packed with tri-*m*-tolyl phosphate on firebrick followed by a pass at 0° through a 4-m column packed with halocarbon oil (11–21) on firebrick were used to obtain final purities above 99.5%. The *trans* isomer is eluted first on these columns. Samples were dried by passing them over phosphorus decoxide. Estimates of isotopic purities of the CFCICFD samples (see spectra) were obtained from the intensities of infrared bands due to undeuterated species.

Boiling points of pure *cis*-CFCICFH (–10.0°) and *trans*-CFCICFH (–13.9°) were calculated from vapor pressure measurements (lit.<sup>5</sup> bp 15° for mixture). Melting points were measured as –133.5° (*cis*) and –134.8° (*trans*).<sup>4</sup>

**Spectroscopy.** Infrared spectra, Figures 1–4, were recorded on a Perkin-Elmer 621 filter-grating spec-

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(2) See N. C. Craig, Y.-S. Lo, L. G. Piper, and J. C. Wheeler, *J. Phys. Chem.*, **74**, 1712 (1970), and other references cited therein.

(3) J. R. Nielsen, C. Y. Liang, and D. C. Smith, *J. Chem. Phys.*, **20**, 1090 (1953).

(4) N. C. Craig and D. A. Evans, *J. Amer. Chem. Soc.*, **87**, 4223 (1965).

(5) J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 2204 (1961).

**Table I:** Infrared and Raman Spectra and Assignments for *cis*-CFCl=CFH (Frequencies in  $\text{cm}^{-1}$ )

Raman, liquid			Infrared, gas			Assignment					
Freq, $\text{cm}^{-1}$	<i>I</i>	pol	Freq, <sup>a</sup> $\text{cm}^{-1}$	$\alpha^b$	Band shape <sup>c</sup>	Freq, $\text{cm}^{-1}$		Symmetry species			
3135	w	p	3137 (14)	0.40	A	Fund	$\nu_1$	$a'$			
			2871 (13)	0.062	A/B	2875	$\nu_2 + \nu_4$	$A'$			
			2822 (13)	0.051	B	2828	$\nu_2 + \nu_5$	$A'$			
			2362	R branch	CO <sub>2</sub> impurity						
			2311 (14)	0.15	A/B	2318	$2 \times \nu_4$	$A'$			
			2264 (13)	0.060	B	2271	$\nu_4 + \nu_5$	$A'$			
			1968		C	1971	$\nu_2 + \nu_{12}$	$A''$			
			1938 (13)	0.004	A/B	1940	$\nu_2 + \nu_9$	$A'$			
			1714	s	p	1716 (13)	1.8	B	Fund	$\nu_2$	$a'$
			1585	0.09	?	1592	$\nu_5 + \nu_7$	$A'$			
1714	s	p	1547 (12)	0.35	B	1552	$2 \times \nu_{10}$	$A'$			
			1550			1550	$\nu_3 + \nu_9$				
			1411 (21)	0.007	C	1414	$\nu_4 + \nu_{12}$	$A''$			
			1382 (14)	0.042	A/B	1383	$\nu_4 + \nu_9$	$A'$			
			1320	w	dp	1326 (12)	2.2	B	Fund	$\nu_3$	$a'$
			1149	w	dp	1159 (13)	6.1	$A^d$	Fund	$\nu_4$	$a'$
			1102	m	p	1112 (12)	14	A/B <sup>d</sup>	Fund	$\nu_5$	$a'$
			1048 (13)	0.95	$A^d$	1046	$2 \times \nu_{11}$	$A'$			
			851	s	p	854 (13)	4.0	$A^d$	Fermi resonance with $\nu_6$		
			781	wm	dp	776 (19)	0.71	$C^d$	Fund	$\nu_6$	$a'$
524	m	dp	667		C	CO <sub>2</sub> impurity					
			523 (20)	0.062	$C^d$	Fund	$\nu_{11}$	$a''$			
			510			510	$2 \times \nu_{12}$	$A'$			
484	s	p	480 (11)	0.052	B	Fermi resonance with $\nu_7$					
			363	s	p	361 (13)	0.042	$A^d$	Fund	$\nu_7$	$a'$
			258	w	dp	255	0.08	C	Fund	$\nu_8$	$a'$
227	w	dp	224	0.19	B?	Fund	$\nu_{12}$	$a''$			
						Fund	$\nu_9$	$a'$			

<sup>a</sup> Spacing between P and R branches in parentheses. <sup>b</sup> Absorption coefficient in  $\text{cm}^{-1} \text{atm}^{-1}$ ; combination bands with intensities  $< 0.05$  omitted unless of special interest. <sup>c</sup> A and B band shape designations are approximate for these molecules of  $C_s$  symmetry. A/B signifies a mixed shape. <sup>d</sup> Multiplet structure suggestive of a chlorine isotope effect or a hot band.

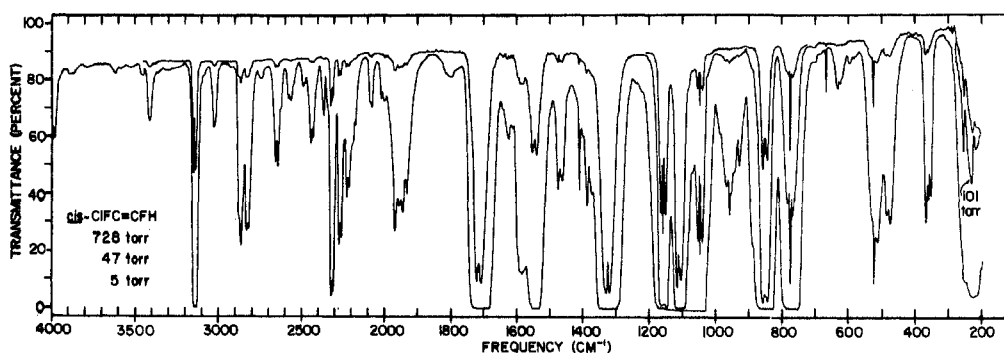


Figure 1. Gas-phase infrared spectrum of *cis*-1,2-difluoro-1-chloroethylene. (The weak features at 2350 and 667  $\text{cm}^{-1}$  are due to impurity carbon dioxide.)

trometer that was purged with dry nitrogen. Gaseous samples were scanned at ambient temperature in 10-cm cells equipped with cesium iodide windows. Frequencies, Tables I–IV, were measured to  $\pm 1 \text{ cm}^{-1}$  under expanded-scale, medium–high resolution conditions. In the spectra bands due to isotopic impurities are shown with dashed lines.

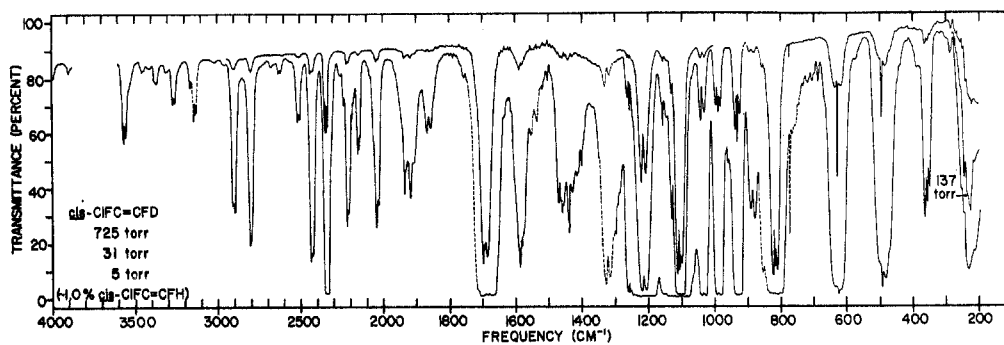
Room temperature, liquid-phase Raman spectra,

Tables I–IV, were recorded photographically on a Hilger E612 spectrograph with 4358-Å excitation from mercury arcs. Capillary cells (2-mm i.d.) were used for samples of about 15 mmol in size. Qualitative depolarizations were obtained by the Edsall–Wilson method. These Raman spectra were obtained by G. Y.-S. Lo at the Dow Chemical Co., Midland, Mich.

Proton nuclear magnetic resonance spectra (type

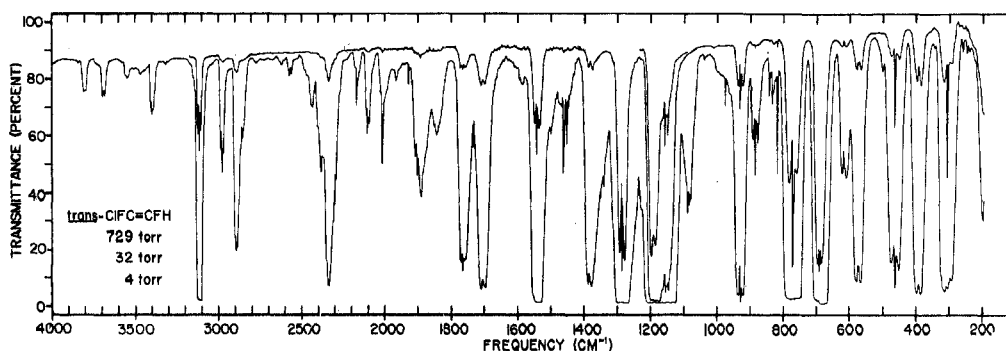
**Table II:** Infrared and Raman Spectra and Assignments for *cis*-CFCl=CFD (Frequencies in  $\text{cm}^{-1}$ )

Raman, liquid			Infrared, gas			Assignment	
Freq., $\text{cm}^{-1}$	<i>I</i>	pol	Freq., $\text{cm}^{-1}$	$\alpha^b$	Band shape <sup>c</sup>	Freq., $\text{cm}^{-1}$	Symmetry species
			3137 (14)		A	3137	<i>cis</i> -CFClCFH impurity
			2801 (10)	0.067	A/B	2806	$\nu_2 + \nu_4$ A'
			2433 (12)	0.082	B	2436	$2 \times \nu_3$ A'
2354?	w	p	2345 (13)	0.42	A	Fund	$\nu_1$ a'
			2215 (12)	0.051	A/B	2220	$2 \times \nu_4$ A'
			1938	0.01	C	1943	$\nu_2 + \nu_{12}$ A''
			1914 (12)	0.035	B	1916	$\nu_2 + \nu_9$ A'
1698	s	p	1696	2.0	B	1931	$\nu_4 + \nu_6$ A'
			1590	0.068	?	Fund	$\nu_2$ a'
			~1546 (14)		B	1606	$\nu_4 + \nu_{11}$ A''
			1469 (11)	0.045	A/B	1589	$\nu_4 + \nu_7$ A'
			1463		C?	1547	<i>cis</i> -CFClCFH impurity
			1437	0.047	B	1471	$\nu_5' + \nu_7$ A'
			1326 (13)		B	1469	$\nu_4 + \nu_8$ A'
			1259 (14)	0.25	A <sup>d</sup>	1465	$\nu_3 + \nu_{12}$ A''
1204	vw		1218 (13)	5.0	B	1438	$\nu_3 + \nu_9$ A'
			1159		C	1326	<i>cis</i> -CFClCFH impurity
			1156 (12)	0.25	B	1260	$2 \times \nu_{10}$ A'
			1128 (12)	0.15	A <sup>d</sup>	Fermi resonance with $\nu_3$	
1100	m	p	1110 (13)	15	A	Fund	$\nu_3$ a'
1045?	vw		1040 (12)	0.37	B	1177	$\nu_9 + \nu_{12}$ A''
			992 (13)	0.27	A	1154	$\nu_5 + \nu_9$ A'
938	w	dp	934 (13)	0.39	A <sup>d</sup>	Fermi resonance with $\nu_4$	
			890 (13)	0.050	B <sup>d</sup>	1126	$\nu_{10} + \nu_{11}$ A'
			853 (14)		A <sup>d</sup>	Fermi resonance with $\nu_4$	
822	s	p	821 (13)	2.4	A	1041	$\nu_6 + \nu_9$ A'
			776		C	Fund	$\nu_4$ a'
633	sm	dp	630 (19)	0.25	C	1041	$\nu_6 + \nu_9$ A'
502	w	dp	496 (19)	0.15	C	Fermi resonance with $\nu_4$ ?	
479	sm	p	~475			992	$2 \times \nu_{11}$ A'
361	sm	p	359 (14)	0.047	A	Fermi resonance with $\nu_5$ ( $\nu_5'$ )	
259	vw	dp	247	0.05	C <sup>d</sup>	Fund	$\nu_5$ a'
226	vw	dp	220	0.28	B?	Fund	$\nu_5$ a'
						877	$\nu_{10} + \nu_{12}$ A'
						838	$\nu_7 + \nu_8$ A'
						Fermi resonance with $\nu_6$	
						854	<i>cis</i> -CFClCFH impurity
						Fund	$\nu_6$ a'
						776	<i>cis</i> -CFClCFH impurity
						Fund	$\nu_{10}$ a''
						Fund	$\nu_{11}$ a''
						Fund	$\nu_7$ a'
						Fund	$\nu_8$ a'
						Fund	$\nu_{12}$ a''
						Fund	$\nu_9$ a'

<sup>a-d</sup> See Table I.Figure 2. Gas-phase infrared spectrum of *cis*-1,2-difluoro-1-chloroethylene-2-*d*<sub>1</sub>.

**Table III:** Infrared and Raman Spectra and Assignments for *trans*-CFCl=CFH (Frequencies in  $\text{cm}^{-1}$ )

Raman, liquid			Infrared, gas			Assignment		
Freq., $\text{cm}^{-1}$	<i>I</i>	pol	Freq., <sup>a</sup> $\text{cm}^{-1}$	$\alpha^b$	Band shape <sup>c</sup>	Freq., $\text{cm}^{-1}$		Symmetry species
3121	wm	p	3120 (16)	0.39	A <sup>d</sup>	Fund	$\nu_1$	a'
			2901 (14)	0.068	A/B	2904	$\nu_2 + \nu_4$	A'
			2342 (13)	0.12	?	2347	$\nu_4 + \nu_5$	A'
			1770 (12)	0.084	A/B	1774	$\nu_4 + \nu_7$	A'
						1728	$\nu_5 + \nu_7$	A'
						Fermi resonance with $\nu_2$ ?		
1709	s	p	1708 (11)	0.16	B	Fund	$\nu_2$	a'
~1551	vw		1547 (13)	0.38	A <sup>d</sup>	1552	$2 \times \nu_{10}$	A'
						1547	$\nu_5 + \nu_8$	A'
			1387 (11)	0.11	B	1396	$\nu_4 + \nu_9$	A'
						1392	$2 \times \nu_6$	A'
1289	m	dp	1290 (14)	1.7	A	Fund	$\nu_3$	a'
1188	vw		1196 (12)	14	A/B <sup>d</sup>	Fund	$\nu_4$	a'
1151	w		1160 (14)	2.8	A <sup>d</sup>	1156	$2 \times \nu_7$	A'
						Fermi resonance with $\nu_5$		
1141	wm	p	1150	2.8	A <sup>d</sup>	Fund	$\nu_5$	a'
~933	vw		935 (14)	0.19	A <sup>d</sup>	934	$2 \times \nu_{11}$	A'
						Fermi resonance with $\nu_6$		
779	m	dp	776 (23)	0.78	C <sup>d</sup>	Fund	$\nu_{10}$	a''
690	s	p	696 (12)	1.9	A <sup>d</sup>	Fund	$\nu_6$	a'
			620 (13)	0.033	A/B	620	$2 \times \nu_{12}$	A'
						597	$\nu_8 + \nu_9$	A'
						Fermi resonance with $\nu_7$		
576	m	p	578 (11)	0.13	A/B	Fund	$\nu_7$	a'
467	m	dp	467 (24)	0.11	C	Fund	$\nu_{11}$	a''
397	m	dp	397 (12)	0.24	B	Fund	$\nu_8$	a'
316	m	dp	310 (23)	0.19	C	Fund	$\nu_{12}$	a''
200	m	dp	~205 R	0.03		Fund	$\nu_9$	a'

<sup>a-d</sup> See Table I.Figure 3. Gas-phase infrared spectrum of *trans*-1,2-difluoro-1-chloroethylene.

AMX) were recorded on a Varian A-60 spectrometer. Samples consisted of 20 mol % olefin in  $\text{CFCl}_3$  solvent with a 1% TMS reference. For *cis*-CFClCFH:  $J_{\text{HF(gem)}} = 72.9$  Hz,  $J_{\text{HF(trans)}} = 12.4$  Hz, and  $\delta = 6.39$  ppm; for *trans*-CFClCFH:  $J_{\text{HF(gem)}} = 74.3$  Hz,  $J_{\text{HF(cis)}} = 1.2$  Hz, and  $\delta = 7.26$  ppm.<sup>6</sup>

**Isomerization Equilibrium.** The equilibrium constant for the *cis*-to-*trans* isomerization of  $\text{CFCl}=\text{CFH}$  in the gas phase was measured at  $318 \pm 1^\circ$ . For the *cis*-to-*trans* reaction  $K = 0.932 \pm 0.022$ .<sup>7</sup> Iodine (about 0.5 Torr) was used as a catalyst, and analyses were per-

formed by gas chromatography. On the 8-m tricresyl phosphate column ( $0^\circ$ ) the two isomers were not quite completely resolved. An experimentally determined correction factor of  $1.008 \pm 0.007$  was applied to the ratio of areas measured with a planimeter. Equilibrium was approached from both the *cis*-rich and *trans*-

(6) Compare P. B. Sargeant, *J. Org. Chem.*, **35**, 678 (1970). For *cis* isomer:  $J = 74$  and  $J = 12$  Hz,  $\delta = 6.05$  (neat); for *trans* isomer:  $J = 74$  and  $J = 1.2$  Hz,  $\delta = 6.90$  (neat).

(7) 0.015 is the standard deviation (SD) based on 8 final measurements; 0.007 is SD in the calibration of the area ratio.

**Table IV:** Infrared and Raman Spectra and Assignments for *trans*-CFCl=CFD (Frequencies in  $\text{cm}^{-1}$ )

Raman, liquid			Infrared, gas			Assignment		
Freq, $\text{cm}^{-1}$	<i>I</i>	pol	Freq, <sup>a</sup> $\text{cm}^{-1}$	$\alpha^b$	Band shape <sup>c</sup>	Freq, $\text{cm}^{-1}$	Assignment	Symmetry species
2348	w	p	3120 (16)		A	3120	<i>trans</i> -CFClCFH impurity	
			2882 (11)	0.092	A/B	2886	$\nu_2 + \nu_3$	A'
			2364 (11) <sup>e</sup>	0.29	A/B	2367	$\nu_3 + \nu_4$	A'
2321	m	p	2326 (15)	0.32	A	2351	$\nu_3 + \nu_6$	A'
			2146 (10)	0.055	A	2340	$2 \times \nu_4$	A'
			2128		C?	Fermi resonance with $\nu_1$		
			2118 (16)		A?	Fund	$\nu_1$	a'
			1766 (13)	0.079	A/B <sup>d</sup>	2151	$\nu_3 + \nu_5$	A'
1683	vs	p	1689 (10) <sup>e</sup>	0.22	B	2129	$\nu_2 + \nu_{11}$	A''
			~1650			2124	$\nu_4 + \nu_5$	A''
1655	vw		1326 (12)	0.10	A/B	1770	$\nu_3 + \nu_7$	A'
			1268			1743	$\nu_4 + \nu_7$	A'
1268	vw		1275 (13)	0.25	A <sup>d</sup>	Fermi resonance with $\nu_2$		
			1235 (12)	0.24	A/B	Fund	$\nu_2$	a'
1154	wm	p	1197 (12)	16	A/B <sup>d</sup>	1653	$\nu_5' + \nu_7$	A'
			1170 (14)	<5.7	A <sup>d</sup>	1330	$2 \times \nu_6$	A'
1137	vw		~1140			1276	$2 \times \nu_{10}$	A'
			1080 (15)	0.24	A/B	Fermi resonance with $\nu_3$		
950	m	p	954 (9) <sup>e</sup>	0.51	B	1238	$\nu_6 + \nu_7$	A'
			882 (15)	0.10	A	Fermi resonance with $\nu_3$		
659	vs	p	776		C <sup>d</sup>	Fund	$\nu_3$	a'
			655 (12)	1.8	A <sup>d</sup>	Fund	$\nu_4$	a'
636	s	dp	639 (~20)	0.63	C <sup>d</sup>	1146	$2 \times \nu_7$	A'
571	sm	p	573 (12)	0.17	A <sup>d</sup>	1152	$\nu_5 + \nu_9$	A'
440	w	dp?	440 (24)	0.13	C	Fermi resonance with $\nu_4$		
393	m	dp?	394 (13)	0.24	A/B	1078	$\nu_{10} + \nu_{11}$	A'
295	m	dp	292 (23)	0.55	C	967	$\nu_7 + \nu_8$	A'
198	m	dp	<200	<0.08		Fermi resonance with $\nu_5$ ( $\nu_5'$ )		
						Fund	$\nu_5$	a'
						880	$2 \times \nu_{11}$	A'
						Fermi resonance with $\nu_6$		
						776	<i>trans</i> -CFClCFH impurity	
						Fund	$\nu_6$	a'
						Fund	$\nu_{10}$	a''
						Fund	$\nu_7$	a'
						Fund	$\nu_{11}$	a''
						Fund	$\nu_8$	a'
						Fund	$\nu_{12}$	a''
						Fund	$\nu_9$	a'

<sup>a-d</sup> See Table I. <sup>e</sup> Probably Q-Q spacing.

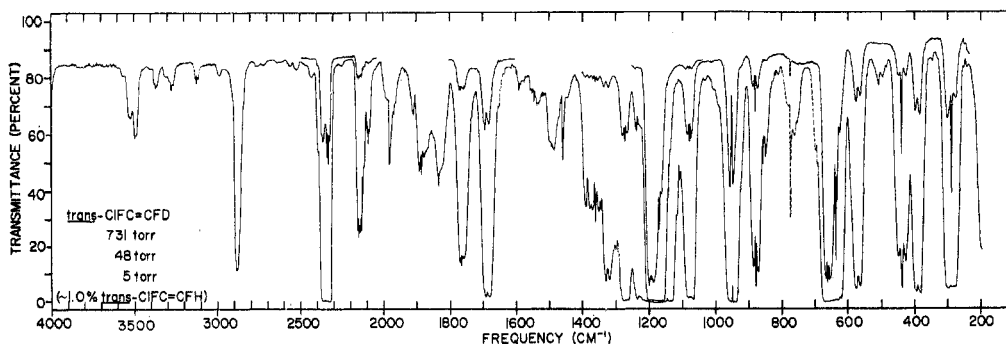


Figure 4. Gas-phase infrared spectrum of *trans*-1,2-difluoro-1-chloroethylene-2-*d*<sub>1</sub>.

rich sides. During equilibrations of several days duration the pressure decreased from an initial value of about 1 atm to about 0.3 atm. This pressure decrease

appeared to be due to polymerization of the haloethylene. An involatile liquid was expelled from the reaction vessel, and a higher molecular weight component

(narrow bands) was observed in the infrared spectrum of the haloethylenes recovered from the isomerization mixture. In addition, hydrogen chloride was found among these reaction products.

## Results and Discussion

**Assignment of Configurations.** Because of the low symmetry of the *cis*- and *trans*-CFCl=CFH molecules, infrared and Raman selection rules do not serve as a simple basis for assigning configurations. However, from a consideration of the relative magnitudes of nmr coupling constants, where, in general,  $J_{\text{HF}(\text{trans})} > J_{\text{HF}(\text{cis})}$ , Sargeant has recently assigned the configurations of these isomers.<sup>6</sup> We have confirmed these nmr assignments. Further support for this assignment of configurations comes from the larger splitting between the CF stretching frequencies of the *cis* isomer compared with that of the *trans*. Consideration of normal coordinates for CX stretching of a simplified CX=CX model and examination of the splittings between these frequencies in haloethylenes of known configurations has established the validity of the rule.<sup>8</sup> The considerably lower intensity of the infrared absorption band due to CC stretching of the *trans* species compared with that of the *cis* is also in accord with this assignment.

**Vibrational Assignment. General.** The *cis* and *trans* isomers of CFCl=CFH and of CFCl=CFD have  $C_s$  symmetry. As a consequence the nine in-plane ( $a'$ ) and three out-of-plane ( $a''$ ) fundamentals are infrared and Raman active with the in-plane fundamentals expected to be polarized in the Raman spectrum. In the gas-phase infrared, bands for in-plane fundamentals have shapes ranging from type A to type B, whereas the bands for the out-of-plane fundamentals are type C. From the moments of inertia (Table VI) and the expressions given by Seth-Paul and Dijkstra<sup>9</sup> we calculate the following PR branch separations at 320°K: *cis*-CFC1CFH ( $\rho^* = 2.97$ ,  $\kappa = -0.860$ ), type A bands 13  $\text{cm}^{-1}$ , type B 12  $\text{cm}^{-1}$ , and type C 20  $\text{cm}^{-1}$ ; *trans*-CFC1CFH ( $\rho^* = 0.872$ ,  $\kappa = -0.060$ ), type A 16  $\text{cm}^{-1}$ , type B 12  $\text{cm}^{-1}$ , and type C 24  $\text{cm}^{-1}$ . Thus, for *cis* molecules the PR separations in bands for in-plane modes should be 12–13  $\text{cm}^{-1}$ , and for *trans* molecules the corresponding range should be 12–16  $\text{cm}^{-1}$ . (This difference in range of PR separations serves as yet another basis for checking the assignment of isomeric configurations.) All of the moments of inertia are large enough so that no detailed rotational structure is observable at a resolution of 0.3  $\text{cm}^{-1}$  and above. However, isotope splitting due to  $^{35}\text{Cl}$ – $^{37}\text{Cl}$  species may be evident for fundamentals that are rich in chlorine motion. As Mann, Acquista, and Plyler have emphasized,<sup>10</sup> one can expect also to find rather intense bands for the first overtones of  $a''$  species, particularly those due principally to CH(D) motion. This generalization is borne out in the spectra of other fluorochloroethylenes which we have studied.<sup>2</sup>

*cis*-1,2-Difluoro-1-chloroethylene. From the infrared spectrum, Figure 1, eight type A/B bands of reasonable frequency, intensity, and PR separation are available for assignment as in-plane fundamentals. The assignments at 3137, 1716, 1112, 854, 480, and 361  $\text{cm}^{-1}$  are confirmed by polarized counterparts in the Raman spectrum (Table I). Although the 1326 and 1159- $\text{cm}^{-1}$  bands are apparently depolarized in the Raman, no substantial doubt exists about their respective assignments as the CH deformation and one of the CF stretches. For two of the out-of-plane fundamentals, 776 and 523  $\text{cm}^{-1}$ , clear type C bands in the infrared and depolarized bands in Raman are found. Finally, the Raman spectrum has two distinct bands in the 300–200- $\text{cm}^{-1}$  region each of which is depolarized. Although the shapes of the corresponding infrared bands are not clearly defined, it appears that the shape of the higher frequency band is type C and that of the lower frequency one is type B. Support for this assignment comes from the repetition of the same pattern in combination bands near 1950 and 1400  $\text{cm}^{-1}$ . The infrared spectrum of *cis*-CFC1CFH in the low-frequency region is reminiscent of the spectra of *trans*-dihaloethylenes and diazenes.<sup>2</sup> This similarity is not surprising as *cis*-CFC1CFH approximates a prolate top in shape, whereas *trans*-CFC1CFH is an asymmetric top. In these near-symmetric top molecules the near degeneracy of the lowest frequency in-plane and out-of-plane fundamentals leads to large distortions in band shapes due to Coriolis coupling.

The fairly intense infrared bands at 1547 and 1048  $\text{cm}^{-1}$  are not fundamentals but are the expected first overtones of the out-of-plane fundamentals,  $\nu_{10}$  and  $\nu_{11}$ . Also the distorted shape of the type C band at 523  $\text{cm}^{-1}$  suggests an overlapped band due to the first overtone of  $\nu_{12}$ . As suggested in the assignments in Table I these intense overtones may profit from Fermi resonance with neighboring fundamentals.

The 47- $\text{cm}^{-1}$  splitting between the two CF stretching fundamentals seems anomalously small when compared with 108  $\text{cm}^{-1}$  for *cis*-CFCl=CFD and 46  $\text{cm}^{-1}$  for *trans*-CFCl=CFH. This small splitting is undoubtedly caused by a depression of the higher CF stretching frequency due to mixing with the CH bend. Apparently, a comparable mixing of the CF stretch and CH bend is not important in the *trans* isomers because the splitting decreases, from 46 to 27  $\text{cm}^{-1}$ , upon deuteration. One might also suppose that mixing of the CD bend with the lower frequency CF stretch would raise this latter frequency and thereby decrease the splitting between the CF stretches. Thus, we consider the split-

(8) N. C. Craig, G. Y.-S. Lo, C. D. Needham, and J. Overend, *J. Amer. Chem. Soc.*, **86**, 3232 (1964).

(9) W. A. Seth-Paul and G. Dijkstra, *Spectrochim. Acta*, **23A**, 2861 (1967).

(10) D. E. Mann, N. Acquista, and E. K. Plyler, *J. Chem. Phys.*, **23**, 2122 (1955).

ting in the deuterated species to be an upper limit and have referred to it in connection with the assignments of configuration presented above.<sup>11</sup>

*cis-1,2-Difluoro-1-chloroethylene-2-d<sub>1</sub>*. For the most part the vibrational assignment for *cis*-CFCICFD follows directly from that of the undeuterated *cis* species after allowance is made for the decrease in frequency of CH-rich modes due to deuteration. The infrared spectrum of *cis*-CFCICFD is given in Figure 2, and the Raman bands are tabulated along with the detailed assignment in Table II. Assignment of the CD bending mode is not obvious in the infrared, however, as three type A/B of comparable intensity are present in the 1050–900-cm<sup>-1</sup> region. Only the lower frequency of the three, the one at 934 cm<sup>-1</sup>, corresponds to a Raman band of significant intensity. Like its equivalent in the *cis*-CFCICFH spectrum this band is apparently depolarized. The middle band is undoubtedly 2ν<sub>11</sub>, strengthened in intensity by Fermi resonance with the CD bending fundamental. The higher frequency band appears to be a consequence of Fermi resonance of ν<sub>4</sub> with ν<sub>6</sub> + ν<sub>9</sub>.

In the infrared spectrum of *cis*-CFCICFD the band structure in the 300–200-cm<sup>-1</sup> region is even more obscure than that of *cis*-CFCICFH. As in the hydrogen case we have assigned the higher frequency feature to the out-of-plane fundamental, ν<sub>12</sub>. Pairs of overlapped combination bands at about 1925, 1450, and 1150 cm<sup>-1</sup> presumably reflect the structure of the low-frequency region.

As in the infrared spectrum of *cis*-CFCICFD first overtones of out-of-plane modes are intense. In addition to 2ν<sub>11</sub>, which is discussed above, 2ν<sub>10</sub> is seen at 1259 cm<sup>-1</sup>. 2ν<sub>12</sub> (510 cm<sup>-1</sup>) would be lost under the overlapped bands due to ν<sub>7</sub> and ν<sub>11</sub>.

*trans-1,2-Difluoro-1-chloroethylene*. In the infrared spectrum of *trans*-CFCICFH, Figure 3, three reasonably intense bands with type C shapes and appropriate PR separations are immediately apparent below 800 cm<sup>-1</sup>. These bands at 776, 467, and 310 cm<sup>-1</sup> correspond to prominent, depolarized Raman bands (Table III) and thus are confidently assigned to the three a'' fundamentals. The first overtones of each of these fundamentals appear with substantial intensity at 1547, 935, and 620 cm<sup>-1</sup>, respectively, and should not be confused with a' fundamentals.

The assignment of the a' fundamentals is not as obvious as that for the a'' fundamentals. Five infrared bands with type A/B band shapes and with reasonable intensities, frequencies, and PR separations, 3120, 1708, 1150, 696, and 578 cm<sup>-1</sup> correspond to polarized Raman bands. These frequencies are assigned to in-plane fundamentals. In the infrared the intensity of the CC stretch is rather weak, but the Raman band is appropriately strong. The position of the lower frequency, symmetric CF stretch in the infrared, is confused by the dominant intensity of the adjacent band

due to the antisymmetric CF stretch and by Fermi resonance with a combination band. Although Raman bands for the other four in-plane fundamentals are apparently depolarized, for three of them well defined type A/B bands are found in the infrared at 1290, 1196, and 397 cm<sup>-1</sup>. Also what appears to be an R branch of the remaining in-plane fundamental is seen just above the low-frequency limit of the spectrometer at 200 cm<sup>-1</sup>.

*trans-1,2-Difluoro-1-chloroethylene-2-d<sub>1</sub>*. As in the case of *trans*-CFCICFH the type-C bands for a'' fundamentals are readily apparent below 800 cm<sup>-1</sup> in the infrared spectrum of *trans*-CFCICFD (Figure 4). The 639-cm<sup>-1</sup> band is partly overlapped by ν<sub>6</sub> (a'), but the ones at 440 and 292 cm<sup>-1</sup> are in the clear. These three fundamentals appear as depolarized bands in the Raman spectrum (Table IV). Once again 2ν<sub>10</sub> (1275 cm<sup>-1</sup>) and 2ν<sub>11</sub> (882 cm<sup>-1</sup>) are rather intense. 2ν<sub>12</sub> (584 cm<sup>-1</sup>) would be masked by ν<sub>7</sub> (a').

Seven of the a' fundamentals have polarized Raman bands. Six of these correspond to type A/B bands at 2326, 1689, 1197, 954, 665, and 573 cm<sup>-1</sup>. The infrared band at 1170 cm<sup>-1</sup>, which is assigned to the symmetric CF stretch, is nearly lost in the wing of the intense 1197-cm<sup>-1</sup> band. The 394-cm<sup>-1</sup> band, which may be depolarized in the Raman, has a clear type B shape in the infrared. The 198-cm<sup>-1</sup> Raman band, though also apparently depolarized, is certainly due to the ninth a' fundamental. Fermi resonance with a combination band must modify the frequency of the CD stretch and possibly several other fundamentals to a lesser degree.

As in the case of the other three molecules in this series the Raman bands assigned to the CCl stretch are characteristically strong and the infrared bands show evidence of chlorine isotope splitting.

*Summary.* Table V summarizes the assignments of vibrational fundamentals for the two *cis* and two *trans* species. We believe that a convincing assignment has been obtained for the twelve fundamentals of each molecule. For each isomer the Rayleigh rule is satisfied as are the product rules as shown in Table VI. In addition the assignments for the *cis* and *trans* isomers are consistent with one another and with the assignment of Nielsen, Liang, and Smith for the gem isomer,<sup>3</sup> which is included for comparison in Table V. Group frequencies have proved to be an excellent guide to the assignments for these molecules of low symmetry and relatively few atoms.

*Thermodynamic Functions.* From a rigid-rotor, harmonic-oscillator treatment of *cis*- and *trans*-CFCICFH, ΔS<sup>o</sup><sub>591</sub> = 86.74 – 86.86 = –0.12 ± 0.26 cal/mol °K<sup>12</sup> for the reaction

(11) Although normal coordinate calculations have not been carried out for these molecules, this discussion is supported by the normal coordinates of related molecules such as CFH=CFH and CFH=CClH (ref 2).

(12) Estimates of uncertainties are based on ±2 cm<sup>-1</sup> uncertainties in fundamental vibration frequencies, 0.01–0.02 Å uncertainties in bond lengths, and 1° uncertainties in bond angles.

**Table V:** Vibrational Fundamentals of the Difluorochloroethylenes and Deuterated Modifications of the *cis-trans* Isomers (Frequencies in  $\text{cm}^{-1}$ )

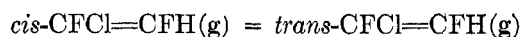
	Approximate description	gem Isomer $\text{CF}_2\text{CClH}$	cis Isomer		trans Isomer	
			CFCICFH	CFCICFD <sup>c</sup>	CFCICFH	CFCICFD <sup>c</sup>
a'						
$\nu_1$	CH(D) str	3130	3137	2345	3120	2326 <sup>a</sup>
$\nu_2$	CC str	1745	1716	1696	1708 <sup>a</sup>	1689 <sup>a</sup>
$\nu_3$	CH(D) bend	1333	1326 <sup>a</sup>	934 <sup>a</sup>	1290 <sup>a</sup>	954 <sup>a</sup>
$\nu_4$	a CF str	1199	1159	1218 <sup>a</sup>	1196	1197 <sup>a</sup>
$\nu_5$	s CF str	970	1112 <sup>a</sup>	1110 <sup>a</sup>	1150 <sup>a</sup>	1170 <sup>a</sup>
$\nu_6$	CCl str	845	854	821	696 <sup>a</sup>	665 <sup>a</sup>
$\nu_7$	a CF bend	579	480	479 <sup>b</sup>	578 <sup>a</sup>	573
$\nu_8$	CCl bend	433	361	359	397	394
$\nu_9$	s CF bend	201 <sup>b</sup>	224	220	200 <sup>b</sup>	198 <sup>b</sup>
a''						
$\nu_{10}$	CH(D) wag	751	776	630	776	639
$\nu_{11}$	CF wag	(572) <sup>b,d</sup>	523	496	467	440
$\nu_{12}$	torsion	243 <sup>b</sup>	255	247	310	292

<sup>a</sup> Uncorrected for probable Fermi resonance. <sup>b</sup> From liquid phase Raman spectrum; all others from gas phase infrared. <sup>c</sup> For the deuterated species numbering of  $\nu_3$ ,  $\nu_4$ , and  $\nu_5$  has been altered for convenience in tabulation. <sup>d</sup> Assignment in doubt.

**Table VI:** Principal Moments of Inertia in  $\text{amu } \text{\AA}^2$ ;<sup>a</sup> Product Rule Check of Assignments

	cis Isomer			trans Isomer		
	$I_a$	$I_b$	$I_c$	$I_a$	$I_b$	$I_c$
CFCICFH	56.56	212.8	269.4	98.92	144.2	243.1
CFCICFD	59.84	213.5	273.4	101.3	147.2	248.4
		Calcd	Obsd	Calcd	Obsd	
$\frac{\text{CFCICFD}}{\text{CFCICFH}}$	a'	0.509	0.512	0.511	0.517	
	a''	0.732	0.745	0.727	0.730	

<sup>a</sup> Geometric parameters:  $r_{\text{CC}} = 1.333 \text{ \AA}$ ,  $r_{\text{CCl}} = 1.726 \text{ \AA}$ ,  $r_{\text{CF}} = 1.348 \text{ \AA}$ ,  $r_{\text{CH}} = 1.079 \text{ \AA}$ ,  $\alpha_{\text{CCCl}} = 123.6^\circ$ ,  $\alpha_{\text{CCH}} = 123.2^\circ$ , and  $\alpha_{\text{CCF}} = 121.0^\circ$ . J. A. Howe, *J. Chem. Phys.*, **34**, 1247 (1961).



From the measured equilibrium constant,  $K_{591} = 0.932 \pm 0.022$ , one calculates  $\Delta G^\circ_{591} = 82.1 \pm 2.8 \text{ cal/mol}$ . Thus,  $\Delta H^\circ_{591} = 10 \pm 160 \text{ cal/mol}$ . From the statistical thermodynamic calculation  $\Delta H^\circ(\text{thermal}) = H^\circ_{591}(\text{trans}) - H^\circ_{591}(\text{cis}) = 9761 - 9780 = -19 \pm 32 \text{ cal/mol}$ ,<sup>12</sup> and from the observed vibrational fundamentals  $\Delta E_0^\circ(\text{zero point}) = 16,994 - 17,044 = -50 \pm 69 \text{ cal/mol}$ .<sup>11</sup> Thus,  $\Delta E_0^\circ(\text{electronic}) = \Delta H^\circ_{591} - \Delta H^\circ(\text{thermal}) - \Delta E_0^\circ(\text{zero point}) = 80 \pm 260 \text{ cal/mol}$ .

Of course, this value of  $\Delta E_0^\circ(\text{electronic})$  rests on the assumption that a true equilibrium constant was measured. Yet, the trihaloethylene isomerization system is not as free of side reactions as we had supposed based on experience with two dihaloethylene systems. The side reaction, presumed to be mostly polymerization, that accompanies the isomerization could prevent *cis-trans* equilibrium from being attained. Such a distortion seems unlikely, however, since the polymerization reactions are presumably possible with both isomers and the equilibrium constant is so near unity.<sup>13</sup>

The small positive value for the electronic energy of the *cis* isomer relative to that of the *trans* is reasonably consistent with the difference of 220 cal/mol between the values of 1090 cal/mol for the  $\text{CFH=CFH}$  case and 870 cal/mol for the  $\text{CFH=CClH}$  case.<sup>2</sup> Consequently, this trihaloethylene example supports the experimental values for the more striking dihaloethylene examples. As has been noted before, the apparent nonbonded attraction between two fluorine atoms is not much greater than that between a chlorine and a fluorine atom. It is also evident that no unexpected effect is introduced by the presence of two halogen atoms on one of the two carbon atoms.

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(13) We do not have a satisfactory explanation for the formation of hydrogen chloride in the isomerization reaction system. This finding was not pursued.