Vibrational assignments and potential constants for cis- and trans-1-chloro-2-fluoroethylenes and their deuterated modifications

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Vibrational Assignments and Potential Constants for

cis- and trans-1-Chloro-2-fluoroethylenes and

Their Deuterated Modifications[1]

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From infrared and Raman spectra a complete assignment of vibrational fundamentals has been obtained for cis- and trans-CClHCFH, CClDCFH, CClHCFD, and CClDCFD. For cis-CClHCFH the a' modes are 3114, 3102, 1661, 1335, 1231, 1062, 812, 656, and 205 cm^{-1}, and the a'' modes are 857, 735, and 442 cm^{-1}. For trans-CClHCFH the a' modes are 3103, 3094, 1647, 1296, 1218, 1127, 876, 447, and 270 cm^{-1}, and the a'' modes are 888, 784, and 270 cm^{-1}. ΔE_0° (electronic) is then found to be 867 ± 90 cal/mol with the cis isomer having the *lower* energy. Urey-Bradley force constants for the in-plane vibrations have been calculated by fitting the frequencies of all eight species at once. General valence force (GVF) constants for the out-of-plane modes have been calculated for the cis and trans species separately. The GVF constants for the two isomers are consistent with each other and with those obtained previously for the cis- and trans-1,2-difluoroethylenes.

The cis isomers of the symmetrically substituted species 1,2-difluoroethylene,[3] 1,2-dichloroethylene,[4] and 1,2-difluorodiazene, NF=NF,[5] are known to be of lower energy than the corresponding trans isomers. This energy difference is believed to be due to a nonbonded attractive force between the halogen atoms in the cis configuration. In an exploratory study Viehe also found the cis isomers of ethylenes containing a fluorine atom and a chlorine, bromine, or iodine atom to be more stable than the corresponding trans isomers.[6] As representatives of these mixed halogen systems the 1-chloro-2-fluoroethylenes appear to be the best choice for a thorough thermodynamic and spectroscopic investigation. For the cis-trans isomerization of the chlorofluoroethylenes we have confirmed Viehe's observation of cis stability and have found $\Delta H^\circ_{615} = 782 \pm 22$ cal/mol and $\Delta S^\circ_{615} = 0.21 \pm 0.04$ cal/mol°K.[7]

The present paper is concerned, however, principally with obtaining complete assignments of the vibrational fundamentals of cis- and trans-CClHCFH as a step toward understanding cis stability in this system. From infrared spectra alone Viehe and coworkers assigned ten of the twelve fundamentals of the cis isomer and eight of the fundamentals of the trans.[8] With the aid of Raman spectra we have completed the assignments of the vibrational fundamentals for these two species and have also obtained assignments for the three deuterated modifications of each isomer. The frequencies of the deuterated species are of interest not only as support for the assignments of the undeuterated molecules but as a basis for exploring the force fields in cis stable isomer pairs. The present paper includes

preliminary results of such normal coordinate calculations.

Experimental Section

Syntheses. A mixture of cis-CClHCFH (bp 15.2°)[6] and trans-CClHCFH (bp −3.8°)[6] was prepared in 70% yield by dehalogenating CCl$_2$HCClFH[9] with zinc dust in refluxing ethanol. The product, which was continuously distilled out of the reaction mixture and trapped at Dry Ice temperature, was about two-thirds cis isomer.

cis- and trans-CClDCFH were obtained by dehalogenating CClBrDCClFH. This ethane mixed with its isomer CCFBrCClHD was prepared by irradiating equimolar gaseous mixtures of hydrogen bromide and CClFCClD[10] in a fused-silica flask with ultraviolet light from a mercury arc. The product of the dehalogenation consisted of about 2 parts of cis- and trans-

(1) Presented, in part, at the 22nd Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, Sept 1967.

(2) Author to whom inquiries should be addressed.

(3) (a) N. C. Craig and E. A. Entemann, *J. Amer. Chem. Soc.*, **83**, 3047 (1961); (b) N. C. Craig and J. Overend, *J. Chem. Phys.*, **51**, 1127 (1969).

(4) (a) K. S. Pitzer and L. J. Hollenberg, *J. Amer. Chem. Soc.*, **76**, 1493 (1954); (b) R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 3259 (1939).

(5) G. T. Armstrong and S. Marantz, *J. Chem. Phys.*, **38**, 169 (1963).

(6) H. G. Viehe, *Ber. Deut. Chem. Ges.*, **93**, 1697 (1960).

(7) To be published. Temperatures in °K.

(8) H. G. Viehe, J. Dale, and E. Franchimont, *Ber. Deut. Chem. Ges.*, **97**, 244 (1964).

(9) N. C. Craig and Y.-S. Lo, *J. Mol. Spectrosc.*, **23**, 307 (1967).

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

CClDCFH and about 1 part of CClFCHD. Small amounts of *cis*- and *trans*-CFClCFH were also found in the product mixture and were believed to have been derived from CClFCClF, present as a contaminant in the starting ethylene.

cis- and *trans*-CClHCFD were prepared by dehalogenating CCl₂HCFBrD. This ethane was made photochemically from gaseous hydrogen bromide and CCl₂CFD.[9]

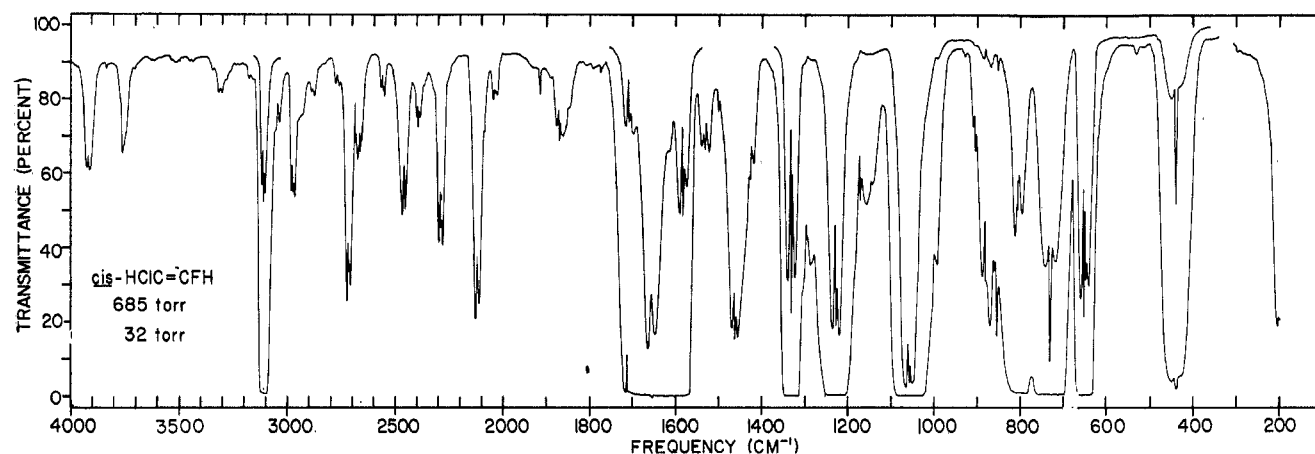*cis*- and *trans*-CClDCFD were synthesized by re-

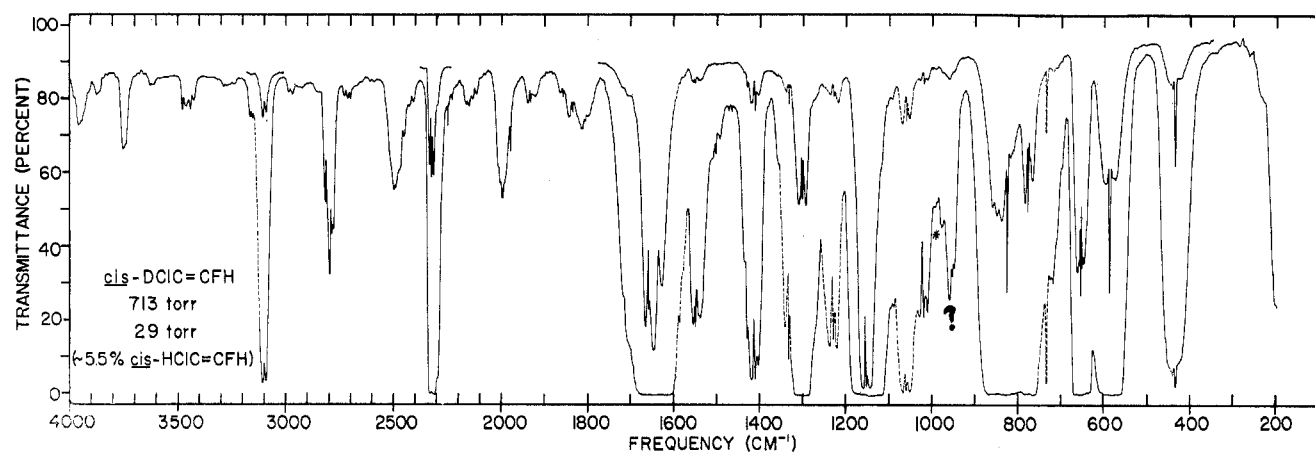Figure 1. Gas-phase infrared spectrum of *cis*-1-chloro-2-fluoroethylene.

Figure 2. Gas-phase infrared spectrum of *cis*-1-chloro-2-fluoroethylene-1-d_1.

Figure 3. Gas-phase infrared spectrum of *cis*-1-chloro-2-fluoroethylene-2-d_1.

Figure 4. Gas-phase infrared spectrum of cis-1-chloro-2-fluoroethylene-1,2-d_2.

Figure 5. Gas-phase infrared spectrum of trans-1-chloro-2-fluoroethylene.

Figure 6. Gas-phase infrared spectrum of trans-1-chloro-2-fluoroethylene-1-d_1.

peated exchange of a cis–trans mixture of CClHCFH with 99.7% deuterium oxide saturated with dried calcium oxide. These reactions were performed in sealed standard-wall Pyrex tubes pressurized externally to 225 psi in a rocking bomb. The temperature was about 125° and exchanges were run about 1 day.[11]

In each case purified samples of the isomers were obtained by gas chromatographic fractionation at room temperature on 6-ft or 12-ft columns packed with

(11) The exchange reaction was stereospecific and proceeded much more rapidly on the chlorinated end of the molecule, a temperature of about 90° being sufficient to effect exchange in 1 day in this case.
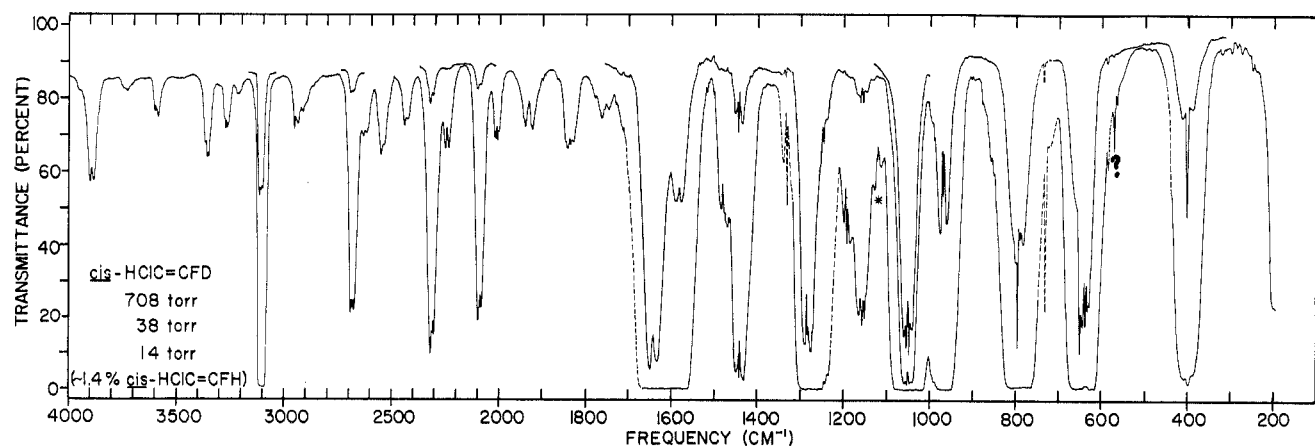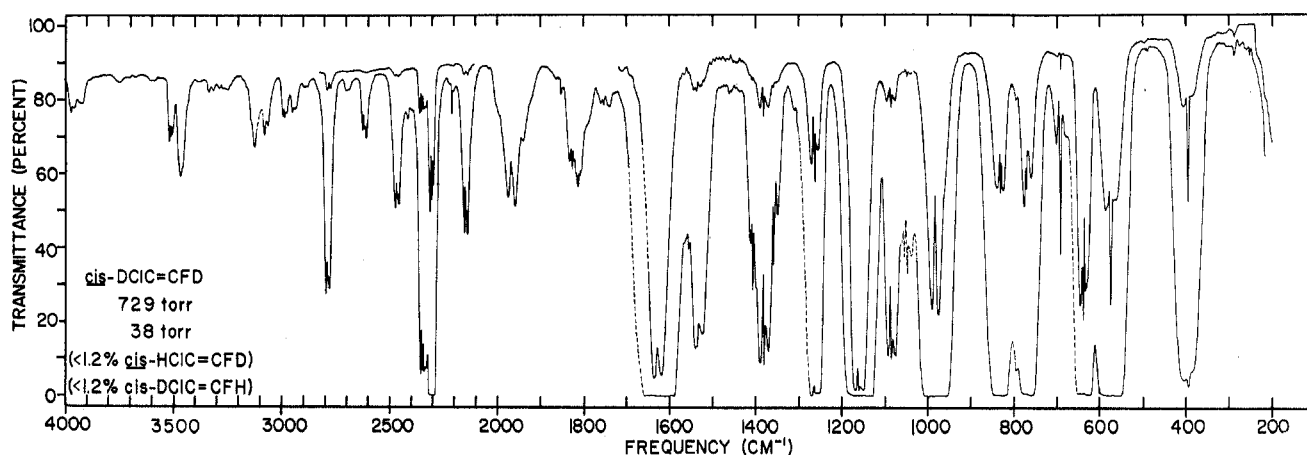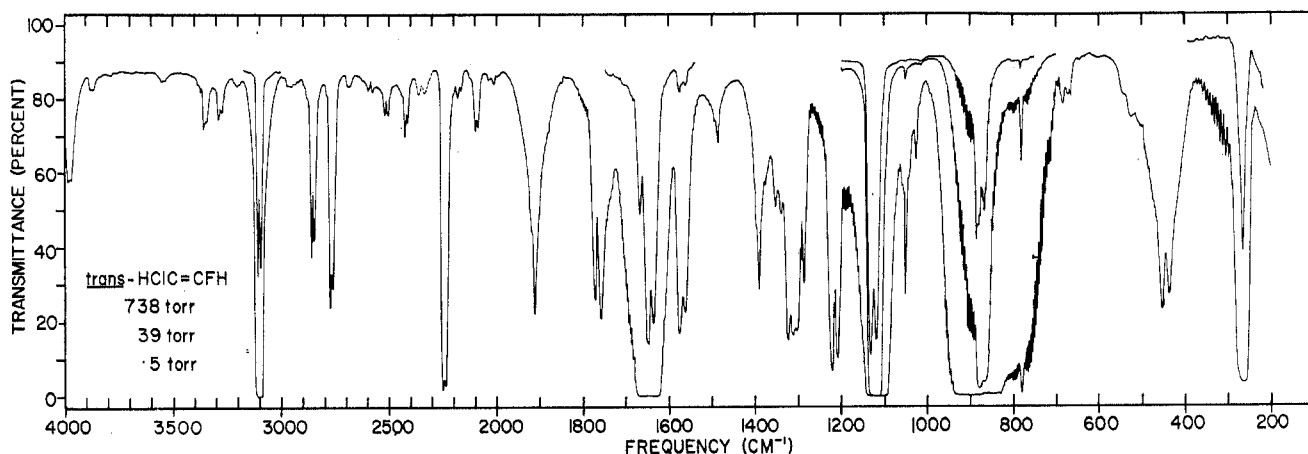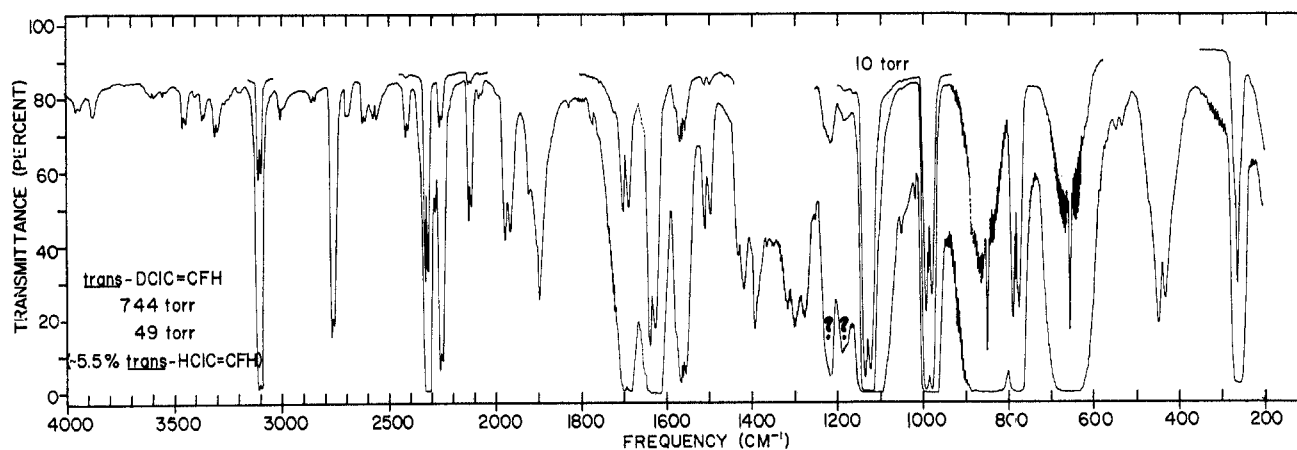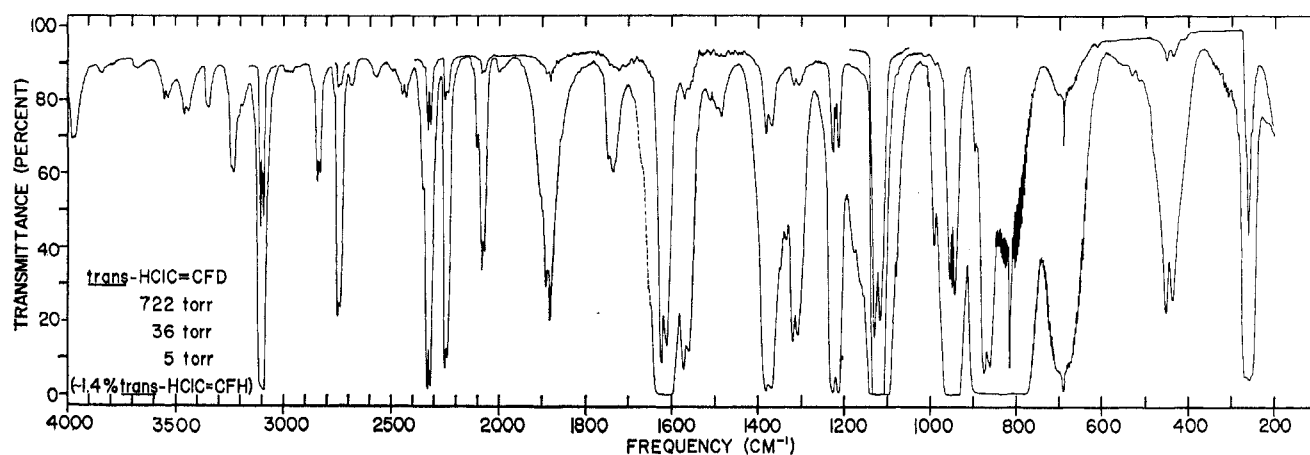
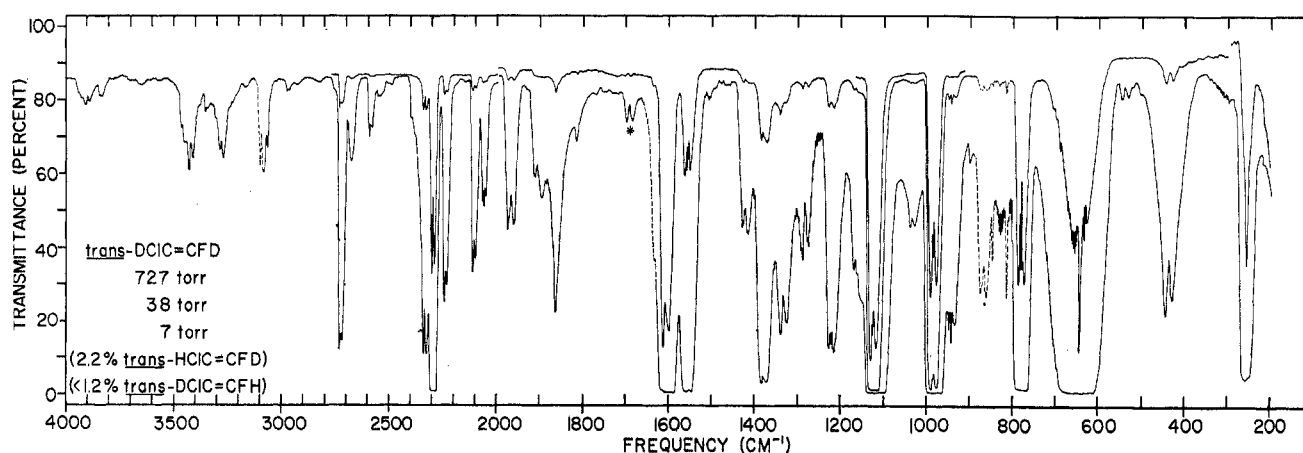Figure 7.   Gas-phase infrared spectrum of *trans*-1-chloro-2-fluoroethylene-2-d_1.

Figure 8.   Gas-phase infrared spectrum of *trans*-1-chloro-2-fluoroethylene-1,2-d_2.

dibutyl phthalate on firebrick. These samples were dried by passing them over phosphorus pentoxide. An attempt to remove impurity carbon dioxide with Ascarite led to a small amount of exchange at the chlorinated end of *trans*-CClDCFD. Thereafter, Ascarite treatment was confined to the undeuturated species. In all cases final purities were greater than 99.5% based on gas chromatographic analysis. In the infrared spectra (Figures 1–8) of *cis*- and *trans*-CClDCFH unidentified weak bands were taken as evidence of somewhat lower purity. Isotopic purities given in Figures 2–4 and 6–8 were estimated from infrared intensities. In these figures bands due to isotopic impurities are shown with dashed lines. Other known impurity bands are marked with asterisks.

Spectroscopy. Gas-phase infrared spectra, Figures 1–8, were obtained on a Perkin-Elmer 621 filter-grating spectrometer with samples held in a 10-cm cell fitted with cesium iodide windows. Frequencies, Tables I–VIII, were measured to ±1 cm^{-1} for well defined bands under expanded-scale, high-resolution conditions.

Liquid-phase Raman spectra, Tables I–VIII, were recorded photographically on a Hilger E612 spectrograph with mercury 4358-Å excitation. Capillary

cells were used, and some samples were as small as 8 mmol. Qualitative depolarizations were obtained by the Edsall–Wilson method.

Results and Discussion

Configurational Assignments. Viehe[6] assigned the isomeric configurations of the 1-chloro-2-fluoroethylenes on the basis of a higher boiling point for the more polar *cis* isomer and the strong infrared band for the out-of-plane CH motion of the *trans* isomer at about 880 cm^{-1}. This assignment of configuration is confirmed, as Viehe also noted for his low resolution spectra, by the abundant rotational structure evident in the gas-phase infrared spectra (see Figures 5–8) of the four *trans* species. The assignment is also consistent with the observed coupling constants from the nuclear magnetic spectra of the *cis* and *trans* isomers. We find $J_{HF(trans)} = 27.3$ Hz for the *cis* isomer (AMX spectrum) and $J_{HF(cis)} = 8.9$ Hz for the *trans* isomer (ABX spectrum) in consonance with the relative magnitudes of HF coupling constants for similar olefins.[10,12]

(12) G. W. Flynn, M. Matsushima, J. D. Baldeschwieler, and N. C. Craig, *J. Chem. Phys.*, **38**, 2295 (1963).

Vibrational Assignments. General. All of the chlorofluoroethylene molecules under consideration have C_s symmetry and consequently have nine a' in-plane and three a'' out-of-plane fundamentals. The a' fundamentals should have gas-phase infrared band shapes ranging between type A and type B and have polarized Raman bands. The a'' fundamentals should have type C band shapes in the gas-phase infrared and depolarized Raman bands. The *trans* isomer is a prolate near-symmetric top, $\kappa = -0.996$, with a moment of inertia of 9 amu $Å^2$ around the unique axis. As a consequence, vibrations which produce dipole

Table I: Infrared and Raman Spectra and Assignments for cis-CClH=CFH

Freq, cm^{-1}	Raman (liquid) I	Polar- ization	Freq, cm$^{-1\,a}$	Ir (gas) a^b	Band shape^c	Freq, cm^{-1}	Assignment	Sym species
			3919 (16)	0.018	B	3926	$\nu_1 + \nu_7$	A'
			3755 (16)	0.015	A/B	3770	$\nu_1 + \nu_8$	A'
			3114 (15) 3115^d	0.52	A	ν_1	Fund.	a'
3105	wm	p	3102	?	?	ν_2	Fund.	a'
			2977 (16)	0.017	A/B	2996	$\nu_3 + \nu_4$	A'
			2717 (15)	0.056	A/B	2733	$\nu_3 + \nu_6$	A'
			2663 (16)	0.016	A/B	2670	$2\nu_4$	A'
			2462 (16)	0.029	B	2473	$\nu_3 + \nu_7$	A'
						2462	$2\nu_5$	A'
			2287 (16)	0.039	A/B	2317	$\nu_3 + \nu_8$	A'
			2119 (16)	0.067	B	2124	$2\nu_6$	A'
			1872 (15)	0.012	A	1874	$\nu_6 + \nu_7$	A'
			1714 (17)	0.29	A/B	1718	$\nu_6 + \nu_8$	A'
						1714	$2\nu_{10}$	A'
							Fermi resonance with ν_3?	
1660	s	p	1661 (17) 1664^d	1.9	B	ν_3	Fund.	a'
			1588 (16)	0.60	A	1624	$2\nu_7$	A'
							Fermi resonance with ν_3?	
						1592	$\nu_{10} + \nu_{11}$	A'
			1534 (15)	0.014	A	1540	$\nu_4 + \nu_9$	A'
			1466 (16)^e	0.092	A	1470	$2\nu_{11}$	A'
						1468	$\nu_2 + \nu_8$	A'
			1459	?	?	$\sim$1456	$\nu_3 - \nu_9$	A'
			1430	0.02	A/B	1436	$\nu_5 + \nu_9$	A'
			1335 (16) 1339^d	1.1	A	ν_4	Fund.	a'
			1298	0.044	A/B	1312	$2\nu_8$	A'
						1299	$\nu_{10} + \nu_{12}$	A'
1214	m	dp	1231 (16) 1232^d	1.8	A	ν_5	Fund.	a'
			1176 (15)	0.03	A/B	1177	$\nu_{11} + \nu_{12}$	A'
1049	m	p	1062 (16)^e 1063^d	3.6	A/B	ν_6	Fund.	a'
			1008	0.05	A/B	1017	$\nu_7 + \nu_9$	A'
			908	0.01	A	?		A'
			884 (17)	0.05	A/B	884	$2\nu_{12}$	A'
$\sim$863	wm	dp	857 $\sim$875^d	0.05	C	ν_{10}	Fund.	a''
803	m	p	812 (16)^e 809^d	0.71	B	ν_7	Fund.	a'
$\sim$737	vw		735^{e,f} 735^d	1.0	C	ν_{11}	Fund.	a''
648	m	p	656 (17)^e 657^d	1.3	A	ν_8	Fund.	a'
444	m	dp	442 443^d	0.18	C	ν_{12}	Fund.	a''
205	w	dp	$\sim$200	0.08	A/B	ν_9	Fund.	a'

^{a} Spacing of P–R branches in parentheses. ^{b} Absorption coefficient in cm^{-1} atm^{-1}. ^{c} A and B band shapes are approximate for this molecule of C_s symmetry. ^{d} Reference 8. ^{e} Structure present due to chlorine isotope shifts or hot bands. ^{f} Rotational structure in P and R branches with spacing of 0.8–0.9 cm^{-1}.

moment changes perpendicular to this rotation axis should lead to nearly perpendicular-type bands with readily resolved rotational structure. The out-of-plane modes necessarily have this structure since the unique axis lies in the plane of the molecule. Rotational structure may also be evident for some in-plane modes in the wings of bands when the vibration has a large component of dipole moment change perpendicular to the unique axis, which passes nearly through the two halogen atoms. The *cis* isomer is a less good approximation to a prolate symmetric top since $\kappa = -0.895$. The least moment of inertia of about 31 amu $Å^2$ is,

Table II: Infrared and Raman Spectra and Assignments for *cis*-CClD=CFH

| Raman (liquid) | | | Ir (gas) | | | Assignment | | |
Freq, cm^{-1}	I	Polarization	Freq, cm^{-1} ^{a}	α^b	Band shape^c	Freq, cm^{-1}		Sym species
			3751(18)	0.013	A/B	3753	$\nu_1 + \nu_8$	A'
			3114	?			*cis*-CClHCFH impurity	
3103	m	p	3098 (17)	0.16	B	ν_1	Fund.	a'
			2807 (15)	0.025	B	2807	$\nu_5 + 2\nu_{10}$	A'
			2786 (16)	0.032	A/B	2792	$\nu_3 + \nu_5$	A'
			2486	0.02	A/B	2524	$\nu_2 + \nu_9$	A'
						2488	$\nu_3 + \nu_6$	A'
			2457	0.01	B	2459	$\nu_4 + \nu_5$	A'
2327	s	p	2322 (17)	0.44	A	ν_2	Fund.	a'
			2250		C	2240	$2\nu_{10} + \nu_{11}$	A''
			2220		C	2225	$\nu_3 + \nu_{11}$	A''
			2000	0.02	?	2006	$\nu_5 + \nu_6$	A'
			1980	0.01	C	1981	$\nu_5 + \nu_{10}$	A''
1663	w	p	1659 (17)^e	1.8	A/B	1652	$2\nu_{10}$	A'
							Fermi resonance with ν_3	
1642	vs	p	1637 (19)	1.2	B	ν_3	Fund.	a'
			1588				*cis*-CClHCFH impurity	
			1552 (16)	0.067	A/B	1556	$2\nu_7$	A'
			1434^e	0.05	C	1439	$\nu_6 + \nu_{11}$	A''
			1414 (16)	0.13	A	1414	$\nu_{10} + \nu_{11}$	A'
			1353		C	1366	$\nu_7 + \nu_{11}$	A''
			1335 (16)	1.3	A		*cis*-CClHCFH impurity	
1298	sm	p	1304 (17)^e	0.62	A	ν_4	Fund.	a'
			1231 (16)	1.6	A		*cis*-CClHCFH impurity	
1135	w	p	1155 (16)	~5	A/B	ν_5	Fund.	a'
~1050	vw		1062 (17)	3.9	A		*cis*-CClHCFH impurity	
			1021 (18)^e	0.066	A	1022	$\nu_{11} + \nu_{12}$	A'
			989		A/B	989	*trans*-CClD=CFH impurity	
			955		A/B		Impurity?	
~870	w	p				868	$2\nu_{12}$	A'
848	s	p	851 (18)	0.64	A/B	ν_6	Fund.	a'
830	w	dp	826^d	0.38	C	ν_{10}	Fund.	a''
~800	vw					803	*cis*-CClHCFH impurity	
772	s	p	778 (16)^e	0.56	A	ν_7	Fund.	a'
			735		C		*cis*-CClHCFH impurity	
649	s	p	655 (16)^e	1.1	A/B	ν_8	Fund.	a'
592	vw	dp?	588^e	0.54	C	ν_{11}	Fund.	a''
			442		C	442	*cis*-CClHCFH impurity	
434	s	dp	434	0.15	C	ν_{12}	Fund.	a''
202	s	p?	~200	0.07	?	ν_9	Fund.	a'

$^{a-c}$ See Table I. ^{d} Rotational structure in P and R branches with 0.8 cm^{-1} spacing. ^{e} See Table I.

however, small enough to lead to rotational structure which can be resolved in favorable regions of the spectrum.

cis-1-Chloro-2-fluoroethylene. In the infrared spectrum of *cis*-CClHCFH in Figure 1 seven prominent type A/B bands for in-plane fundamentals are located at 3114, 1661, 1335, 1231, 1062, 812, and 656 cm⁻¹. Each of these bands with the exception of the 3114-cm⁻¹ band has a counterpart in the Raman spectrum (Table I). All but the 1231-cm⁻¹ band are definitely polarized. Well defined type C bands in the infrared spectrum at 735 and 442 cm⁻¹ account for two of the out-of-plane fundamentals. The Raman spectrum has a very weak

band corresponding to the higher frequency out-of-plane fundamental and a depolarized band of medium intensity corresponding to the lower frequency one. Though not apparent in the survey scan in Figure 1, rotational spacing of about 0.8 cm⁻¹ was resolved in the 735-cm⁻¹ band. Only the spike of the Q branch of the third out-of-plane fundamental (ν_{10}) appears at 857 cm⁻¹ in the infrared, but this assignment is well supported by a depolarized Raman band. The low infrared intensity of ν_{10} is attributable to a CH torsion with a_2-like symmetry. The shoulder of a band seen at the low-frequency edge of the infrared spectrum must be due to an in-plane fundamental even though

Table III: Infrared and Raman Spectra and Assignments for *cis*-CClH=CFD

Raman (liquid)			Ir (gas)			Assignment		
Freq, cm⁻¹	I	Polar- ization	Freq, cm⁻¹[a]	α[b]	Band shape[c]	Freq, cm⁻¹		Sym species
			3899 (18)	0.018	B	3903	$\nu_1 + \nu_7$	A'
			3365 (16)	0.014	A/B	3369	$\nu_2 + \nu_5$	A'
						3287	$\nu_2 + \nu_6$	A'
3110	wm	p	3112 (15)	0.40	A/B		ν_1 Fund.	a'
			2691 (15)	0.064	A/B	2695	$\nu_3 + \nu_5$	A'
			2549 (15)	0.013	B	2566	$2\nu_4$	A'
2325	s	p	2318 (16)	0.091	A/B		ν_2 Fund.	a'
			2249 (16)	0.014	B	2252	$\nu_4 + \nu_6$	A'
			2100 (15)	0.067	A/B	2102	$2\nu_5$	A'
			2022 (16)	0.012	B	2020	$\nu_5 + \nu_6$	A'
			1934 (15)	0.010	B	1938	$2\nu_6$	A'
			1840 (17)	0.013	A/B	1842	$\nu_6 + \nu_7$	A'
1641	vs	p	1644 (16)	2.7	B		ν_3 Fund.	a'
			1584 (14)	0.48	B	1606	$\nu_6 + \nu_8$	A'
						Fermi resonance with ν_3		
						1592	$2\nu_{10}$	A'
			1482 (16)	0.027	B	1488	$\nu_4 + \nu_9$	A'
			1446 (17)	0.16	A	1446	$\nu_{10} + \nu_{11}$	A'
			1335	1.2	A		*cis*-CClHCFH impurity	
1268	vw	dp	1283 (15)[e]	2.3	B		ν_4 Fund.	a'
			1245		C?	~1244	$\nu_3 - \nu_{12}$	A''
			1196 (15)	0.030	A	1196	$\nu_{11} + \nu_{12}$	A'
			1162 (16)	0.066	A/B	1174	$\nu_6 + \nu_9$	A'
			1127 (15)	0.016	A/B		*trans*-CClHCFD impurity	
1038	sm	p	1051 (17)	4.1	B		ν_5 Fund.	a'
			990		A?	996	$\nu_7 + \nu_9$	A'
965	m	p?	969 (16)[d,e]	0.80	A		ν_6 Fund.	a'
804	w	dp?	796[d]	~0.6	C		ν_{10} Fund.	a''
789	s	p	791 (16)	0.72	A		ν_7 Fund.	a'
			735	1.3	C		*cis*-CClHCFH impurity	
652	wm	dp	650[d]	~0.5	C		ν_{11} Fund.	a''
632	s	p	637[e]	1.2	A		ν_8 Fund.	a'
			588		C		*cis*-CClDCFH impurity	
			575[e]		C		*cis*-CClDCFD impurity	
			567		C	~569	$\nu_6 - \nu_{12}$?	A''
404	m	dp	400	0.20	C		ν_{12} Fund.	a''
205	sm	p?	200	~0.07	?		ν_9 Fund.	a'

[a–c] See Table I. [d] Rotational structure in P and/or R branches with 0.85–0.95 cm⁻¹ spacing. [e] See Table I.

its Raman counterpart is depolarized. Only the second CH-stretching mode remains to be assigned. It appears an an indistinct shoulder on the low-frequency side of the 3114-cm^{-1} infrared band and as a polarized Raman band at 3105 cm^{-1}. Table I also includes the ten assignments of Viehe, *et al.*[8] Agreement is within a few cm^{-1} for all but ν_{10}.

cis-1-Chloro-2-fluoroethylene-1-d$_1$. Bands for all twelve fundamentals of *cis*-CClDCFH are clearly apparent in the gas-phase infrared in Figure 2. Each of the nine with a type A/B shape corresponds to a polarized Raman band (Table II), and each of the three with a type C shape corresponds to a depolarized Raman band. Although ν_6 and ν_{10} overlap in the gas-phase infrared, the characteristic shapes are evident, and

0.8 cm^{-1} rotational spacing is present in the P branch of the ν_{10} band.

cis-1-Chloro-2-fluoroethylene-2-d$_1$. At first glance the gas-phase infrared spectrum of *cis*-CClHCFD in Figure 3 appears to have only eight type A/B bands, even if the shoulder at about 200 cm^{-1} is included, and only two type C bands. Closer inspection reveals overlap between bands for in-plane and out-of-plane fundamentals at both 800 and 650 cm^{-1}. This interpretation is confirmed by the Raman spectrum (Table III) in which a pair of polarized and depolarized bands is present in each of these regions. The assignment of bands due to out-of-plane fundamentals to these two regions is also supported by the 0.9 cm^{-1} rotational spacing in R branches of the type C parts of the bands.

Table IV: Infrared and Raman Spectra and Assignments of *cis*-CClD=CFD

Raman (liquid)			Ir (gas)			Assignment		
Freq, cm^{-1}	I	Polarization	Freq, cm^{-1} ^{a}	α^b	Band shape^c	Freq, cm^{-1}		Sym species
			3505 (15)	0.010	A	3504	$\nu_1 + \nu_4$	A'
			3460	0.017	?	3459	$\nu_2 + \nu_4$	A'
			3120	0.011	?	3128	$\nu_2 + \nu_6$	A'
			2782 (15)	0.050	B	2791	$\nu_3 + \nu_6$	A'
			2459 (16)	0.023	B	2460	$\nu_3 + \nu_6$	A'
2342	s	p	2342 (17)	0.13	A	ν_1	Fund.	a'
2305	m	dp	2297 (16)	0.44	A	ν_2	Fund.	a'
			2138 (16)	0.031	B	2146	$\nu_4 + \nu_6$	A'
			1964 (17)	0.023	B	1993	$\nu_4 + \nu_6$	A'
			1825 (15)	0.016	A	1832	$\nu_3 + \nu_9$	A'
			1810	?	?	1815	$\nu_5 + \nu_6$	A'
1624	vs	p	1629 (16)	2.9	B	ν_3	Fund.	a'
			1537 (16)	0.079	B	1540	$2\nu_7$	A'
			1406	0.034	C	1406	$\nu_6 + \nu_{11}$	A''
			1381 (17)	0.095	A	1408	$\nu_7 + \nu_8$	A'
						1382	$2\nu_{10}$	A'
			1356	0.037	C	1378	$\nu_5 + \nu_{12}$	A''
						1345	$\nu_2 + \nu_{11}$	A''
			1303	?	?		*cis*-CClDCFH impurity	
			1263 (15)^e	0.28	A	1276	$2\nu_8$	A'
						1266	$\nu_{10} + \nu_{11}$	A'
						1187	$\nu_5 + \nu_9$	A'
						Fermi resonance with ν_4		
1142	vw	p	1162 (17)	5.2	A	ν_4	Fund.	a'
			1085 (16)	0.095	A	1085	$\nu_{10} + \nu_{12}$	A'
			1051	~3.3	A/B		*cis*-CClHCFD impurity	
977	m	p	984 (15)^d	1.2	B	ν_5	Fund.	a'
830	s	p	831 (16)^{e,f}	0.42	A	ν_6	Fund.	a'
			745^e		C?		*cis*-CClHCFD impurity?	
764	s	p	770 (16)	0.42	A	ν_7	Fund.	a'
690	s	dp	691^f	0.012	C	ν_{10}	Fund.	a''
632	s	p	638 (15)^e	1.1	A	ν_8	Fund.	a'
578	vw	p?	575^e	0.52	C	ν_{11}	Fund.	a''
395	m	dp	394	0.16	C	ν_{12}	Fund.	a''
203	s	p	<200	?	?	ν_9	Fund.	a'

$^{a-c}$ See Table I. ^{d} Rotational spacing of 0.71 cm^{-1} in R branch; poorly resolved structure in *P*. ^{e} See Table I. ^{f} Poorly resolved rotational structure.

Of the nine bands assigned to in-plane modes only the one at 1283 cm^{-1} corresponds to a depolarized Raman band, but there can be no doubt about this assignment. cis-1-Chloro-2-fluoroethylene-1,2-d$_2$. In contrast to the spectra of the other three cis species, the infrared spectrum of cis-CClDCFD does not have any overlapping bands due to fundamentals. In Figure 4 eight prominent type A/B bands and a wing of a band

Table V: Infrared and Raman Spectra and Assignments for trans-CClH=CFH

Raman (liquid)			Ir (gas)			Assignment		
Freq, cm^{-1}	I	Polar- ization	Freq, cm^{-1} a	α b	Band shape c	Freq, cm^{-1}		Sym species
			3977 (13)	0.02	B	3979	$\nu_1 + \nu_7$	A'
			3350	0.008	B	3364	$\nu_2 + \nu_9$	A'
							$\nu_2 + \nu_{12}$	A''
			3103 (12)^f 3115^d	0.82	A/B	ν_1	Fund.	a'
3094	m	p				ν_2	Fund.	a'
			2854 (12)	0.035	B	2865	$\nu_3 + \nu_5$	A'
			2769 (11)	0.044	A/B	2774	$\nu_3 + \nu_6$	A'
			2247 (12)	0.20	A/B	2254	$2\nu_6$	A'
			2090	0.01	B	2094	$\nu_3 + \nu_8$	A'
							$\nu_5 + \nu_7$	A'
			1914^f	0.062	~C	1917	$\nu_3 + \nu_9$	A'
							$\nu_3 + \nu_{12}$	A''
			1768 (13)^f	0.060	B	1776	$2\nu_{10}$	A'
						1764	$\nu_7 + \nu_{10}$	A''
			1666 (14)	0.51	B	1672	$\nu_{10} + \nu_{11}$	A'
						1665	$\nu_5 + \nu_8$	A'
							Fermi resonance with ν_3	
1643	s	p	1647 (12) 1647^d	1.5	B	ν_3	Fund.	a'
			1572 (14)	0.061	B	1574	$\nu_6 + \nu_8$	A'
							Fermi resonance with ν_3	
						1568	$2\nu_{11}$	A'
			1489	0.011	~C	1488	$\nu_5 + \nu_9$	A'
							$\nu_5 + \nu_{12}$	A''
			1395	0.051	~C	1397	$\nu_3 + \nu_9$	A'
							$\nu_6 + \nu_{12}$	A''
			1375	0.02	C	1377	$\nu_3 - \nu_9$	A'
							$\nu_3 - \nu_{12}$	A''
			1349 (14)	0.025	B		?	
			1321 (11) 1317^d	0.079	B	1323	$\nu_7 + \nu_8$	A'
1294	s	p	1296 (15)	0.047	A/B	ν_4	Fund.	a'
1218	m	p	1218 (13)^f 1217^d	0.11	B	ν_5	Fund.	a'
1112	m	p	1127 (13) 1127^d	12	A/B	ν_6	Fund.	a'
			1054^e	0.052	~C	1054	$\nu_9 + \nu_{11}$	A'
							$\nu_{11} + \nu_{12}$	A''
			1028^e	0.014	~C	1026	$\nu_4 - \nu_9$	A'
							$\nu_4 - \nu_{12}$	A''
~896	vw	dp?	888^f ~885^d	1.3	C	ν_{10}	Fund.	a''
871	m	p	876 (13) 875^d	2.8	A/B	ν_7	Fund.	a'
785	m	dp	784^f 784^d	0.12	C	ν_{11}	Fund.	a''
			678 (13)	0.005	B	679	$\nu_6 - \nu_8$	A'
			525	0.007	?	540	$2\nu_9$	A'
							$\nu_9 + \nu_{12}$	A''
							$2\nu_{12}$	A'
447	s	p	447 (15)	0.060	B	ν_8	Fund.	a'
274	m	dp	270^g	0.82	~C	ν_9	Fund.	a'
							ν_{12}	Fund.	a''

$^{a-e}$ See Table I. ^{f} Rotational structure with spacing of 3.0–3.6 cm^{-1} in wings of band. ^{g} 6.4 cm^{-1} spacing in R branch.

near 200 cm^{-1} account for the nine in-plane fundamentals, and three type-C bands account for the three out-of-plane fundamentals. All but the 2305-cm^{-1} in-plane fundamental have definitely polarized bands in the Raman spectrum (Table IV). Depolarized bands in the Raman spectrum correspond to two of the out-of-plane modes, and the polarization of the third band, which is of very low intensity, is in doubt. As in the case of *cis*-CClHCFH, the weakest band in the infrared for an out-of-plane fundamental corresponds to a well defined, depolarized Raman band and thus to a CD torsion with a_2-like symmetry.

trans-1-Chloro-2-fluoroethylene. The infrared spectrum of *trans*-CClHCFH in Figure 5 has five prominent type-A/B bands located at 3103, 1647, 1112, 876, and 447 cm^{-1}, which are undoubtedly due to in-plane fundamentals. The corresponding Raman bands (Table V) are polarized. A partly overlapped band at 1296 cm^{-1}, supported by a strong, polarized counterpart in the Raman, is the sixth in-plane fundamental. A stronger band at 1218 cm^{-1}, also supported by a polarized Raman band, is the seventh. The second CH-stretching frequency is observed only in the Raman spectrum as a polarized band at 3094 cm^{-1}. Without a more detailed analysis of the spectra there is no evidence for the ninth in-plane fundamental.

Three type C bands attributable to out-of-plane fundamentals seem to be present in the gas-phase infrared

Table VI: Infrared and Raman Spectra and Assignments for *trans*-CClD=CFH

Raman (liquid)			Ir (gas)			Assignment		
Freq, cm^{-1}	I	Polarization	Freq, cm^{-1} ^{a}	α^b	Band shape^c	Freq, cm^{-1}		Sym species
			3360	0.005	$\sim$C	3365	$\nu_1 + \nu_9$	A$'$
							$\nu_1 + \nu_{12}$	A$''$
3093	wm	p	3099 (12)	0.25	B	ν_1	Fund.	a$'$
			2757 (12)	0.072	B	2762	$\nu_2 + \nu_8$	A$'$
							$\nu_3 + \nu_5$	A$'$
2313	m	p	2318 (12)^d	0.71	B	ν_2	Fund.	a$'$
			2280	0.02	C	2287	$\nu_3 + \nu_{11}$	A$''$
			2253 (12)	0.11	B	2264	$2\nu_5$	A$'$
			2120 (13)	0.025	B	2121	$\nu_5 + \nu_6$	A$'$
			1973 (13)	0.030	B	1978	$2\nu_6$	A$'$
			1915	<0.02	B?	1914	$\nu_5 + \nu_7$	A$'$
			1896	0.053	$\sim$C	1896	$\nu_3 + \nu_9$	A$'$
							$\nu_3 + \nu_{12}$	A$''$
			1695 (13)	0.37	B	1702	$2\nu_{10}$	A$'$
1626	vs	p	1630 (12)	1.1	B	ν_3	Fund.	a$'$
$\sim$1550	vw		1563 (11)	0.14	A	1564	$2\nu_7$	A$'$
			1506 (12)	0.026	B	1508	$\nu_{10} + \nu_{11}$	A$'$
			1429 (13)	0.036	A/B	1439	$\nu_7 + \nu_{11}$	A$'$
						1433	$\nu_6 + \nu_9$	A$'$
			1395	0.064	$\sim$C	1398	$\nu_5 + \nu_9$	A$'$
							$\nu_5 + \nu_{12}$	A$''$
			1309 (13)^d	0.06	B	1314	$2\nu_{11}$	A$'$
1283	s	p	1284 (14)	0.074	B	ν_4	Fund.	a$'$
			1218	0.28	?	1226	$\nu_7 + \nu_8$ Impurity?	A$'$
			1183	0.15	?	1186	$\nu_8 - \nu_8$ Impurity?	A$'$
1115	m	p	1132 (13)	8.9	B	ν_5	Fund.	a$'$
			1046 (12)	0.037	A	1048	$\nu_7 + \nu_9$	A$'$
							$\nu_7 + \nu_{12}$	A$''$
			1016	0.021	C	1018	$\nu_4 - \nu_{12}$	A$''$
980	sm	p	989	4.0	B	ν_6	Fund.	a$'$
			$\sim$875				*trans*-CClHCFH impurity	
853	m	dp	851^{d,e}	0.40	C	ν_{10}	Fund.	a$''$
782	sm	p	782 (13)	0.88	B	ν_7	Fund.	a$'$
654	m	dp	657^{d,e}	0.38	C	ν_{11}	Fund.	a$''$
			546 (12)	0.006	B	545	$\nu_6 - \nu_8$	A$'$
442	vs	p	444 (14)^d	0.058	B	ν_8	Fund.	a$'$
270	s	dp?	266^f	0.79	$\sim$C	ν_9	Fund.	a$'$
							ν_{12}	Fund.	a$''$

$^{a-c}$ See Table I. ^{d} Rotational spacing of 2.5–2.9 cm^{-1} in P and R branches. ^{e} See Table I. ^{f} Rotational spacing of 5.1 cm^{-1} in R branch.

spectrum. The assignment of one at 888 cm⁻¹, which overlaps the ν_7 band, is supported by the well developed rotational structure in the R branch and an apparently depolarized Raman band. Rotational structure also supports the assignment of the second type C band at 784 cm⁻¹ to ν_{11} and apparently also the third one at 274 cm⁻¹. The ν_{11} fundamental, which has a prominent, depolarized Raman band and a relatively weak infrared band, must be the CH motion which correlates with b_g symmetry in a symmetrically substituted dihaloethylene. The 6.4-cm⁻¹ spacing of the rotational structure of the R branch of the 274-cm⁻¹ band is nearly twice the normal spacing of 3.3 cm⁻¹. Furthermore, the general appearance of this lowest frequency band is almost identical with that of the corresponding band in the spectrum of trans-CFHCFH. For the difluoroethylene

Table VII: Infrared and Raman Spectra and Assignments for trans-CClH=CFD

Raman (liquid)			Ir (gas)			Assignment		
Freq, cm⁻¹	I	Polarization	Freq, cm⁻¹ ᵃ	α ᵇ	Band shapeᶜ	Freq, cm⁻¹		Sym species
			3968 (16)	0.012	A/B	3971	$\nu_1 + \nu_7$	A′
			3348	0.006	?	3361	$\nu_1 + \nu_9$	A′
							$\nu_1 + \nu_{12}$	A″
			3233 (11)	0.018	B	3240	$2\nu_3$	A′
3095	m	p	3099 (13)	0.54	A	ν_1	Fund.	a′
			2835 (12)	0.021	B	2841	$\nu_3 + \nu_4$	A′
			2740 (11)	0.062	A/B	2745	$\nu_3 + \nu_5$	A′
			2570	0.003	?	2585	$\nu_2 + \nu_9$	A′
							$\nu_2 + \nu_{12}$	A″
						2571	$\nu_3 + \nu_6$	A′
			2340	<0.02	?	2346	$\nu_4 + \nu_5$	A′
2330	m	p	2323 (12)ᵈ	0.21	B	ν_2	Fund.	a′
			2242 (12)	0.10	A/B	2250	$2\nu_5$	A′
			2093 (12)	<0.15	B	2093	$\nu_4 + \nu_7$	A′
			2072 (12)	0.042	A	2076	$\nu_5 + \nu_6$	A′
			1900	<0.024	?	1902	$2\nu_6$	A′
			1892	0.069	~C	1882	$\nu_3 + \nu_9$	A′
			1882				$\nu_3 + \nu_{12}$	A″
			1742 (11)	0.019	?	1744	$2\nu_7$	A′
1619	vs	p	1620 (12)	1.8	B	ν_3	Fund.	a′
			1567 (12)	0.12	A/B	1569	$\nu_5 + \nu_8$	A′
			1480	0.007	~C	1483	$\nu_3 + \nu_9$	A′
							$\nu_3 + \nu_{12}$	A″
			1378 (12)ᵈ	0.21	B	1395	$\nu_6 + \nu_8$	A′
						1382	$2\nu_{11}$	A′
			1341	<0.04			?	
			1315	0.10	B	1316	$\nu_7 + \nu_8$	A′
1213	s	p	1221 (13)ᵈ,ᵉ	0.31	A	ν_4	Fund.	a′
			<1140			1133	$\nu_7 + \nu_9$	A′
							$\nu_7 + \nu_{12}$	A″
1112	m	p	1125 (13)ᵈ,ᵉ	11	B	ν_5	Fund.	a′
			1080	<0.04	~C	1079	$\nu_{10} + \nu_{12}$	A′
							$\nu_9 + \nu_{10}$	A″
			988 (10)ᵉ	<0.04	A/B	953	$\nu_{11} + \nu_{12}$	A′
							Fermi resonance with ν_6	
~945	vw	dp	951 (12)ᵉ	1.0	A	ν_6	Fund.	a′
			894 (10)	<0.3	A/B	888	$2\nu_8$	A′
869	m	p	872 (13)ᵉ	2.3	B	ν_7	Fund.	a′
813	vw	dp	817ᵈ	0.75	C	ν_{10}	Fund.	a″
~775	vw	dp				785	trans-CClHCFH impurity	
689	m	dp	691ᵈ	0.15	C	ν_{11}	Fund.	a″
			523	0.003	B	524	$2\nu_9$	A′
							$2\nu_{12}$	A′
446	s	p	444 (14)	0.062	B	ν_8	Fund.	a′
266	m	dp?	262ᶠ	0.75	~C	ν_9	Fund.	a′
							ν_{12}	Fund.	a″

ᵃ⁻ᶜ See Table I. ᵈ Rotational structure in P and R branches with 2.4–2.9 cm⁻¹ spacing. ᵉ See Table I. ᶠ Rotational structure in P and R branch with 5.2-cm⁻¹ spacing.

Table VIII: Infrared and Raman Spectra and Assignments for trans-CClD=CFD

Raman (liquid) Freq, cm⁻¹	I	Polar-ization	Ir (gas) Freq, cm⁻¹ ᵃ	α^b	Band shapeᶜ	Assignment Freq, cm⁻¹		Sym species
			3424 (15)	0.013	B	3425	$\nu_2 + \nu_4$	A'
			3284 (12)	0.012	B	3286	$\nu_2 + \nu_5$	A'
						3284	$\nu_1 + \nu_6$	A'
			3099 (13)	0.008	B	3099	trans-CClDCFH impurity trans-CClHCFD impurity	
			3078 (13)	0.012	B	3081	$\nu_2 + \nu_7$	A'
			2730 (11)	0.084	A/B	2738	$\nu_2 + \nu_8$	A'
						2737	$\nu_3 + \nu_4$	A'
			2680	0.013	?	2690	$\nu_4 + 2\nu_7$	A'
			2598	0.012	~C	2598	$\nu_1 + \nu_9$	A'
							$\nu_1 + \nu_{12}$	A''
			~2390	0.01	A/B	2393	$\nu_3 + \nu_7$	A'
2345	s	p	2339 (14)ᵈ	0.20	B	ν_1	Fund.	a'
~2304	vw	dp	2299 (12)	1.0	B	ν_2	Fund.	a'
			2244 (12)	0.052	B	2252	$2\nu_4$	A'
			2111 (12)	0.040	B	2113	$\nu_4 + \nu_5$	A'
			2066 (11)	0.021	A	2071	$\nu_4 + \nu_6$	A'
			1975 (13)	0.030	B	1974	$2\nu_5$	A'
			1911 (14)	0.018	B	1908	$\nu_4 + \nu_7$	A'
			1866 (14)	0.06	~C	1870	$\nu_3 + \nu_9$	A'
							$\nu_3 + \nu_{12}$	A''
			1695	w	B		cis-CClFCFD impurity	
			~1630				trans-CClDCFH impurity	
1609	vs	p	1611 (13)	1.8	B	ν_3	Fund.	a'
			1560 (12)	0.41	A	1565	$\nu_4 + \nu_8$	A'
						1564	$2\nu_7$	A'
			1427 (12)	0.028	B	1426	$\nu_5 + \nu_8$	A'
			1382 (11)ᵈ	0.25	A/B	1384	$\nu_6 + \nu_8$	A'
							$2\nu_{10}$	A'
			1336 (12)	0.070	B	1338	$\nu_{10} + \nu_{11}$	A'
			1287 (12)ᵈ	0.033	B	1292	$2\nu_{11}$	A'
			1224 (12)	0.13	~B	1221	$\nu_7 + \nu_8$	A'
			1166	0.06	B	1172	$\nu_3 - \nu_8$	A'
1113	s	p	1126 (13)ᵉ	8.7	B	ν_4	Fund.	a'
			1038 (10)	0.029	B	1041	$\nu_7 + \nu_9$	A'
							$\nu_7 + \nu_{12}$	A''
984	s	p	987 (13)ᵉ	4.7	B	ν_5	Fund.	a'
~944	vw	dp	945 (14)	0.065	A	ν_6	Fund.	a'
						951	$\nu_{10} + \nu_{12}$	A'
							$\nu_9 + \nu_{10}$	A''
			904	0.01	~C	905	$\nu_{11} + \nu_{12}$	A'
							$\nu_9 + \nu_{11}$	A''
			871 (12)		A/B		trans-CClHCFD impurity	
						878	$2\nu_8$	A'
			850		C		trans-CClDCFH impurity	
			817ᶠ		C		trans-CClHCFD impurity	
782	s	p	782 (12)	1.1	B	ν_7	Fund.	a'
691	s	dp	692	<0.05	C	ν_{10}	Fund.	a''
~642	vw	dp?	646ᵈ	0.78	C	ν_{11}	Fund.	a''
			546 (13)	0.004	B	548	$\nu_3 - \nu_5$	A'
442	vs	p	441 (14)ᵈ	0.061	B	ν_8	Fund.	a'
262	s	dp?	259ᵍ	1.0	~C	ν_9	Fund.	a'
							ν_{12}	Fund.	a''

ᵃ⁻ᶜ See Table I.   ᵈ Rotational spacing of 1.7–2.4 cm⁻¹ in P and R branches.   ᵉ See Table I.   ᶠ Rotational spacing of 2.5 cm⁻¹ in R branch, 2.9 cm⁻¹ in P branch.   ᵍ Rotational spacing of 4.3 cm⁻¹ in R branch.

Table IX: Vibrational Fundamentals of *cis*-1-Chloro-2-fluoroethylene and Deuterated Modifications (Frequencies in cm^{-1})

| | Obsd | | | | Calcd | | | |
	CClHCFH	CClDCFH	CClHCFD	CClDCFD	CClHCFH	CClDCFH	CClHCFD	CClDCFD
a'								
ν_1	3114	3098	3112	2342	3136	3135	3113	2311
ν_2	3102	2322	2318	2297	3112	2289	2310	2289
ν_3	1661^a	1637^a	1644^a	1629	1649	1638	1621	1609
ν_4	1335	1304	1283	1162^a	1351	1322	1273	1171
ν_5	1231	1155	1051	984	1209	1144	1075	974
ν_6	1062	851	969	831	1086	854	962	837
ν_7	812	778	791	770	795	778	793	775
ν_8	656	655	637	638	650	643	627	623
ν_9	205^b	202^b	205^b	203^b	204	203	203	203
a''								
ν_{10}	857	826	796	691	857	826	797	691
ν_{11}	735	588	650	575	737	587	650	573
ν_{12}	442	434	400	394	442	434	400	395

^{a} Uncorrected for probable shift due to Fermi resonance with a combination tone. ^{b} From liquid-phase Raman spectra; all others from gas-phase infrared.

case much evidence has been found in support of this band being due to two almost degenerate fundamentals distorted by a strong Coriolis perturbation.[3b] We therefore confidently assign both ν_9 and ν_{12} to the 274-cm^{-1} band. Table V also includes the eight frequencies which Viehe, *et al.*, assigned to fundamentals.[8] Agreement with our assignments is within a few cm^{-1} in every case.

trans-1-Chloro-2-fluoroethylene-1-d₁. Given the interpretation that the band in the 270-cm^{-1} region is due to overlap of the ν_9 and ν_{12} fundamentals as in *trans*-CClHCFH, one finds the vibrational assignment for *trans*-CClDCFH to be straightforward. Seven type A/B bands are quickly found in the gas-phase infrared spectrum in Figure 6 and are assigned to in-plane fundamentals. The eighth band, 1284 cm^{-1}, is sufficiently weak in the infrared that the strong, polarized Raman band (Table VI) at this frequency becomes the basis for the assignment. Two type C bands stand out clearly with well defined rotational structure in the gas-phase infrared and have depolarized counterparts in the Raman. In the low-frequency region, where ν_9 and ν_{12} overlap, exaggerated rotational spacing of 5.1 cm^{-1}, compared with a normal value of about 2.7 cm^{-1}, is again present.

trans-1-Chloro-2-fluoroethylene-2-d₁. The gas-phase infrared spectrum in Figure 7 of *trans*-CClHCFD contains seven prominent type A/B bands which we have assigned to fundamentals. All but the 951-cm^{-1} band are supported by polarized bands in the Raman spectrum (Table VII). The 951-cm^{-1} mode causes a weak, apparently depolarized Raman band. The eighth in-plane fundamental must correspond to the type A/B band at 1221 cm^{-1} and not to the band of comparable intensity at 1378 cm^{-1}. A frequency of 1378 cm^{-1} is too high for this fundamental, and the 1221-cm^{-1} as-

signment is supported by a strong, polarized Raman band. Well defined type C bands with obvious rotational structure are at 813 and 689 cm^{-1} in the infrared spectrum. These fundamentals also produce medium intensity, depolarized Raman bands. With eight of the in-plane and two of the out-of-plane fundamentals assigned we turn, as in the *trans*-CClHCFH and *trans*-CClDCFH cases, to the distorted band at the low-frequency end of the spectrum. We assign this band with its 5.2-cm^{-1} rotational spacing to both the ν_9 and ν_{12} fundamentals. The spectrum of this molecule provides, however, further support for this interpretation beyond that found for *trans*-CClHCFH and CClDCFH. Although the band for the overlapped fundamentals looks like the corresponding bands for the other two species, but with more poorly defined rotational structure in the R branch, the combination band at 1885 cm^{-1} has two distinct features. This band is assigned as $\nu_3 + \nu_9$ and $\nu_3 + \nu_{12}$ and has a shape strongly suggestive of overlapped type A/B and type C bands.

trans-1-Chloro-2-fluoroethylene-1,2-d₂. Six prominent type A/B bands seen at 2339, 1611, 1126, 987, 782, and 441 cm^{-1} in the gas-phase infrared spectrum of *trans*-CClDCFD in Figure 8 correspond to polarized Raman bands (Table VIII) and are confidently assigned as in-plane fundamentals. The unusual intensity of the band for the CD-bending mode at 987 cm^{-1} is due to considerable CF-stretching character in this vibration. Although the type A/B band at 2304 cm^{-1} corresponds to a very weak, depolarized Raman band, it must certainly be the second CD stretch. The location of the second CD-bending mode is less certain. Compared with the values of the CD-bending frequencies in the *trans*-CClDCFH and CClHCFD the low-intensity infrared band at 945 cm^{-1} seems to be the correct assignment, even though the corresponding

Table X: Vibrational Fundamentals of *trans-*1-Chloro-2-fluoroethylenes and Deuterated Modifications (Frequencies in cm^{-1}).

	Obsd				Calcd			
	CClHCFH	CClDCFH	CClHCFD	CClDCFD	CClHCFH	CClDCFH	CClHCFD	CClDCFD
a'								
ν_1	3103	3099	3099	2339	3120	3118	3111	2301
ν_2	3094[a]	2318	2323	2299	3110	2288	2298	2284
ν_3	1647[b]	1630	1620	1611	1666	1652	1635	1619
ν_4	1296	1284	1221	1126	1287	1279	1210	1124
ν_5	1218	1132	1125	987	1214	1128	1123	995
ν_6	1127	989	951[b]	945	1117	986	952	931
ν_7	876	782	872	782	886	781	877	781
ν_8	447	444	444	439	452	449	450	448
ν_9	270	266	262	259	277	271	268	263
a''								
ν_{10}	888	851	817	692	888	851	817	692
ν_{11}	784	657	691	646	784	657	691	646
ν_{12}	270	266	262	259	268	266	262	259

[a] From liquid-phase Raman spectra; all others from gas-phase infrared. [b] Uncorrected for probable Fermi resonance with a combination tone.

Raman band is very weak and apparently depolarized. The corresponding fundamental in *trans-*CClHCFD also has a weak, apparently depolarized Raman band. Further, there is no other candidate in the infrared spectrum of reasonable intensity and shape in this region. For the out-of-plane fundamentals only the type C band at 646 cm^{-1} stands out clearly in the infrared. This band has rich rotational structure and an apparently depolarized version in the Raman spectrum. Close examination of the infrared spectrum reveals the Q branch of a weak type C band at 691 cm^{-1}, which is confirmed by a strong depolarized Raman band. As in the three other *trans* species we assign the spike-like band in the low-frequency region to a near degeneracy in

Table XI: Product Rule Check of Assignments and Principal Moments of Inertia in amu Å^2 [a]

		*cis-*Isomer		*trans-*Isomer	
		Calcd	Obsd	Calcd	Obsd
CClDCFH	a'	0.512	0.508	0.509	0.523
CClHCFH	a''	0.754	0.757	0.798	0.791
CClHCFD	a'	0.515	0.523	0.510	0.520
CClHCFH	a''	0.742	0.743	0.793	0.787
CClDCFD	a'	0.264	0.271	0.260	0.272
CClHCFH	a''	0.557	0.562	0.622	0.616

	I_a	I_b	I_c	I_a	I_b	I_c
CClHCFH	31.22	136.1	167.3	8.99	210.6	219.6
CClDCFH	34.97	136.2	171.2	11.30	210.7	222.0
CClHCFD	32.91	140.3	173.2	11.12	211.5	222.6
CClDCFD	36.63	140.4	177.0	13.48	211.5	225.0

[a] Geometric parameters: r_{CC} = 1.333 Å, r_{CCl} = 1.726 Å, r_{CF} = 1.348 Å, r_{CH} = 1.079 Å, α_{CCCl} = 123.6°, α_{CCH} = 123.2°, and α_{CCF} = 121.0°. J. A. Howe, *J. Chem. Phys.,* **34,** 1247 (1961).

ν_9 and ν_{12}. Rotational spacing of 4.3 cm^{-1} in the R branch and two features for the combination band, $\nu_1 + \nu_9$ and $\nu_1 + \nu_{12}$ at 2598 cm^{-1}, provide further support for this assignment.

Summary. For the four *cis* species we are confident of the assignments of the vibrational fundamentals, which are summarized in Table IX. Although some of the evidence is less direct, we believe that we have also obtained complete assignments of the fundamentals of the *trans* species, Table X. All of the assignments are consistent with the isotope product rule (Table XI) and with the Rayleigh rule. As shown in Tables I–IV for the *cis* species and Tables V–VIII for the *trans*, it is possible in almost every case to assign the weaker bands as binary combinations. This agreement was also found for very weak bands with absorption coefficients less than 0.01 cm^{-1} atm^{-1}. These very weak bands were omitted from the tables except where they were of special interest such as combinations involving the entangled ν_9 and ν_{12} fundamentals of the *trans* species.

Thermodynamic Functions. With a complete vibrational assignment of the fundamentals in hand one may check the $\Delta S°$ obtained from the thermodynamic measurements and extract $\Delta E_0°$ (electronic), the electronic energy difference between the two isomers, from $\Delta H°$. A rigid-rotor, harmonic-oscillator treatment of *cis-* and *trans-*CClHCFH gives $\Delta S°_{615}$ = 0.24 ± 0.04 cal/mol °K and $\Delta H°_{615}$ (thermal) = 184 cal/mol for the *cis-*to-*trans* reaction. The calculated value of $\Delta S°_{615}$ is in satisfactory agreement with the experimental value of 0.21 cal/mol °K. From the calculated value of $\Delta H°_{615}$(thermal), the experimental value of $\Delta H°_{615}$ = 782 ± 22 cal/mol, and $\Delta E_0°$(vibration) = −269 ± 70 cal/mol, one obtains $\Delta E_0°$(electronic) = 867 ± 90 cal/mol. This value for $\Delta E_0°$(electronic) is very nearly

Table XII: Potential Constants for Vibrations
of 1-Chloro-2-fluoroethylenes

A. In-Plane Modes; Modified Urey–Bradley Field
[K, F, and C in mdyn/Å; H in mdyn Å/radian²]

	Zero-order[a]	Overlay	Dispersion
K_{CC}	7.48	7.50	0.14
K_{CH}	4.83	4.82	0.051
K_{CF}	5.20	4.67	0.22
K_{CCl}	2.66	2.75	0.32
H_{CCH}	0.335	0.187	0.065
H_{HCF}	0.500[b]	0.491	0.074
H_{CCF}	0.172	1.14	0.21
H_{HCCl}	0.383	0.273	0.079
H_{CCCl}	0.207		
F_{CH}	0.450	0.394	0.086
F_{CF}	1.37	0.754	0.21
F_{HF}	0.34[b]	0.557	0.089
F_{CCl}	0.92	0.769	0.10
F_{HCl}	0.30	0.524	0.087
C_{HH}	0.0	−0.009	0.022
C_{FCl}	0.080	−0.004	0.028
C_{HF}	−0.045	−0.043	0.038
C_{HCl}	0.030	−0.077	0.040
T_δ	0.0	0.097	0.031

B. Out-of-plane Modes; General Valence Field
[mdyn Å/radian²]

	cis		trans	
	Refined[c]	Dispersion	Refined[c]	Dispersion
$F_\gamma H(Cl)$	0.356	0.0006	0.345	0.0004
$F_\gamma H$ (F)	0.353	0.0007	0.363	0.0005
F_τ	0.529	0.0017	0.468	0.0029
$F_{\gamma\gamma}$	0.064	0.0005	0.143	0.0004
$F_{\tau\gamma}H(Cl)$	−0.267	0.0016	−0.220	0.0028
$F_{\tau\gamma}H(F)$	−0.211	0.0010	−0.195	0.0023

[a] Reference 11. [b] Reference 16. [c] Zero-order force constants: $F_\delta = 0.30$ and $F_\tau = 0.30$; all others 0.0.

the mean of the values for CFHCFH, 1086 cal/mol,[3b] and CClHCClH, 642 cal/mol.[4a]

Normal Coordinate Calculations. In-Plane Modes. For the in-plane normal coordinate calculations five valence bond stretching coordinates and six unscaled valence angle bending coordinates were used. Two rocking and two scissors coordinates and two angle redundancy relationships were then defined as before for halogenated ethylenes.[10,13] The geometric parameters (Table XI) were based in part on microwave results for the *cis* isomer. The calculations were performed with the Minnesota normal coordinate programs, which employ a modified GF formalism.[14] These programs were adapted for use on an IBM 360/44 computer.

The four *cis* species and the four *trans* species were treated together in an overlay calculation with a modified Urey–Bradley force field (MUBFF). All force constants except those for the *cis* interaction were considered to be the same for the two isomers. In addition, the same stretching (K_{CH}), bending (H_{CCH}),

and *gem* interaction (F_{CH}) constants were used for the hydrogen atoms on the two ends of the molecule. A *trans* CH-bend interaction force constant (T_δ), which had proved useful before for *trans* haloethylenes,[8b,15] was added to improve the frequency fit and reduce the force constant dispersions. This interaction constant compensated in part for the constraint imposed by using only one H_{CCH} constant. Even though this normal coordinate problem with 22 force constants seemed well determined by the 72 observed frequencies, it proved necessary to hold the H_{CCCl} constant at its zero-order value. Of course, frequency changes due to deuteration provide little new information about the force constants for carbon–halogen-rich modes, and the MUBFF is a questionable approximation.

The zero-order force constants (Table XII) are the same as those used in our earlier CClFCClH calculations,[10] except where supplemented with force constants from the CFHCFH calculations.[8b] The average differences between calculated and observed frequencies (Tables X and XI) are 1%. With the exception of the CH-stretching frequencies, where neglect of anharmonicity corrections is most serious, almost all of the calculated frequencies are within 15 cm⁻¹ of the observed ones. The refined force constants (Table XII) compare favorably with the zero-order values except in the case of H_{CCF}. Attempts to hold this force constant to a smaller value were unsuccessful. Dispersions of refined force constants are of reasonable magnitude except for those of the *cis* interaction constants. The satisfactory overlay calculation is added evidence in support of the assignments of the vibrational fundamentals.

Exploratory calculations with the MUBFF for the *cis* and *trans* species separately were unrewarding as the calculations either diverged or refined to unacceptable force constants. We expect, however, to make a more thorough study of the normal coordinates with several force field approximations for separate isomers.

One of the goals of this study of *cis–trans* isomerism in haloethylenes is to find evidence for *cis* stability in the force constants. In contrast to the CFHCFH case the *cis*-type interaction constants are apparently too poorly defined to permit any, even tentative, deductions. We do find, however, the same pattern in the fit of the CC-stretching frequencies. The overlay values for the *cis* isomers are, on the average, 14 cm⁻¹ too low and those for the *trans* isomers are 15 cm⁻¹ too high. This result may imply a larger K_{CC} force constant for the *cis* isomer, which correlates with its lower electronic energy.

Out-of-Plane Modes. As in our previous haloethylene calculations two wagging coordinates and one torsion

(13) J. R. Scherer and J. Overend, *J. Chem. Phys.*, **32**, 1720 (1960).
(14) (a) J. R. Scherer and J. Overend, *ibid.*, **32**, 1289 (1960); (b) C. D. Needham, Ph.D. Thesis, University of Minnesota, 1965.
(15) J. R. Scherer and J. Overend, *J. Chem. Phys.*, **33**, 1681 (1960).

coordinate were defined for out-of-plane vibrations.[3b,16] One wagging coordinate, $R_\gamma FH$, was the change in angle between a CH bond and the plane defined by the CCF atoms, and the other was the change in angle between the second CH bond and the plane defined by the CCCl atoms. The change in the dihedral angle between the CCF and CCCl planes was the torsion coordinate. The *cis* and *trans* isomers were treated separately with six-parameter general valence force fields.

As shown in Tables X and XI, calculated frequencies fit the experimental ones within 1 cm^{-1} in all but three instances, and all of the calculated force constants, Table XII, have convincingly low dispersions. The diagonal force constants are in good agreement with the ones obtained in the separate calculations for the *cis* and *trans* isomers of CFHCFH.[3b] For *cis*-CFHCFH, $F_\gamma = 0.362$, $F_\tau = 0.551$, $F_{\gamma\gamma} = 0.0534$, and $F_{\gamma\tau} = -0.246$; for *trans*-CFHCFH, $F_\gamma = 0.347$, $F_\tau = 0.460$, $F_{\gamma\gamma} = 0.141$, and $F_{\gamma\tau} = -0.190$. The pattern of a wagging force constant that is nearly independent of configuration and a torsion force constant that is signifi-cantly larger for the *cis* isomer is repeated. The off-diagonal force constants are also in good agreement with those for the difluoroethylenes. The difference in torsion force constants correlates with the lower electronic energy of the *cis* isomer. Furthermore, the 13% difference in the F_τ force constants for the chloro-fluoroethylenes is less than the 20% difference for the difluoroethylenes in parallel with the order of the difference in the electronic energies of the *cis* and *trans* isomers.

(16) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Publications, New York, N. Y., 1955, pp 58–62.