vestigate, in a preliminary way, the contributions of conformer populations *vs.* intrinsic asymmetry to the observed magnetic nonequivalence of protons 1 and 2. Although the temperature range was small, there was no evidence of change in the details in the chemical shift difference for the 1,2-protons. Thus it could be reasonably concluded that either there was a predominant conformer whose contribution to the asymmetry was reduced slowly throughout the temperature range investigated or that the system was in reasonably "rapid" rotation even at the lowest temperatures and the change with temperature is that appropriate to a system subjected to an averaging process that changes slowly with temperature.[8]

The observed magnetic nonequivalence of the 1,2-protons in the compounds investigated which have an asymmetric grouping in the molecule and the parallel observation of the apparent equivalence of these protons in molecules which have a plane of symmetry clearly demonstrate a longer range effect of the asymmetric system than might be expected from results previously reported in the literature. While the origin of this effect is not now clear, one might have to con-

sider not only the field effects through space, such as for conformers, but also the possible influence of asymmetry introduced in the electronic system of the molecule by the asymmetric group. The observed effect would seem to have considerable potential importance in problems involving structural elucidation.

Experimental

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Vibrational Assignment for *cis*- and *trans*-1,2-Dichloro-1-fluoroethylenes: FClC=CClH and FClC=CClD

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Infrared, Raman, and proton nuclear magnetic resonance spectra are presented for *cis*- and *trans*-FClC=CClH and FClC=CClD. Assignments of vibration frequencies are obtained for the twelve fundamentals of the *cis* species and for eleven fundamentals of the *trans* species. The assignments for the nine planar modes in each species are supported by normal coordinate calculations. In determining the isomeric configurations, advantage is taken of the significantly greater splitting between the two carbon–chlorine stretching frequencies for the *cis* isomer than for the *trans* isomer. The dynamic origin of this generally useful splitting rule is explored.

The substituted ethylenes are interesting molecules. As *cis–trans* isomers, they provide pairs of distinct chemical species with minimal structural differences. Their well-defined geometry provides a useful basis for studying the energetics of configurational stability.[1] Although in many cases it has been found that the configuration of lower energy is the *trans* isomer, in several halogenated ethylenes it appears to be the *cis*.[2-4] It, however, generally remains to be shown that these are differences in electronic energy and are not merely due to differences in heat capacity or zero-point vibrational energy. For this reason, a careful study of the vibrational and rotational energy levels of *cis–trans* isomeric pairs is desirable. The chlorofluoroethylenes are well suited to such a study because within the series we find an interesting range of relative stabilities. Moreover, they are tractable from a spectroscopic viewpoint. As a fundamental part of this study, it is our intention to examine the vibrational spectra of a number of chlorofluoroethylenes.

In the present paper we have used normal coordinate analysis primarily to confirm the vibrational assignment. We hope that when all of the spectroscopic data are in hand, it will also be possible to determine reliable force constants for this series of molecules and to establish where there are, in fact, differences in force constants between the *cis* and *trans* configurations which can be related to differences in electronic energy. In addition, for the particular case of an unsymmetrically substituted ethylene such as FClC=CClH, there are problems in the assignment of configuration, for the well-recognized differences between the infrared and Raman spectra of two symmetrically substituted isomers are no longer useful.[5] In the present paper, the utility of the frequency difference between the two carbon–halogen stretching modes in *cis–trans* isomer pairs is brought out.

cis–trans fluorinated olefins have also proved to be of considerable interest in n.m.r. studies where the greater magnitude of the *trans* coupling constant, compared with the *cis* coupling constant, appears to be well established experimentally, but not fully understood.[6,7]

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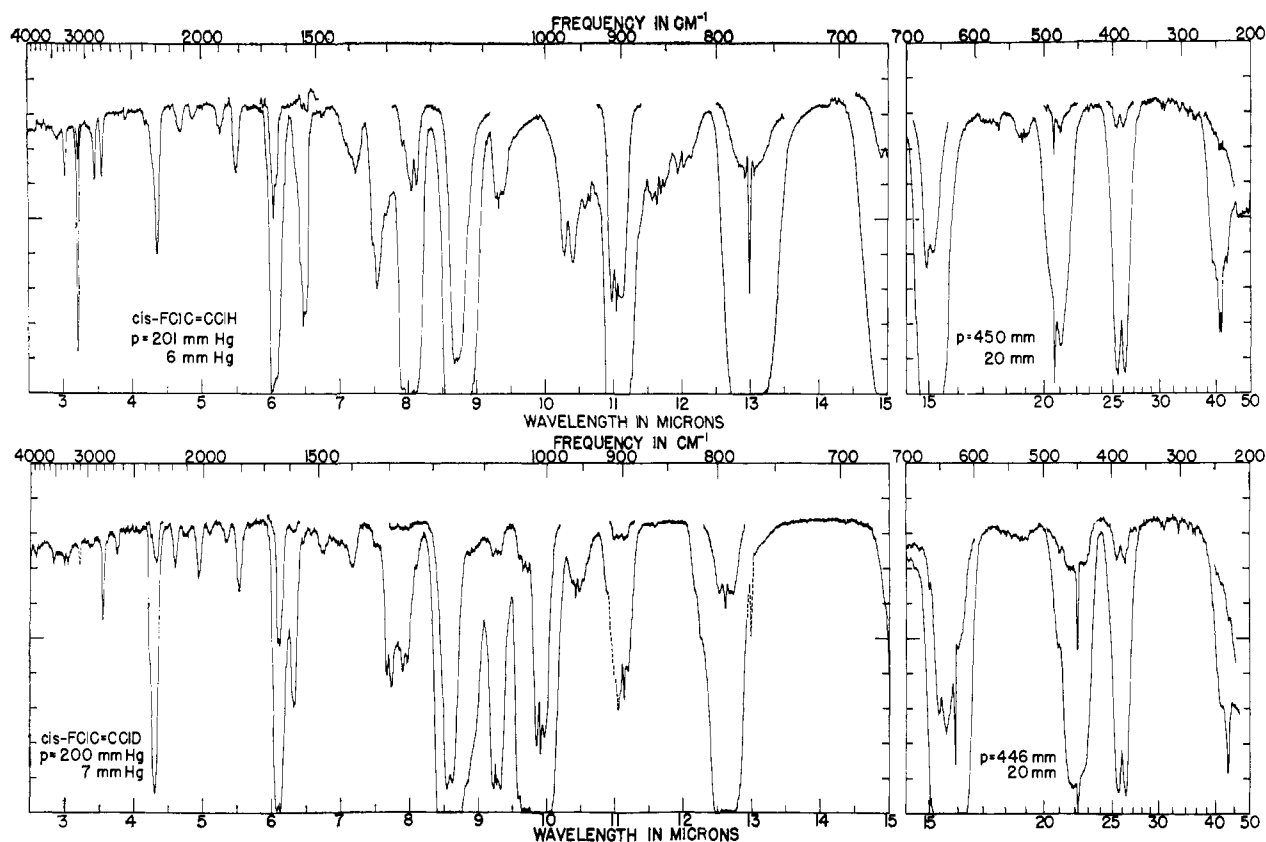
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Fig. 1 (Upper curve).—Infrared spectrum of *cis*-FClC =CClH.
Fig. 2 (Lower curve).—Infrared spectrum of *cis*-FClC=CClD.

Experimental

A mixture of *cis*- and *trans*-1,2-dichloro-1-fluoroethylenes was prepared in 95% yield by zinc dust dehalogenation of 1,1,2,2-tetrachloro-1-fluoroethane[8] in refluxing ethanol.[4] Gas chromatography of the isomeric mixture at 50° on a 4 m. × 1 cm. column packed with 30% dibutyl phthalate on 30–60 mesh firebrick gave pure samples of each isomer. For the *trans* isomer the elution time was 1.3 times longer than that of the *cis* isomer. Molar weight determinations by gas density measurements of the separated isomers agreed within 2% with the calculated value. The possible presence of 1,1-dichloro-2-fluoroethylene among the fractionated isomers as a consequence of 1,1,1,2-tetrachloro-2-fluoroethane as an impurity in the starting ethane was eliminated by synthesizing a sample of this isomer[9] and examining its infrared spectrum. This spectrum of 1,1-dichloro-2-fluoroethylene was the same as that subsequently reported by Muelleman, *et al.*[10] On the basis of gas chromatograms, *cis*-1,2-dichloro-1-fluoroethylene (m.p. −116.1°, b.p. 31.0° cor.) and *trans*-1,2-dichloro-1-fluoroethylene (m.p. −114.8°, b.p. 37.5° cor.) were each obtained in 99.9% purity.

Deuterated 1,2-dichloro-1-fluoroethylenes were prepared by repeated base-catalyzed exchange of the ethylene[11] with 99.5% deuterium oxide[12] in sealed Pyrex tubes at 70–80°. Excess dried calcium oxide served as the base, and exchange reactions were generally run overnight. After final drying over phosphorus pentoxide and gas chromatographic fractionation, the *cis* and *trans* isomers were obtained in 99.8% purity. From the infrared spectra isotopic purity of the deuterated species was found

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 335.

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

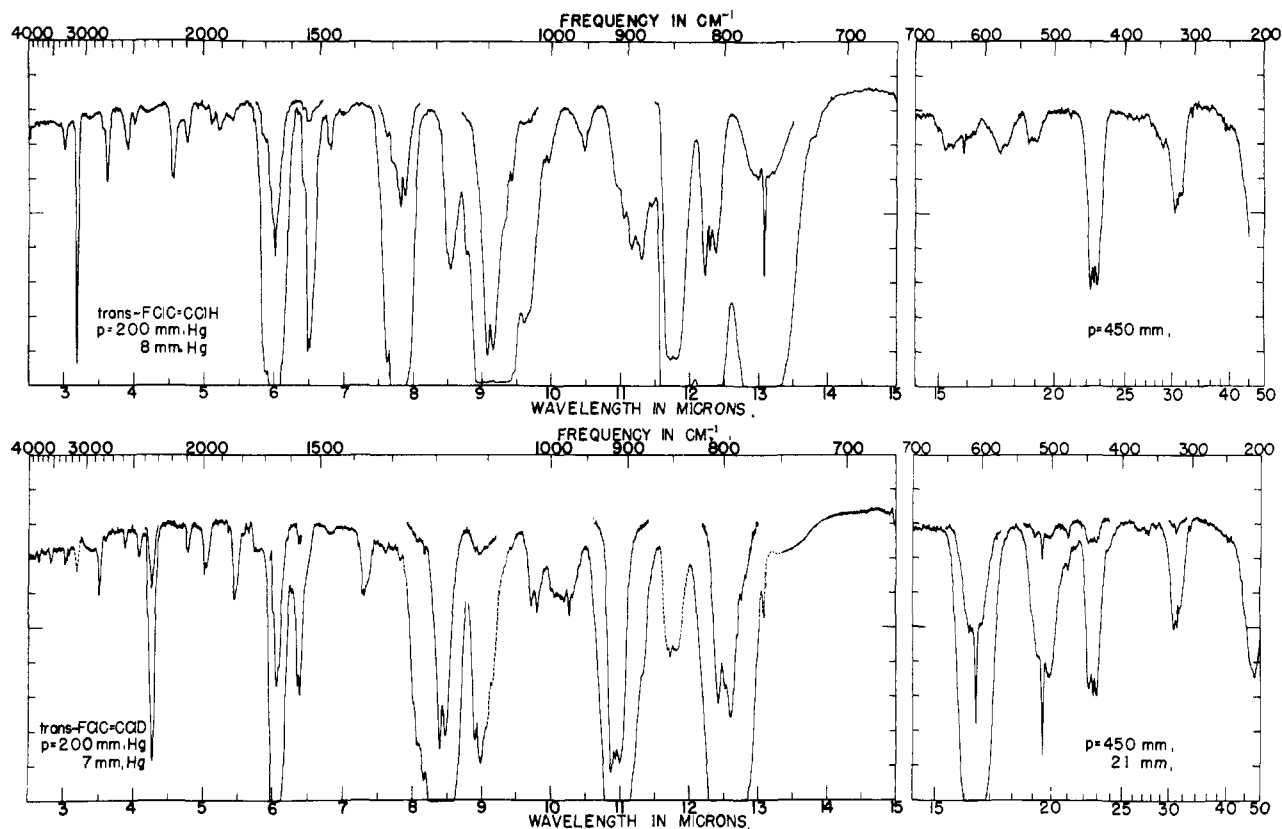(8) Columbia Organic Chemical Co., Charleston, S. C.

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(10) C. J. Muelleman, K. Ramaswamy, F. F. Cleveland, and S. Sundaram, *J. Mol. Spectry.*, **11**, 262 (1963).

(11) J. E. Francis and L. C. Leitch, *Can. J. Chem.*, **35**, 348 (1957); S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

(12) General Dynamics Corp., Liquid Carbonic Division, San Carlos, Calif.

to be 98.5%. This result was confirmed by an analysis on a Consolidated mass spectrometer, Model 21–401, where, with an ionizing voltage of about 8 v., a ratio of 0.016 for parent mass peaks 114/115 was observed.

Infrared spectra, Fig. 1–4, were obtained on a Beckman IR-4 equipped with sodium chloride optics and on a Beckman IR-7 equipped with the cesium iodide prism-grating interchange. Calibration of these spectrometers with polystyrene, water vapor, and carbon dioxide bands gave wave lengths reliable within ±0.01 μ in the sodium chloride region and frequencies reliable within ±1 cm.⁻¹ in the cesium iodide region. A 10-cm. gas cell equipped with cesium iodide windows was used. The pressures indicated with Fig. 1–4 are somewhat uncertain owing to the solubility of the halogenated ethylenes in the grease on the stopcock of the cell. In addition, far-infrared spectra were obtained in the region from 400 to 50 cm.⁻¹ on a single beam spectrometer designed by L. R. Herscher at Dow Chemical Co. For these spectra sample pressures were about 250 mm. in a 10-cm. cell equipped with polyethylene windows.

Raman spectra, summarized in Tables I and II, were obtained photographically on a Hilger E612 spectrograph with a dispersion of 16 Å./mm. Excitation was by means of the 4358.3 Å. line of mercury. Liquid samples of approximately 1 ml. were used in capillary tubes of 3 mm. i.d. Qualitative depolarizations were obtained by the Edsall–Wilson method.[13]

Proton nuclear magnetic resonance spectra were obtained for the *cis*- and *trans*-1,2-dichloro-1-fluoroethylenes on a Varian A-60 n.m.r. spectrometer. The liquid samples contained 1% tetramethylsilane (TMS) and 10% olefin in a carbon tetrachloride solvent. As was to be expected for an AX spin system,[6] the proton spectrum of each isomer was a symmetrical doublet. For the *cis* isomer the H–F coupling constant was found to be 4.0 c.p.s. and the chemical shift relative to TMS 6.23 p.p.m.; for the *trans* isomer, 17.8 c.p.s. and 5.60 p.p.m.

Assignments of Vibrational Frequencies and Isomeric Configurations.—The 1,2-dichloro-1-fluoroethylenes are assumed to be planar molecules of C_s symmetry. As a consequence, the nine planar vibration modes of species A′ and the three nonplanar vibration modes of species A″ should be infrared active. In the gas phase infrared spectra, hybrid type A/B bands, consisting of triplets or doublets with peaks of comparable intensity,

(13) J. T. Edsall and E. B. Wilson, *J. Chem. Phys.*, **6**, 124 (1938).

Fig. 3 (Upper curve).—Infrared spectrum of *trans*-FClC=CClH.
Fig. 4 (Lower curve).—Infrared spectrum of *trans*-FClC=CClD.

are expected for the planar modes, and type C bands, having a strong central Q branch, are expected for the nonplanar modes.[14] On the basis of these considerations and of previous assignments for similar halogenated ethylenes, most of the fundamentals were readily located as the most intense bands in the infrared. These assignments are summarized in Tables I and II.

For the normal *trans* isomer, absorption due to the skeletal out-of-plane mode ν_{11} does not appear with significant intensity, although a hint of a weak type C band is visible on the low frequency side of the band at $\sim$530 cm.$^{-1}$. For the deuterated *trans* species, only one C–Cl stretching mode could be located with certainty. In the spectra of both the normal and deute-

TABLE I

cis-1,2-Dichloro-1-fluoroethylene: Fundamentals Observed in Infrared and Raman; Zero-Order Calculations
(Frequencies in cm.$^{-1}$)

	Approximate description	FClC=CClH				FClC=CClD			
		Infrared[b]	Raman[a,d]		Calcd.	Infrared[c]	Raman[a,e]		Calcd.
ν_1	$\nu_{CH(D)}$	3106	3094	s, p	3088	2320	2309	s, p	2274
ν_2	ν_{CC}	1650	1648	vs, p	1666	1642	1638	vs, p	1650
ν_3	$\rho_{CH(D)}$	1239	1234	m, p	1271	1009	1003	w, ?	1047
ν_4	ν_{CF}	1149	1143	vw, ?	1170	1167	1154	wm, p	1170
A′ ν_5	$a\nu_{CCl} + \nu_{CF}$	907	901	w	869	794	792	m, p	760
ν_6	$s\nu_{CCl} + \nu_{CF}$	669	662	s, p	667	652	645	s, p	652
ν_7	$a\delta_{CCl}$	$\sim$480	472	m, p	477	$\sim$470	470	m, p	474
ν_8	$a\delta_{ClCF} + \nu_{CCl}$	390	389	wm, ?	382	389	386	m, p	381
ν_9	$s\delta_{CCl}$	167	171	vs, p	192	165	170	vs, p	192
ν_{10}	$\omega_{CH(D)}$	771	772	w		633	628	s	
A″ ν_{11}		486	484	m		451	452	wm	
ν_{12}		245	251	wm		233	238	m	

[a] Relative intensities and polarization given for each Raman line. [b] Also obsd. in infrared: $\sim$122 w and $\sim$83 w. [c] Also obsd. in infrared: $\sim$119 w and $\sim$83 w. [d] Also obsd. in Raman: 1258 w. [e] Also obsd. in Raman: 1582 w, 1250 vw, and 902 w.

Several uncertainties entered into the preliminary infrared assignments. One is due to the apparent overlapping of several A′ and A″ bands of the *cis* isomers. In Fig. 1 and 2, this effect is seen at $\sim$480 cm.$^{-1}$ in the spectrum of the undeuterated species and at $\sim$640 and $\sim$450 cm.$^{-1}$ in the spectrum of the deuterated species. Comparison of the two *cis* spectra gives, however, considerable support to this interpretation, since the frequencies of the two carbon–halogen-rich planar modes involved, which should be relatively insensitive to deuteration, remain essentially unchanged while the two type C bands shift significantly.

rated *trans* isomers the interpretation of the bands at $\sim$325 cm.$^{-1}$ is unclear. The distorted shapes of these bands and the comparison with the *cis* isomers suggests overlap between the frequencies of the planar rocking motion and one of the out-of-plane skeletal motions, although a frequency of 325 cm.$^{-1}$ seems unduly high for this out-of-plane mode. It is also quite possible that the missing fundamental is part of the $\sim$190 cm.$^{-1}$ band, for which only a rough contour was observed.

Also summarized in Tables I and II are the results of zero-order normal coordinate calculations for the planar modes. These calculations, which are described in more detail below, were made using Urey–Bradley force constants transferred from ethylene, tetrachloroethylene, and tetrafluoroethylene. The

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TABLE II

trans-1,2-DICHLORO-1-FLUOROETHYLENE: FUNDAMENTALS OBSERVED IN INFRARED AND RAMAN; ZERO-ORDER CALCULATIONS

(Frequencies in cm.$^{-1}$)

		Approximate description	FClC=CClH				FClC=CClD			
			Infrared[c]	Raman[a,d]		Calcd.	Infrared[c]	Raman[a,e]		Calcd.
	ν_1	$\nu_{CH(D)}$	3115	3113	s, p?	3091	2342	2328	m, p	2277
	ν_2	ν_{CC}	1650	1645[b]	s, p	1661	1650	1647	vs, p	1645
	ν_3	$\rho_{CH(D)}$	1274	1265	w, p	1334	916	912	s, p	961
	ν_4	$\nu_{CF} + \rho_{CH(D)}$	1097	1088	m, p	1114	1189	~1170	vw	1201
A'	ν_5	a$\nu_{CCl} + \nu_{CF}$	853	842	w, p	835	801	798	vs, p	804
	ν_6	sν_{CCl}	815	811	s, p	802	. . .	786	s, p	756
	ν_7	s$\nu_{CCl} + \rho_{CF}$	447	444	s, p	436	445	444	s, p	435
	ν_8	a$\delta_{CCl} + \nu_{CCl}$	~326	322	vs, p	336	~324	322	s, p	335
	ν_9	sδ_{CCl}	192	193	vw	209	190	192	m, p	208
	ν_{10}	$\omega_{CH(D)}$	766	768	w		611	609	s	
A''	ν_{11}		. . .	530	m		514	512	m	
	ν_{12}		. . .	. . .			. . .	. . .		

[a] Relative intensity and polarization given for each Raman line.   [b] Also obsd. in Raman: 1657 w, p (842 + 811 = 1653) and 1688, m, p (2 × 842 = 1684).   Fermi resonance may be involved here.   [c] Also obsd. in infrared: ~90 w.   [d] Also obsd. in Raman: 1620 w, 1535 w, and 1303 w.   [e] Also obsd. in Raman: 1824 w, 1218 vw, and 1020 w.

satisfactory agreement between these calculations and the qualitative infrared assignments provides strong support for these assignments and is the basis for coordinate descriptions given for each planar mode. The most striking difference between the fundamental frequencies of the two isomers occurs in the splitting between the two C–Cl stretching frequencies. In both the spectra and calculations for the *cis* isomers this splitting is 240–150 cm.$^{-1}$, whereas it is only 40–12 cm.$^{-1}$ for the *trans* isomers. As a consequence, the *cis* and *trans* configurations have been assigned with considerable confidence to the low boiling and high boiling compounds, respectively.

Raman spectra were also obtained for these ethylenes. For molecules with C_s symmetry, transitions involving the twelve fundamentals are allowed in the Raman effect with the nine symmetric A' species polarized and the three A'' species depolarized. In general, the Raman results confirm the interpretation of the infrared spectra, with most of the bands missing from the infrared due to low intensity being found in the Raman spectra. Unfortunately, the Raman spectra also fail to yield a firm assignment for the low frequency out-of-plane mode of the *trans* isomer.

For the *trans*-FClC=CClD, the splitting of only 12 cm.$^{-1}$ between the two carbon–chlorine stretching frequencies, which are of the same symmetry, A', is at first unexpected. The Raman spectrum and the zero-order calculations give, however, strong support to this assignment. In addition, no other band of reasonable intensity is to be found in this region in the infrared spectrum, whereas some suggestive structure is seen at low pressures at about 790 cm.$^{-1}$. Further support comes from an analysis of the splitting between carbon–halogen stretching frequencies in *trans* isomers given below.

For each spectrum reasonable assignments for bands not attributed to fundamentals were readily found among the binary combinations and first overtones. Only the low frequency infrared bands apparently present at ~120 and ~85 cm.$^{-1}$, which would have to be due to difference bands, could not be satisfactorily assigned. These latter observations deserve careful experimental re-examination.

The proton nuclear magnetic resonance spectra provide further support for the assignments of configurations based on the infrared and Raman results; the species which has been assigned as the *cis* isomer has the smaller HF coupling constant. This difference in magnitude of *cis* and *trans* coupling constants is consistent with that observed for other HF coupling constants in similar *cis* and *trans* isomers.[6,7]

Normal Coordinate Analysis

For the planar modes, a normal coordinate analysis was carried out by the Wilson GF method,[15] primarily as a further check on the vibrational assignment. A Urey–Bradley force field was chosen as Urey–Bradley force constants have previously been determined for other halogenated ethylenes and have been

shown to be reasonably transferable.[16] G and Z^{17} matrices were evaluated by a computer program; the molecular parameters, assumed to be the same for both *cis* and *trans* species, were taken as: $r_{CC} = 1.31$ Å., $r_{CCl} = 1.72$ Å., $r_{CF} = 1.31$ Å., $r_{CH} = 1.07$ Å., $\alpha_{CCCl} = 123°$, $\alpha_{CCF} = 123°$, $\alpha_{CCH} = 123°$.

Internal coordinates were defined as the stretchings of the five bonds and the bendings of the six valence angles and the designation of the force constants in Table III is consistent with this notation. The potential energy is written as

$$2V = \sum_i [2K'\Delta r_i + K(\Delta r_i)^2] + \sum_i [2H'\Delta\alpha_i + H(\Delta\alpha_i)^2] + \sum_i [2F'q\Delta q_i + F(\Delta q_i)^2] + \sum_i [2C'c\Delta c_i + C(\Delta c_i)^2] \quad (1)$$

The Δr_i represent valence-bond stretching coordinates, the $\Delta\alpha_i$ valence-bond angle deformations, the Δq_i the change in separation of *gem* nonbonded atoms, and the Δc_i the change in separation of the *cis* atoms. The redundant coordinates are taken care of in the usual way, leaving the linear terms F' and C' in the potential energy. There is no intramolecular tension associated with the angle redundancies at the carbon atoms.[18] The linear terms present a minor problem; if they are left in the potential there are insufficient data to determine them. They can be expressed in terms of the corresponding quadratic terms if the nonbonded potential is assumed to have a simple experimental repulsive form. Although the latter approach is questionable,[1] we have in this work followed convention, assuming V(nonbonded) $= kr^{-9}$, and have set $F' = -0.1F$ and $C' = -0.1C$. There is some justification for this procedure as the force constants we wish to transfer from related molecules were determined from a similar potential function and also the linear force constants do not make a large contribution[19] to the intramolecular potential, particularly the C' terms.

(15) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw–Hill Book Co., Inc., New York, N. Y., 1955.

(16) J. R. Scherer and J. Overend, *J. Chem. Phys.*, **33**, 1681 (1960).

(17) J. Overend and J. R. Scherer, *ibid.*, **32**, 1289 (1960).

(18) B. Crawford and J. Overend, *J. Mol. Spectry.*, **12**, 307 (1964).

(19) Of course, if the linear force constants were large, they could make a significant contribution; however, for any potential function between r^{-12} and r^{-6} they could be considered small.

Table III

Urey-Bradley Force Constants for Planar Modes of cis- and trans-FClC=CClH(D) [K, F, and C in mdynes/Å.; H in mdynes Å./(radian)^2]

	(i) Zero order	(ii) Overlay	σ	(iii) cis refine	σ	(iv) trans refine	σ
K_{CC}	7.48	7.719	0.088	7.422	0.048	7.742	0.135
K_{CH}	4.83	4.921	.024	5.113	.024	4.863	.060
K_{CF}	5.20	4.294	.248	4.742	.061	4.822	.256
K_{CCl}	2.66	3.208	.119	3.012	.047	2.965	.193
H_{CH}	0.335	0.138	0.032	0.142		0.233	0.074
H_{CF}	.172	.172		.172		.172	
H_{HCl}	.383	.283	0.062	.626	0.019	.142	0.123
H_{ClF}	.549	.755	.107	.647		.647	
H_{CCl}	.207	.652	.142	.196	0.030	.192	0.130
F_{CH}	0.450	0.450		0.084	0.037	0.450	
F_{CF}	1.370	1.110	0.094	1.370		1.370	
F_{HCl}	0.300	0.300		0.300		0.534	0.107
F_{ClF}	.635	.635		.635		.635	
F_{CCl}	.920	.360	0.115	.920		.716	0.175
C_{ClCl}	0.16	0.047	0.038	0.097	0.016		
C_{FH}	− .045	.119	.055	−0.045			
C_{ClH}	.030	.136	.052			0.030	
C_{FCl}	.080	− .037	.040			0.080	

As a check on the vibrational assignment, we first calculated the in-plane frequencies from a set of force constants transferred from ethylene[20] and the perhaloethylenes.[21] In those cases where there is a direct structural correspondence, the values were transferred directly, e.g., K_{CCl} was taken to be the same as in C_2Cl_4. Where the value of a force constant might be expected to fall between two known ones, the arithmetic mean was used.

The in-plane vibrational frequencies from this first calculation are shown in Tables I and II, together with the observed fundamentals previously assigned. The several uncertain assignments of the in-plane fundamentals discussed in the preceding section are substantiated by the zero-order force-constant calculation and it seems reasonable to consider the vibrational assignments firmly established for the in-plane vibrations.

Next we attempted a least-squares adjustment of the in-plane force constants to the assigned fundamental frequencies, first treating each isomer separately, and then both together in an overlay calculation.[22] It was immediately apparent that, even with complete assignments for both normal and deuterated species, there were insufficient data to permit simultaneous adjustment of all the parameters in the potential function, and that it would be necessary to constrain some at their transferred values. We explored a number of alternative, physically reasonable, constraints but with little success. In the overlay calculation, we were unable to determine a set of force constants which gave a satisfactory frequency fit for both cis and trans isomers. Although, when we treated each isomer separately, we were able to fit the vibrational frequencies, the force constants were unsatisfactory; there was little correspondence between similar force constants in the two isomers and some had quite unreasonable values.

This failure led us to use a statistical criterion to select the set of force constants to be adjusted. In this method,[23,24] a force constant is chosen for adjustment

if the reduction of the variance V when that force constant is adjusted meets the tests

$$\Delta V d / V > F_1$$

where d is the number of degrees of freedom and F_1 is a number usually taken between 1 and 4. If, for any force constant

$$\Delta V d / V < F_2$$

that force constant is constrained. In the present work the force constants were divided into two sets. Those in the first set were invariably adjusted; those in the second were adjusted if they satisfied the F test. Thus the choice of which force constants were held at values transferred from related molecules was made by entirely statistical reasoning and there was no chemical argument.

Both cis and trans isomers were treated this way in overlay. All the stretching force constants K_{CX} and all the bending force constants H_{XY}, with the exception of H_{CF}, were chosen for the first set and forced into adjustment. The remaining force constants were subjected to the F test, with F_1 taken as 1.25 and F_2 as 1.20, and C_{FH}, F_{CCl}, F_{CF}, C_{ClH}, C_{FCl}, and C_{ClCl} were found to have decreasing, but significant, effects on the variance. These force constants were then adjusted by least squares to give the values shown in Table III. The corresponding calculated frequencies are shown in Table IV.

Table IV

Calculated Frequencies for Planar Modes of cis- and trans-FClC=CClH(D) in Cm.$^{-1}$

	Normal					Deuterated			
	Overlay		Separate			Overlay		Separate	
	cis	trans	cis	trans		cis	trans	cis	trans
1	3130	3128	3117	3139	1	2303	2305	2305	2308
2	1656	1653	1661	1660	2	1646	1641	1632	1649
3	1240	1273	1234	1273	3	1169	1187	1167	1189
4	1142	1109	1152	1100	4	1009	923	1012	919
5	917	844	901	853	5	787	800	800	800
6	669	813	671	815	6	655	774	649	785
7	477	445	474	441	7	474	444	468	440
8	389	328	392	321	8	389	328	391	320
9	171	191	171	199	9	171	190	171	198

The differences between observed and calculated frequencies are generally less than 10 cm.$^{-1}$ except for the vibration at 907 cm.$^{-1}$ in cis (H), that at 1097 cm.$^{-1}$ in trans (H), that at 786 cm.$^{-1}$ in trans (D), and the CH and CD stretching frequencies. The errors in the latter are quite normal and are attributable to anharmonicity. The adjusted force constants have apparently reasonable magnitudes although they do, in some cases, differ considerably from the zero-order ones, especially H_{CCl} and F_{CCl}. As these two force constants are stochastically correlated, we expected to be able to obtain better values for both force constants by constraining H_{CCl} at 0.207 mdyne Å./(radian)^2 without significantly increasing the variance; our attempt to do this was unsuccessful.

In an effort to discover differences between the cis and trans configurations, we next refined separately

(20) J. R. Scherer and J. Overend, J. Chem. Phys., 33, 1681 (1960).

(21) D. E. Mann, L. Fano, J. H. Meal, and T. Shimanouchi, ibid., 27, 51 (1957).

(22) J. Overend and B. Crawford, Jr., paper presented at Symposium on Molecular Spectroscopy, Columbus, Ohio, 1961.

(23) M. A. Efroymson, "Mathematical Methods for Digital Computers," A. Ralston and H. S. Wilf, Ed., John Wiley and Sons, Inc., New York, N. Y., 1960.

(24) J. H. Schachtschneider and R. G. Snyder, Spectrochim. Acta, 19, 117 (1963).

the force constants of the *cis* isomer to its observed frequencies. In this way, we arrived at the set of force constants in column iii of Table III. The *cis* frequencies corresponding to these values of the force constants agree with the observed frequencies within 2–3 cm.$^{-1}$, but the *trans* frequencies calculated from the same force constants are off by as much as 25 cm.$^{-1}$. This procedure was repeated, *mutatis mutandis*, for the *trans* isomer with similar results.

If there are differences in the electronic energy of the *cis* and *trans* configurations, we might reasonably expect such differences to be reflected in the force constants, and it is tempting to interpret in this way the results of the separate calculations for the *cis* and *trans* configurations. However, in working with the observed vibrational frequencies and a harmonic-oscillator model, we neglect all corrections due to anharmonicity. It is not presently possible to determine the precise magnitude of these corrections, but they are probably of the order of 10 cm.$^{-1}$ which corresponds to the differences between observed and calculated frequencies when the same force constants are assumed for both isomers. We interpret this result to mean that there is no real evidence for any difference in the in-plane force constants and that the differences found, when the force constants corresponding to the two configurations were adjusted separately, are not reliable and possibly spurious.

In an effort to confirm the out-of-plane assignments for the *cis* configuration and to supply the missing frequencies for the *trans*, we attempted a normal coordinate calculation for the out-of-plane modes using four different force fields of the type described by Manneback and Rahman[25] and taking the same values for the force constants of both isomers. These calculations were unsatisfactory as the calculated frequencies did not correspond to the assigned values in Tables I and II. It appears either that the potential function used is not appropriate or that the assumption that the same force constants obtain for both *cis* and *trans* configurations is invalid.

Splitting of Symmetric and Asymmetric Stretching Frequencies.—We have used the observed separations of the symmetric and asymmetric C–Cl stretching frequencies as a criterion in assigning the configurations of the two isomers. The *cis* and *trans* configurations of the symmetrical molecules HXC=CXH are readily distinguished spectroscopically as the vibrational selection rules are much more exclusive for the centrosymmetric *trans* species. Even in the case of molecules of the type HXC=CYH, there can be no real doubt as to which isomer is which, for the out-of-plane hydrogen deformations are good group frequencies in the infrared and are well characterized.[5] But in HClC=CClF the hydrogen deformation frequency does not differentiate between *cis* and *trans* and we have turned to another criterion to assign the configurations of the two isomers; namely, that the separation of symmetric and asymmetric C–Cl stretching frequencies is considerably greater in the *cis* isomer than in the *trans*. As is shown in Table V, the effect seems to be general. In view of its importance we have investigated its dynamic origin.

(25) C. Manneback and A. Rahman, *Ann. soc. sci. Bruxelles*, **I67**, 28 (1953).

TABLE V

SPLITTING BETWEEN ASYMMETRIC AND SYMMETRIC STRETCHING FREQUENCIES FOR HALOGENATED ETHYLENES (Frequencies in cm.$^{-1}$)

	cis isomer		*trans* isomer		
	CX stretch freq.[a]	Splitting	CX stretch freq.[a]	Splitting	Reference
HFC=CFH	1127	113	1159	37	b
	1014		1122		
HFC=CFD	1167	134	1166	. .	b
	1033		. . .		
DFC=CFD	1225	171	1175	66	b
	1054		1109		
HClC=CClH	848	137	817	−27	c
	711		844		
HClC=CClD	781	78	775	−48	d
	703		823		
DClC=CClD	761	72	784	19	c
	689		765		
HBrC=CBrH	746	166	680	−66	e
	580		746		
HBrC=CBrD	707	131	668	−49	f
	576		717		
DBrC=CBrD	671	105	648	−22	e
	566		670		
HIC=CIH	672	178	589	−74	g
	494		663		

[a] Frequency for asymmetric mode listed first. [b] N. C. Craig and E. A. Entemann, *J. Chem. Phys.*, **36**, 243 (1962), and unpublished Raman spectra. [c] See ref. 2b and H. J. Bernstein and R. A. Ramsay, *J. Chem. Phys.*, **17**, 556 (1949). [d] H. J. Bernstein and A. D. E. Pullin, *Can. J. Chem.*, **30**, 963 (1952). [e] J. M. Dowling, P. G. Puranik, and A. G. Meister, *J. Chem. Phys.*, **26**, 233 (1957). [f] M. deCroes, M. Perlinghi, and R. Van Riet, *Bull. classe sci., acad. roy. Belg.*, **42**, 379 (1956). [g] S. I. Miller, A. Weber, and F. F. Cleveland, *J. Chem. Phys.*, **23**, 44 (1955).

Since the detailed vibrational analysis of the substituted ethylenes is rather complicated, we have taken as a simplified model, the tetraatomic system X—C=C—X in both *cis* and *trans* configurations. Previously, Trenkler[26] found a similar effect for the *cis* and *trans* configurations of the X–Y–Y–X system in a comparison of the frequencies of mechanical models with those calculated with the valence-force treatment of Lechner.[27] He concluded, from calculations with several values for the mass of X, that the two stretching frequencies of the *cis* configuration are split further apart than those of the *trans*. Although Trenkler observed this splitting with ball-and-spring models and in calculations, insufficient spectroscopic data were then available for comparison and he made no effort to determine the dynamic origin of the effect.

Internal coordinates, shown in Fig. 5, were taken in the linear combinations and the symmetrized G

$$S_1 = R_1$$
$$S_2 = 1/\sqrt{2}\,(R_2 + R_3)$$
$$S_3 = 1/\sqrt{2}\,(R_4 + R_5)$$
$$S_4 = 1/\sqrt{2}\,(R_2 - R_3)$$
$$S_5 = 1/\sqrt{2}\,(R_4 - R_5) \qquad (2)$$

matrices were written in terms of these coordinates. The G matrix elements for both *cis* and *trans* configurations, expressed in terms of the elements G_{ij} of the unsymmetrized $\mathbf{G}$ matrix for the *cis* configuration, are

(26) V. F. Trenkler, *Physik. Z.*, **36**, 423 (1935).

(27) F. Lechner, *Sitzber. Akad. Wiss. Wein*, [IIa] **141**, 633 (1932).

cis-C_2X_2 trans-C_2X_2

$$\mathcal{G}_{11} = G_{11} \qquad\qquad \mathcal{G}_{11} = G_{11}$$

$$\mathcal{G}_{22} = G_{22} \qquad\qquad \mathcal{G}_{22} = G_{22}$$

$$\mathcal{G}_{33} = G_{44} + G_{45} \qquad \mathcal{G}_{33} = G_{44} - G_{45}$$

$$\mathcal{G}_{12} = \sqrt{2}G_{12} \qquad\qquad \mathcal{G}_{12} = \sqrt{2}G_{12}$$

$$\mathcal{G}_{13} = \sqrt{2}G_{14} \qquad\qquad \mathcal{G}_{13} = \sqrt{2}G_{14}$$

$$\mathcal{G}_{23} = G_{24} + G_{25} = 0 \qquad \mathcal{G}_{23} = G_{24} - G_{25}$$

$$\mathcal{G}_{44} = G_{22} \qquad\qquad \mathcal{G}_{44} = G_{22}$$

$$\mathcal{G}_{55} = G_{44} - G_{45} \qquad \mathcal{G}_{55} = G_{44} + G_{45}$$

$$\mathcal{G}_{45} = G_{24} - G_{25} \qquad \mathcal{G}_{45} = G_{24} + G_{25} = 0 \quad (3)$$

where

$$G_{11} = 2\mu_c$$

$$G_{22} = \mu_x + \mu_c$$

$$G_{44} = \rho_1{}^2\mu_x + \rho_3{}^2\mu_c + (\rho_1{}^2 + \rho_3{}^2 - 2\rho_1\rho_2 \cos \alpha)\mu_c$$

$$G_{45} = -2\rho_3(\rho_3 - \rho_1 \cos \alpha)\mu_c$$

$$G_{12} = \mu_c \cos \alpha$$

$$G_{14} = -\rho_1\mu_c \sin \alpha$$

$$G_{24} = -\rho_3\mu_c \sin \alpha$$

$$G_{25} = \rho_3\mu_c \sin \alpha \qquad\qquad (4)$$

and $\mu_x = 1/m_x$, $\mu_c = 1/m_c$, and ρ_i is the reciprocal of the ith equilibrium bond length.

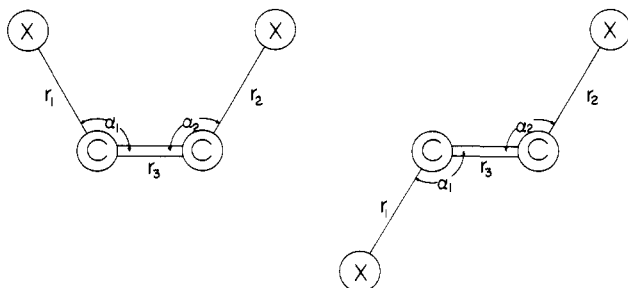In the particular case where the C atoms are joined by a double bond with a high force constant, it is a

Fig. 5.—Definitions of internal coordinates: $R_1 = \Delta r_3$, $R_2 = \Delta r_1$, $R_3 = \Delta r_2$, $R_4 = \Delta \alpha_1$, $R_5 = \Delta \alpha_2$.

fair approximation to split out the high C=C stretching frequency from the symmetry blocks for the totally symmetric species in the secular equation.[28]

In doing this, we drop the C=C force constant, but must modify the original 3×3 $\mathcal{G}$ matrix, to obtain a new 2×2 matrix for the CX stretching and bending coordinates. The original elements $\mathcal{G}_{22}$, $\mathcal{G}_{33}$, and $\mathcal{G}_{23}$ are now reduced by terms depending on $\mathcal{G}_{11}$, $\mathcal{G}_{12}$, and $\mathcal{G}_{13}$ originally associated with the C=C group, leading to a lowering of the symmetric CX stretching and CX deformation frequencies. This modified $\mathcal{G}$ matrix is given by

$$\begin{bmatrix} (\mathcal{G}_{22} - \mathcal{G}_{12}{}^2/\mathcal{G}_{11}) & (\mathcal{G}_{23} - \mathcal{G}_{12}\mathcal{G}_{13}/\mathcal{G}_{11}) \\ (\mathcal{G}_{23} - \mathcal{G}_{12}\mathcal{G}_{13}/\mathcal{G}_{11}) & (\mathcal{G}_{33} - \mathcal{G}_{13}{}^2/\mathcal{G}_{11}) \end{bmatrix}$$

If we then further assume a simple valence force field with K as the CX stretching force constant and H as the CCX bending force constant and with no cross

(28) B. L. Crawford, Jr., and J. T. Edsall, J. Chem. Phys., 7, 223 (1939); M. A. Pariseau, E. Wu, and J. Overend, ibid., 39, 217 (1963).

terms, we find the following approximate expressions for the stretching-frequency parameters, $\lambda = 4\pi^2 \cdot N^{-1}c^2\nu^2$ where ν is the CX stretching frequency in cm.$^{-1}$

$$\text{sym.} \quad \lambda \cong (\mathcal{G}_{22} - \mathcal{G}_{12}{}^2/\mathcal{G}_{11})K + (\mathcal{G}_{23} - \mathcal{G}_{12}\mathcal{G}_{13}/$$

$$\mathcal{G}_{11})^2 KH[(\mathcal{G}_{22} - \mathcal{G}_{12}{}^2/\mathcal{G}_{11})K - (\mathcal{G}_{33} - \mathcal{G}_{13}{}^2/$$

$$\mathcal{G}_{11})H]^{-1} \quad (5)$$

$$\text{asym.} \quad \lambda \cong \mathcal{G}_{44}K + \mathcal{G}_{45}{}^2 KH[\mathcal{G}_{44}K - \mathcal{G}_{55}H]^{-1} \quad (6)$$

It is instructive to evaluate (5) and (6) for some appropriate molecular skeletons (viz., X = F, Cl, and Br) using the values for bond lengths and force constants given in Table VI and taking $\alpha = 120°$. The calculated symmetric and asymmetric CX stretching frequencies and the predicted splittings are given in Table VII. These show trends similar to the observed splittings for some haloethylenes (Table V) although there are differences in detail. Of particular interest is the crossover of symmetric and asymmetric stretching frequencies in the trans molecule as the mass of X increases and the CX force constant decreases. This crossover was found by Trenkler[26] in his calculations, although at that time experimental molecular-vibration frequencies were not available to confirm it.

TABLE VI

ADDITIONAL PARAMETERS USED IN CALCULATIONS FOR THE XC=CX MODEL

Atom X	μ_X, a.m.u.$^{-1}$	r_{CX}, Å.	K, mdynes/Å.	$H, \times 10^{11}$ mdyne Å./ (radian)^2
F	0.0526	1.30	5.20	0.18
Cl	.0286	1.72	2.66	.21
Br	.0127	1.89	2.11	.18

In our model calculations using a simple valence potential, we have found the different splittings for the cis and trans configuration when we used the same force constants for both molecules. This indicates that the origin of the splitting is steric rather than chemical, and we should seek the critical terms in the G matrix rather than the F.

In the secular equations for the asymmetric vibrations, there is a sizable stretch–bend cross term, $\mathcal{G}_{45}{}^2 \cdot KH$, in the cis molecule, whereas that in trans is zero. This causes the cis asymmetric stretching frequency to be higher than the trans, which has the same value as a diatomic CX molecule with the same force constant.

In the modified secular equations for the symmetric vibrations, there are now two factors to consider. The first is the effect of the $\mathcal{G}_{23}{}^2$ term; in the cis molecule this is zero; in the trans, it is equal to $\mathcal{G}_{45}{}^2 KH$ (the term responsible for raising the asymmetric frequency of the cis configuration). The second factor, which results from splitting out the C=C stretching frequency, reduces the diagonal terms of both cis and trans and causes both symmetric frequencies to be depressed by an amount d. The cross terms are also modified slightly. The effect on that of the cis configuration is apparently negligible for all cases considered, and for practical purposes it may still be taken as zero; the cross term in the symmetric trans species is increased somewhat and the frequency is raised by c' which is greater than c (cf. Table VII). The splitting in the cis configuration is then given by $\Delta\lambda = (d + c)$ and that in the trans configuration by $\Delta\lambda = (d - c')$.

TABLE VII

CALCULATED SPLITTINGS FOR STRETCHING FREQUENCIES OF *cis* AND *trans* CONFIGURATIONS OF XC=CX

	cis-XCCX				*trans*-XCCX		
	F	Cl	Br		F	Cl	Br
$g_{22}K = g_{44}K$	0.7067	0.2976	0.2026	$g_{22}K = g_{44}K$	0.7067	0.2976	0.2026
c^a	.0172	.0280	.0294	c'^b	.0322	.0508	.0554
$d = g_{12}^2 K/g_{11}$	.1077	.0550	.0437	$d = g_{12}^2 K/g_{11}$	.1077	.0550	.0437
$\lambda(\text{asym.}) = g_{44}K + c$	.7239	.3256	.2320	$\lambda(\text{asym.}) = g_{44}K$	.7067	.2976	.2026
$\lambda(\text{sym.}) = g_{22}K - d$	.5990	.2426	.1589	$\lambda(\text{sym.}) = g_{22}K + c' - d$	.6312	.2934	.2143
$\nu(\text{asym.})$, cm.$^{-1}$	1109	743	628	$\nu(\text{asym.})$, cm.$^{-1}$	1095	711	587
$\nu(\text{sym.})$, cm.$^{-1}$	1008	642	519	$\nu(\text{sym.})$, cm.$^{-1}$	1035	706	603
$\Delta\nu$, cm.$^{-1}$	101	101	109	$\Delta\nu$, cm.$^{-1}$	60	5	-16

^{a} $c = g_{45}^2 KH[g_{44}K - g_{55}H]^{-1}$. ^{b} $c' = (g_{23} - g_{12}g_{13}/g_{11})^2 KH[(g_{22} - g_{12}^2/g_{11})K - (g_{33} - g_{13}^2/g_{11})H]^{-1}$.

Our results indicate that $d + c > d - c'$ for a wide range of masses and force constants.[29]

Thus it seems that we should find quite generally that the splitting between symmetric and asymmetric stretching frequencies is greater in the *cis* configuration than the *trans* in any molecular grouping which corresponds to our simple model. Figures 6 and 7 summarize the argument. It seems reasonable to expect this result to carry over to the substituted ethylenes and ethanes although there may be complications arising from the neglect of the vibrational frequencies associated with the other substituents. Qualitatively, we expect the model to be more appropriate where the symmetric and asymmetric CX stretching frequencies are reasonably good group frequencies.
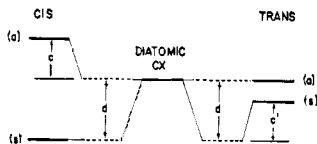

Fig. 6.—Sketch showing splitting of symmetric and asymmetric stretching frequencies in *cis*- and *trans*-C$_2$X$_2$ (see Tables VII and VIII for definitions of c, c', and d).

In conclusion, it now appears that the vibrational assignments of the *cis* FClC=CClH and FClC=CClD are essentially complete. There remain several gaps in the assignment of the *trans* isomers which we are

(29) In principle, the difference between c and c' could outweigh the sign difference (*i.e.*, $(c - c') > 2d$), but in all the cases investigated there is no suggestion of this possibility occurring. Even if $(c - c') > 2d$, we should find the highest *trans* frequency to be symmetric and the highest *cis* to be asymmetric, and it might still be possible to distinguish between the two configurations.

presently unable to resolve. It is expected that studies, now in progress, on related molecules will contribute to our understanding of this entire series
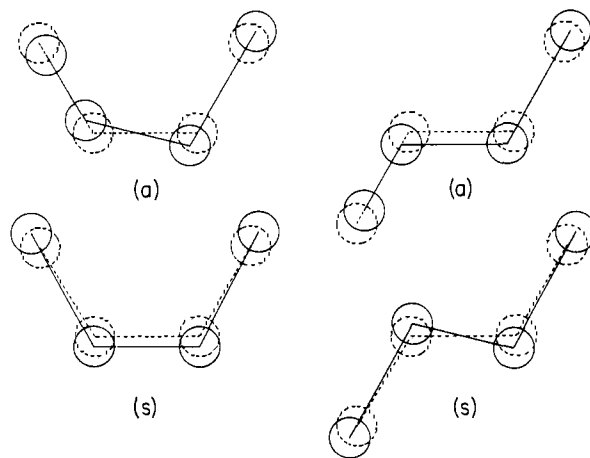

Fig. 7.—Approximate normal coordinates showing significant contributions of angle bending to the asymmetric stretch for the *cis* configuration and to the symmetric stretch for the *trans*.

of chlorofluoroethylenes and presumably allow us to complete the *trans* assignment.