

Normal-mode analysis of infrared and Raman spectra of poly(vinyl fluoride)

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Abstract

Infrared and Raman spectra of samples of poly(vinyl fluoride) (PVF) have been recorded. The vibrational spectra have been analyzed by means of normal-mode calculations. A force field was derived by using 2-fluorobutane as a model compound. Crowder's force field for hydrofluorocarbons was employed as a starting point and subsequently refined in application to secondary fluorides. A planar zigzag, syndiotactic single-chain model of crystalline PVF was submitted to be analyzed by this scheme. A comparison of observed infrared and Raman bands with frequencies calculated for syndiotactic PVF shows that PVF produced by conventional free radical polymerization has an atactic structure, supporting the ^{19}F -NMR results and conclusions reached by Koenig and Boerio. Band assignments in terms of atactic structure are proposed.

Keywords: Infrared spectrometry; Raman spectrometry; 2-Fluorobutane; Normal-mode analysis; Poly(vinyl fluoride)

Several researchers have reported infrared and Raman spectra of poly(vinyl fluoride) (PVF), and tentative band assignments have been made. The infrared spectra of PVF were used by Koenig and Mannion [1] as a basis for analyzing enchainment, conformational and configurational defects in the material. The Raman spectrum subsequently obtained by Koenig and Boerio [2] led to the interpretation of the stereochemical configuration of the polymer. The polarized infrared spectrum of PVF has also been interpreted by Zerbi and Cortelli [3]. However, there are still many aspects of the vibrational spectrum that are not completely understood. The stereoregularity of PVF, in particular, has been the subject of controversy. Both the x-ray work of Natta et al. [4] and Koenig's Raman spectra [2] subsequently ob-

tained have led to the conclusion that the polymer is atactic. In addition, the tacticity of PVF has been recently studied by ^{19}F solution NMR, and has been shown to be atactic [5–7]. Zerbi and Cortelli [3], on the other hand, have suggested a syndiotactic structure for PVF.

In the general case, the straightforward nature of interpreting NMR data would favor the atactic structural assignment. However, in the case of PVF, like PVC, the differential solubility of alternative chain configurations may play an important role. It is suspected that highly syndiotactic PVF, like highly syndiotactic crystalline PVC [8], is marginally soluble even in good solvents. This would imply that NMR analysis of syndiotactic PVF chain segments, localized in insoluble crystallites, would suffer a negative bias due to spin-

lattice saturation effects [9]. Although the solubility of PVF would be expected to be less affected by tacticity than that of PVC, it is desirable to resolve analytical uncertainties related to this potential solubility factor by a solid state technique capable of studying both the ordered and amorphous regions of the sample.

Distinctions between different local configurations of a regular polymer chain can be made on the basis of normal-mode analysis of the vibrational spectrum, since the infrared and Raman bands, particularly in the 1500–700 cm^{-1} region, are sensitive to those structures. However, to date, the reliability of normal-mode calculations for PVF has been limited by the lack of an available force field appropriate to the secondary fluorides. We are presently in a position to carry out normal-mode calculations for PVF by having available vibrational spectra of 2-fluoropropane and 2-fluorobutane as well as their vibrational assignments. In this paper, we therefore present further experimental studies and the results of normal-mode calculations on PVF. We have recorded the infrared and Raman spectra of PVF. The polarized infrared spectra of oriented, and the Raman spectra of non-oriented PVF samples, have been obtained. In the normal-mode calculations, valence force constants have been transferred from the low-molecular-weight model compound, 2-fluorobutane.

EXPERIMENTAL

Laboratory-generated samples of PVF obtained from DuPont were used. Infrared spectra were recorded on a Digilab Model FTS-60 FT-IR spectrometer. Oriented samples were obtained by stretching the film four times its original length. Polarized infrared spectra were obtained with the electric vector parallel and perpendicular to the stretching direction. Raman spectra were obtained with a Spec 1403 double monochromator equipped with holographic gratings. Spectra were excited by the 514.5-nm line of a Coherent Radiation 52 Argon Ion Laser and 90° scattering geometry was used.

NORMAL-MODE CALCULATIONS OF MODEL COMPOUNDS

Derivation of the force field for secondary fluorides

Although secondary hydrocarbon chlorides, bromides, and iodides have been extensively investigated spectroscopically [10–16], only a few studies have reported on secondary fluorides [17–19]. The infrared spectrum of 2-fluoropropane has been recorded by Griffiths et al. [19] in the vapor state and in CS_2 solution, and a very approximate qualitative description of the vibrational modes has been made. The vibrational spectra were also obtained for 2-fluoropropane and 2-fluorobutane by Crowder et al. [17,18], and vibrational assignments of these two materials were made with the aid of normal coordinate calculations. However, force constants were not given, and the potential energy distribution was reported only for 2-fluoropropane. We approached the task of obtaining an accurate force field for secondary fluoride by the method described here. A set of force constants for primary fluorides was available [20,21], which required only a few additional constants to make it suitable for secondary fluorides. A reliable valence force field has also been published for saturated hydrocarbons [22,23]. The force field constants in this potential function were transferred, where applicable, to 2-fluorobutane. These combined sets of force constants were used to fit the frequencies in the 200–1200 cm^{-1} region reported by Crowder [17], for the three conformations of 2-fluorobutane. The final set of force constants is given in Table 1.

RESULTS AND DISCUSSION

Figure 1 presents the 2-fluorobutane molecule with its internal coordinates and Fig. 2 shows the possible conformations and their nomenclature. The full roster of coordinates used in the normal-mode calculations are listed in Table 2. In Table 3 are given the calculated frequencies and potential energy distributions for the three conformations of this molecule. A detailed compari-

TABLE 1

Force constants for secondary fluorides

No.	Constant ^a	Environment	Calculated value ^b
1	MH	ME	4.7522
2	CH	HX	4.902
3	CH	HH	4.487
4	MC	MEHH	4.4858
5	MC	MEHX	4.413
6	CC	HXHH	4.413
7	CX	HX	5.100
8	HCH	HH	0.5084
9	HMH	ME	0.5397
10	CMH	HXME	0.600
11	CMH	HHME	0.6172
12	MCH	MEHX	0.680
13	MCH	MEHH	0.7041
14	CCH	HXHH	0.610
15	MCX	MEHX	1.262
16	CCX	HHHX	1.162
17	HCX	HX	1.000
18	MCC	MEHXHH	1.100
19	M·C	MEHX	0.05
20	M·C	MEHH	0.0784
21	C·C	HXHH	0.05
22	MH,MH	ME	0.001
23	CH,CH	HH	0.0167
24	MC,CC	MEHXHH	0.1480
25	MC,CX	MEHX	0.740
26	CC,CX	HHHX	0.840
27	CM,CMH	MEHX	0.206
28	CM,CMH	MEHH	0.1845
29	MC,MCH	MEHX	0.206
30	MC,MCH	MEHH	0.3065
31	MC,MCX	MEHX	0.567
32	MC,MCC	MEHXHH	0.273
33	CC,CCH	HHHX	0.206
34	CC,CCX	HHHX	0.567
35	CC,CCM	HHHXME	0.274
36	CX,HCX	HX	0.200
37	CX,MCX	MEHX	0.500
38	CX,CCX	HHHX	0.500
39	CX,MCC	MEHXHH	-0.05
40	MC,HCC	MEHHHX	0.106
41	CC,HCM	HHHXME	0.006
42	MC,XCC	MEHXHH	0.567
43	CC,XCM	HHHXME	0.567
44	HMH,HMH	ME	0.0091
45	HMH,CMH	MEHH	0.0039
46	CMH,CMH	MEHH	0.010
47	CMH,CMH	MEHX	-0.0237
48	CCH,CCH	HXHH	0.05
49	MCH,MCH	MEHH	0.074
50	MCH,HCC	MEHXHH	0.10
51	MCH,HCC	MEHHHX	0.050
52	MCH,MCX	MEHX	0.10

TABLE 1 (continued)

No.	Constant ^a	Environment	Calculated value ^b
53	MCX,XCC	MEHXHH	0.1
54	MCC,MCH	MEHXHH	-0.05
55	MCC,CCH	MEHXHH	0.05
56	M·C,C·C	MEHXHH	0.08
57	HMC,MCHT ^c	MEHH	0.1037
58	HMC,MCHG	MEHX	0.05
59	HMC,MCHG	MEHH	-0.046
60	HMC,MCXT	MEHX	0.063
61	HMC,MCXG	MEHX	0.055
62	CCM,CMHT	HHHXME	0.207
63	CCM,CMHG	HHHXME	0.056
64	MCC,CCHG	MEHXHH	0.106
65	HCC,CCXT	HHHX	0.063
66	HCC,CCXG	HHHX	0.055
67	HCC,CCHG	HXHH	-0.05
68	MCC,CCMT	MEHXHHME	-0.036

^a M is the carbon atom of CH₃ group, X is the F atom.
^b Stretch and stretch,stretch force constants are in mdyn/Å, while stretch,bend and bend force constants are in mdyn. ^c T and G: *trans* and *gauche*.

son of observed and calculated frequencies is difficult because of the presence of three isomers in the liquid. However, the availability of published data on both liquid and solid forms of 2-fluorobutane permits certain inferences to be made based on observations of the effect of decreasing temperature on the spectrum of the material. Table 4 lists observed frequencies for solid and liquid 2-fluorobutane with calculated frequencies of the three isomers (S_{hh} , S_{ch} , and $S_{hh'}$) shown in Fig. 2. We have assigned those bands which decrease in intensity in the solid state to the S_{ch} and $S_{hh'}$ conformations. Since the frequencies calculated for the S_{hh} conformation fit the observed solid state frequencies better than those calculated for S_{ch} , the solid state spectrum has been assumed to be accounted for mainly by the S_{hh} conformation.

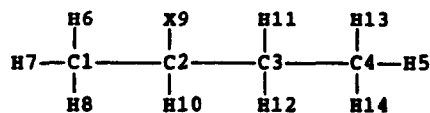


Fig. 1. 2-Fluorobutane with numbering corresponding to that used for internal coordinates (X = fluorine).

TABLE 2

Internal coordinates for 2-fluorobutane

No. Bond ^a			Bond length		
<i>Stretching</i>					
1	(M---C)	(1-2)	1.5400		
2	(M---H)	(1-6)	1.0900		
3	(M---H)	(1-7)	1.0900		
4	(M---H)	(1-8)	1.0900		
5	(C---C)	(2-3)	1.5400		
6	(C---X)	(2-9)	1.3600		
7	(C---H)	(2-10)	1.0900		
8	(C---M)	(3-4)	1.5400		
9	(C---H)	(3-11)	1.0900		
10	(C---H)	(3-12)	1.0900		
11	(M---H)	(4-5)	1.0900		
12	(M---H)	(4-13)	1.0900		
13	(M---H)	(4-14)	1.0900		
<i>Bending</i>					
14	(H-M-C)	(6-1-2)			
15	(H-M-C)	(7-1-2)			
16	(H-M-C)	(8-1-2)			
17	(H-M-H)	(6-1-7)			
18	(H-M-H)	(6-1-8)			
19	(H-M-H)	(7-1-8)			
20	(M-C-C)	(1-2-3)			
21	(M-C-X)	(1-2-9)			
22	(M-C-H)	(1-2-10)			
23	(X-C-C)	(9-2-3)			
24	(X-C-H)	(9-2-10)			
25	(H-C-C)	(10-2-3)			
26	(C-C-M)	(2-3-4)			
27	(C-C-H)	(2-3-11)			
28	(C-C-H)	(2-3-12)			
29	(H-C-M)	(11-3-4)			
30	(H-C-H)	(11-3-12)			
31	(H-C-M)	(12-3-4)			
32	(C-M-H)	(3-4-5)			
33	(C-M-H)	(3-4-13)			
34	(C-M-H)	(3-4-14)			
35	(H-M-H)	(13-4-5)			
36	(H-M-H)	(14-4-5)			
37	(H-M-H)	(13-4-14)			
<i>Torsions</i>					
			Connected atom indices		
38	(M·C)	(1-2)	6	7	8 3 9 10
39	(C·C)	(2-3)	1	9	10 4 11 12
40	(C·M)	(3-4)	2	11	12 5 13 14

^a Atomic weights: M = 12.0111500; C = 12.0111500; H = 1.0078250; X = 18.9984000; H = 1.0078250.

TABLE 3

Calculated frequencies and potential energy distribution for 2-fluorobutane

Band	
<i>S_{hh} conformation</i>	
1448	77(ME1 AB-2) 10(ME1 AB-1)
1414	33(ME1 SBND) 15(2 3 CC S) 12(HX2 H-PD) 11(1 2 CC S)
1398	55(ME4 SBND) 18(HH3 WAG)
1381	36(HH3 WAG) 36(ME4 SBND) 15(3 4 CC S) 12(ME1 SBND)
1276	37(HX2 H-PL) 32(ME1 SBND)
1220	41(HH3 TWS) 23(ME4 R-2)
1142	32(HX2 CX-S) 10(1 2 CC S) 10(HX2 DEF)
1084	18(ME1 R-2) 15(1 2 CC S) 14(3 4 CC S)
1028	30(HX2 H-PL) 13(1 2 CC S) 13(3 4 CC S) 11(HH3 WAG)
1010	36(ME1 R-1) 14(ME4 R-1) 11(3 4 CC S)
985	34(3 4 CC S) 24(ME4 R-1) 16(HH3 WAG)
971	32(HH3 TWS) 27(ME1 R-2) 19(ME4 R-2)
892	49(HX2 CX-S) 26(ME1 R-2) 12(ME1 R-1)
820	38(2 3 CC S) 16(ME4 R-1) 15(1 2 CC S) 14(ME1 R-1)
751	63(HH3 ROC) 43(ME4 R-2)
486	84(HX2 X-PD)
462	48(HX2 X-PL) 22(HH3 DEF) 14(1 2 CC S)
348	68(HX2 DEF) 12(HX2 X-PL) 12(2 3 CC S) 10(HH3 DEF)
257	52(HH3 DEF) 20(HX2 DEF) 19(HX2 X-PL)
<i>S_{ch} conformation</i>	
1448	85(ME4 AB-2)
1421	24(ME1 SBND) 17(2 3 CC S) 13(ME4 AB-1) 11(HX2 H-PL)
1402	41(HH3 WAG) 19(ME1 SBND) 13(HX2 H-PD)
1391	90(ME4 SBND) 15(3 4 CC S)
1279	42(ME1 SBND) 32(HX2 H-PL)
1218	42(HH3 TWS) 25(ME4 R-2)
1150	23(HX2 CX-S) 12(1 2 CC S) 12(ME1 R-1) 10(HX2 DEF)
1095	28(ME1 R-2) 15(HX2 CX-S) 11(HX2 H-PL)
1042	43(3 4 CC S) 17(ME4 R-1)
1015	31(HX2 H-PL) 11(3 4 CC S) 10(HH3 WAG)
975	26(ME4 R-1) 17(ME1 R-1) 11(ME1 R-2)
957	26(HH3 TWS) 19(ME4 R-1) 14(1 2 CC S) 13(ME4 R-2)
903	43(HX2 CX-S) 35(ME1 R-2) 15(ME1 R-1)
802	36(2 3 CC S) 24(1 2 CC S) 10(ME1 R-1)
750	57(HH3 ROC) 39(ME4 R-2)
482	80(HX2 X-PD)
438	33(HX2 DEF) 32(HH3 DEF) 14(HX2 X-PD)
390	81(HX2 X-PL)
247	47(HX2 DEF) 47(HH3 DEF) 14(3 4 CCTO)

TABLE 3 (continued)

Band	$S_{hh'}$ conformation
1458	42(ME4 AB-1) 13(HH3 BND) 10(2 3 CC S)
1452	71(HH3 BND)
1451	38(ME1 AB-2) 30(ME1 AB-1)
1449	50(ME1 AB-2) 27(ME1 AB-1) 12(ME4 AB-1)
1448	84(ME4 AB-2)
1433	17(ME1 SBND) 16(ME1 AB-1) 12(ME4 AB-1) 11(ME4 SBND)
1405	50(HH3 WAG) 14(ME4 AB-1) 13(3 4 CC S)
1385	71(ME4 SBND) 15(ME1 SBND)
1282	42(ME1 SBND) 32(HX2 H-PL)
1218	42(HH3 TWS) 25(ME4 R-2)
1152	28(HX2 CX-S) 12(1 2 CC S) 11(HH3 ROC) 10(HX2 DEF)
1100	23(ME4 R-1) 19(3 4 CC S) 11(ME1 R-1)
1086	23(HX2 H-PL) 22(ME1 R-2) 13(1 2 CC S)
986	32(ME4 R-1) 23(ME1 R-2) 15(HH3 WAG) 10(HX2 H-PL)
967	33(ME1 R-1) 22(HH3 TWS) 18(3 4 CC S) 12(ME4 R-2)
933	26(3 4 CC S) 19(1 2 CC S) 18(HH3 TWS) 11(ME4 R-2)
892	47(HX2 CX-S) 31(ME1 R-2)
813	41(2 3 CC S) 18(1 2 CC S)
747	61(HH3 ROC) 41(ME4 R-2)
601	48(HX2 X-PD) 23(HH3 DEF)
422	73(HX2 X-PL) 10(2 3 CC S)
366	80(HX2 DEF)
215	64(HH3 DEF) 36(HX2 X-PD)

From the potential energy distribution indicated in Table 3, the most interesting parts of the spectra are the essentially delocalized frequencies of the C-F stretching modes. This result contrasts with other carbon-halogen stretching frequencies in primary and secondary alkyl halides. Crowder's results on primary and secondary fluo-

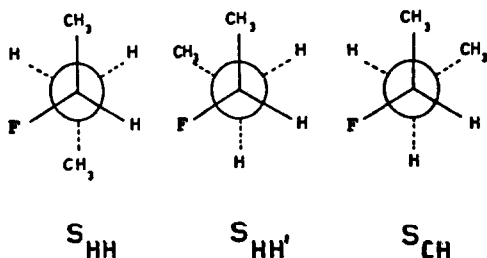


Fig. 2. Conformations of secondary fluorides.

TABLE 4

Assignments to observed frequencies of 2-fluorobutane

Observed		Calculated		
Solid	Liquid	S_{hh}	S_{ch}	$S_{hh'}$
	1470 m			
	1458 m			
1449 mw	1450 w			1448
1386 mw	1387 m	1398	1391	1405
1378 w	1380 sh	1381		1385
1351 w	1350 sh			
1341 w	1342 mw			
1303 vw	1306 vw			
1272 vw	1273 vw	1276	1279	1282
1180 mw	1177 mw			
1155 vvw	1154 w			
1128 mw	1133 ms			
1116 ms	1120 ms	1142	1150	1152
	1103 m		1095	1100
1033 m	1033 ms	1028	1042	
998 mw	993 m	1010	1015	
984 w	985 m	985	975	986
	978 w			967
971 m	970 s	971	957	
889 s	895 s	892	903	892
824 m	824 m	820	802	813
765 w	765 w	751	750	747
	595 vw		601	
495 w	495 w	486	482	
462 w	461 w	462	438	
	422 vw		422	
	383 w		390	
	360 vw	348		366
	253 w	257	247	
	228 vw			215

rides showed the same phenomena. A study of Table 4 indicates that the fit between calculated and observed frequencies below 1200 cm^{-1} is quite satisfactory. On the other hand, the fit in the region above 1200 cm^{-1} grows increasingly poorer with increased wavenumber. Problems with the force field related to this region are present, but it can be said that the force constants represent the best derivable fit to the available data. In order to have a more reliable force field for secondary fluorides, both infrared and Raman data for 2-fluoropropane and 2-fluorobutane are required. The resulting force field should additionally be tested on other related model compounds, such as 3-fluoropentane and 2,4-difluorobutane. Therefore, although the

present force field cannot be considered totally general in application to secondary fluorides, it represents a starting point on which to build, and should be capable of lending insight to the interpretation of the vibrational spectra of this class of compounds. In particular, we feel that its application to the analysis of the spectra of poly(vinyl fluoride) is justified.

NORMAL-MODE CALCULATION OF PVF

The normal-mode calculations were done on a single chain for the stereoregular and regioregular structures, i.e., no interchain forces are considered. Although the classical approach to the vibrational analysis of polymers in terms of an infinite chain mode with perfect chemical, stereoregular and conformational structures is not valid for real polymers, the vibrational analysis of a disordered material can be more easily performed if the vibrational spectrum of the infinite perfect model is well known and is used as a reference point in the comparison.

The structural parameters used were the same as for the secondary fluorides. The bond angles were assumed to be tetrahedral. Cartesian coordinates were calculated for the planar zigzag structures of the isolated syndiotactic PVF chain. The symmetry coordinates, constructed from the internal coordinates defined in the standard way (Table 5), are listed in Table 6 with numbering of

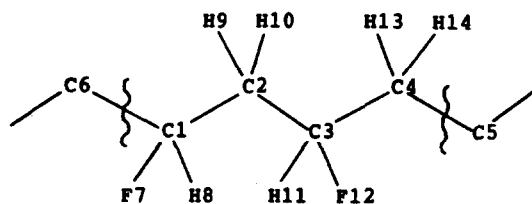


Fig. 3. Structural unit of syndiotactic PVF, with atom numbering.

atoms shown in Fig. 3. The force field for the single chain was the same as that used for secondary fluorides. The calculated frequencies are compared with the observed in Table 7 in which the assignments of the bands based on the calculated potential energy distribution are also given.

RESULTS AND DISCUSSION

For atactic poly(vinyl fluoride), all the spectrally active vibrational modes occur both in the infrared and Raman spectra. Planar syndiotactic PVF has a symmetry isomorphous with the factor group C_{2v} [4]. The normal modes for the planar syndiotactic structure are distributed among the species as Raman and infrared active (A_1 , B_1 , B_2) modes and only Raman active A_2 modes [24]. PVF with a planar isotactic structure has a symmetric isomorphous with the factor group C_s . The normal modes for this isotactic structure may be divided among the symmetry species as A' (in phase) and A'' (out of phase). All vibrations are active in both the infrared and Raman spectra. The symmetry analysis indicates that only syndiotactic placements lead to differences in infrared and Raman selection rules in PVF.

Polarized infrared spectra of the oriented PVF film are shown in Fig. 4 and the Raman spectrum is shown in Fig. 5. The observed infrared and Raman frequencies are listed in Table 6 and compared with calculated frequencies of the syndiotactic structure. In this table we listed only modes in the $1500\text{--}700\text{ cm}^{-1}$ region. Analysis of Figs. 4 and 5 with Table 7 indicates that some Raman bands deserve special consideration, among them are the bands at 1150 cm^{-1} and at 1436

TABLE 5

Internal coordinates for syndiotactic PVF

Bond lengths		Bond angles			
R^I	1-2	ϕ_1^{II}	6-1-2	Θ^I	1-2-9
R^{II}	2-3	ϕ_2^{II}	1-2-3	Θ^{II}	1-2-10
R^{III}	3-4	ϕ_3^{II}	2-3-4	Θ^{III}	9-2-3
R^{IV}	4-5	ϕ_4^{II}	3-4-5	Θ^{IV}	10-2-3
r_1^I	1-7	ϕ_1^{III}	7-1-8	θ^I	2-3-11
r_2^I	1-8	ϕ_2^{III}	9-2-10	θ^{II}	2-3-12
r_1^{II}	2-9	ϕ_3^{III}	11-3-12	θ^{III}	4-3-11
r_2^{II}	2-10	ϕ_4^{III}	13-4-14	θ^{IV}	4-3-12
r_1^{III}	3-11	ϕ_1^{IV}	6-1-7	ϕ_1^I	3-4-13
r_2^{III}	3-12	ϕ_2^{IV}	6-1-8	ϕ_2^I	3-4-14
r_1^{IV}	4-13	ϕ_3^{IV}	7-1-2	ϕ_3^I	5-4-13
r_2^{IV}	4-14	ϕ_4^{IV}	8-1-2	ϕ_4^I	5-4-14

cm^{-1} . As assigned by Koenig and Boerio [2], these bands may correspond to infrared bands at 1144 cm^{-1} . However, the band at 1144 cm^{-1} ,

which was assigned as $\nu(\text{CF})$, should be weaker in the Raman than in the IR spectrum, which is the opposite of the observed.

TABLE 6

 Symmetry coordinates for syndiotactic poly(vinyl fluoride) (C_{2v} symmetry)

a_1 coordinates	b_1 coordinates
$S_1 = \frac{1}{2}(\Delta R^I + \Delta R^{II} + \Delta R^{III} + \Delta R^{IV})$	$S_1 = \frac{1}{2}(\Delta R^I - \Delta R^{II} - \Delta R^{III} + \Delta R^{IV})$
$S_2 = \frac{1}{2}(\Delta r_1^{II} + \Delta r_2^{II} + \Delta r_1^{IV} + \Delta r_2^{IV})$	$S_2 = \frac{1}{2}(\Delta r_1^{II} - \Delta r_2^{II} - \Delta r_1^{IV} - \Delta r_2^{IV})$
$S_3 = \frac{1}{\sqrt{2}}(\Delta r_2^I + \Delta r_1^{III})$	$S_2 = \frac{1}{\sqrt{2}}(\Delta r_2^I - \Delta r_1^{III})$
$S_4 = \frac{1}{\sqrt{2}}(\Delta r_1^I + \Delta r_2^{III})$	$S_4 = \frac{1}{\sqrt{2}}(\Delta r_1^I - \Delta r_2^{III})$
$S_5 = \frac{1}{\sqrt{2}}(\Delta \theta^I + \Delta \theta^{III})$	$S_5 = \frac{1}{\sqrt{2}}(\Delta \theta^I - \Delta \theta^{III})$
$S_6 = \frac{1}{\sqrt{2}}(\Delta \theta^{II} + \Delta \theta^{IV})$	$S_6 = \frac{1}{\sqrt{2}}(\Delta \theta^I - \Delta \theta^{III})$
$S_7 = \frac{1}{\sqrt{2}}(\Delta \theta^I + \Delta \theta^{III})$	$S_7 = \frac{1}{\sqrt{8}}(\Delta \phi_1^{II} + \Delta \phi_2^{II} - \Delta \phi_3^{II} - \Delta \phi_4^{II} - \Delta \phi_1^{IV}$ $- \Delta \phi_2^{IV} + \Delta \phi_3^{IV} + \Delta \phi_4^{IV})$
$S_8 = \frac{1}{\sqrt{2}}(\Delta \theta^{II} + \Delta \theta^{IV})$	$S_8 = \frac{1}{\sqrt{8}}(\Delta \phi_1^{II} - \Delta \phi_2^{II} + \Delta \phi_3^{II} - \Delta \phi_4^{II} + \Delta \phi_1^{IV}$ $- \Delta \phi_2^{IV} + \Delta \phi_3^{IV} - \Delta \phi_4^{IV})$
$S_9 = \frac{1}{\sqrt{8}}(\Delta \phi_1^{II} + \Delta \phi_2^{II} + \Delta \phi_3^{II} + \Delta \phi_4^{II} + \Delta \phi_1^{IV}$ $+ \Delta \phi_2^{IV} + \Delta \phi_3^{IV} + \Delta \phi_4^{IV})$	$S_9 = \frac{1}{2}(\Delta \phi_2^I + \Delta \phi_4^I - \Delta \phi_1^{III} - \Delta \phi_3^{III})$
$S_{10} = \frac{1}{\sqrt{8}}(\Delta \phi_1^{II} - \Delta \phi_2^{II} - \Delta \phi_3^{II} + \Delta \phi_4^{II} - \Delta \phi_1^{IV}$ $+ \Delta \phi_2^{IV} + \Delta \phi_3^{IV} - \Delta \phi_4^{IV})$	$S_{10} = \frac{1}{2}(\Delta \phi_1^I + \Delta \phi_3^I - \Delta \phi_2^{III} - \Delta \phi_4^{III})$
$S_{11} = \frac{1}{2}(\Delta \phi_2^I + \Delta \phi_4^I + \Delta \phi_1^{III} + \Delta \phi_3^{III})$	
$S_{12} = \frac{1}{2}(\Delta \phi_1^I + \Delta \phi_3^I + \Delta \phi_2^{III} + \Delta \phi_4^{III})$	
a_2 coordinates	b_2 coordinates
$S_1 = \frac{1}{2}(\Delta R^I + \Delta R^{II} - \Delta R^{III} - \Delta R^{IV})$	$S_1 = \frac{1}{2}(\Delta R^I - \Delta R^{II} + \Delta R^{III} - \Delta R^{IV})$
$S_2 = \frac{1}{2}(\Delta r_1^{II} + \Delta r_2^{II} - \Delta r_1^{IV} - \Delta r_2^{IV})$	$S_2 + \frac{1}{2}(\Delta r_1^{II} - \Delta r_2^{II} - \Delta r_1^{IV} + \Delta r_2^{IV})$
$S_3 = \frac{1}{\sqrt{2}}(\Delta \theta^{II} - \Delta \theta^{IV})$	$S_3 = \frac{1}{\sqrt{8}}(\Delta \phi_1^{II} + \Delta \phi_2^{II} - \Delta \phi_3^{II} - \Delta \phi_4^{II} + \Delta \phi_1^{IV}$ $+ \Delta \phi_2^{IV} - \Delta \phi_3^{IV} - \Delta \phi_4^{IV})$
$S_4 = \frac{1}{\sqrt{2}}(\Delta \theta^{II} - \Delta \theta^{IV})$	$S_4 = \frac{1}{\sqrt{8}}(\Delta \phi_1^{II} - \Delta \phi_2^{II} + \Delta \phi_3^{II} - \Delta \phi_4^{II} - \Delta \phi_1^{IV}$ $+ \Delta \phi_2^{IV} - \Delta \phi_3^{IV} + \Delta \phi_4^{IV})$
$S_5 = \frac{1}{\sqrt{8}}(\Delta \phi_1^{II} + \Delta \phi_2^{II} + \Delta \phi_3^{II} + \Delta \phi_4^{II} - \Delta \phi_1^{IV}$ $- \Delta \phi_2^{IV} - \Delta \phi_3^{IV} - \Delta \phi_4^{IV})$	$S_5 = \frac{1}{2}(\Delta \phi_2^I - \Delta \phi_4^I + \Delta \phi_1^{III} - \Delta \phi_3^{III})$
$S_6 = \frac{1}{\sqrt{8}}(\Delta \phi_1^{II} - \Delta \phi_2^{II} - \Delta \phi_3^{II} + \Delta \phi_4^{II} + \Delta \phi_1^{IV}$ $- \Delta \phi_2^{IV} - \Delta \phi_3^{IV} + \Delta \phi_4^{IV})$	$S_6 = \frac{1}{2}(\Delta \phi_1^I - \Delta \phi_3^I + \Delta \phi_2^{III} - \Delta \phi_4^{III})$
$S_7 = \frac{1}{2}(\Delta \phi_2^I - \Delta \phi_4^I - \Delta \phi_1^{III} + \Delta \phi_3^{III})$	
$S_8 = \frac{1}{2}(\Delta \phi_1^I - \Delta \phi_3^I - \Delta \phi_2^{III} + \Delta \phi_4^{III})$	

As can be seen from Table 7, however, the calculated frequencies of syndiotactic structure are not in agreement with the observed bands. Particularly the calculated A_2 modes do not fit the observed frequencies based on the vibrational selection rules. Zerbi [3] preferred the syndiotactic model to analyze the IR spectrum of PVF particularly because of the occurrence of the two C–F stretching modes (at 1144 and 1094 cm^{-1}) with proper polarization. However, normal coordinate calculation suggests that the band at 1144 cm^{-1} is not a single mode but a mixed one. This suggestion is supported by normal coordinate calculations of 2-fluoropropane by Crowder [18] and 2-fluorobutane by us. In Table 3 for 2-fluorobutane, there are two modes strongly involving the stretching of the C–F bond (1142 and 892 cm^{-1}). Moreover, it is not the high-frequency

mode which contains the larger contribution from the C–F stretching mode, though it is usually assumed as a representative of the C–F stretching in the empirical assignments. If we consider the observed band at 1144 cm^{-1} having a potential energy distribution, $\nu(\text{CF})$ will be contributing mainly in the IR and $\gamma_t(\text{CH}_2)$ in the Raman so that we can explain the behavior of the Raman 1150 and IR 1144 cm^{-1} bands in the observed spectra. In addition, the three infrared active species, A_1 , B_1 , and B_2 should have parallel dichroism when the molecular chains are oriented along the stretching direction. As shown in Table 7, however, the observed parallel bands do not correspond to calculated B_2 frequencies. They thus provide additional support for the atactic configuration in the crystal structure of PVF.

In order to have more conclusive evidence,

TABLE 7

Observed frequencies and calculated frequencies of syndiotactic PVF

Observed		Calculated				
Infrared	Raman	A_1	A_2	B_1	B_2	Potential energy distribution
		1460				94(HH-b)
1444 w ^a						
1426 s	1436 s		1446			98(HH-b)
1410 s					1407	37(HH-w)
1367 m	1366 m					
1354 m	1354 m					
1300 vw	1302 m					
	1256 m					
1249 m				1247		53(HH-w) 34(C–C s) 11(CH-pl)
1232 m			1223			42(HH-w) 35(C–C s)
	1194 m					
1185 vw						
	1150 s				1186	45(HH-w) 24(CH-pl)
1144 s		1149				61(HH-tw) 25(CX-s)
1094 s	1095 m			1087		56(CX-s) 22(HH-r)
1084 s			1062			84(HH-tw)
1033 s	1032 w	1011				21(C–C s) 19(CH-pl) 12(HH-tw)
						11(CX-s)
966 vw	961 w					39(CH-pl) 10(HH-tw)
			950		960	52(CH-pl) 17(HH-tw) 11(C–C s)
				944		61(C–C s)
888 m	890 m	851				37(CX-s)
831 s	834 s			825		81(HH-r)
815 w						
765 w ^a					805	38(HH-r) 31(CX-s) 15(C–C s)
722 w ^a						

^a Band due to head-to-head, tail-to-tail defect structure.

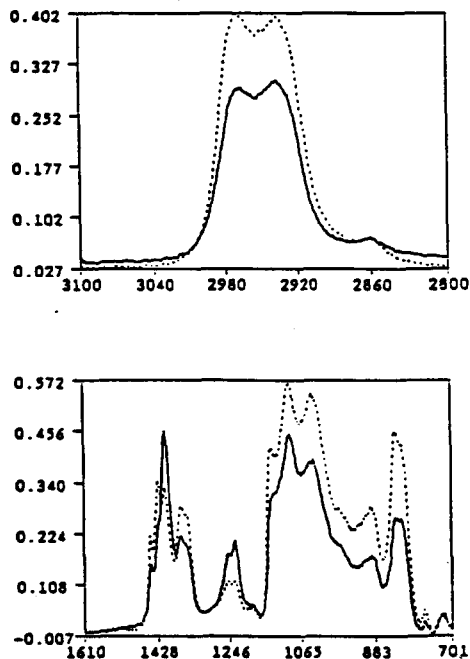


Fig. 4. Infrared spectra of an oriented sample of PVF in polarized light. — electric vector parallel to drawing direction; ····· electric vector perpendicular to drawing direction.

however, we need a more precise force field from additional model compounds like *di*- and *eso*-2,4-difluoropentane, and 2,4,6-trifluoroheptane.

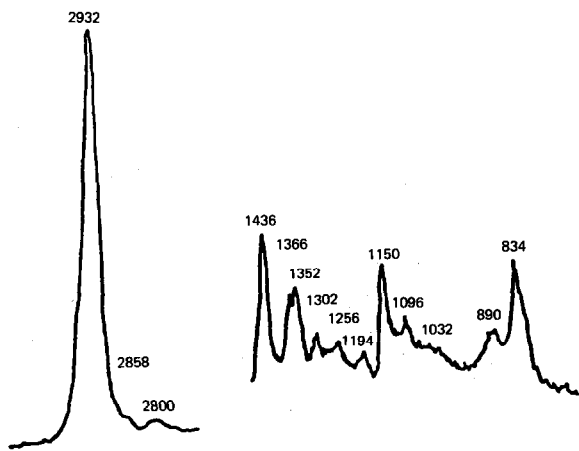


Fig. 5. Raman spectrum of poly(vinyl fluoride).

We turn now to an approximate normal coordinate analysis of the spectra of PVF based on the atactic model of the chain configuration.

ASSIGNMENTS OF BANDS IN THE SPECTRUM OF POLY(VINYL FLUORIDE)

Before discussing the assignments of the bands in the infrared spectrum of PVF it is appropriate that we consider what frequencies may be expected to appear. For molecules with any appreciable symmetry this can be done by means of a group theoretical approach. In the present case the uncertainty in structure occasioned by the random location of the fluorine atoms does not make the group theory analysis particularly useful. We will therefore begin by classifying the normal modes of the molecule in terms of the separable modes of component groups in the chain. Later it will become more evident to what extent we may consider the modes to be separable and what influence neighboring chain interactions can be expected to have on the spectrum.

It seems reasonable to choose the monomer unit $-\text{CH}_2\text{CHF}-$ as the fundamental spectroscopic unit, since, although two types of such units occur (depending on the position of the F), these are essentially independent of each other as a result of their random location in the chain. We therefore do not expect that interactions between these two types of units will give rise to any new frequencies in the spectrum.

With this assumption we expect $3 \times 6 - 4 = 14$ normal modes of the $-\text{CH}_2\text{CHF}-$ group in the polymer chain. In terms of separable modes of the component groups, the frequencies will be distributed as follows: 6 CH_2 (2 stretching, bending, wagging, twisting, rocking), 3 CH, 3 CF (each consisting of a stretching plus 2 bending modes, one perpendicular to the chain axis and one parallel), and 2 CC (skeletal vibrations).

The vibrational assignment of PVF in terms of the atactic model is attempted below. The vibrational analysis is based on the infrared polarization and Raman data, and on the comparison with the normal coordinate analysis data of model compounds 2-fluoropropane and 2-fluorobutane.

For the head-to-head defect structure, the infrared data [7] of isotactic PVF is used.

(1) *Carbon-hydrogen stretching modes.* Three bands are expected for the atactic structure: $\nu(\text{CH})$, $\nu_a(\text{CH}_2)$, and $\nu_s(\text{CH}_2)$ which are the typical localized modes. The asymmetric and the symmetric $\nu(\text{CH}_2)$ can be assigned to the perpendicular bands at 2969 and 2932 cm^{-1} , respectively, which have the proper polarization and frequency. However, an explanation of the disappearance of the band at 2969 cm^{-1} in the Raman spectrum is puzzling because the asymmetric CH_2 stretching vibration should be also Raman active due to its change of polarizability ellipsoid during the vibration. The assignment of the $\nu(\text{CH})$ is difficult due to its low intensity as occurs in other vinyl polymers. The band at 2861 cm^{-1} is due to the isolated ethylene molecules in the tail-to-tail portion of polymer. This assignment is based on (a) the absence of such a band in the spectrum of isotactic PVF and (b) the presence of a similar band in polyvinylidene fluoride [25].

(2) *CH_2 deformation modes.* Examination of potential energy distribution in the normal coordinate calculation for 2-fluorobutane suggests that only bending [$\delta(\text{CH}_2)$] and rocking [$\gamma_r(\text{CH}_2)$] modes can be regarded as localized deformation modes (Table 3).

The assignment of the $\delta(\text{CH}_2)$ to the 1426 cm^{-1} is based on the proper polarization (perpendicular) and presence of such a mode in the frequency range of the model compound (2-fluorobutane). The very high dichroic ratio and disappearance of this band in the molten state suggests its origin to an ordered structure with a localized mode. Normal coordinate analysis of syndiotactic PVF shows no coupling of this mode so a localized mode can be accepted.

The strong perpendicular band at 831 cm^{-1} can be undoubtedly assigned as a $\gamma_r(\text{CH}_2)$ mode. Normal coordinate analysis of 2-fluorobutane and syndiotactic PVF supports this assignment as a localized mode.

The bands at 1444 and 760 cm^{-1} are due to the tail-to-tail structure because of their absence in the spectrum of isotactic PVF. Although normal-mode analysis of model compounds such as 2,5-difluoroheptane is required, these bands can

be assigned with some confidence as $\delta(\text{CH}_2\text{CH}_2)$ and $\gamma_r(\text{CH}_2\text{CH}_2)$, respectively. The fact that its polarization properties are the same as those of the two neighboring localized bands [$\delta(\text{CH}_2)$ and $\gamma_r(\text{CH}_2)$, respectively], supports these assignments.

The assignment of the remaining deformation modes is difficult due to extensive coupling. Infrared polarization, the intensities of the infrared and Raman spectra, and the general frequency positions from normal coordinate analysis of model compound and syndiotactic PVF are helpful in assigning bands.

The band at 1410 cm^{-1} shows a relatively high parallel dichroism indicating that it is predominantly a $\gamma_w(\text{CH}_2)$ mode. However, the disappearance of this band in the Raman spectrum is unexpected because carbon-fluorine stretching modes are not in this region.

We have a reasonable suggestion for the location of the $\gamma_t(\text{CH}_2)$ mode. Although this mode is predicted to be very weak in the infrared spectrum, the normal coordinate analysis of 2-fluorobutane and syndiotactic PVF and Raman data suggest that this mode contributes predominantly to the Raman band at 1150 cm^{-1} . As discussed, this mode is strongly mixed with the $\nu(\text{CF})$ mode. The Raman band at 1302 cm^{-1} can also be assigned to the $\gamma_t(\text{CH}_2)$ mode which is absent from the infrared spectra.

(3) *Carbon-fluorine stretching modes.* One of the most striking characteristics of infrared spectra of fluorinated organic structures is the strong intensity of the carbon-fluorine stretching vibrations. It is due to the fact that the stretching vibrations of highly polar linkages are associated with high infrared intensities due to the changes in the permanent dipole moment. The intensities of the Raman lines, which are governed by changes in the induced dipole moment during vibration, are in contrast low for these vibrations and are thus not a distinguishing feature of the spectra. A second important aspect of the infrared spectra of carbon-fluorine stretching vibrations is the possibility of coupling (notable with skeletal stretching), which prohibits its providing unique group frequencies and results in very complex absorption patterns. In spite of the

above facts, we will attempt to make assignments for bands involving carbon-fluorine stretching modes based on the normal coordinate analysis of 2-fluoropropane [18] and 2-fluorobutane and on the relative intensities of infrared and Raman spectra.

In 2-fluoropropane, the $\nu(\text{CF})$ modes lie within the range 1264–819 cm^{-1} . According to our work on 2-fluorobutane, this mode falls in the 1142–892 cm^{-1} region, respectively. Therefore, the perpendicularly polarized bands at 1144, 1033, and 888 cm^{-1} can be assigned to the modes involving $\nu(\text{CF})$. A comparison of the intensities in infrared and Raman spectra with the required polarization supports these assignments. For the band at 888 cm^{-1} , it is believed to be coupled strongly with the $\nu(\text{CC})$ mode. The fact of the strong intensity in infrared and the weak in the Raman band at 1033 cm^{-1} suggest that this band is predominantly the $\nu(\text{CF})$ mode. As discussed, the band at 1144 cm^{-1} can be assigned to contributions from the $\gamma_t(\text{CH}_2)$ and $\nu(\text{CF})$ modes.

(4) *Carbon-fluorine deformation modes.* There is little doubt that the two bands at 450 and 402 cm^{-1} can be assigned to $\gamma_r(\text{CF})$ and $\gamma_w(\text{CF})$ which have the proper polarization and frequency. Normal coordinate analyses of 2-fluorobutane and syndiotactic PVF support these assignments.

(5) *Carbon-carbon stretching and carbon-hydrogen deformation modes.* The assignment of the remaining bands is more difficult due to extensive coupling of the modes and the lack of data from deuterated polymers. The above mentioned studies on carbon-carbon frequencies of small molecules and syndiotactic PVF show that the $\nu(\text{CC})$ modes occur in a broad frequency range; that is, these are delocalized modes. Therefore, it is hard to make unambiguous assignments of the $\nu(\text{CC})$ modes of PVF. However, the fact that an intense Raman band arises from bonds having nearly symmetrical charge distributions such as C–C can lead to a fairly reliable assignment of this mode. Although couplings are expected, the $\gamma_w(\text{CH})$ and $\gamma_r(\text{CH})$ modes occur in fairly restricted frequency ranges, around 1200 and 1300 cm^{-1} . The group of bands at 1232 and 1249 cm^{-1} and at 1354 and 1367 cm^{-1} are proba-

TABLE 8

Proposed vibrational assignment of PVF in terms of atactic configuration

Observed		Infrared polarization	Approximate assignment
Infrared	Raman		
2970 s		⊥	$\nu_a(\text{CH}_2)$
2932 s	2932 s	⊥	$\nu_s(\text{CH}_2)$
2861 w	2859 w		$\nu(\text{CH}_2\text{CH}_2)$
1446 w		⊥	$\delta(\text{CH}_2\text{CH}_2)$
1427 s	1436 s	⊥	$\delta(\text{CH}_2)$
1410 s			$\gamma_w(\text{CH}_2)$
1368 m	1366 m	⊥	$\gamma_r(\text{CH}) + \gamma_w(\text{CH}_2)$
1351 m	1354 m	⊥	$\gamma_r(\text{CH}) + \nu(\text{CC})$
1295 vw	1302 m		$\gamma_t(\text{CH}_2)$
1250 m	1256 m		$\gamma_w(\text{CH}) + \nu(\text{CC})$
1232 m			$\gamma_w(\text{CH CH}) + \gamma_w(\text{CH})$
1189 vw	1194 m		$\nu(\text{CC})$ of T-T
1144 s	1150 s	⊥	$\nu(\text{CF}) + \gamma_t(\text{CH}_2)$
1092 s	1095 m	⊥	$\nu(\text{CC}) + \nu(\text{CF})$
1033 s	1032 w	⊥	$\nu(\text{CF})$
965 vw	961 vw	⊥	
888 m	890 m	⊥	$\nu(\text{CF}) + \nu(\text{CC})$
831 s	834 s	⊥	$\gamma_r(\text{CH}_2)$
763 w		⊥	$\gamma_r(\text{CH}_2\text{CH}_2)$
722 w	720 vw		
510 vw	506 w		
465 m	454 m	⊥	$\gamma_r(\text{CF})$
394 m	395 w		$\gamma_w(\text{CF})$

bly assignable to the modes involved in $\gamma_w(\text{CH})$ and $\gamma_r(\text{CH})$, respectively. The strong parallel polarization of these former two bands and the strong perpendicular polarization of the latter two bands support these assignments. Comparison of the Raman and infrared intensities and the normal-mode analyses suggest that the band at 1249 cm^{-1} is the coupled $\gamma_w(\text{CH})$ and $\nu(\text{CC})$ mode, the band at 1232 cm^{-1} being the uncoupled $\gamma_w(\text{CH})$ mode. It is also suggested that the 1367 cm^{-1} is the coupled $\gamma_r(\text{CH})$ and $\gamma_w(\text{CH}_2)$ mode, and the 1354 cm^{-1} band the coupled $\gamma_r(\text{CH})$ and $\nu(\text{CC})$ mode.

Although uncertainties will always exist, the overall set of proposed assignments for PVF is quite satisfactory. The assignments proposed tentatively are in Table 8. Several assignments require additional confirmation which could be achieved by studies of deuterated PVF and extended studies on low-molecular-weight model compounds.

Conclusions

We have developed a force field for secondary fluorides based on the extension of existing force fields for hydrocarbons and primary fluorides. We recognize that this force field cannot be regarded as a general force field for secondary fluorides. However, the agreement between the observed and calculated frequencies below 1200 cm^{-1} indicates that it is presently useful to apply to the analysis of the spectra of poly(vinyl fluoride).

A comparison of observed infrared and Raman bands with frequencies calculated for syndiotactic PVF shows that PVF produced by conventional free radical polymerization has an atactic structure, supporting ^{19}F -NMR results and conclusions reached by Koenig and Boerio.

Band assignments in terms of atactic structure are also proposed.

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