Raman Scattering from Finite Polytetrafluoroethylene Chains and a Highly Oriented TFE–HFP Copolymer Monofilament

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ABSTRACT: Raman polarization studies on a highly oriented tetrafluoroethylene–hexafluoropropylene (TFE–HFP) copolymer have been used to make band assignments for the PTFE homopolymer. In addition, band progressions observed in the Raman spectra of a series of isostructural perfluoro-*n*-alkanes have been used to plot out portions of the ω_3, ω_6, and ω_8 experimental dispersion curves for PTFE. Comparisons of band assignments and experimental dispersion curves with previous normal mode calculations indicated a lack of agreement between mode symmetries and a sizable discrepancy in the ω_6 branch for phase values greater than 120°. Normal mode calculations, based on an isolated chain model, have been performed in which the valence force field constants have been refined to improve the agreement with experimental results.

Experimental estimates of the dependence of vibrational frequencies on the phonon wave vector (dispersion curves) are useful in force field refinement calculations aimed at improved force fields and band assignments. The use of vibrational frequencies obtained from short chain oligomers to determine the shape of dispersion curves of the infinite polymer has been well established in the case of the *n*-alkanes.[1–4] Unfortunately, the lack of a suitable set of oligomers for other polymer systems has limited the applicability of the method to the *n*-alkanes and polyethylene. In addition, with the further absence of highly oriented, optically clear materials on which polarized Raman data could be obtained the complete determination of specific band assignments in polymers has been limited.[5–9] Recently we reported preliminary results of our studies on a series of perfluoro-*n*-alkanes as a model system for investigating polytetrafluoroethylene (PTFE).[10] Using the observed frequencies of the longitudinal acoustic modes together with knowledge of the chain length, it was possible to plot out a portion of the ω_8 longitudinal acoustical branch and compare it with the theoretical curves obtained from normal coordinate calculations on PTFE using force fields currently found in the literature.[11,12] In this way, the accuracy of force fields in predicting the experimental frequencies can be evaluated. In a similar way, additional regions of the spectrum, in which a noticeable dispersion in frequency is noted among the members of a set of oligomers, can be used to obtain information about the shape of other polymer dispersion curves.[13] It is the purpose of this work to present additional Raman data on a series of perfluoro *n*-alkanes together with a polarized Raman study on a highly oriented monofilament of a tetrafluoroethylene and hexafluoropropylene (TFE–HFP) random copolymer. In the latter case, it was found that previous assignment schemes on which subsequent force field refinements had been made were not entirely consistent with polarization measurements. These assignments are examined in the context of a least-squares refinement on parameters of a local symmetry coordinate valence force field. We found that it was possible to improve the agreement between calculated and experimental frequencies in a manner consistent with the polarization results.

Experimental Section

The perfluoro-*n*-alkanes, $C_{20}F_{42}$, $C_{16}F_{34}$, $C_{12}F_{26}$, and $C_{10}F_{22}$, were high purity (99.999%) research samples provided by the Dupont Co.[25] A sample of C_9F_{20} was furnished by the Minnesota Mining and Manufacturing Co. All samples were used as received without further purification or chemical treatment.

The highly oriented tetrafluoroethylene–hexafluoropropylene (TFE–HFP) random copolymer monofilament was a commercial Dupont product (FEP 100). A transparent sample with a diameter of 20 mils (1 mil = 2.54×10^{-5} m) was supplied. Infrared intensity measurements indicated that this copolymer contained 13–14 mol % of HFP. Slightly opaque fibers (approximately 0.1 mm in diameter) of PTFE homopolymer were obtained from the Dupont Co.

A Spex 1401 double monochromator equipped with Jobin-Yvon holographic gratings (1800 lines/mm) was used in conjunction with a Coherent Radiation CR-12 Ar^+ laser to record the Raman spectra. All spectra were recorded using 90° scattering geometry. For polarization measurements a polarization analyzer followed by a quartz scrambler was used in front of the entrance slit of the monochromator.

Solid state spectra of the perfluoro-*n*-alkanes were recorded by compressing small amounts of material into a capillary tube which was subsequently sealed. Spectra of C_9F_{20} which is a liquid at room temperature were recorded by passing a stream of cold nitrogen over a capillary tube containing the liquid perfluoro-*n*-alkane in a Harney-Miller cell. When the material was observed visually to crystallize, the temperature was stabilized and the spectrum was recorded. In this way, the chances of encountering any solid–solid phase transitions were minimized.

Results and Interpretation

A. Raman Spectra of a Highly Oriented TFE–HFP Random Copolymer. Crystalline PTFE is known to have a 15/7 helical form above 19 °C.[14] The effect of $-CF_3$ branches on this helical form has not been determined. However, it has been shown that the hexagonal lattice parameters of the TFE–HFP copolymer are dependent on the comonomer content, increasing with increased HFP content.[15] This may suggest a disturbance of the hexagonal close packing in the copolymer lattice. In PTFE, the vibrational bands in the 570–625-cm^{-1} region have been shown to be particularly sensitive to helical conformation.[16,17] Comparisons between the Raman spectrum of the TFE–HFP random copolymer and that of PTFE indicate that its chain conformation is identical to that of PTFE at room temperature, i.e., a 15/7 helix. Therefore, the symmetry analysis for the TFE–HFP copolymer is the same as that for PTFE in the 15/7 helical form. For this structure, the factor group is $D(14\pi/15)$ and the vibrations are distributed among the symmetry species as follows: 4 A_1 (Raman active), 3 A_2 (IR active), 8 E_1 (IR and Raman active), and 9 E_2 (Raman active).

Polarized Raman experiments can be designed which select out modes belonging to each of the Raman active symmetry species from knowledge of the chain orientation with respect to the filament axis, the factor group symmetry, and the Raman scattering activities. The latter quantities have been derived by Snyder for partially oriented polymer molecules.[18] Scattering activities were tabulated by Snyder in terms of derived polarizability tensor elements for the usual point groups in both 90 and 180° scattering. Although helical symmetry groups such as the $D(14\pi/15)$ group of PTFE were not

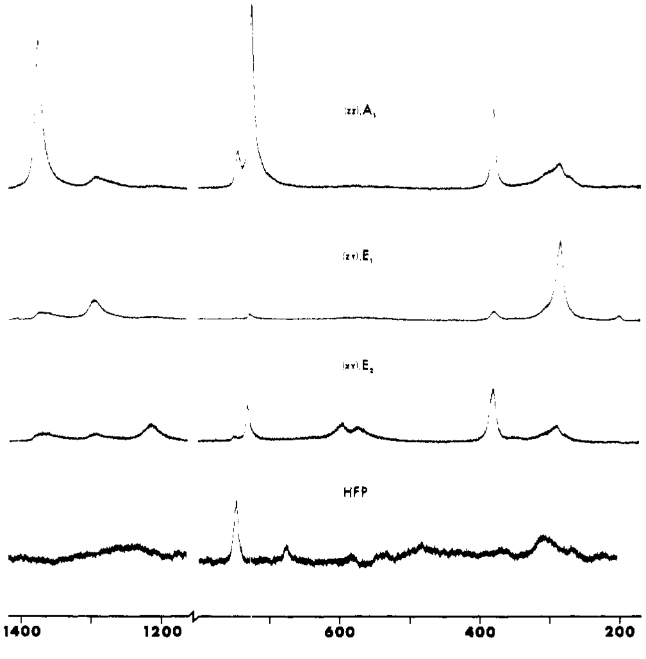

Figure 1. Polarized Raman spectra from TFE–HFP copolymer monofilament (top three traces) and unpolarized Raman spectrum of poly(hexafluoropropylene) (bottom trace). Letters in brackets refer to polarization directions of incident and scattered light; *z* is the monofilament axis.

considered explicitly by Snyder, we can make use of his tables by correlating Raman active symmetry species of the helical group to those of one of the point groups considered. For example, the Raman scattering activities of the Raman active symmetry species of $D(14\pi/15)$ are identical to those of the point group D_5.

According to our low-angle X-ray investigations of the TFE–HFP specimens, which yielded a four-point pattern, the lamellae are oriented at an angle of approximately 32° with respect to the filament axis. From our previous investigation[10] of the polarization properties of the Raman active longitudinal acoustic mode in the TFE–HFP copolymer monofilament, it was determined within experimental error that the chain axis is parallel to the filament axis. Hence, the helical axis and the filament axis are parallel to the *z* axis in Snyder's notation. Only A_1 modes are active in 90° scattering when both the incident and scattered polarization directions are parallel to the filament axis (*zz* scattering). Similarly, it is found that *zy* scattering selects E_1 modes and *xy* scattering selects E_2 modes.

In Figure 1, the results of our Raman polarization measurements are shown. All spectra were recorded using right-angle scattering geometry. The small letters found in parentheses indicate the direction of the incident and scattered polarization directions respectively. In our reference system, as indicated above, the *z* axis was taken along the filament axis. In addition to the A_1, E_1, and E_2 spectra, a spectrum of atactic hexafluoropropylene (HFP) is included to indicate the contribution made by $-CF_3$ branches in the 700–750- and 300–350-cm^{-1} regions. An indication of the high orientation present in the copolymer sample can be seen by comparing the intensity of the 729-cm^{-1} band in the *zz* and *xy* spectra.

In previously reported normal coordinate analyses based on force field refinements, the Raman band at 288 cm^{-1} has been assigned along with the 1377-, 729-, and 383-cm^{-1} bands to the A_1 symmetry species.[11,12] As can be seen in Figure 1, this is incompatible with observed Raman polarization measurements which clearly show that the 288-cm^{-1} band belongs to the E_1 symmetry species. This observation was further confirmed from Raman polarization measurements on a bundle of highly oriented PTFE fibers. Although there was some polarization scrambling due to the opacity of the fibers it was concluded that the 288-cm^{-1} band does indeed exhibit E_1 symmetry. This misassignment will be discussed in conjunction with the perfluoro-*n*-alkane data in the following section.

The sharp band located at 740 cm^{-1} is attributed to the presence of $-CF_3$ branches as can be seen by comparison with the atactic HFP spectrum. The remaining three strong bands at 1377, 729, and 383 cm^{-1} belong to the A_1 symmetry species as has been previously designated.[11]

In addition to the already mentioned 288-cm^{-1} band, the 207- and 1296-cm^{-1} bands are observed to also belong to the E_1 representation. Residual intensity of the A_1 modes is also present and results from a lack of complete orientation in the sample. Masetti et al.[19] have assigned IR bands at 1242, 1153, 553, and 312 cm^{-1} to the E_1 symmetry species. These bands are not observed in the room-temperature Raman spectrum of either PTFE or the TFE–HFP copolymer.

The assignment of the two Raman bands at 575 and 595 cm^{-1} has been the subject of speculation and discussion for some time.[19–21] These two bands have been observed to change their relative intensity with temperature and Boerio and Koenig (BK) have suggested that they arise from thermal defects.[20] Masetti et al., on the other hand, favor an assignment of these bands to overtones since no fundamentals are predicted in this frequency region. As can be seen from Figure 1, both band intensities are consistent with E_2 symmetry and cannot, therefore, be due to overtones as suggested by Masetti et al.[19] Since the only E_2 modes predicted[22] between 500 and 700 cm^{-1} are at 522 and 677 cm^{-1}, the shape of ω_4 and ω_5 dispersion curves in the region of 24° must be adjusted. A force field refinement incorporating the new polarization results and the oligomeric data will be discussed in section C.

Two other bands at 378 and 1215 cm^{-1} are found in the *xy* spectrum and are assigned to E_2 modes. The 378-cm^{-1} band is the lower frequency component of a doublet found in the 380-cm^{-1} region. The assignment of the lower frequency component of the 380-cm^{-1} doublet to planar zigzag segments[19] is inconsistent with the polarization results and with the observation of the doublet with approximately the same intensity ratio in the perfluoro-*n*-alkanes. An analysis of the polarization behavior of the Raman active vibrations of planar zigzag PTFE shows that the appearance of bands with only *xy* scattering intensity is incompatible with planar zigzag conformations. As the chain length decreases, for example in the perfluoro-*n*-alkane series, the occurrence of conformational defects decreases and the doublet should disappear. As can be seen in Figure 2 this is not the case even for the shortest perfluoro-*n*-alkanes investigated. The splitting of the doublet is observed to change slightly as the chain length decreases, but this reflects a slight band broadening because of the proximity of the melting point of the shorter chain oligomers to the actual temperature at which the spectra were recorded.

The observed bands, their symmetry species, calculated values, and assignments are given in Table I.

B. Raman Spectra of a Series of Perfluoro-*n*-alkanes. In Figure 3, the Raman spectra of the four perfluoro-*n*-alkanes which are solid at room temperature are compared with that of the polymer. The oligomers are isostructural with the polymer as has been discussed previously.[10] There exist several regions of the spectrum notably in the 0–250- and 700–1000-cm^{-1} range in which bands whose frequencies change with chain length, *n*, can be seen. These bands can be used to plot out portions of dispersion curves for the polymer.[13]

An analogous situation exists in the case of *n*-paraffins and

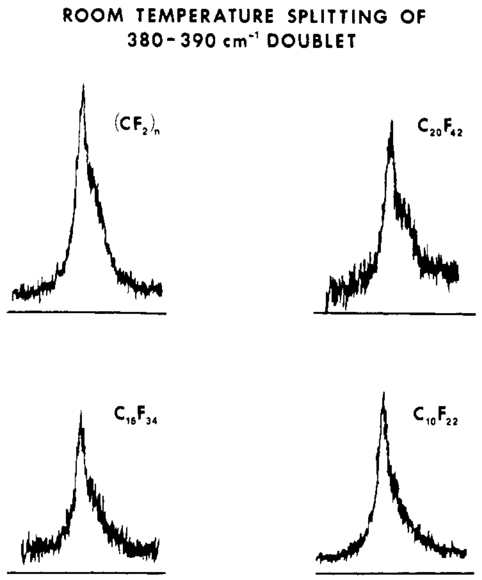

Figure 2. Room temperature Raman spectra of the 380–390-cm^{-1} doublet of selected perfluoro-*n*-alkanes and poly(tetrafluoroethylene).

Table I
Calculated and Observed Spectroscopically Active Modes of PTFE

Symmetry species	Calcd, cm^{-1}, for force field I	II	Obsd, cm^{-1} Raman	IR	Assignments
A_1	285	285			CF_2 twist
	384	386	383		CF_2 scissors
	729	730	729		Sym CF_2 stretch, CF_2 wag
	1377	1385	1377		Asym CF_2 stretch, CF_2 rock
A_2	0	0			Chain axis translation
	0	0			Chain axis rotation
	507	502		503	CF_2 wag
	614	637		638	CF_2 wag, CF_2 rock
	1211	1207		1213	CCC bend, CC stretch
E_1	0	0			Chain translations
	25	25			CCC bend, torsion
	197	207	207	203	CF_2 rock, torsion
	291	291	288	293	CF_2 twist
	315	317		312	CF_2 wag
	551	553		553	CF_2 scissors
	1155	1154		1153	Sym CF_2 stretch, CF_2 scissors
	1246	1241		1242	Asym CF_2 stretch, CF_2 rock
	1297	1296	1296	1300	CC stretch, CCC bend, CF_2 wag
E_2	14	14			Torsion
	150	150	140		CCC bend, CF_2 wag, CC stretch
	282	282			CF_2 twist
	378	380	378		CF_2 scissors
	558	560	575		CF_2 wag, CF_2 rock
	612	628	595		CF_2 rock, CF_2 wag
	752	754			Sym CF_2 stretch, CF_2 wag
	1217	1210	1215		CCC bend, CC stretch
	1370	1376			Asym CF_2 stretch, CF_2 rock

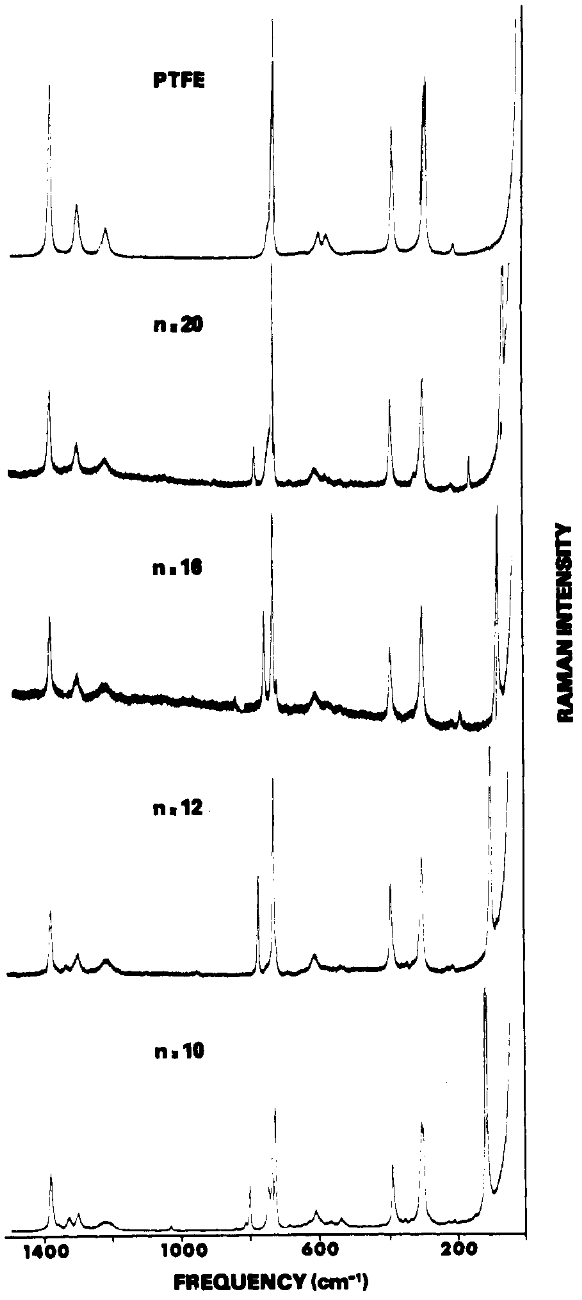

Figure 3. Room temperature unpolarized Raman spectra of perfluoro-*n*-alkanes and poly(tetrafluoroethylene).

Snyder has shown that in a simple model of a chain of identical oscillators with negligible end group effects the solution of the secular equation is a function of only one variable, ϕ, the phase difference between identical displacements in adjacent oscillators when the molecule undergoes a normal mode of vibration.[1] For a chain of N oscillators, the solutions of the secular equation correspond to discrete values of the phase difference:

$$\phi = m\pi/(N + 1) \qquad (m = 1, 2, \ldots, N)$$

Hence, in the spectrum of an oligomer, it should be possible to identify a series of bands corresponding to the same molecular motion and assign to each one a particular m value. When these bands have been assigned for a homologous series of oligomers, it is then possible to test their dependence on ϕ. A plot of frequency vs. phase angle should provide a smooth curve indicating that modes corresponding to this type of motion are a function of ϕ only. Once the actual shape of this dispersion curve is known adjustment of the force field parameters so that the calculated dispersion curves will fit the experimental data can be undertaken.[4]

This has been done for the longitudinal branch (ω_8) of

Table II
Assignment of m Values for the ω_3 Branch

	m		
n	0	2	4
20	730	744	778
18[a]	731	746	802
16	730	754	839
14[a]	732	760	888
12	734	776	941
10	735	780	1034
9	739	829	1076

[a] Data from Boerio and Koenig.[16]

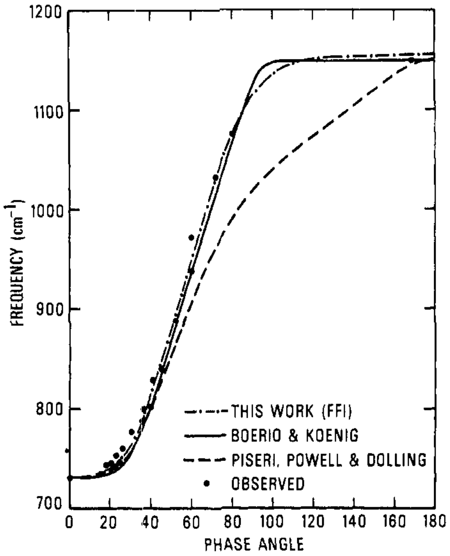

Figure 4. Experimental and theoretical ω_3 dispersion curves of poly(tetrafluoroethylene); experimental values are taken from Table II.

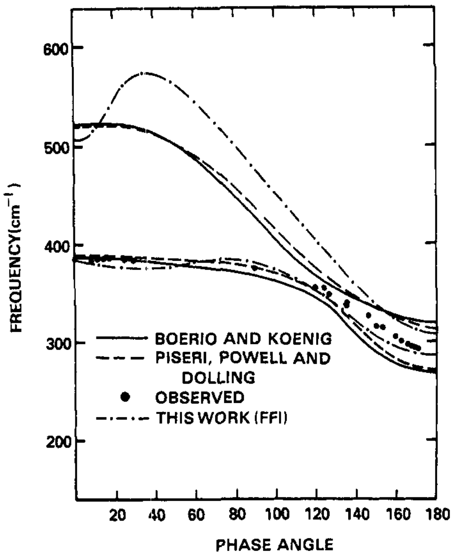

Figure 5. Experimental and theoretical ω_5 and ω_6 dispersion curves of poly(tetrafluoroethylene); experimental values are taken from Table III.

Table III
Assignment of m Values for the ω_6 Branch

			m
n[a]	1	3	5
20	292	314	340
16	294	326	355
12	296	338	
10	300	348	
9	305	355	
6[b]	315	375	

[a] Raman data from BK for n = 14 and 18 could not be used because of overlap with Rayleigh line. [b] Data of Piaggio et al.[24] on solid C_6F_{14}.

PTFE using the frequencies obtained from the low-frequency Raman spectrum of the perfluoro-n-alkanes ranging in length from 7–20 carbon atoms. The accordion-like motion of the chain associated with this branch is such that only phase values with odd values of m will give rise to a change in polarizability which is required for Raman activity. Calculated dispersion curves, using two different force fields from the literature, were then compared with the experimentally determined points.[10]

In Table II is listed a series of bands in the 700–1000-cm^{-1} region with their associated m values. In Figure 4, these experimental points have been plotted and compared to theoretical dispersion curves calculated from literature force fields and a force field determined in this work. Although previous force fields give reasonable agreement with the experimental data at phase values less than 40°, the Boerio and Koenig model[11] predicts more accurately the shape of the ω_3 branch for ϕ greater than 40°. The data points at 1153 cm^{-1} (ϕ = 168°) correspond to the E_1 IR active mode assigned by Masetti et al.[19]

Of particular interest is the ω_6 branch which is shown in Figure 5 (lower set of curves). Based on the reassignment of the 288-cm^{-1} band to an E_1 mode discussed earlier, it becomes apparent that the experimental data will not necessarily agree with the theoretical dispersion curve calculated using a force field which was refined on the assumption that the 288-cm^{-1} band exhibited A_1 symmetry. This is borne out as seen in Figure 5. Several points should be made concerning the experimental data. First of all, the observed frequencies for the perfluoro-n-alkanes listed in Table III are entirely consistent with the assignment of the 288-cm^{-1} band to E_1 symmetry. That is to say that the 288-cm^{-1} mode together with the observed perfluoro-n-alkane frequencies, with their associated m values, fall on a smooth curve. Second, the E_2 mode assigned at 378 cm^{-1} which appears in Figure 5 at 24° lies on a smooth curve passing through the points corresponding to m = 1 which have been obtained from the perfluoro-n-alkane spectra. In addition, the ϕ = 0° frequency of 383 cm^{-1} obtained from the copolymer also falls on this curve.

It is obvious that in this case there exists a large discrepancy between the theoretical dispersion curves, taken from the literature, and the experimental dispersion curves. A force field refinement taking into consideration the results of our polarization measurements and the perfluoro-n-alkane data will be presented in the next section.

As can be seen in Figure 3, there are no other regions of the perfluoro-n-alkane spectra which exhibit significant frequency dispersion with chain length. There are several Raman bands whose intensity increases with decreasing chain length. These can be attributed to end groups which increase in proportion to the CF_2 groups as the chain length decreases. In Table IV, all the observed bands for the perfluoro-n-alkanes studied are listed and assigned to their respective dispersion curves. The region below 200 cm^{-1} has been treated in detail in a previous publication.[10] Bands assignable to end group motions are designated as such in Table IV.

C. Normal Mode Calculations. Previous force fields of PTFE have been developed by Boerio and Koenig[11] from IR and Raman data using an isolated chain model and by Piseri

Table IV
Observed Raman Bands for C_nF_{2n+2} (n = 9, 10, 12, 16, 20)

C_9F_{20}	$C_{10}F_{22}$	$C_{12}F_{26}$	$C_{16}F_{34}$	$C_{20}F_{42}$	Assignment
125 vs	112 vs	96 vs	74 vs	60 vs	ω_8
	202 w	205 w	184 w	154 w	ω_8
			205 vw	207 vw	ω_8
	219 vw	220 vw	215 sh	214 sh	ω_7
295 s	295 s	296 s	294 s	292 s	ω_6
305 s	300 s				ω_6
328 vw	328 vw	323 vw			End group
355 vw	348 vw	338 vw	326 vw	314 vw	ω_6
			355 vw	340 vw	ω_6
380 s	381 s	380 s	381 s	379 s	ω_6
385 s	385 s	385 s	385 s	383 s	ω_6
536 m	533 w	533 vw	533 vw	533 vw	
560 vw	563 vw		569 vw	575 vw	
602 m	595 sh		596 sh	598 sh	ω_5, ω_4
608 m	606 m	607 m	606 m	607 m	
721 vs	723 vs	722 m	720 m	720 m	End group
739 vs	735 s	734 vs	730 vs	730 m	ω_3
750 s	745 s				End group
829 m	780 m	776 m	754 m	744 m	ω_3
848 vw					
859 vw					
1076 vw	1034 vw	941 vw	839 vw	778 w	ω_3
1213 w	1216 w	1212 w	1215 w	1217 w	ω_2
1304 w	1300 w	1300 w	1300 w	1295 w	ω_1
1325 w	1325 w		1323 vw	1323 vw	End group
		1339 vw			
1354 w	1357 w		1350 vw	1355 vw	End group
1381 s	1380 s	1378 s	1379 s	1378 s	ω_1

Table V
Force Fields of PTFE in Local Symmetry Coordinates

Force constant type[a]	Force field I		Force field II	
	Value	SD	Value	SD
022	6.31336	0.163	6.278	0.041
012	1.51277	0.08	1.51277	0.08
028	0.01202	0.08	0.0345	0.04
024	0.25478	0.068	0.25478	0.068
033	6.18405	0.082	6.18405	0.073
036	1.09245	0.034	1.2144	0.077
011	5.463	0.193	5.463	0.193
018	−0.53944	0.046	−0.53944	0.046
014	−0.0327	0.098	−0.0327	0.017
015	−0.5898	0.058	−0.5898	0.058
088	1.763	0.179	1.763	0.075
048	0.11622	0.112	0.11622	0.112
044	1.471	0.059	1.486	0.019
055	1.0658	0.041	1.0658	0.017
066	1.367	0.046	1.5296	0.024
077	1.074	0.064	1.074	0.064
099	0.05133	0.126	0.05133	0.126
136	−0.094	0.063	−0.094	0.026
111	0.1452	0.086	0.170	0.026
181	−0.0872	0.07	−0.0872	0.036
141	−0.0046	0.064	−0.0046	0.064
158	0.0473	0.064	0.022	0.022
145	−0.1184	0.063	−0.1184	0.072
155	−0.1071	0.023	−0.1207	0.009

[a] Middle and right most integers refer to local symmetry coordinates. Left most integer refers to chemical repeat unit of the second coordinate. 1, r_{cc}, 2, sym CF_2 stretch; 3, asym CF_2 stretch; 4, scissors; 5, wag; 6, rock; 7, twist; 8, CCC bend; 9, torsion.

et al.[12] from coherent inelastic neutron scattering results in addition to IR and Raman data for a hexagonal lattice model with interactions between fluorines approximated by a nonbonded potential of the exponential 6 type. The Boerio and Koenig force field has subsequently been used to calculate frequencies of PTFE in a number of chain conformations even though it was recognized that this force field is inadequate in that it produced negative eigenvalues over a small range of phase values. Furthermore, IR polarization data and investigations of crystallinity effects by Masetti et al.[19] as well as the Raman results discussed above indicate that neither force field was derived from a wholly consistent set of band assignments.

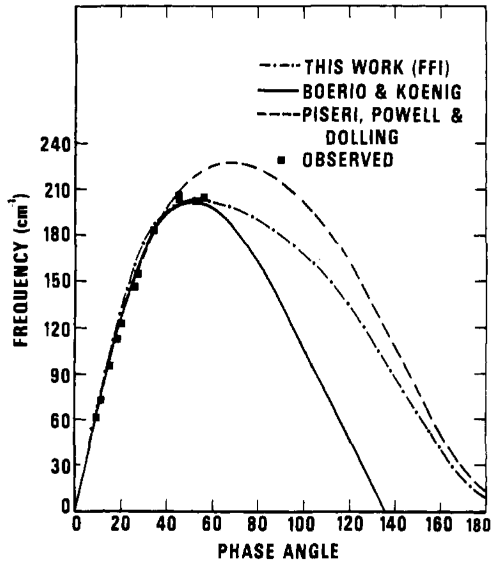

Figure 6. Experimental and theoretical longitudinal acoustic dispersion curves of poly(tetrafluoroethylene).

Piseri et al.[12] found that predicted lattice effects on the intramolecular frequencies were small, and hence we restricted our calculations to the isolated chain model. On the basis of success achieved in a previous lattice dynamical calculation of polyethylene we have used localized symmetry coordinates and thereby removed the degeneracy in the bending internal coordinates.[4] Examples of localized symmetry coordinates are fluoromethylene scissors, wag, twist, and rock. These coordinates are linear combinations of the internal bending coordinates and for the molecular geometry used in this calculation have the coefficients given in Table VI. Some simplification in refinement, by the method of least squares, could be achieved through use of localized symmetry coordinates. The description given in Table VI is for PTFE in the 15/7 helical form. The starting force field for refinement was derived by suitable transformation of the force field of Piseri et al.[12] labeled I. The 19 parameters of this field yielded a total of 28 nonzero elements in the local symmetry coordinate force field. Four of the 28 parameters could be set equal to zero without affecting the overall frequency agreement after refinement. The average frequency difference between calculated and observed values was 6 cm^{-1} for the case in which the Raman bands at 575 and 595 cm^{-1} were assigned to E_2 modes. Significantly better agreement was obtained by removing the 575 and 595 cm^{-1} pair from the refinement for which case the difference was reduced to 3.5 cm^{-1}. The final force fields for both assignment schemes are presented in Table V along with standard deviations associated with force field parameters. A comparison of calculated and experimental frequencies for each of the two force fields is given in Table I along with the assignments as determined by examination of the **J** matrix elements. In Figures 4–6 are shown comparisons of calculated dispersion curves for our force field I, the Boerio and Koenig force field,[11] and the Piseri et al. force field[12] with experimental dispersion curves. Better agreement has been achieved

Table VI
Local Symmetry Coordinate Definitions

Symmetry coordinates	Internal coordinates[a]							
	CF bond stretch	CF′ bond stretch	$\mathrm{C_-CC_+}$ angle bend	FCF′ angle bend	$\mathrm{C_-CF}$ angle bend	$\mathrm{C_-CF'}$ angle bend	$\mathrm{C_+CF}$ angle bend	$\mathrm{C_+CF'}$ angle bend
Symmetric CF_2 stretch	$2^{-1/2}$	$2^{-1/2}$						
Antisymmetric CF_2 stretch	$2^{-1/2}$	$2^{-1/2}$						
Skeletal angle bend			a	$-b$	$-c$	$-c$	$-c$	$-c$
CF_2 bend				d	$-e$	$-e$	$-e$	$-e$
CF_2 wag					f	f	$-f$	$-f$
CF_2 rock					f	$-f$	f	$-f$
CF_2 twist					f	$-f$	$-f$	f

[a] $a = -0.90469$; $b = -0.180038$; $c = -0.193082$; $d = 0.906338$; $e = 0.211277$; $f = 0.5$.

with the present force fields, including the assignments, based on Raman polarization data, for other dispersion curves.

The mode assignments for the optical points, phase angles of 0 (A_1, A_2), 24° (E_2), and 168° (E_1), are similar to those of Boerio and Koenig[11] with the reversal of the rocking and wagging modes. At 0 phase we assign wagging mode to the lower of the 503, 638 cm^{-1} pair and a combination of wagging and rocking to the higher frequency member, whereas Boerio and Koenig[11] have assigned the lower frequency member of the pair to rocking and the higher frequency member to the fluoromethylene wagging mode. The same reversal in assignments persists at the other phase values with spectroscopic activity. Our lowest frequency A_1 mode, 285 cm^{-1}, is somewhat lower than that calculated by Boerio and Koenig due to removing the need to fit the 291-cm^{-1} band to an A_1 mode. It is instructive to compare the ω_8 branch between these two calculations since with the Boerio and Koenig force field it is found that negative eigenvalues persist near the E_1 phase value, 168°, for this branch. The Piseri et al. force field I does not suffer this fate; however, from the comparisons in Figure 6, it is evident that the overall agreement is better with the present force field, especially near the peak frequencies.

Conclusions

Raman polarization measurements obtained on a highly oriented TFE–HFP copolymer monofilament indicate that some previous band assignments on PTFE must be revised. In particular, the 288-cm^{-1} band, earlier believed to belong to the A_1 symmetry species, has been reassigned to the E_1 symmetry species. In addition, several bands whose symmetry has previously been in doubt have been assigned. The current assignments have been evaluated by a normal mode calculation based on the isolated chain model. Although the agreement between the calculated E_2 modes and the observed bands at 575 and 595 cm^{-1} has been substantially improved in comparisons with previous calculations[11,12] there remains a discrepancy of 17 cm^{-1} for each frequency. The experimental results support assignment of the 575- and 595-cm^{-1} bands to E_2 symmetry and the lack of agreement with calculated values must be viewed as arising from deficiencies in the force field or isolated chain model.

In a recent paper by Chantry et al.[23] concerning assignments of low-frequency IR spectra of $C_{14}F_{30}$ and drawn PTFE, a band observed in the polymer at 312 cm^{-1} was assigned to the E_1 intersection ($\phi = 168°$) of ω_6 while that at 292 cm^{-1} is considered to arise from the activation of the 291 cm^{-1} A_1 Raman band as a result of conformational irregularity. Masetti et al.,[19] on the other hand, have assigned the 292-cm^{-1} IR band to an E_1 fundamental based on its strong perpendicular dichroism. Our polarization results suggest that the 288-cm^{-1} Raman and the 292-cm^{-1} IR bands (allowing for instrumental effects) can both be assigned to the E_1 intersection of the ω_6 branch. This would then raise the possibility that the 312-cm^{-1} IR band and the 311-cm^{-1} Raman band (observed only at low temperature in PTFE) are the E_1 intersection of the ω_5 branch. Infrared studies on the highly oriented copolymer may provide some additional information concerning this region of the spectrum.

The assignment of Raman bands in a series of isostructural perfluoro-*n*-alkanes to groups involving similar motions has been used to determine the shape of parts of the ω_3, ω_6, and ω_8 experimental dispersion curves. Comparison of these with the theoretical dispersion curves calculated for both the isolated chain approximation and in the lattice from existing force fields shows reasonable agreement for the ω_3 and ω_8 branches, but a sizable discrepancy exists for the ω_6 branch for phase values in excess of 120°. This point in conjunction with the new assignments obtained from polarization data indicated that adjustment of the existing force field parameters was warranted. Two refinements of force field parameters in local symmetry coordinate basis set were carried out. The final sets of force field parameters are given in Table V for the case (I) where the 575- and 595-cm^{-1} bands are assigned to E_2 modes and for the case (II) where these two bands are not assigned. Considerable improvement is found for ω_6 branch with both force fields.

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(25) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for this purpose.