# Vibrational spectra of crystalline polytetrafluoroethylene

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Existing literature sources on the experimental vibrational spectroscopy of polytetrafluorethylene are reviewed and new detailed evidence in this field is presented. It has been proposed elsewhere on spectroscopic grounds that a structure exists involving two chains per unit cell at low temperatures, but X-ray support for this proposal is lacking. We explore this point in detail by referring to new spectroscopic data.

## INTRODUCTION

### *Structure of polytetrafluoroethylene*

The vibrational spectrum of polytetrafluoroethylene (PTFE) has been determined by Raman spectroscopy and also by infra-red, far infra-red absorption and also inelastic neutron scattering. As we shall describe, there is no absolute agreement about the details and explanation of the spectra and this paper attempts to clarify the situation.

PTFE undergoes several phase transitions at different temperatures. The different transitions may be described by the following diagram:

$$\mathrm{Ph}_1 \xleftrightarrow{292\mathrm{K}} \mathrm{Ph}_2 \xleftrightarrow{303\mathrm{K}} \mathrm{Ph}_3 \quad \text{increasing evidence of crystalline defects}$$

In addition, several high pressure phases have been observed by Nakafuku[4] and Nicol[5].

There is wide agreement that a transition occurs at 292K between a structure for $\mathrm{Ph}_2$ with a 15/7 helix (line factor group $D_{15}$, helix angle $14\pi/15$) and for $\mathrm{Ph}_1$, a 13/6 helix (line factor group $D_{13}$, helix angle $12\pi/13$)[2]. The crystal structure of $\mathrm{Ph}_2$ is hexagonal, with $a=0.566$ nm and $c=1.95$ nm[1], but the phase is considered to be imperfectly developed, the cell contains only one chain. The morphology of the low temperature phase $\mathrm{Ph}_1$ is a little uncertain, since it has been considered to be both triclinic and monoclinic[3]. Bunn[2] favoured a hexagonal (probably triclinic) structure with $a=0.55$ nm and $c=1.68$ nm when he studied fibres. He concluded in this case that $\gamma=119.5°$. Clark[1] came to the same conclusi with $a=0.56$ nm, $c=1.69$ nm and $\gamma=119.3°$ but Kilian[6] described phase $\mathrm{Ph}_1$ as triclinic with dimensions $a=0.4882$ nm, $b=0.4875$, $c=0.51$, $\alpha=90°$m $\beta=\gamma=87°$, i.e. there is a small but significant difference between $a$ and $b$. There is some evidence to indicate that $\mathrm{Ph}_1$ contains more than one chain per unit cell, particularly at low temperatures but since there is no X-ray support for this view this point is explored below.

Since PTFE always exists, at normal pressure, in the form of a helix, an analysis of the vibrational spectrum for an isolated infinite helix would be useful in understanding the spectrum of PTFE. Such an analysis has been carried out by Higgs[11]. Boerio and Koenig[12] have also proposed a vibrational assignment. Using the latter and a damped least squares method to calculate force constants, they obtained dispersion curves for PTFE. The results obtained were found to be in good agreement with those from inelastic neutron scattering. They calculated a 19 parameter valence force field by using Raman and infra-red fundamentals and optically inactive modes determined by inelastic neutron scattering. The vibrational spectrum of PTFE has also been calculated by Zerbi and Sacchi[13], who computed vibrational frequencies using classical lattice dynamics. The calculations were first carried out assuming a perfect crystalline system. After allowing for the effects of the disorder, the calculated dispersion curves were found to be in good agreement with experimental data.

The two phases of crystalline PTFE (the 15/7 and 13/7 helices) have the following modes:

$D_{15}$–$4A_1, 3A_2, 8E_1$ and 9 each of $E_2, E_3, E_4, E_5, E_6$ and $E_7$
$D_{13}$–$4A_1, 3A_2, 8E_1$ and 9 each of $E_2, E_3, E_4, E_5$ and $E_6$.

Out of these only the modes having symmetries $A_1, A_2, E_1$ and $E_2$ are spectroscopically active. The $A$ class modes correspond to vibrations with a phase angle of zero between adjacent $\mathrm{CF}_2$ units. For $E_1$ and $E_2$ modes, the phase angles are $\psi$ and $2\psi$, respectively, where $\psi$ is the screw angle per repeat unit: for a 15/7 helix, $\psi=14\pi/15=168°$.

The phase angle for vibrations of class $E_1$ is 168° and that for $E_2$ vibrations is 336° or 24°. The $E_2$ modes have frequencies close to those of the corresponding $A_1$ modes. The four $A_1$ and nine $E_2$ modes are Raman active, whilst three $A_2$ modes are infra-red active, and the eight $E_1$ modes are infra-red and Raman active, while the nine $E_2$ modes are only Raman active.

Several investigators have recorded the spectrum of PTFE. Thus, the infra-red spectrum has been recorded by Liang and Krimm[14], the effect of pressure and tempera-

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*Table 1* Assignments of the vibrational spectrum of PTFE by: A, Boerio and Koenig[12]; B, Piseri *et al.*[20]; C, Peacock *et al.*[21]

| Branch and description | | | $A_1$ | $A_2$ | $E_2$ | $E_1$ |
|---|---|---|---|---|---|---|
| $B_1$ | $\nu_s(CF_2)$ | A | 1379 | | 1347 | 1298 |
| | | B | 1380 | – | 1384 | 1207 |
| | | C | 1381 | | 1301 | 1153 |
| $B_2$ | $\nu_{as}(CF_2)$ | A | | 1212 | 1216 | 1241 |
| | | B | – | 1450 | 1449 | 1298 |
| | | C | | 1240 | 1330 | 1217 |
| $B_3$ | $\nu(CC)$ | A | 731 | | 741 | 1150 |
| | | B | 731 | – | 741 | 1150 |
| | | C | 732 | | 743 | 932 |
| $B_4$ | $\rho(CF_2)$ | A | | 636 | 675 | 552 |
| | | B | – | 638 | 676 | 552 |
| | | C | | 638 | 678 | 576 |
| $B_5$ | $\omega(CF_2)$ | A | | 522 | 523 | 322 |
| | | B | – | 520 | 524 | 321 |
| | | C | | 516 | 449 | 551 |
| $B_6$ | $\delta(CF_2)$ | A | 387 | | 385 | 271 |
| | | B | 387 | – | 385 | 277 |
| | | C | 385 | | 401 | 277 |
| $B_7$ | $t(CF_2)$ | A | 304 | | 300 | 188 |
| | | B | 291 | – | 288 | 203 |
| | | C | 290 | | 308 | 203 |

ture on the infra-red spectra has been recorded by Brown[15] and Chantry has published several papers describing the far infra-red absorption[8-10,16]. Hathaway and Neilson[17] were the first to describe the Raman spectrum of this material whilst the Raman spectrum and its variation with temperature was studied by Boerio and Koenig[18,19]. Based on experimental evidence vibrational assignments were proposed by Piseri[20], by Peacock[21], and by Chantry[10] (for infra-red only).

The assignments proposed by Boerio[12], Piseri[20] and Peacock[21] are listed in *Table 1*, wherein it will be seen that there is reasonable agreement between theoretical predictions of frequency and experimental data*. However, some specific details of the assignment are still debatable. For instance referring to *Table 1*, the band at 385 cm$^{-1}$ has been assigned to an $E_2$ mode by Boerio and Piseri, while it has been assigned to an $A_1$ mode by Peacock *et al.* Similarly, the band at 552 cm$^{-1}$ has been assigned to a $CF_2$ rocking motion by Boerio and Piseri, while it has been attributed to a $CF_2$ wag by Peacock and there are other disagreements. These are, however, minor differences and, in general, the assignments agree well with each other and with the theoretical 'predictions'.

It also must be mentioned that the entire observed vibrational spectrum cannot be attributed to the crystalline phase exclusively, e.g. the band at 615 cm$^{-1}$ has been assigned to reversal of the helical conformation.

### *Low frequency spectrum*

As outlined above on X-ray evidence, all normal pressure phases of PTFE are thought to contain one chain per unit cell. Thus, no lattice modes are expected. The occurrence of low frequency spectral bands and the possible incidence of correlation multiplets leads to the inevitable proposition that this premise is inaccurate.

Thus, the low temperature phase is thought by Boerio and Koenig[17] to contain more than one chain per unit cell because they attribute the bands observed at 577/581, 1214/1218 and 383/389 to doublets originating in the room temperature species at 575, 1215 and 385 cm$^{-1}$, respectively. They go on to conclude that the cell at low temperatures is monoclinic but no corroborating X-ray diffraction evidence seems to exist. Chantry takes a similar view on the evidence of low frequency infra-red observations.

### *Vibrational spectra of $C_{14}F_{30}$*

In order to assist the detailed assignment of the vibrational spectrum of a polymer and particularly to evaluate the form of the dispersion curves it is traditional to study oligomers. Several have been investigated elsewhere, including $C_{10}F_{22}$, $C_{16}F_{34}$ and we discuss here the spectra of $C_{10}F_{22}$ and $C_{14}F_{30}$.

It is of value to make comparisons of vibrational behaviour only if the structure of the various oligomers and the polymer in question can be reliably described as 'identical'. This is not always the case, but fortunately $C_{14}F_{30}$ is known to be closely related to PTFE[2] and it is assumed that those used here are similar in structure to $C_{16}F_{34}$.

An oligomer chain is of finite length and hence has modes distributed at widely spaced points along the dispersion curves. Further, these modes are optically active and are, in principle, detectable as series of closely spaced bands in the vibrational spectra.

The low resolution Raman spectra of $C_{14}F_{30}$ (and several other oligomers) have been reported by Koenig and Boerio[23]. The infra-red spectrum has been recorded by Willis and the far infra-red spectrum by Chantry[24]. *Figure 1* shows the dispersion curves obtained from their data. We intend to report the vibrational spectrum of

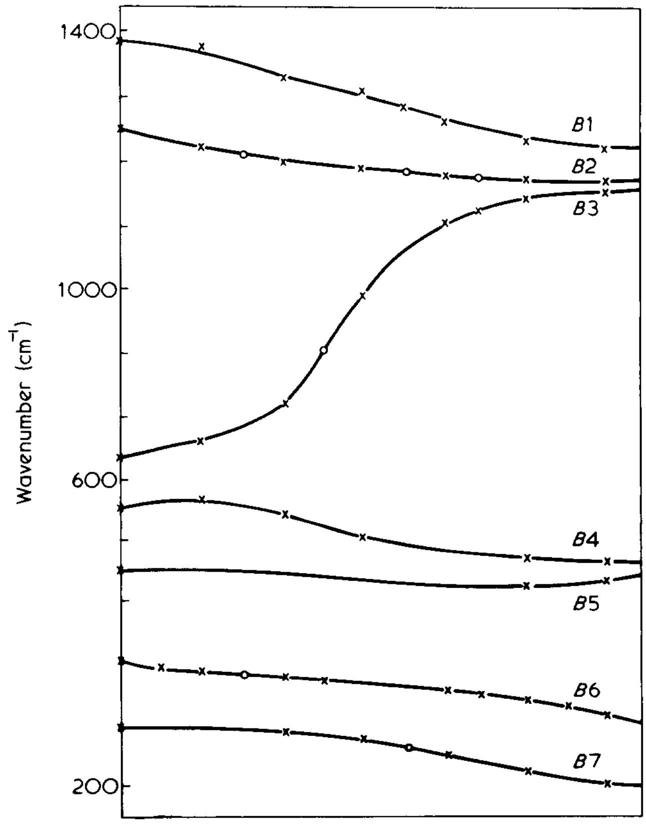

*Figure 1* Dispersion curves for $C_{14}F_{30}$

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* Assignments by Piseri[20] and Peacock[21] are based upon experimental work, while the one proposed by Boerio[12] is a theoretical prediction.

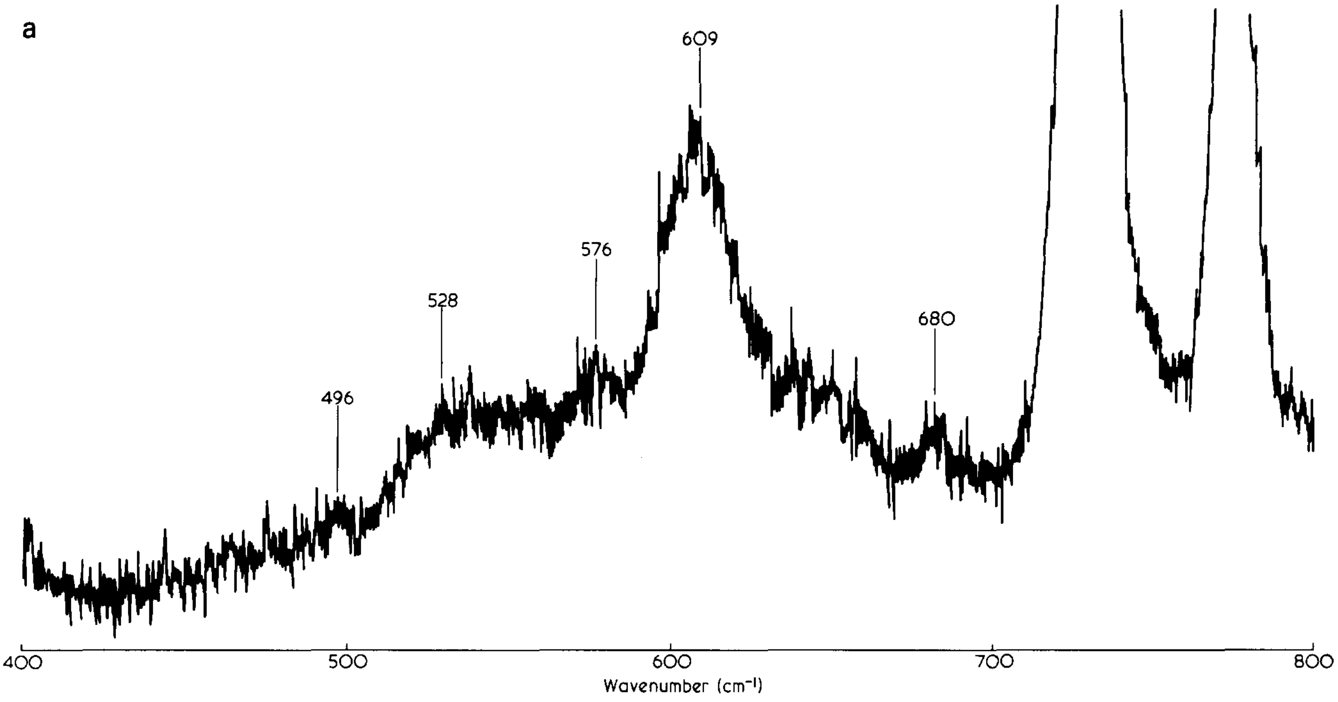

*Figure 2(a)* Raman spectrum of $C_{14}F_{30}$ at 120K

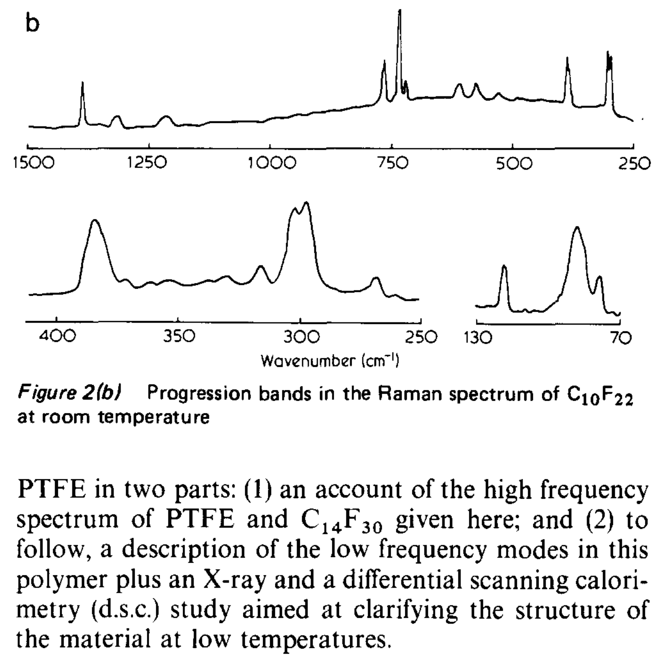

*Figure 2(b)* Progression bands in the Raman spectrum of $C_{10}F_{22}$ at room temperature

*Table 2* Progression bands of $C_{14}F_{30}$. Frequencies in $cm^{-1}$. Definitions of *B* numbers as in *Table 3*

| Branch *B*2 | | Branch *B*3 | |
|---|---|---|---|
| Raman | I.r. | Raman | I.r. |
| 1235 | 1236 | 733 | 731 |
| 1225 | 1225 | 764 | 760 |
| 1214 | | | |
| 1204 | 1205 | | 822 |
| | | 895 | |
| 1193 | 1190 | | |
| | | | 988 |
| 1182 | 1180 | | |
| 1168 | | 1101 | 1099 |
| | | | 1118 |
| | 1163 | 1134 | 1132 |
| | 1154 | | 1148 |

| Branch *B*6 | | Branch *B*7 | |
|---|---|---|---|
| Raman | I.r. | Raman | I.r. |
| 402 | 402 | | 290 |
| | 392 | | |
| 385 | 384 | | |
| 381 | | | |
| 374 | 374 | | 284 |
| | 367 | | |
| | 364 | 268 | 268 |
| 362 | 360 | 260 | |
| 355 | 353 | | 252 |
| | 349 | | |
| 334 | 336 | 226 | 226 |
| 330 | 328 | | |
| 316 | 314 | 202 | 203 |
| 298 | 300 | | |

PTFE in two parts: (1) an account of the high frequency spectrum of PTFE and $C_{14}F_{30}$ given here; and (2) to follow, a description of the low frequency modes in this polymer plus an X-ray and a differential scanning calorimetry (d.s.c.) study aimed at clarifying the structure of the material at low temperatures.

## EXPERIMENTAL

The PTFE used in these experiments was supplied by ICI Plastics Division Ltd. The Raman spectra were measured using a CODERG T 800 instrument fitted with an Ortec Brookdeal 5C1 photon counting system. A detailed description of the system is given elsewhere[25]. The sample of $C_{14}F_{30}$ was kindly supplied by Dr Chantry of the National Physical Laboratory, Teddington, Middlesex. The sample of $C_{10}F_{22}$ was purchased from Lancaster Synthesis Ltd and was purified by vacuum sublimation.

## RESULTS AND DISCUSSION

The Raman spectra of $C_{10}F_{22}$ and $C_{14}F_{30}$ are shown in *Figure 2*. The Raman spectrum of $C_{14}F_{30}$ shown here contains more detailed information than that due to Koenig. In particular, it is possible to discern several sequences of bands expected for this limited length 'polymer'. As a result, we can evaluate the precise form of the dispersion curve for this molecule (but not, of course, for PTFE). The dispersion diagram for the branches $B_2$, $B_3$, $B_6$ and $B_7$ are constructed and are shown in *Figure 1* and *Table 2*. The filled circles indicate intersections

*Table 3* Vibrational assignment of polytetrafluoroethylene on the basis of the dispersion diagrams shown in ***Figure 1.*** The values in parenthesis refer to the assignment for $C_{14}F_{30}$

| Branch and description | | $A_1$ | $A_2$ | $E_2$ | $E_1$ |
|---|---|---|---|---|---|
| $B_1$ | $\nu_s(CF_2)$ | 1382<br>(1379) | – | 1380<br>(1370) | 1213<br>(1211) |
| $B_2$ | $\nu_{as}(CF_2)$ | – | 1250<br>(1236) | 1218<br>(1227) | 1154<br>(1154) |
| $B_3$ | $\nu_s(CC)$ | 735<br>(731) | – | 746<br>(756) | 1154<br>(1148) |
| $B_4$ | $\rho(CF_2)$ | – | 642<br>(648) | 676<br>(654) | 555<br>(555) |
| $B_5$ | $\omega(CF_2)$ | – | 502<br>(550) | 524<br>(548) | 516<br>(527) |
| $B_6$ | $\delta(CF_2)$ | 395<br>(402) | – | 383<br>(384) | 312<br>(311) |
| $B_7$ | $t(CF_2)$ | 294<br>(290) | – | 294<br>(290) | 206<br>(203) |

$\nu_s(CF_2)$ = symmetric $CF_2$ stretch
$\nu_{as}(CF_2)$ = assymmetric $CF_2$ stretch
$\nu_s(CC)$ = CC stretch
$\rho(CF_2)$ = $CF_2$ rock
$\omega(CF_2)$ = $CF_2$ wag
$\delta(CF_2)$ = $CF_2$ bend
$t(CF_2)$ = $CF_2$ stretch

observed only in the Raman spectrum. The Raman data for $C_{14}F_{30}$ support the dispersion curves proposed by Chantry[24]. *Table 3* lists the full vibrational assignment of $C_{14}F_{30}$ on the basis of dispersion diagrams. *Table 3* also lists a vibrational assignment for PTFE, which is obtained by assuming that the dispersion curves for PTFE closely resemble those for $C_{14}F_{30}$. Comparing *Tables 3* and *1*, it will be seen that there are many features in common between the new assignment and those listed previously.

### *Effect of temperature on the Raman spectrum*

*Figure 3* shows the Raman spectra of PTFE at 300, 280 and 120K. There is little change in the spectrum upon cooling from 300 to 280K. However, the spectrum changes significantly upon cooling from 280 to 120K. Most of the bands are sharper and the doublets referred to by Koenig and Boerio become clearly resolved (especially at 580 and 1215 $cm^{-1}$) at 120K†. Since PTFE is known to undergo a transition $Ph_2 \rightarrow Ph_1$ when the polymer is cooled from 300 to 280K, the spectrum is surprisingly insensitive to the phase change at 292K. One possibility is that the vibrational behaviour of the two phases is similar. Another is that the transition is slow and the material studied at low temperatures is similar to $Ph_2$.

Several factors are responsible for any changes which may be observed in the vibrational spectrum as a result of the temperature change, e.g. phase changes, defect removal and band narrowing due to the changes in multiplet intensities and positions. The effect of phase change (structure of the unit cell and configuration of the helix) is considered first. To investigate the effect of these factors on the Raman spectra, a PTFE sample was stored at 256K for 3 months to facilitate the conversion to $Ph_1$ and was then quenched into liquid nitrogen before study. The Raman spectrum was recorded at 120K. For comparison purposes, another sample was kept at 280K for a long period and then quenched to 90K. The spectra of both these samples are shown in *Figure 4*. They are similar, the only prominent difference being the increase in intensities of the band pair at 580 $cm^{-1}$. Thus, if there is a phase change at or below 273K, Raman spectroscopy is insensitive to it. We also conclude that the phases $Ph_2$ and $Ph_1$ have similar spectra and, further, that the transition between the phases is relatively facile.

The lowering of temperature without phase change has several well-known vibrational phenomena associated with it.

(1) If correlation splitting occurs, the band intensity usually increases in magnitude and the splitting increases as the lattice contracts.

(2) The bands arising from excitement from already excited vibrational state (the so-called 'hot bands') are reduced in intensity. This factor is particularly important at low frequencies and results normally in the removal of a low frequency 'tail' on an otherwise symmetrical band.

(3) In fluids, band narrowing occurs when translational freedom is reduced. This is not typical of crystals. In

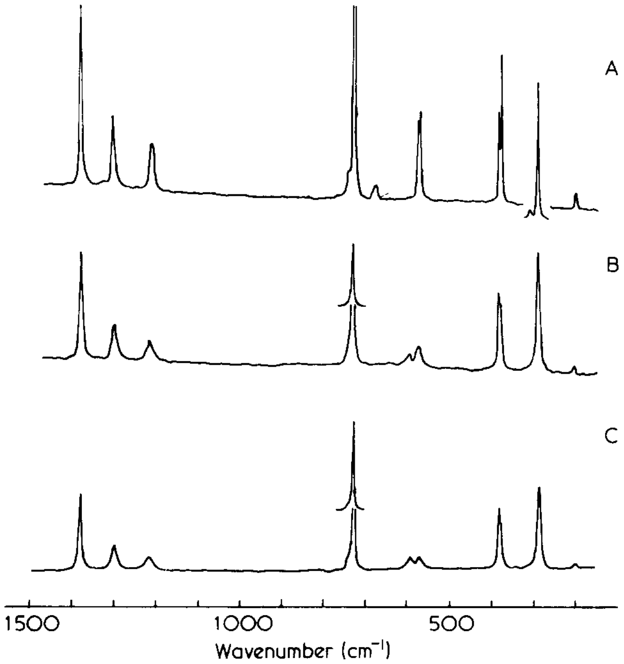

***Figure 3*** Raman spectrum of polytetrafluoroethylene at different temperatures A, 120K; B, 280K; C, 300K

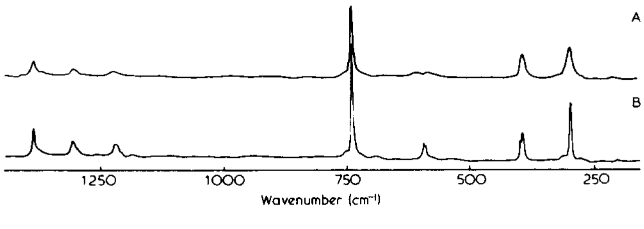

***Figure 4*** Raman spectrum of samples of polytetrafluoroethylene which has been stored at: A, 256K and B, 280K prior to quenching in liquid nitrogen. Spectra recorded at 120K

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† Also the doublet at 380 $cm^{-1}$ reverses in intensity.

paracrystalline materials such as PTFE, broad bands due to amorphous material and forming a diffuse background frequently underlying the crystalline modes can change in shape significantly. This can result in apparent narrowing of vibrational bands in crystalline polymer with temperature reduction.

Turning now to the proposition that a structure with two or more chains traversing the unit cell exists at low temperatures, we would expect in this case that lattice modes of vibration would be spectroscopically apparent. Chantry *et al.* contend that they can find such bands in the far infra-red absorption spectrum of all samples of PTFE, and particularly in those of high crystallinity. Surprisingly, we do not find supporting evidence in the Raman spectrum. Thus, it is apparent that the vibrational characteristics of this material need further study, and before a 'new' structural phase can be definitely identified, X-ray and thermal measurements must be made in parallel with the vibrational studies. The outcome of this work will be reported elsewhere.

Thus, to conclude, it is apparent that the existing descriptions of the vibrational spectrum of PTFE are correct since we have been able to corroborate them from high resolution oligomer spectra. We also conclude that to date we see little evidence in the Raman spectra to support the view porposed elsewhere that at low temperatures PTFE adopts a new crystal structure involving two or more chains per unit cell. This point deserves considerable effort and we intend to report the outcome in the near future.

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