

On the vibrational assignment problem for polytetrafluoroethylene: 1. The far infra-red spectrum

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Studies of the polarized far infra-red spectra of drawn specimens of polytetrafluoroethylene (PTFE) and of the spectrum of the oligomer $C_{14}F_{30}$ both at room and liquid nitrogen temperatures have given results which strongly confirm the general form of recently published dispersion diagrams. However the absolute values of band intensities and their variation with specimen morphology suggest that some minor changes to the optical intersections are necessary. Intensity arguments also strongly indicate that the labelling, adopted by most recent workers, for the branches *B6* and *B7* should be interchanged.

INTRODUCTION

The complexities of the macromolecular state introduce considerable difficulties into the problem of assigning the vibrational spectra of polymers. It is usually the crystalline bands which are of interest but these may be difficult to pick out from the overall spectrum which contains contributions from the amorphous (i.e. conformationally irregular) regions and from modes of the chain in the crystalline regions which are made active by imperfections. The crystalline regions themselves are usually small and assembled into spherulites, so the selection rules which would apply for an isolated macromolecule are always violated and the degree of violation will depend on the way the specimen was prepared and on its subsequent history. Both of these difficulties are encountered for polytetrafluoroethylene (PTFE), but in addition there are the complications due to the two phase transitions at 30° and 19°C. The nature of these transitions is still not fully understood, but the crystalline regions of the polymer are certainly disordered above 30°C and some measure of disorder is probably present down to 19°C. Below this temperature the unit cell changes from having just one molecular segment to having two^{1,2}. With this complexity it is not surprising that published spectra disagree with one another not only in intensities (where large discrepancies are encountered) but also in the values of the frequencies quoted.

Nevertheless considerable progress has been made in understanding the vibrational spectrum of PTFE. Several assignments²⁻⁶ have been suggested for the $k = 0$ modes, with some measure of agreement, and valence force fields have been proposed and these used to calculate the dispersion diagrams⁴⁻⁶. Some uncertainties do however remain and since these cannot be resolved without a correct assignment of the low frequency region, we have sought to provide some additional information by studying spectra of uniaxially drawn specimens and by studying the spectrum of the oligomer perfluorotetradecane ($C_{14}F_{30}$). We now report our results and discuss the light they throw on the assignment problem for PTFE.

EXPERIMENTAL

Drawn specimens were prepared as described previously⁷. The specimens of the oligomer were found to possess a high vapour pressure and it was necessary to confine them between 'Melinex'* windows in vacuum-tight cells to prevent the severe sublimation which would have occurred if unprotected specimens were placed in the evacuated specimen chamber of the interferometer. The far infra-red spectra at room and liquid nitrogen temperatures were recorded by standard methods^{7,8} and the results are shown in *Figures 1-3*. For purposes of comparison, some spectra of thermally degraded specimens were obtained using a Perkin-Elmer 580 spectrometer.

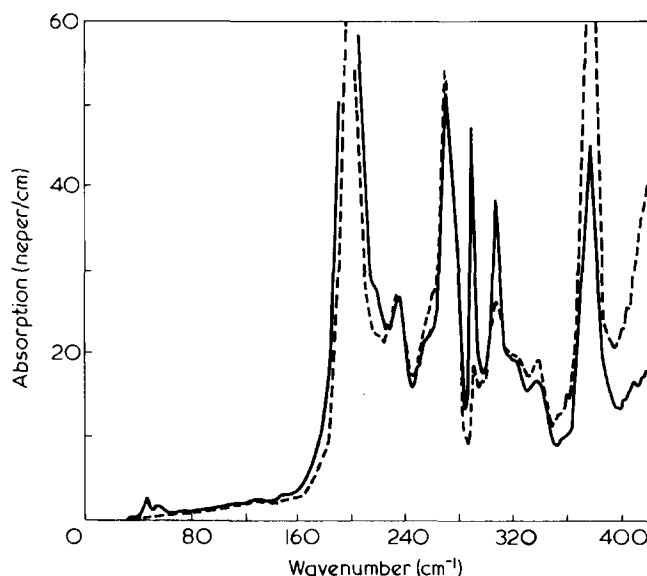


Figure 1 Spectra of a drawn specimen of PTFE at liquid nitrogen temperature observed with polarized radiation. —, Electric vector perpendicular to draw direction; ---, electric vector parallel to draw direction

* ICI trademark—a form of poly(ethylene terephthalate) film.

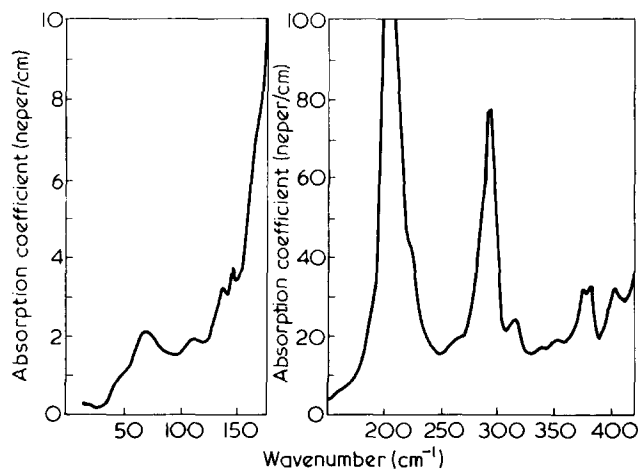


Figure 2 Room temperature spectrum of perfluorotetradecane, $C_{14}F_{30}$

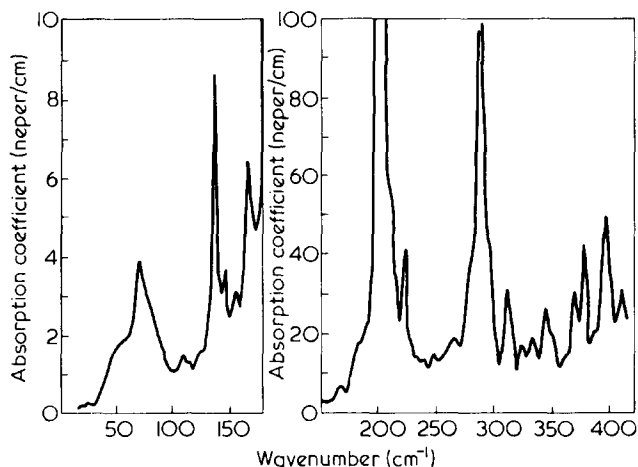


Figure 3 Liquid nitrogen temperature spectrum of $C_{14}F_{30}$

THEORY

The most suitable format for discussing the vibrations of macromolecular helices, and especially when these are to be compared with those of corresponding oligomers, is the dispersion diagram with phase angle as abscissa. The appropriate schematic diagram for isolated PTFE helices is shown in Figure 4. This diagram is constructed on the usual hypothesis that the room temperature (i.e. $T > 19^\circ C$) form has a 15_7 helix and that therefore $\phi = 168^\circ$. The selection rules are that only modes with phase angles $\theta = 0^\circ$ (A_1 , A_2), $\phi(E_1)$ and $360 - 2\phi(E_2)$, where ϕ is the geometrical helix angle are potentially active optically (i.e. in infra-red absorption or Raman scattering) so the amount of information available from vibrational spectroscopy is distinctly limited. Inelastic neutron scattering is potentially capable of exploring wide regions of the dispersion diagram and the rising part of branch B8 is well known from neutron work. In i.r. absorption, E_1 modes are perpendicularly polarized and A_2 modes are parallel polarized. A_1 and E_2 modes are forbidden in the infra-red but are potentially active in the Raman effect where the former give rise to polarized bands.

Group theoretical analysis of the helix shows that 'twisting' or 'scissors' branches will have $\theta = 0$ intersections of A_1 symmetry whereas 'rocking' or 'wagging' branches will have $\theta = 0$ intersections of A_2 symmetry. A simple geometrical picture of the origin of this can be visualized by imagining a local coordinate system x , y , z , set up and

fixed in each CF_2 group such that z is the bisector of the CF_2 angle, x is perpendicular to the CF_2 plane and y is perpendicular to z in the plane. For all helix angles except $\phi = 180^\circ$, the planes of the CF_2 groups are not perpendicular to the helix axis but nevertheless each local z -axis is. Motions of the CF_2 groups which are symmetric with respect to the local z -axis therefore give oscillating dipoles which are strictly perpendicular to the helix axis and it follows that twisting or scissors branches at $\theta = 0$ must be of A_1 symmetry since they will have no component along the direction of the helix axis. For the perfect infinite helix there will be no resultant dipole moment change perpendicular to the axis either and the mode will occur only in the Raman effect as a polarized line, but if there is any perturbation which makes the mode active, it will be observed to be polarized *perpendicular* to the helix axis. Rocking or wagging motions (i.e. motions with respect to x or y) will have components both perpendicular and parallel to the helix axis and the direction of the resulting dipole moment change will depend on the value of the phase angle θ . At $\theta = \phi$ the motion gives a purely perpendicular direction whereas at $\theta = 0$ it gives a purely parallel direction. A good example of this is provided by the branch B8. For low values of θ it corresponds to nearly pure motion along the chain axis - in fact to the propagation of sound waves along the chain; at values of θ near ϕ it corresponds to transverse motion of the helix. The direction of the resulting vector representing the motion goes smoothly therefore from pure perpendicular at $\theta = \phi$ to pure parallel at $\theta = 0$.

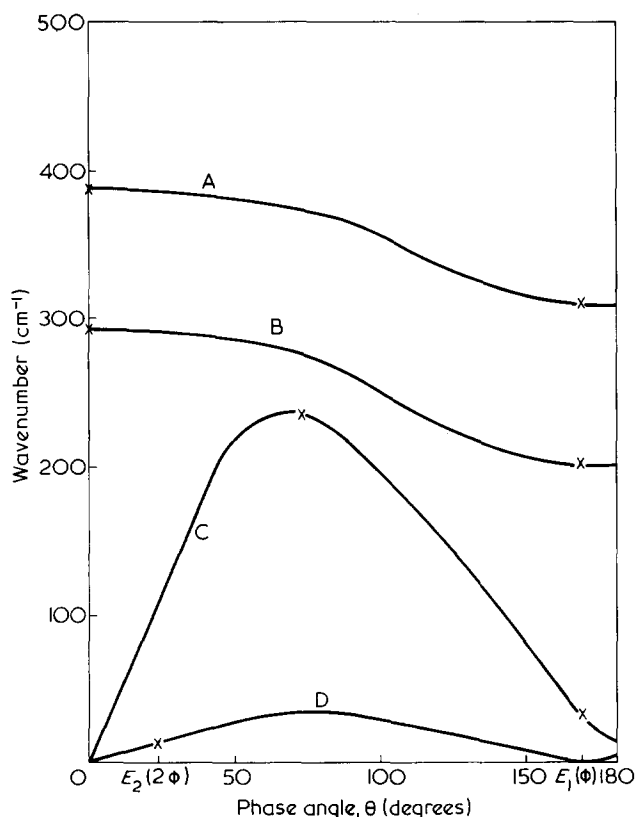


Figure 4 Schematic dispersion diagram for PTFE. Although to a certain extent hypothetical, this diagram is constrained to agree with the present assignment and to resemble as closely as possible previous diagrams, based on valence-force field calculations⁴⁻⁶. Branches: A, B6; B, B7; C, B8; D, B9

DISCUSSION*

The higher frequency range polarized spectra shown in *Figure 1* complement the lower frequency results already reported^{7,9} and also serve for comparison with results quoted by previous workers¹⁰. The extremely intense band at 203 cm^{-1} and its perpendicular polarization are both well known. The band at 292 cm^{-1} is known in the Raman effect (A_1) and we have reported its activation in the infra-red spectrum by conformational irregularity¹¹. The present specimens are sintered and the band appears as expected—its sharpness and high degree of perpendicular polarization are new observations and these confirm its assignment to the A_1 intersection of the branch $B7$ corresponding to 203 cm^{-1} which is the E_1 intersection. The band at 236 cm^{-1} is naturally assigned as the 'head' of the branch $B8$ made active by conformational irregularity and owes its intensity to the density-of-states maximum which occurs where the slope of the dispersion diagram is zero. From the arguments given earlier this line will appear unpolarized since it will have roughly equal components in each direction. The band at 277 cm^{-1} has several times been quoted as a fundamental of the crystalline regions but our earlier observations¹¹ put this in question and this together with our present observation that it is not clearly polarized either way strongly suggest that it arises in the amorphous regions. The band at 312 cm^{-1} (whose reported frequency seems to vary from specimen to specimen) has been assigned as the E_2 intersection of $B7$ but this has been criticized⁵ on the grounds that it is hard to see why the E_2 ($\theta = 24^\circ$) intersection should have a higher frequency than the A_1 ($\theta = 0$). The available information seems to be that it is a permanent feature of the spectrum of PTFE and is found even with unsintered specimens. Liang and Krimm^{10,12} observed a band at 321 cm^{-1} but no-one subsequently has observed any absorption in this region. It is plausible therefore to suggest that their band was actually at 312 cm^{-1} and to follow their suggestion that it is an E_1 fundamental. The natural assignment then is to the E_1 intersection of $B6$. The strong band near 380 cm^{-1} presents some problems. Liang and Krimm^{10,12} originally assigned it as an amorphous band but did note its parallel polarization. In the Raman effect a polarized line at 389 cm^{-1} is known, which splits¹ into a doublet, at low temperatures, with components at 383 and 389 cm^{-1} . It is not easy to see how the Raman polarization data can be reconciled with the parallel polarization observed in the infra-red spectrum. Piseri and his colleagues⁵ have suggested that the effects of interchain forces could lead to the intersection E_6 (at $\theta = 72^\circ$) becoming active and have calculated that there could therefore be an A_2 mode at 384 cm^{-1} , the intersection with $B6$. However $B6$ appears to involve inherently small dipole moment changes and one could not assume plausibly that more than a small part of the observed intensity comes from this cause. The band at 384 cm^{-1} does however increase markedly in intensity upon sintering and studies of specimens which have received various types of thermal treatment (varying time at various temperatures) show that its intensity is always proportional to that of

the band at 277 cm^{-1} . It is reasonable therefore to assume that both of these bands arise in a common environment and that this common environment is not the crystalline part of the material. The Raman data is best interpreted as meaning that the A_1 intersection of $B6$ does lie near 383 cm^{-1} and therefore we are postulating a coincidence between a non-crystalline band (seen in the i.r. spectrum) with a crystalline band or bands seen in the Raman spectrum. This is not an unreasonable postulate because Raman intensities do not usually vary inherently over wide ranges so the strong bands observed in the Raman spectrum of a highly crystalline specimen must arise in the crystalline regions. In the infra-red on the other hand, intensities can vary over huge limits and a 1% component could easily give lines more intense than some of the lines of the other 99%. The parallel polarization of the 384 cm^{-1} band in the infra-red could be explained if it is assumed that the band arises in the chain-folds since a transition moment locally perpendicular in the fold would have a strong component in the draw direction (that is the direction of the helix axes in the crystalline regions). If this is correct then there is a strong inference that the 277 cm^{-1} band arises in the chain-folds too. This is supported by careful measurements which have shown that 277 cm^{-1} is likewise polarized parallel, albeit slightly. Nevertheless one must be careful not to take this argument too far for one cannot exclude the possibility that both bands have contributions from both the amorphous (i.e. interlamellar non-helical material) and the chain-fold (i.e. lamellar edge) regions.

The suggested assignments are gathered together in *Figure 4* which is schematic but constrained to be as similar to previously published dispersion diagrams as is possible bearing in mind the revisions. These revisions are however relatively minor and one would not expect them to introduce major changes into the force field. The weak bands at 320 and 342 cm^{-1} are probably the E_5 ($\theta = 120^\circ$) and the E_3 ($\theta = 144^\circ$) intersections of $B6$ made active by conformational irregularity or interchain forces.

We now turn to consider the spectrum of $C_{14}F_{30}$. This substance belongs to the class of materials often called 'plastic' crystals though that term is best avoided in discussions ranging over polymer physics! These substances condense to the solid state with a very small change in entropy and are therefore highly disordered. They undergo one or more solid state transitions at the lowest of which there is a large entropy change and the material becomes ordered. At room temperature, X-ray studies have revealed¹³, through the absence of the layer lines, that the material is very disordered, probably having random degrees of lateral slip between the molecules. There is some evidence that the molecules are helical and, since it is usually assumed that PTFE itself departs from the planar zig-zag configuration because of steric forces, we will assume a helical conformation for the molecule. This is supported by the work of Bunn and Howells¹⁴ who found that $C_{16}F_{34}$ was helical with almost the same conformation as PTFE.

The room temperature spectrum of $C_{14}F_{30}$ is shown in *Figure 2* and the liquid nitrogen temperature spectrum in *Figure 3*. The former may be compared with the Raman spectrum determined by Koenig and Boerio¹⁵. The room temperature bands are very broad, doubtless due to the disorder, but the bands at 203 cm^{-1} and 290 cm^{-1} are well worthy of comment. The analogies with the bands at 203 cm^{-1} and 292 cm^{-1} in PTFE are very striking. At liquid nitrogen temperature which is, apparently, below the final

* Bulk PTFE by analogy with the fibrous form¹³, is commonly assumed to adopt the 13_6 helix form at temperatures below 19°C . However there is little spectral evidence to confirm this and even if it is so, the effect on the spectrum will be small. We have therefore chosen to continue to use the concepts appropriate to a 15_7 helix in the analysis of low temperature spectra since this makes intercomparison very much easier.

Table 1 Low temperature far infra-red spectrum of $C_{14}F_{30}$

Wavenumber (cm ⁻¹)	Intensity	θ (n)*	Branch
25	vw broad	180 (13)	B8
54	w broad	166.2 (12)	B8
69	m broad	13.8 (1)	B8
83	w broad	152.3 (11)	B8
110	vw —	138.5 (10)	B8
114	vvw —	?	?
124	vw —	?	?
136	s sharp	27.7 (2)	B8
145	w sharp	124.6 (9)	B8
153	vw broad	?	?
168	s broad	110.8 (8)	B8
184	w shoulder	96.9 (7)	B8
190	w shoulder	41.5 (3)	B8
203	vvvs sharp	166.2 (12)	B7
214	m shoulder	83.1 (6)	B8
226	vs sharp	69.2 (5), 55.3 (4) also 138.5 (10)	B8 B7
252	s broad	110.8 (8)	B7
268	s broad	83.1 (6)	B7
284	vs shoulder	55.3 (4)	B7
290	vvs sharp	27.7 (2), 0 (0)	B7
300	vs shoulder	180 (13)	B6
314	vs sharp	166.2 (12)	B6
328	m broad	152.3 (11)	B6
336	m broad	138.5 (10)	B6
349	s sharp	124.6 (9)	B6
353	m shoulder	110.8 (8)	B6
367	w —	69.2 (5)	B6
374	vs sharp	55.3 (4)	B6
384	vs shoulder	27.7 (2)	B6
392	w —	13.8 (1)	B6
402	vs sharp	0 (0)	B6
416	s sharp		B6

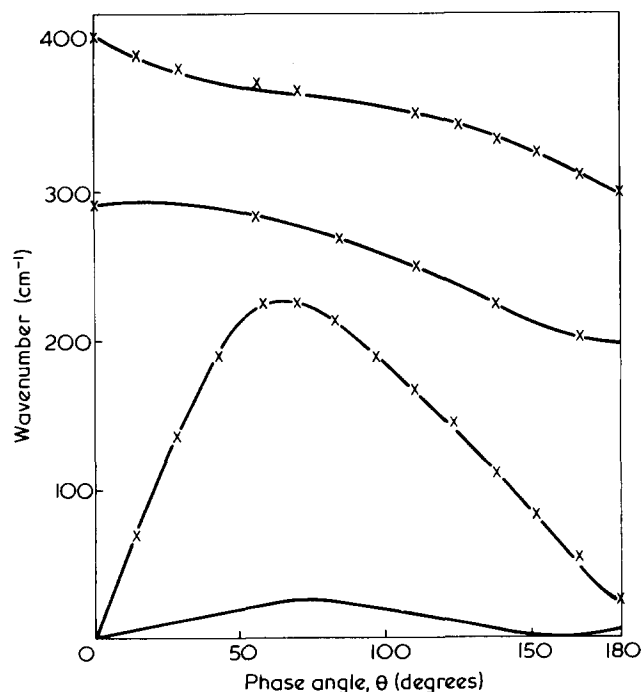
* $n\pi/13 = \theta$ 

Figure 5 Observed bands for $C_{14}F_{30}$ at low temperature presented in the form of a suggested dispersion diagram. The lowest branch is purely tentative since no intersections have been observed for certain

transition temperature, the lines are sharp and very many more have made their appearance. They are listed in Table 1. The simplest interpretation of this observation is that to a first approximation, $C_{14}F_{30}$ being a finite molecule has its normal

mode frequencies distributed, like beads on a string, along the dispersion curves for the infinite molecule PTFE. Secondly, and this is not an approximation, all the normal modes are potentially infra-red and Raman active though the larger the oligomer is, the more closely are the selection rules for PTFE observed. Making finally, by analogy with the low temperature forms of PTFE and $C_{16}F_{34}$, the simplest assumption that the helix angle in $C_{14}F_{30}$ is such that looking along the chain the first and final carbon atoms eclipse (i.e. $\phi = 12\pi/13$), one predicts the spectrum. Using this predicted spectrum as a guide one adjusts slightly the dispersion curves to give the best fit. The results of this procedure are shown in Figure 5. It will be noted from this Figure that observed intersections occur not only for $\theta = 12\pi/13$ (and its folded successors) but also for $\theta = n\pi/13$. This phenomenon is in principle also possible in the extended helix of PTFE if interchain forces are significant. For the finite helical molecule belonging to point group C_2 it has its origin in the restriction imposed by dynamics, that the terminal atoms must vibrate either in phase or out of phase.

It will be seen that all the observed bands for $C_{14}F_{30}$ fall onto branches which look remarkably like those of PTFE. In general the intersections which correspond to allowed transitions in PTFE are strongest and those which arise from the series based on $2\pi/13$ are stronger than those based on $\pi/13$. There is no possibility of there being a branch connecting the 292 cm^{-1} intersection with the 314 cm^{-1} intersection and by inference one can assume that such a branch does not occur for PTFE either. Thus Piseri's conclusion that the strong neutron interaction at 300 cm^{-1} and for high β -values does not arise from a branch of the isolated helix is supported.

CONCLUSION

Our new results support the general shapes for the lowest four branches of PTFE deduced by earlier workers. However we prefer to assign the E_1 intersection of B6 to the weak band at 312 cm^{-1} , rather than to the band at 277 cm^{-1} which is almost certainly an amorphous band. With this revision one has the situation that B7 clearly involves large changes of dipole moment whereas B6 involves very small changes. Recent workers have tended to assign these to the twisting and scissors motions respectively, basing their conclusions solely on frequency arguments. However this assignment cannot possibly be reconciled with the observed intensities, after all 203 cm^{-1} is one of the strongest known polymer bands, so we prefer to relabel the branches so that B7 becomes the scissors branch and B6 the twisting branch. Since the branches are nearly parallel (Figure 4) this relabelling will merely involve a readjustment of the force constants. Some reassignments at higher frequencies may prove necessary and these may serve to remove some of the anomalies in published values for the force constants.

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