Conformational Order and Disorder in Poly(tetrafluoroethylene) from the Infrared Spectrum

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ABSTRACT: In this paper (paper II) a new set of experimental data on the infrared spectrum of poly(tetrafluoroethylene) is presented and discussed in order to verify or disprove the theoretical predictions presented in the preceding work (paper I). Samples of different origin have been analyzed under various experimental conditions. Absorptions from ordered and disordered regions of the material have been located. New bands have been observed in the low-frequency region and the assignment of the low-frequency fundamentals has been modified. Absorptions due to geometries different from the most stable $D_{14\pi/15}$ chain have been located suggesting the existence of defects or segments of chain with planar-zigzag conformation. More coiled chains are also likely to occur. A comprehensive and critical discussion is presented of the presently available experimental data from the vibrational spectrum of poly(tetrafluoroethylene) (including the Raman and the far-infrared spectrum). The structural implications are analyzed.

The infrared spectrum of poly(tetrafluoroethylene) (PTFE) has been the subject of several investigations in the past.[1-3] For a short detailed review of the main results of these studies we refer to the preceding paper (paper I).[4] With the availability of laser sources much more attention has been focussed in the last years at the Raman scattering properties of this polymer. Two groups of workers[5-8] have recently reported on the Raman laser spectrum of PTFE and have independently proposed an assignment of several infrared and Raman bands to fundamental modes of the PTFE chain taken as isolated. In such an analysis they used the infrared data taken from previous authors. Even if the agreement in the conclusions of these two groups of authors is rather good, there is still some uncertainty in the interpretation of several spectral features both in the Raman and the infrared spectra. The room-temperature transition of PTFE is likely to be the reason of this uncertainty; namely, the experimental data may originate from the two structures stable above and below 19°, respectively. Moreover other structures are also likely to occur. For a comprehensive review of the nature of this transition, see paper I. In paper I the density of vibrational states $g(\omega)$ and $k = 0$ phonon frequencies have been calculated for several geometrical models of PTFE which should be the most stable ones on the basis of theoretical considerations.[9] Similar calculations have been carried out on polymer chains containing randomly distributed conformational defects. Conclusions have been derived on the main changes which should be observed in the vibrational spectrum of PTFE when either particular chain geometries or conformational defects occur in a real sample. In this paper we report on new experimental results on the infrared absorption spectrum of PTFE. The purpose of the present work is twofold: (i) verify the validity of the force field adopted in the calculations, (ii) collect experimental data in order to verify or disprove the theoretical predictions regarding the existence of geometrical defects and their effect on the spectrum as discussed in paper I.

Experimental Section

The infrared spectra were obtained with a Perkin-Elmer Model 180 (4000–180 cm^{-1}) and a Hitachi Perkin-Elmer Model Fis-3 (400–30 cm^{-1}) grating spectrophotometers. The polymer as powder was studied either as a suspension in Nujol and in KBr or CsI matrix for the 4000–400 cm^{-1} range, or by pressing it at room temperature into films of the desired thickness (400–30 cm^{-1}). Commercial samples of PTFE of various origins were purchased in the form of films and plates and directly analyzed. For the dichroic measurements only commercial products were employed which, after orientation induced by drawing at room temperature, were analyzed under tension. In order to reduce the effect of the polarizing properties of the gratings the specimens were positioned with their stretching direction at 45° with respect to the monochromator slits. A wire grid polarizer in the common beam of both spectrophotometers was used. Rotation of ±45° was allowed to obtain spectra with light polarized parallel and perpendicular to the drawing direction. The first set of low-temperature measurements was obtained by placing the specimen in a conventional, commercially available, low-temperature cell using liquid nitrogen as refrigerant. Still lower temperatures were reached by employing a helium Cryo-Tip refrigerator Model AC-3L. With this device spectra near the liquid hydrogen temperature were obtained. The determination of the true temperature of very thin films of polymer turned out to be a rather difficult task. While this fact is not particularly important when experiments are carried out at low temperatures with any of the cryostats used, much more careful attention had to be payed when the temperature had to be slowly and gradually changed just below the room temperature. Since experiments in this temperature range are particularly meaningful, attempts were made to reach good and reliable reproducibility. In order to avoid any possible temperature gradient across the sample, a device was realized in which the sample was immersed in a stream of nitrogen gas cooled at the desired temperature. In such a case the junction of the thermocouple was in contact with the gas stream flowing near the sample and the indicated value was assumed to represent the "true" temperature of the sample. For thicker samples the cold junction of the thermocouple was inserted in a hole drilled in the polymer and no serious problems were encountered in the measure of the temperature. For the high-temperature measurements an electrically heated furnace, which was built in our laboratory, was employed. The sample, clamped between cesium iodide plates, was heated at temperatures as high as 400°. In this case the junction of the thermocouple was inserted in a hole drilled in one of the CsI plates.

Results and Discussion

It is known that PTFE in the form of fine microcrystalline powder shows some differences in its optical,[10] mechanical,[11] and magnetic[12] properties when compared

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(1) C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **25**, 563 (1956).

(2) R. E. Moynihan, *J. Amer. Chem. Soc.*, **81**, 1045 (1959).

(3) R. G. Brown, *J. Chem. Phys.* **40**, 2900 (1964).

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(10) C. A. Sperati and H. W. Starkweather, Jr., *Fortschr. Hochpolym. Forsch.*, **2**, 465 (1961).

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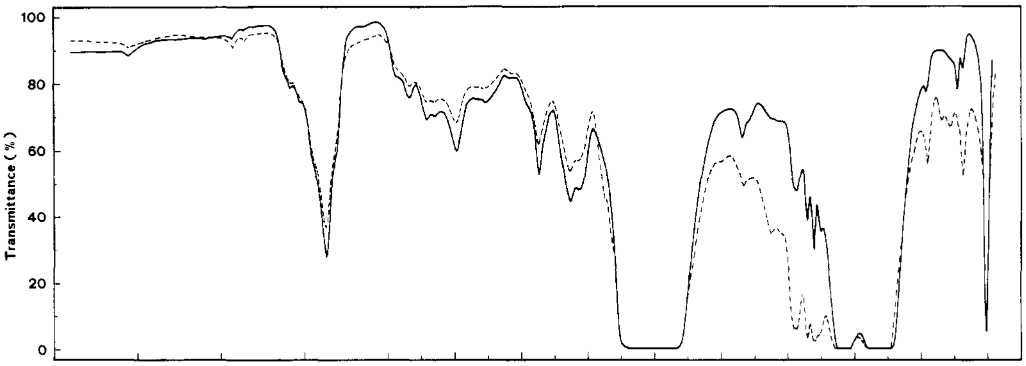

Figure 1. Infrared absorption spectrum from 4000 to 190 cm^{-1} of PTFE, 25-mm diameter disk: (——) powder, 140 mg; (- - -) commercial film, 115 mg.

with commercial products of the same chemical nature. This fact has been ascribed to a possible lowering of crystallinity which should occur when the original polymer is subjected to very high temperatures in all technological processes which yield commercial articles. By comparing spectroscopic and density data, Moynihan[2] has suggested that the ratio of the infrared absorption intensities at 778 and 2367 cm^{-1} could be taken as a relative measure of the degree of crystallinity of the polymer. Such a method has been and is presently used in many laboratories in order to determine the relative content of the crystalline phase in PTFE samples. Since the present work deals with the interpretation of particular features in the infrared spectrum of PTFE which might be correlated to specific conformational defects, as suggested by theory,[4] it has been thought necessary to examine several specimens of polymer of different origin and having different thermal and mechanical history. In addition to powderlike polymerized material, several commercial PTFE films were then studied. The latter had been obtained either by compressing rhe powder at high temperatures from an aqueous suspension or through a skiving process from polymer moldings of cylindrical shape.

The infrared spectra of all commercial products were nearly identical independently of their origin; little differences were observed only in very minor absorption features which can confidently be attributed to different technological production processes. On the contrary, the spectrum of the powder shows peculiar features in frequency as well in intensity when compared with that of commercial films (Figure 1). Moreover the observed spectral differences tend to cancel out when the powder is heated above the softening point and then reanalyzed after cooling at room temperature. If the method of Moynihan is adopted, for the time being, the intensities of the bands near 780 cm^{-1} (Figure 1) seem to indicate that the PTFE powder is much more crystalline than the commercial product as film.

In the discussion of the experimental results reference will be made constantly to paper I and particularly to Figure 4 of paper I which correlates the calculated fundamental frequencies for several chain geometries which have been considered to be the most probable ones on the basis of theoretical considerations.

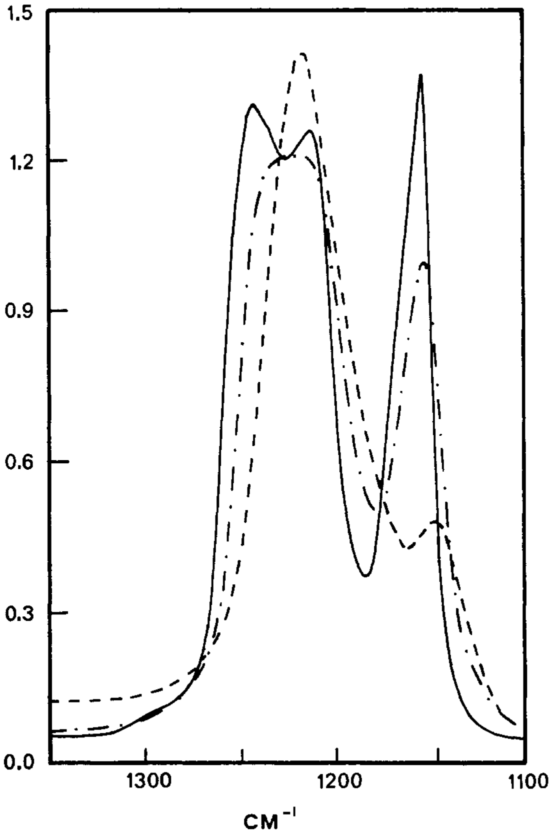

Figure 2. Infrared absorption spectrum from 1350 to 1100 cm^{-1} of powder of PTFE in KBr matrix at different temperatures: (——) room temperature; (-·-·-·) 320°; (- - -) 395°.

1400-1100-cm^{-1} Region. The infrared spectrum of PTFE in the 1400-1100-cm^{-1} range has received relatively little attention in the past, mainly because of the very strong absorption intensity. Very thin films of polymer ($\sim$0.003 mm), now commercially available, should allow an easier study of the fundamentals in this region. This is only partly true since several difficulties are encountered when dichroic measurements are performed if perpendicular illumination of oriented samples is used. It follows that an unequivocal assignment of the only one theoretically predicted parallel fundamental in this region is not yet possible on an experimental basis only. It has been reported by Moynihan[2] that the absorption pattern between 1300 and 1100 cm^{-1} depends on the nature of the sample. In addition to the always occurring band at 1152 cm^{-1}, Moynihan finds two strong absorption maxima at 1242 and 1213 cm^{-1} in the spectra obtained by pressing a fine powder of PTFE in KBr; he finds instead one band at 1212 cm^{-1} when reflection techniques are used and when thin oriented films are studied under parallel polarized radiation, and only one band at 1225 cm^{-1} with diluted water dispersions. Moynihan suggests that

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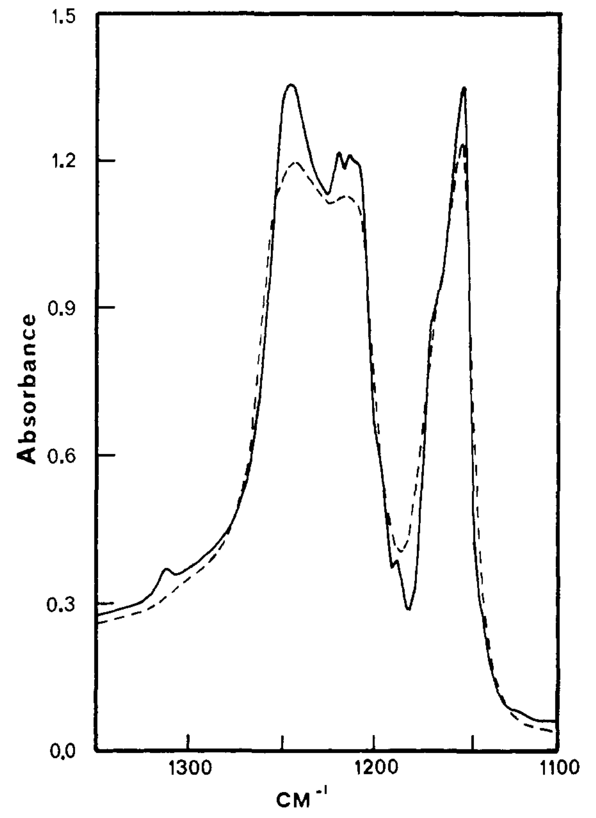

Figure 3. Low-temperature infrared absorption spectrum from 1350 to 1100 cm^{-1} of powder of PTFE in CsI matrix: (- - -) room temperature; (——) −190°.

strong reflection maxima in this region somehow affect the experimental results on thin films. We agree on these results; in addition we find that the intensity reproducibility for the 1242-1213-cm^{-1} doublet of powder in KBr matrix is rather poor.

Current assignments[2,7] based on $D_{14\pi/15}$ or $D_{12\pi/13}$ line group (hereafter referred to as models D_{15} and D_{13}) associate the bands at 1242 and 1152 cm^{-1} with $k = 0$ phonon of E_1 species on the basis of dichroic measurements, the band at 1213 cm^{-1} with an optical A_2 phonon mainly on the basis of the dichroic properties of its two phonon transitions. Based on several coincidences with the Raman spectrum and other considerations, Peacock *et al.*[8] have recently inverted the assignment of the 1242- and 1213-cm^{-1} bands (1242 cm^{-1} → A_2; 1213 cm^{-1} → E_1). Figure 2 shows the infrared spectrum from 1350 to 1100 cm^{-1} of PTFE powder in KBr matrix at several temperatures. In addition to the very weak, ill-defined band near 1300 cm^{-1} three well-resolved absorption maxima are observed at 1242, 1213, and 1154 cm^{-1} at room temperature. Whereas the lowest frequency peak is sharp but clearly asymmetric at higher frequencies the maxima at 1242 and 1213 cm^{-1} strongly overlap and are broad thus suggesting they represent an envelope of many transitions arising from C-F bond embedded in various structural environments. These structural features might well originate from regions of conformationally disordered chains in the polymer. It is then possible to postulate that even in the "highly crystalline" PTFE powder such disordered regions occur. At higher temperatures remarkable changes are observed in the same spectral range (Figure 2). When the temperature rises, the two distinct peaks at 1242 and 1213 cm^{-1} disappear into a broad absorption at about 1225 cm^{-1}. A nonnegligible lowering of the intensity at 1300 and 1154 cm^{-1} is also observed. At temperatures above the softening point (327°) of the polymer a much more well-defined absorption maximum appears at 1217 cm^{-1}, the intensity of the 1154-cm^{-1} peak is very reduced and the feature at 1300 cm^{-1} cancels out completely. Furthermore the overall absorption pattern is generally slightly shifted toward lower frequencies. The reversibility of this spectral behavior was carefully tested. Starting from the melt upon cooling the band at 1300 cm^{-1} is again found, and the intensity change near 1150 cm^{-1} and the broadening of the band at about 1225 cm^{-1} are again observed. The splitting of the broad 1225-cm^{-1} band into 1242-1213-cm^{-1} doublet and the asymmetry of the 1150-cm^{-1} band are not reobserved by cooling. It can then be concluded that the powder contains peculiar structural characteristics which cannot be regenerated by cooling a fused sample, if cooling rates as high as 2°/min are employed. For sake of completeness low-temperature measurements have been performed also (Figure 3). A number of details are better resolved at low temperatures even if no dramatic changes are observed in the overall absorption pattern. Of particular interest are: (i) the frequency shift toward higher frequencies (1312 cm^{-1}) of the highest frequency band and (ii) the splitting in at least two components of the 1213-cm^{-1} peak. The same behavior has been reported recently in the low-temperature Raman spectrum of PTFE[8,13]. A complete reversibility has been observed in these experiments.

As given in Figure 4 of paper I, four infrared active fundamentals are expected in this spectral range for the polymer chain containing 15 CF_2 groups in the repeat unit. The calculated values are 1298 (E_1), 1241 (E_1), 1213 (A_2), and 1150 (E_1) cm^{-1}.

First the experimental weak band at about 1300 cm^{-1} is assigned to an E_1 optical phonon for the following reasons: (a) it coincides with a well-defined Raman band for a sample at room temperature; (b) this coincidence is even more evident if one considers the behavior at low temperatures—both bands shift to higher frequency, namely, from 1300 to 1308 cm^{-1} at −150° in the Raman[8] and from 1300 to 1312 cm^{-1} at −190° in the infrared; (c) the infrared band is clearly perpendicular as found by dichroic measurements on oriented films. The very low infrared intensity of this band is reasonably accounted for by the fact that a small transition moment is probably associated to this phonon. In fact in the case of the planar-zigzag model such a mode belongs to the B_{1g} infrared inactive species: the very small geometrical change associated to the coiling of the chain from the planar to a D_{13} or D_{15} model generates a very small dipole moment change.

The three main absorptions at 1242, 1213, and 1154 cm^{-1} should be distributed among the ir active A_2 (parallel) and E_1 (perpendicular) optical phonons. Several criteria have guided the authors in proposing an assignment of these bands in the past. We wish to discuss our viewpoint based on our experiments. From Table II of paper I four spectroscopically active vibrations are predicted by calculations in the 1250-1140-cm^{-1} range: two ir Raman coincidences, corresponding to E_1 species, are expected at about 1240 and 1150 cm^{-1}. Failure in observing these frequencies in the Raman is accounted for possibly by considering that such vibrations are Raman inactive for the planar-zigzag model. As discussed before it is then expected that the Raman transition moment of these two modes should be very small for the D_{13} or D_{15} helical chain. The two other frequencies in this range are predicted to be very close, namely, one E_2 mode (Raman active

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[13] F. J. Boerio and J. L. Koenig, *J. Chem. Phys.*, 54, 3667 (1971).

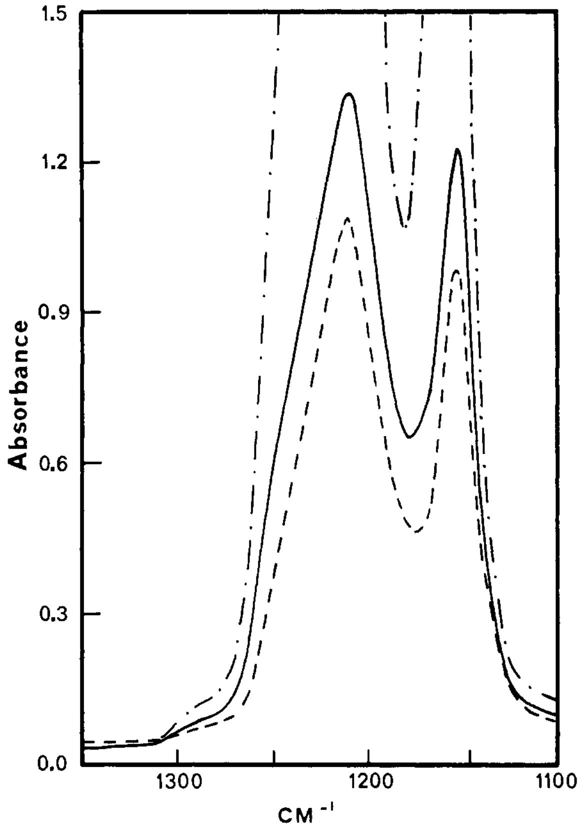

Figure 4. Infrared absorption spectrum from 1350 to 1100 cm^{-1} of an oriented commercial film of PTFE: (——) unpolarized radiation; (- - -) radiation with electric vector polarized parallel to stretching direction; (······) radiation with electric vector polarized prependicular to stretching direction.

only) is expected at 1217 cm^{-1}, one A_2 (ir active only) at 1213 cm^{-1}. Preliminary results obtained in our laboratory by Raman scattering experiments on PTFE oriented fibers seem to confirm the assignment of the 1217-cm^{-1} frequency to an E_2 fundamental, hence we do not consider the 1217- (Raman) and 1213-cm^{-1} (ir) bands as coincidents.

For the experimental verification of the symmetry of the modes in this frequency range, we resort to dichroic measurements (Figure 4). The spectrum of the oriented film in unpolarized light differs sensibly from that of the powder at room temperature. Only two intense maxima are found at 1210 and 1153 cm^{-1}, whereas a very weak unresolved prominence is observed near 1250 cm^{-1}; moreover, the asymmetry of the 1153-cm^{-1} band has nearly disappeared in the commercial product. Surprisingly this spectrum is rather similar to that of the powder at temperatures above the softening point. While the overall absorption intensity is clearly reduced under parallel light the intensity under perpendicular illumination is so strong that the absorption maxima cannot be observed directly. The weak feature at about 1250 cm^{-1} appears to be a little more pronounced in the unpolarized spectrum when compared with the parallel spectrum. The 1153-cm^{-1} peak, which occurs both in the original and in the commercial polymer at nearly the same frequency, is definitely assigned by us to an E_1 perpendicular infrared active $k = 0$ phonon, in agreement with the reported calculated data. The assignment of the two remaining E_1 and A_2 $k = 0$ phonon is not so unequivocal and is rather difficult. A suggestion for the resolution of this uncertainty comes from the spectrum of the powder at different temperatures (Figure 2). From Figure 2 and from the previous discussion it becomes apparent that the possible existence of geometrical disorder affects more the band at 1213 cm^{-1} than the band at 1242 cm^{-1}. An unequivocal perpendicular dichroism is observed in the 1250–1180-cm^{-1} range with a very pronounced enhancement near 1240 cm^{-1}. We failed instead to observe any parallel band in this frequency range. The band at 1242 cm^{-1} of the powder is reasonably taken as originating from the E_1 mode. There is then no other choice for the A_2 mode which necessarily has to be associated with the 1213-cm^{-1} band of the powder. Failure in observing a parallel band may be due to the following reasons: (i) the band is intrinsically weak since it originates from a B_{3g} infrared inactive mode of the planar-zigzag chain; (ii) the sample for dichroic measurements is a commercial film obtained after the substance has been heated to high temperatures above the softening point. From Figure 2 at such a temperature a peak develops at 1217 cm^{-1} which does not split upon cooling, as discussed previously. It is then likely that additional conformational structures are responsible for the peak at 1210 cm^{-1} in Figure 4 and has nothing to do with the A_2 mode sought for (paper I shows that the conformational disorder causes a broadening of the density of states in this spectral region).

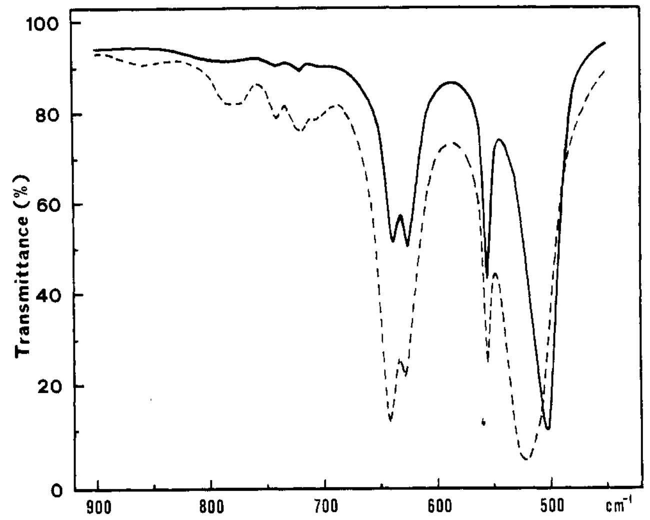

Figure 5. Infrared absorption spectrum from 900 to 450 cm^{-1} of PTFE: (——) powder in CsI matrix; (- - - -) commercial film.

Because of the complexity of the interpretation of the spectrum of PTFE in this frequency range already in terms of a D_{15} or D_{13} ideal model, any attempt to derive evidence for other regular structures as treated in paper I is meaningless.

900-450-cm^{-1} Region. The spectral region between 900 and 450 cm^{-1} is that which has been investigated in more details by most of the authors. Most of the investigations were carried out with the main hope to correlate specific infrared absorptions with the physical properties of the polymer. It was recognized that the crystallinity of PTFE seems to be related to the absorption intensity in the 900–700-cm^{-1} range[2] and that the room temperature transition can be revealed by the change in intensity of the infrared doublet at 638–626 cm^{-1}.[3] We rediscuss in this work the problem in the light of our new experimental data.

Let us first compare the infrared spectrum of the powder and the film (Figure 5). The spectrum of the powder (perhaps more crystalline) shows sharp peaks at 638, 626, 553, and 503 cm^{-1}. The spectrum of the film shows peaks at 638, 626, and 553 cm^{-1}. The peak at 503 cm^{-1} in the powder shifts to 520 cm^{-1} and becomes noticeably broader in the film. The relative intensity of the doublet at

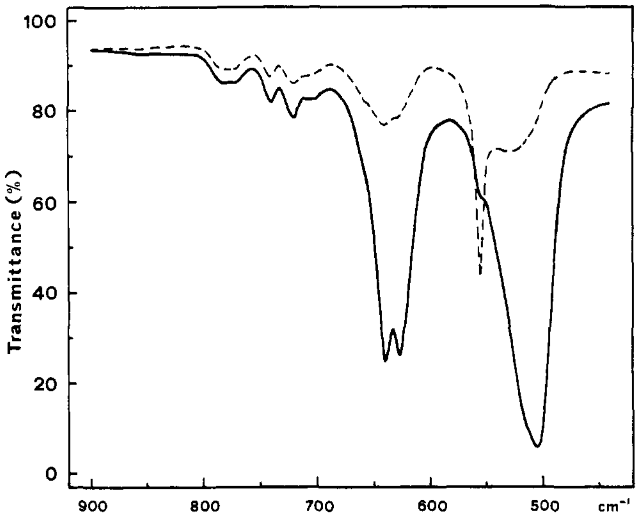

Figure 6. Infrared absorption spectrum from 900 to 450 cm^{-1} of an oriented commercial film of PTFE: (——) radiation with electric vector polarized parallel to stretching direction; (- - -) radiation with electric vector polarized perpendicular to stretching direction.

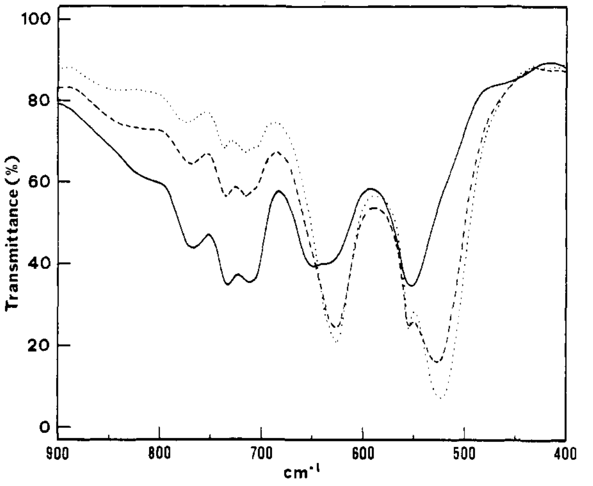

Figure 7. Infrared absorption spectrum from 900 to 450 cm^{-1} of a commercial film of PTFE at high temperature: (· · · ·) 230°; (- - -) 320°; (——) 360°.

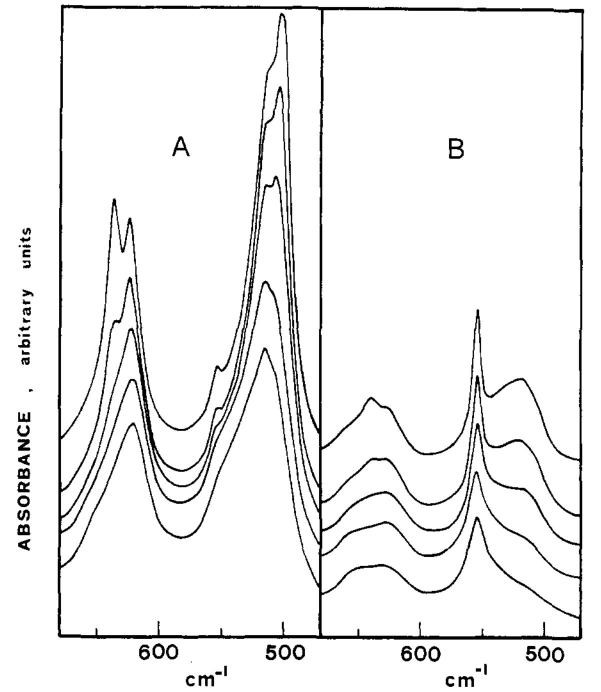

Figure 8. Infrared absorption spectrum from 680 to 470 cm^{-1} of an oriented commercial film of PTFE at several temperatures: (A) radiation with electric vector polarized parallel to stretching direction; (B) radiation with electric vector polarized perpendicular to stretching direction. Temperatures (from top to bottom): 35, 100, 200, 305, 320°.

638-626 cm^{-1} for the film is rather strange if compared with that of the powder since, on the basis of the commonly accepted assignment, would indicate for the film a larger concentration of crystalline compound with respect to the powder. This is in sharp contrast with the conclusive evidence previously discussed in this paper which has shown that the film contains a larger concentration of amorphous substance. This contrast is overcome when the polarized spectrum of the film is analyzed (Figure 6). In such a case the parallel spectrum becomes rather similar to that of the powder regarding the relative intensity of the 638-626-cm^{-1} doublet and the peak position of the band at 503 cm^{-1}. It is then possible to assign with confidence the peaks at 638 (parallel), 553 (perpendicular), and 503 cm^{-1} (parallel) to the A$_2$, E$_1$, and A$_2$ $k = 0$ phonon of the D_{15} or D_{13} helix, respectively. The residual broad absorptions at 640 and 530 cm^{-1} in perpendicular light (Figure 6) can be ascribed to the disordered regions of the commercial sample and are responsible for the differences between the spectra of the powder and the film reported in Figure 5. The existence of peaks due to disordered regions is confirmed in the spectra of samples heated at higher temperatures below and above the softening point (540 and 512 cm^{-1}, Figures 7 and 8). The disorder does exist also at low temperature as revealed from the spectrum in Figure 9 (512 cm^{-1}).

While the observed shift 503 → 520 cm^{-1} from the powder to the film can be ascribed to changes in the amorphous content, the behavior of the peak at 626 cm^{-1} is instead somehow anomalous, namely: (i) the peak at 626 cm^{-1} is clearly parallel (Figure 6); (ii) its intensity is very low below 0° (Figure 9); (iii) increases progressively with the temperature with a sudden enhancement at the transition point (19°);[2] (iv) disappears at the softening point giving rise to a broad absorption centered near 640 cm^{-1} (Figure 7). It seems reasonable to assume that the energy provided to the sample at the transition point cannot introduce drastic geometrical changes which generate a large concentration of amorphous substance (X-rays see a lattice above 19°).[14,15] From energy calculations[9] the planar form turns out to be quite probable. The calculations of paper I suggest that the introduction of a planar-zigzag structure should give rise to a parallel band at about 620 cm^{-1}. The dichroism and the temperature behavior of the peak at 626 cm^{-1} are in agreement with this prediction. From calculations, the existence of the planar structure should also be revealed by the existence of a perpendicular infrared band near 548 cm^{-1}. A sudden increase at the transition temperature of the half-bandwidth of the peak near 520 cm^{-1} has been reported by Brown[3] (and his experiments have been repeated and confirmed by us). It is concluded that such a broadening can be due to the increase in concentration of the planar form even if a defined peak cannot be resolved from the complex structure of the spectrum in this frequency interval. If this interpretation is correct from Figures 7 and 8 it is concluded that the planar form continues to exist at higher temperatures

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(14) C. W. Bunn and E. R. Howells, *Nature (London)*, 174, 549 (1954).

(15) E. S. Clark, *J. Macromol. Sci. Phys.*, 1, 795 (1967).

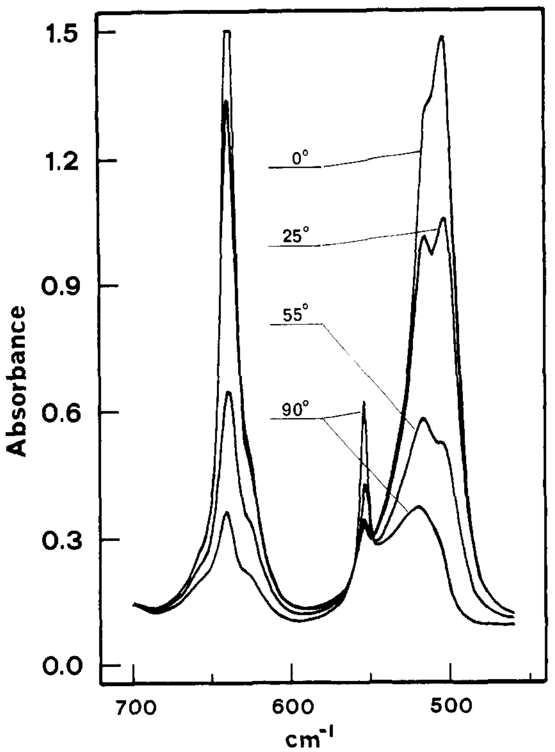

Figure 9. Infrared absorption spectrum from 700 to 450 cm^{-1} of an oriented commercial film of PTFE. Temperature −20°. Radiation with electric vector polarized at different angles with respect to the stretching direction.

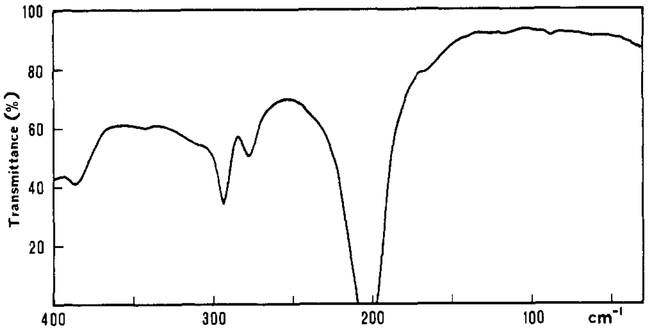

Figure 10. Infrared absorption spectrum from 400 to 30 cm^{-1} of powder of PTFE at room temperature.

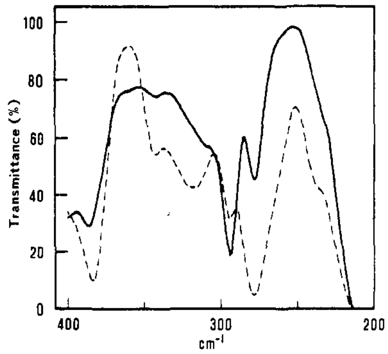

Figure 11. Infrared absorption spectrum from 400 to 200 cm^{-1} of PTFE at room temperature: (——) powder; (- - -) commercial film.

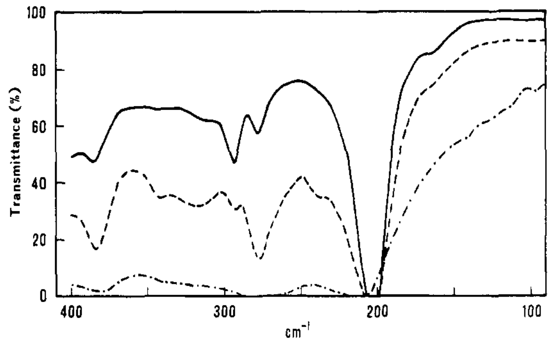

Figure 12. Infrared absorption spectrum from 400 to 100 cm^{-1} of powder of PTFE: (——) room temperature; (·······) 350°; (-----) room temperature, after cooling from 350°.

and is completely destroyed at the softening point. A complicating feature in this spectral region is the absorption at about 515 cm^{-1} due to the disorder which has been shown in the spectrum under polarized light (Figure 9).

Further information can be derived from the complex structure between 850 and 680 cm^{-1}. In this spectral range several peaks are observed whose intensity increases along with the increase of the concentration of the amorphous material. Among these Moynihan chooses the peak at 778 cm^{-1} as characteristic of the amorphous phase to be used for the quantitative determination of the relative content of the crystalline material. A slightly parallel dichroism for this band has been reported by Liang and Krimm[1] and has been verified by us in this work. Calculations of paper I predict that models 3 and 4 should exhibit one parallel band in this frequency range. The occurrence of the peak at 778 cm^{-1} may be taken as a possible indication that in the amorphous material segments of more coiled chains can exist.

400-50-cm^{-1} Region. Four infrared active $k = 0$ phonon of species E_1 (perpendicular) are predicted from theoretical considerations in the region below 400 cm^{-1} for the D_{15} model. One of these is calculated at very low frequencies, below the range covered by all commercial instruments, and has never been observed. Liang and Krimm associate the three other fundamentals to the peaks at 321, 277, and 203 cm^{-1}.[1] The sample they analyzed was of commercial nature. To our knowledge no other experimental works have been performed in this frequency range. Since no infrared bands have been observed below 200 cm^{-1} (Figure 10) our analysis will be limited to the 400-200-cm^{-1} range.[16]

In Figure 11 the absorption pattern between 400 and 200 cm^{-1} of a powder sample is compared with that obtained from a commercial film. As already noticed at higher frequencies also in this range the observed differences disappear when the powder is heated above the softening point and cooled again to room temperature (Figure 12). The main observation concerns the relative intensity of the 293-277-cm^{-1} doublet which appears to be related to different molecular structures occurring, with different concentrations, in specimens of various origin. For the identification of the three perpendicular E_1 transitions the spectrum of an oriented commercial film in polarized light has been examined. In the spectrum at room temperature (Figure 13) the weak feature at 277 cm^{-1} shows a weak parallel dichroism and is then left out in this discussion and it will be considered later in this paper. The strong perpendicular band at 203 cm^{-1} is obviously one of the E_1 fundamentals; another E_1 fundamental is located at 293 cm^{-1} because it is perpendicular and becomes stronger in the spectrum of the powder. The last fundamental is located at 312 cm^{-1} from the spectrum at low

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(16) Several infrared peaks below 100 cm^{-1} have been reported recently in low-temperature experiments. For a few comments on these results see section 7 of the conclusions of this paper.

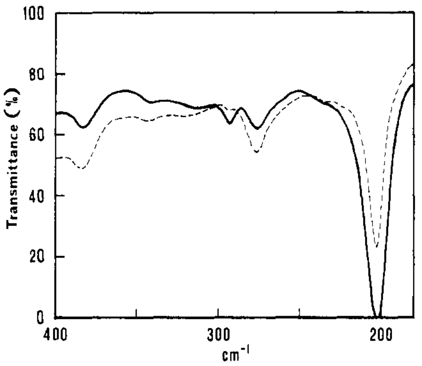

Figure 13. Infrared absorption spectrum from 400 to 180 cm^{-1} of an oriented commercial film of PTFE at room temperature: (- - - -) radiation with electric vector polarized parallel to stretching direction; (——) radiation with electric vector polarized perpendicular to stretching direction.

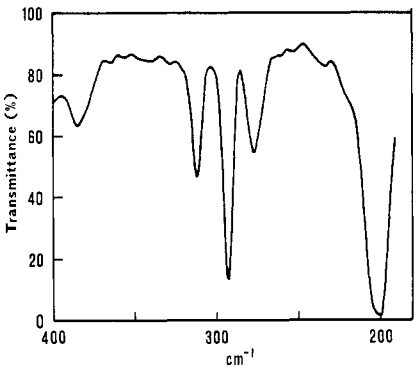

Figure 14. Infrared absorption spectrum from 400 to 190 cm^{-1} of powder of PTFE at −150°.

temperatures of the powder (Figure 14) and its E_1 species has been verified from its dichroism from an oriented commercial film at low temperatures.[17]

Temperature-dependence studies have shown that the bands at 312 and 293 cm^{-1} are temperature dependent; their intensity decreases with increasing temperature with a sudden change near the transition temperature (Figure 15). From Figure 4 of paper I two bands in the 300-cm^{-1} range are predicted to disappear in the infrared if a planar structure is generated. The agreement between theory and experiments gives a further support to the interpretation of the mechanism of the phase transition near 19° as proposed in paper I. Further temperature-dependence studies at high temperatures below and above the softening point allow to suggest an interpretation of the spectral differences observed between the powder and the film. The main absorption bands due to the disordered substance are observed at 384 and 277 cm^{-1} as shown in the spectrum of the molten state (Figure 12). It follows again that the commercial product contains a larger amount of amorphous material.

The surprising coincidence of the infrared peak at 384 cm^{-1} with a A_1 Raman active mode in a spectral range free from neighboring fundamental transitions suggests the logical possibility that the lack of symmetry within the disordered region and/or the disorder (lack of translational symmetry) activates an infrared mode or phonon only Raman active for the ordered substance.

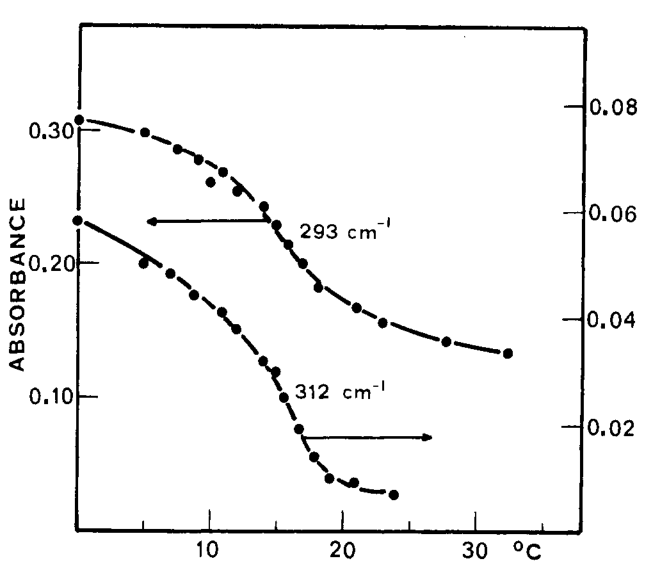

Figure 15. Intensity *vs.* temperature of the infrared absorption bands at 312 and 293 cm^{-1}.

Since a slightly parallel dichroism has been observed for the amorphous peak at 277 cm^{-1} it is possible to postulate, following the theoretical predictions of paper I, Figure 4, that it may arise from the strongly geometry-dependent A_2 parallel mode of some other types of more coiled helices (see, for example, the models 3 and 4 of paper I). From Figure 4 of paper I only the latter two models can exhibit a parallel fundamental in this frequency range. This mode is correlated (Figure 4 of paper I) to the parallel mode at 503 cm^{-1} for the D_{15} model. As previously discussed by raising the temperature the band at 503 cm^{-1} decreases in intensity while the one at 277 cm^{-1} increases. Thus the increase in concentration of one structure at the expense of the other can be safely postulated when the temperature is raised.

Conclusions

In what follows the results both of paper I and of this work are taken into account at the same time in order to give a comprehensive view of the vibrational problem of PTFE.

(1) Of the two types of materials studied, the powder certainly contains a more ordered structure than the film. We wish to point out that we are mainly concerned with the conformational order and/or disorder within the chain of PTFE and wish to avoid the term "crystallinity"[18] since unequivocal evidence of Davidov's splittings or static splittings has not been collected.

In addition to the pair of bands proposed by Moynihan for the determination of the relative content of disordered material, we can suggest for thick samples the doublet at 293-277 cm^{-1}; I_{293}/I_{277} increases with increasing order.

(2) The analysis of the spectrum of the more ordered powder material throughout the whole vibrational spectrum has allowed a better identification of the fundamental transitions of the D_{15} model. Comparison with the assignments of the infrared active modes by the previous authors shows that the main disagreement lies in the low-frequency region (see Table I). Since the force field has been refined on the previously reported experimental data (obtained from commercial samples) a further refinement may be needed. However the theoretical predictions of paper I are still valid on the whole as shown by the experiments.

(3) In the literature[2] it has also been proposed that the transition at 19° involves a change from D_{13} to D_{15} helix.

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(17) Furthermore it may coincide with the Raman band reported at 308 cm^{-1} by Koenig *et al.* at low temperatures (ref 5).

(18) G. Zerbi, F. Ciampelli, and V. Zamboni, *J. Polym. Sci., Part C*, 7, 141 (1964).

Table I
Infrared Active $k = 0$ Phonon of Poly(tetrafluoroethylene)

Calculated[a] ($D_{14\pi/15}$ Model of Isolated Chain)		Experimental			
		Previous Authors[b]		This Work	
cm^{-1}	Symmetry Species	cm^{-1}	Dichroism	cm^{-1}	Dichroism
1298	E_1			1300	⊥
1241	E_1	1242	⊥	1242	⊥
1213	A_2	1213		1213	
1150	E_1	1152	⊥	1153	⊥
640	A_2	638	∥	638	∥
552	E_1	553	⊥	553	⊥
519	A_2	516	∥	503	∥
322	E_1	321		312	⊥
271	E_1	277		293	⊥
187	E_1	203	⊥	203	⊥
6.2	E_1				

[a] Paper I. [b] References 1 and 2.

As shown by the calculations of Hannon *et al.*[6] the calculated normal frequencies for the two models are practically identical, hence no appreciable changes in the vibrational spectrum are to be expected. The observed spectral changes reported here can then more reasonably be assigned to the planar-zigzag conformation in agreement with calculations. This does not mean that the $D_{13} \rightarrow D_{15}$ transformation cannot occur, but simply it cannot be revealed by the vibrational spectrum.

In paper I a mechanism for the phase transition near 19° has been postulated as consisting of an increase of concentration of a planar-zigzag form with respect to the D_{15} chain. Paper I predicts that from model 2 to model 1 the E_1 mode at 1298 cm^{-1} and the A_2 mode at 1213 cm^{-1} should disappear in the infrared spectrum. The A_2 mode at 638 cm^{-1} should shift downward to 626 cm^{-1}. The E_1-A_2 doublet at 552-518 cm^{-1} should coalesce into a singlet at 542 cm^{-1}. The two E_1 modes calculated near 320 and 270 cm^{-1} should disappear. Because of the complexity of the spectrum nothing certain can be derived from the experimental viewpoint from the 1300-1200-cm^{-1} range. Instead a nice verification of the theoretical predictions is found for the lower frequency region where we do indeed find evidence for the planar-zigzag form. Temperature-dependence studies of the 638-626-cm^{-1} doublet indicate that the material at room temperature is a mixture of the two conformational structures. It has to be pointed out that the planar-zigzag structure may occur as a defect even within the single chain because the energy required for such a deformation is very low. We do not have any possibility to suggest a minimum length of such a conformational defect. This conclusion offers an alternative explanation of some of the temperature-dependent features of the Raman spectrum of PTFE reported by Koenig *et al.*[19] and by Boerio *et al.*[13] These authors have shown that the Raman doublets at 384-389 and 575-595 cm^{-1} change their relative intensity with temperature. The same authors have proposed that this fact may be ascribed to either the introduction of thermal defects or to a crystal field splitting arising from a lattice with more than one chain per unit cell. We suggest instead the following explanation. The component at 384 cm^{-1} arises from the A_1 mode of the D_{15} chain, the other component at 389 cm^{-1} arises from the A_g mode of the planar-zigzag form. From Figure 2 of ref 13 it is clear that the sample is a mixture of the two forms whose relative concentration changes in the way which has been previously discussed. The same interpretation can be suggested for the other doublet at 575-595 cm^{-1}. Since no fundamentals are expected in this frequency range we assign the peak at 575 cm^{-1} to the first overtone of the A_1 fundamental at 291 cm^{-1} of the D_{15} model: $2 \times 291 = 582$, $A_1 \times A_1 = A_1$, Raman active. The second component at 595 cm^{-1} may be the first overtone of the corresponding fundamental of the planar-zigzag model which is Raman and infrared inactive, and is calculated in paper I at 305 cm^{-1}: $A_u \times A_u = A_g$, Raman active. The temperature behavior of this doublet is parallel to that observed for the Raman doublet at 384-389 cm^{-1} and for the infrared doublet at 638-626 cm^{-1}.[20]

(4) The existence of helical segments with geometries approaching the models 3 and 4 of paper I seems to be revealed in the commercial products by the weakly parallel peaks at 778 and 277 cm^{-1}.

(5) The disordered material shows main absorptions at 1215, 640, near 520, and 277 cm^{-1} in very good agreement with the predictions of the calculations of paper I.

(6) Evidence of possible activation in the infrared of Raman active modes can only be found at 384 cm^{-1}. However it cannot be excluded that the disordered material can contribute to this infrared band.

(7) A puzzle still remains in the interpretation of the vibrational spectrum of PTFE, namely: (i) the splittings at low temperatures reported for the Raman spectrum by Boerio *et al.*[13] at 577-581 cm^{-1} and at 1214-1218 cm^{-1}; (ii) the absorption bands in the far-infrared region at 46, 55, 70, and 85 cm^{-1} recently reported by Chantry *et al.*[21] We have independently observed for samples at low temperature the same bands in the far infrared and located a splitting in the infrared at 1214-1218 cm^{-1} (Figure 3) in nice coincidence with the Raman.

Following the interpretation originally proposed by Boerio *et al.*[13] Chantry *et al.*[21] take the absorptions in the far-infrared region as further evidence of lattice bands arising from a crystalline structure containing more than one chain per unit cell.

The existence of splittings in the vibrational spectrum and of absorption or scattering in the low-frequency region is not an unequivocal evidence of the existence of more than one chain per unit cell. As clearly demonstrated by Piseri *et al.*[22] splittings are predicted by group theory because of symmetry also for the hexagonal or triclinic lattices with one chain per unit cell. Furthermore the same authors have shown that additional absorptions may arise in going from the isolated chain model to the three-dimensional model because of the change of symmetry. Calculations indicate that this fact should be particularly noticeable in the low-energy region where the ω_9 dispersion branch has to occur. Obviously, the amount of splitting, the location of the ω_9 branch, and the corresponding polarization vectors depend upon the force field which is not yet definitely settled especially for the torsional motions.

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(19) J. L. Koenig and F. J. Boerio, *J. Chem. Phys.*, **52**, 4170 (1970).

(20) The fact that the Raman line at 389 cm^{-1} occurs even at −180° when the Raman line at 595 cm^{-1} and the infrared band at 625 cm^{-1} disappear at ~0° may depend on the intrinsic intensities of the corresponding vibrational transitions.

(21) G. W. Chantry, J. W. Fleming, E. A. Nicol, H. A. Willis, and M. E. A. Cudby, *Chem. Phys. Lett.*, **16**, 141 (1972).

(22) L. Piseri, B. M. Powell, and G. Dolling, *J. Chem. Phys.*, **57**, 158 (1973).