wt., 2.83 g.) had positive specific rotations of the order of $+1°$. The last fraction gave $[\alpha]_D$ $-34°$ (0.5 g.) and was impure $[Pt(d\text{-}pn_2]Cl_2$. The dextrorotatory material (2.6 g.) in cold water (150 ml.) was shaken with silver oxalate, and after filtration to remove silver chloride the solution was evaporated to 40 ml. Addition of methanol (10 ml.) caused the separation of a white amorphous material that crystallized out as needles on standing overnight. A 0.5% aqueous solution gave $[\alpha]_D$ $+10°$, and in 0.05 *N* hydrochloric acid gave $[\alpha]_D$ $+1°$. By repeated recrystallization from water by the addition of ethanol the pure oxalate (0.5 g.) was obtained, $[\alpha]_D$ $+15°$; $[\alpha]_{5461}$ $+18°$ in water and $[\alpha]_D$ $+13°$; $[\alpha]_{5461}$ $+16°$ in 0.015 *N* sodium hydroxide.

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_3](C_2O_4)_2 \cdot 5H_2O$: C, 22.83; H, 5.90; N, 12.29. Found: C, 22.96; H, 5.88; N, 12.25. Calcd. for $[Pt(C_3H_{10}N_2)_3]Cl_4 \cdot H_2O$: C, 18.72; H, 5.59; N, 14.56. Found: C, 18.97; H, 5.43; N, 14.47.

A 1.5% aqueous solution gave α_D $+0.04°$, whence $[\alpha]_D$ $+1.3°$. From a total amount of tris-complex isolated (17.2 g.) an estimated quantity of 2.5 g. of pure D-*ddd* isomer was obtained, *i.e.*, approximately 15%.

Bis-(*d*-propylenediamine)-platinum(II) Tetra-iodocadmiate(II) 1-Hydrate.—The filtrate remaining after the separation of the isomers of the tris-complex as oxalate was strongly levorotatory. Oxalate ion was removed as before by precipitation as calcium oxalate at *p*H 8. The filtered solution was acidified and on the addition of cadmium(II) acetate 2-hydrate and sodium iodide gave a white crystalline precipitate. The tetra-iodocadmiate(II) was repeatedly recrystallized from hot water by the addition of a little sodium iodide and gave $[\alpha]_D$ $-20°$; $[\alpha]_{5461}$ $-24°$ in acetone.

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_2][CdI_4] \cdot H_2O$: C, 7.34; H, 2.26; Cd, 11.45; I, 51.7. Found: C, 7.30; H, 2.22; Cd, 11.53; I, 52.07.

The chloride was prepared by the elimination of cadmium ion as the carbonate by the addition of a slight excess of lithium carbonate and then of the iodide ion by shaking with excess of freshly precipitated silver chloride. The aqueous filtrate then was made acid with hydrochloric acid, evaporated to dryness and the lithium chloride extracted with a little ethanol. The salt was recrystallized from water by the addition of acetone and ether. A 0.5% aqueous solution gave $[\alpha]_D$ $-44°$; $[\alpha]_{5461}$ $-53°$ (for the monohydrate), which compares well with the previous value $[\alpha]_D$ $-46°$ (for the anhydrous material) recorded by Tschugaeff and Sokoloff.[4]

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_2]Cl_2 \cdot H_2O$: C, 16.66; H, 5.13; N, 12.96. Found: C, 16.48; H, 5.03; N, 12.82.

D-Tris-(*l*-propylenediamine)-platinum(IV) Oxalate 1-Hydrate and Chloride 1-Hydrate, D-*lll* Isomer.—This isomer was prepared from *l*-propylenediamine, ($[\alpha]_D$ in benzene $-34.1°$) and purified through the oxalate as described above. A 0.5% solution in 0.05 *N* hydrochloric acid gave $[\alpha]_D$ $+188°$, $[\alpha]_{5461}$ $+244°$.

Anal. Found: C, 25.54; H, 5.3; N, 13.4.

The chloride gave $[\alpha]_D$ $+212°$, $[\alpha]_{5461}$ $+252°$ in 0.5% aqueous solution.

Anal. Found: C, 19.08; H, 5.55; N, 14.58.

L-Tris-(*l*-propylenediamine)-platinum(IV) Oxalate 5-Hydrate, L-*lll* Isomer.—This isomer was separated from the D-*lll* isomer as described previously and gave $[\alpha]_D$ $-10°$, $[\alpha]_{5461}$ $-12°$ in aqueous solution. A 1.11% solution in 0.03 *N* hydrochloric acid gave α_D $-0.04°$, α_{5461} $-0.05°$ whence $[\alpha]_D$ $-1.8°$, $[\alpha]_{5461}$ $-2.25°$.

Anal. Found: C, 23.2; H, 5.6; N, 12.56.

Bis-(*l*-propylenediamine)-platinum(II) Tetra-iodocadmiate(II) 1-Hydrate.—This was obtained from the mother liquor after the removal of the D-*lll* and L-*lll* isomers as the oxalates. A 1.0% solution in acetone gave $[\alpha]_D$ $+20°$ and $[\alpha]_{5461}$ $+24°$.

Anal. Found: C, 7.53; H, 2.26; Cd, 11.62; I, 51.9.

Bis-(*l*-propylenediamine)-platinum(II) Chloride 1-Hydrate.—The chloride was isolated from the tetra-iodocadmiate(II) as described above. A 0.5% aqueous solution gave $[\alpha]_D$ $+45°$ and $[\alpha]_{5461}$ $+54°$.

Anal. Found: C, 16.30; H, 5.36; N, 12.84.

Bis-(*l*-propylenediamine)-platinum(II) Iodide.—The iodide was prepared from the tetra-iodocadmiate(II) after removal of the cadmium as cadmium(II) carbonate. A 0.5% aqueous solution gave $[\alpha]_D$ $+31°$ and $[\alpha]_{5461}$ $+37°$.

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_2]I_2$: C, 12.06; H, 3.38; N, 9.38. Found: C, 12.28; H, 3.39; N, 9.27.

Reaction of D-Tris-(*l*-propylenediamine)-platinum(IV) Chloride with *l*-Propylenediamine.—The tris complex (0.5 g.) in water (15 ml.) was heated on the steam-bath with *l*-propylenediamine (1 ml., 67% w./w.) at 80–90° for 2 hr. and finally allowed to become dry. The orange yellow residue was dissolved in water and the solution adjusted to *p*H 5 with acetic acid. Addition of potassium oxalate gave no precipitate of $[Pt(l\text{-}pn)_3](C_2O_4)_2$. The solution was then made strongly acid by the addition of hydrochloric acid when the color darkened to brown. Addition of cadmium acetate 2-hydrate and sodium iodide gave a yellowish crystalline precipitate of bis-(*l*-propylenediamine)-platinum-(II) tetra-iodocadmiate(II) 1-hydrate. After recrystallization from hot water this gave $[\alpha]_D$ $+20.0°$; $[\alpha]_{5461}$ $+24.0°$ in acetone. These values agree exactly with the rotations reported above.

CANBERRA, AUSTRALIA

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

The Molecular Structure of Perfluorocarbon Polymers. Infrared Studies on Polytetrafluoroethylene[1]

BY R. E. MOYNIHAN

RECEIVED JANUARY 13, 1958

The infrared absorption spectrum of polytetrafluoroethylene was studied in the 5000–270 cm.$^{-1}$ region. The variations in the spectrum with crystallinity were investigated to make possible an extrapolation to the crystalline spectrum. Several absorption bands were shown to be associated with vibrations of the amorphous configurations. The bands in the crystalline spectrum have been assigned on the basis of selection rules derived from the symmetry of the crystalline chain configuration. A crystalline density of 2.30 g./cc. was determined by an extrapolation based on an amorphous band intensity. The first-order transition at 19° was found to be accompanied by spectral changes.

Introduction

While the application of group theoretical methods to the analysis of high polymer spectra might seem to be a profitless undertaking, the tremendous length of a polymer molecule actually results in simplification rather than complexity. The treatment of a polymer molecule as a one-dimensional crystal was discussed by Tobin.[2] Polytetrafluoroethylene is an interesting subject for such a study because of its high symmetry, high crystallinity and its helical structure.

Several spectra of polytetrafluoroethylene have been published, but in general the regions of strong

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[1] Presented at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

[2] M. C. Tobin, *J. Chem. Phys.*, **23**, 891 (1956).

absorption are obscured. Robinson and Price[3] obtained the reflection spectrum and noted that the number of parallel bands in the spectrum is not consistent with a planar zig-zag structure. Krimm and Liang reported fundamental band assignments based on symmetry and calculated frequencies for a planar zig-zag infinite chain.[4]

Experimental

The infrared spectra were obtained with Perkin–Elmer Model 21, 13 and 112 spectrophotometers. CaF_2, NaCl, KBr and CsBr prisms were employed in the appropriate spectral regions. Film samples generally were prepared by microtoming bars molded from commercial forms of Teflon[5] tetrafluoroethylene resins or various experimental forms of polytetrafluoroethylene. Powder was pressed at room temperature to give transparent films for the study of highly crystalline samples. The strong absorption in the 1200 and 650–400 cm.$^{-1}$ regions were also studied by suspending powdered polymer in KBr, with aqueous suspensions and with reflection techniques. The orientation spectra were obtained with highly-crystalline films stripped from a calendered but unsintered sheet and oriented by cold-drawing. AgCl polarizers and the natural polarization of the double-pass instrument were used to study dichroism. X-Ray crystallinity determinations were based on graphical resolution of the overlapping amorphous halo and the 100 diffraction peak. Density measurements were carried out by liquid (tetrachloroethylene) displacement. The samples were placed under vacuum and wet first with tetrachloroethylene vapor as a precaution against trapping air. The low temperature spectra were obtained by placing the sample in an inverted "Dewar" having openings to allow the passage of the infrared beam and cooling with a stream of dry nitrogen of the desired temperature. A thermocouple with one junction at the surface of the film was used to measure the approximate temperature.

Discussion

Crystalline Effects.—The symmetry of the crystalline chain structure cannot be used immediately to aid in interpreting the observed spectrum, because a polymer sample is in general only partially crystalline, and this is reflected in its spectrum. Therefore, the effects of crystallinity on the polytetrafluoroethylene spectrum were studied. These data made an extrapolation to the crystalline spectrum possible.

The spectra of samples with crystallinities covering the range from 40 to *ca.* 95% were obtained. The most pronounced changes in the spectrum with crystallinity occur in the 850–700 cm.$^{-1}$ region and at 384 cm.$^{-1}$. Several bands were found in these regions which decrease regularly in intensity with increasing crystallinity. For example, see Fig. 1. Within the scatter of the data, the band intensities are linear functions of crystallinity and the intercept is at or near the origin, suggesting that these bands are due only to vibrations of the amorphous material. The dashed line in Fig. 1 indicates the intensity of the 780 cm.$^{-1}$ band in samples with crystallinities too high for determination by X-ray and supports this assertion. Except for these, the bands in the spectrum vary in intensity with crystallinity to a lesser extent, indicating that they are due to overlapping absorption by the crystalline and amorphous material.

The existence of amorphous bands in the polytetrafluoroethylene spectrum is reasonably expected on the basis of the considerable data that have been published concerning rotational isomers in simpler compounds. The situation is similar to that of the 1,2-disubstituted ethanes, for which bands are found in the spectrum that can be assigned to *trans* and *gauche* configurations. For polymers, the rotational configurations are, of course, more complex. However, since vibrational coupling does not extend over many carbon atoms in the amorphous regions, a given perfluoromethylene group is influenced principally by the configurations about its own two C–C bonds. The vibrational entities can thus be visualized as *trans, trans; trans, gauche;* etc. Each configuration has perhaps different frequencies and certainly different selection rules, and, therefore, bands peculiar to the amorphous material can appear in the spectrum. The fact that several, definite bands occur, rather than broad regions of absorption, is attributed to the existence of discrete configurations resulting from the high rotational barriers. This model suggests also the possibility of different temperature dependences for these bands.

On the assumption that a polymer can be treated as a two component mixture of amorphous and crystalline regions with no regard for the boundary material, both density and the amorphous band intensities are linear functions of volume fraction crystallinity, and, thus, of each other. The amorphous bands can be used in conjunction with density measurements to extrapolate to the crystalline density, Fig. 2. The extrapolated value of 2.304 (±0.006) at 23° is in good agreement with the value of 2.30 calculated for the form existing at this temperature from the unit cell parameters and assuming 15 CF_2 groups in the repeat unit. Since the band intensities are measured from an estimated baseline, the accuracy of the crystalline density value is affected to some extent. It is believed that the accuracy is of the order of the indicated standard deviation. A similar experiment was reported recently by Miller and Willis.[5a] These authors extrapolated a curve to obtain agreement with a value of 2.35, which we believe to be outside our experimental error.

A routine, relative crystallinity determination based on the amorphous bands in the polytetrafluoroethylene spectrum proved valuable. It is more rapid and precise than the X-ray method. In practice, the ratio of the 778 and 2367 cm.$^{-1}$ band intensities are measured. This eliminates the thickness measurement and increases precision. The precision is of the order of ±1% at 50% crystallinity and correspondingly better at higher levels. A density measurement and an infrared crystallinity determination when combined give an estimate of the micro-void content often found in molded specimens of polytetrafluoroethylene. To determine the micro-void content, the density of a sample is predicted on the basis of its crystallinity, as measured by the infrared method, and the difference between this density and its actual density is a measure of the micro-void content. The determination is precise to about ±0.2% voids by

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(3) T. S. Robinson and W. C. Price, *Proc. Phys. Soc. (London)*, **66B**, 969 (1953).

(4) Krimm and Liang, *J. Chem. Phys.*, **25**, 563 (1956).

(5) Du Pont Registered Trade Mark.

(5a) R. G. J. Miller and H. A. Willis, *J. Polymer Sci.*, **19**, 489 (1956).

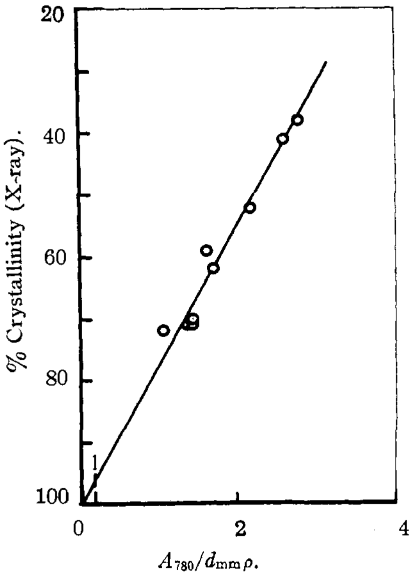

Fig. 1.—Absorbance per unit thickness and density of 780 cm.$^{-1}$ absorption band *vs.* crystallinity.

volume and has proved useful in practical work on the technology of polytetrafluoroethylene.[6]

Quantitative studies of dichroism were not made. It is evident that the amorphous bands are much less sensitive to orientation, as would be expected.

Group Theory Results.—The symmetry of the crystalline chain configuration can be used to predict the number of infrared active fundamentals, the orientation of their transition moments and to describe, approximately, the corresponding vibrations. For this purpose, only a single, isolated, infinite chain is considered, having the same configuration it would have in the crystal. This approximation is correct to the extent that the intermolecular forces are small in comparison with the intramolecular forces and interchain vibrational coupling can be neglected. The first condition should be satisfied, at least, quite well for a fluorocarbon polymer. In this model the chain is a one-dimensional crystal and the repeat unit plays the role of the unit cell. The theory of crystal spectra by Hornig,[7] Winston and Halford[8] and others can be applied.

X-Ray studies indicate that the crystalline polytetrafluoroethylene chain configuration is a helical zig-zag of CF_2 groups.[9–12] The number of CF_2 groups in the repeat unit depends upon the temperature.[10–12] Above 19° the repeat unit contains 15 CF_2 groups, or the helix requires 30 CF_2 groups to make one complete turn (2π). Below 19° the repeat unit contains 13 CF_2 groups.

The configuration of the chain allows two types of symmetry operations other than pure translations.

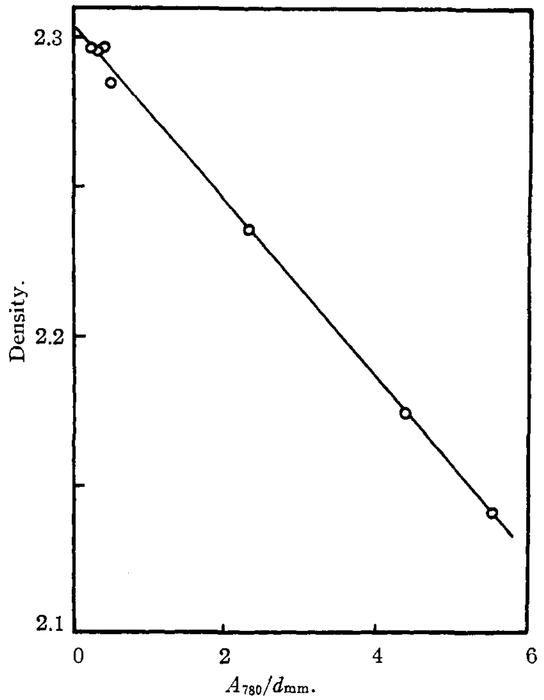

Fig. 2.—Extrapolated crystalline density for polytetrafluoroethylene.

The first type is a screw operation. That is, for the room temperature form, the chain is rotated about its axis by $\pi \pm \pi/15$ and translated one-fifteenth of the repeat unit along the chain. This brings a given CF_2 group in turn into the position occupied by the next, the next plus one, etc. The second type of symmetry operation is equivalent to a rotation by π about a twofold axis perpendicular to the chain axis and bisecting the FCF angle. There are fifteen such operations, each one of which transforms a given CF_2 group back into itself, while exchanging the others. The collection of these operations forms the factor group of the space group. The factor group is isomorphous with the dihedral point group D_{15}.

Fundamental absorption corresponds to vibrational motions in which each of the corresponding atoms in the different unit cells is moving in exactly the same manner, *i.e.*, the vibrational eigenfunction must be totally symmetric to translation. This requirement reduces the number of vibrations to be considered to $3(45) - 3 = 132$. The representation of these motions can be reduced among the 9 factor group irreducible representations to give the number of vibrations of each species $-\Gamma = 4A_1 + 3A_2 + 8E_1 + 9\,(E_2 + \ldots + E_7)$. The infinitesimal rotation R_z (A_2) becomes a low frequency vibration in the three-dimensional crystal; the infinitesimal translations T_x, $T_y(E_1)T_z(A_2)$ correspond to small translations of the entire crystal. The representation of the dipole moment operator includes the A_2 and E_1 species and thus these vibrations can be infrared active. The change in dipole moment associated with the vibrations of the A_2 species is parallel to the chain axis; that associated with the E_1 species is perpendicular to the chain axis. It is of interest that of the nearly infinite number of modes of the chain, or the 135

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(6) P. E. Thomas, J. F. Lontz, C. A. Sperati and J. L. McPherson, *SPE Journal*, **89**, (1956).

(7) D. F. Hornig, *J. Chem. Phys.*, **16**, 1063 (1948).

(8) H. Winston and R. S. Halford, *ibid.*, **17**, 607 (1949).

(9) R. H. H. Pierce, W. M. D. Bryant and J. F. Whitney, Buffalo Meeting of American Chemical Society, March, 1952; Chicago Meeting of the American Chemical Society, September, 1953.

(10) C. W. Bunn and E. R. Howell, *Nature*, **174**, 549 (1954).

(11) R. H. H. Pierce, E. S. Clark, J. F. Whitney and W. M. D. Bryant, Atlantic City Meeting of the American Chemical Society, September, 1956.

(12) E. S. Clark and L. T. Muus, New York Meeting of the American Chemical Society, September, 1957.

modes of the repeat unit, the number of active vibrations is reduced to only eleven. An attempt at a force-field calculation would not be more difficult than for a simple molecule, since the dimensions of the secular equations would be 4, 3, 8 and 9.

The selection rules for overtones and combination bands are given in Table I on the basis of the factor group selection rules. This is not a complete description but will apply to the fundamentals observed in the spectrum.[7,8] It is evident that no overtones of the active fundamentals are allowed on this basis. However, the inactive modes are probably not shifted greatly in frequency from the active ones, and the analysis is confused by two inactive modes combining to yield an active one.

TABLE I

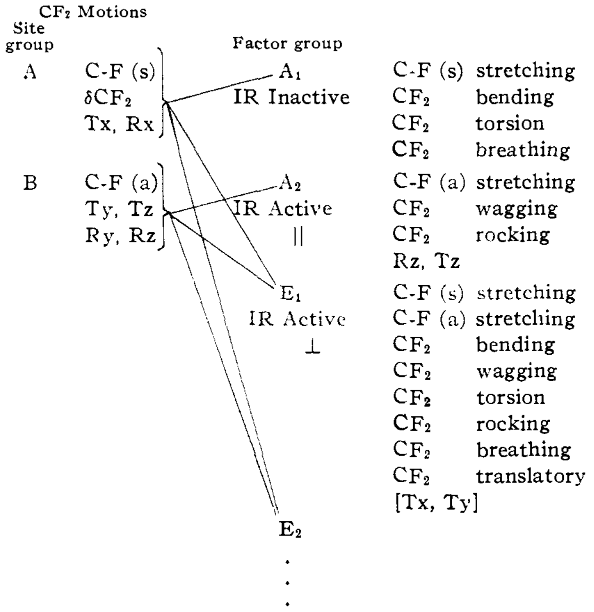
SELECTION RULES FOR OVERTONE AND COMBINATION BANDS

Overtones	Combination
$A_1^2 = A_1$	$A_1 \times A_1 = A_1$
$A_2^2 = A_1$	$A_1 \times A_2 = A_2$
$E_k^2 = A_1 + E_{2k}$	$A_1 \times E_n = E_n$
	$A_2 \times A_2 = A_1$
	$A_2 \times E_n = E_n$
	$E_j \times E_k = E_{j+k} + {}_{\lvert j-k \rvert}$

The type of motion in a given vibration can be described roughly by the following procedure. For each of the CF_2 groups, a rotation about one of the twofold axis merely interchanges the two fluorine nuclei. In other words, the CF_2 group is invariant in respect to itself, or converted back into itself, by two operations—the identity and one of the twofold rotations. These two operations form a site group of the CF_2 group.[8] The site group is a subgroup of the factor group and a correlation table can be constructed as given in Table II. For a given isolated CF_2 group, the motions can be divided into two species according to their behavior in respect to a rotation by π about the twofold axis. These are the familiar motions of a non-linear XY_2 molecule (of lower symmetry, however). Only three vibrations are possible for this isolated group, the symmetric C–F stretching and scissors deformation belonging to the totally symmetric A species and the asymmetric C–F stretching belonging to the B species. The rotations are divided as shown, remembering that the twofold axis coincides with the X (or Y)-axis to be consistent with the factor group. The motions of the 15 CF_2 groups in the unit cell can be synthesized by combining the motions of the individual groups according to the correlation table.

TABLE II

CORRELATION TABLE



For example, the A species of the site group enter into the A_1 species of the chain factor group. Since the A_1 species of the chain is totally symmetric to the screw rotation, each CF_2 group along the chain is vibrating in exactly the same manner. The symmetric stretching of the CF_2 group becomes a chain motion in which each of the fluorine nuclei move outward along the bonds as the carbon atoms move toward the chain axis. Similarly, the A rotation of the lone CF_2 group becomes a torsional or twisting vibration of the CF_2 groups in the chain. The A translational motion becomes a breathing motion of the chain, in which the CF_2 groups as a unit move in and out perpendicular to the chain. In the E_n chain vibrations, the lone CF_2 group motions are combined to form degenerate pairs. The E_n species differ in the phasing of the vibrations between the different CF_2 groups along the chain. Since the degrees of freedom do not remain separated to this extent, of course, in the actual vibrations, the description arrived at by this process is only an approximate one.

The predictions for a helix with 13 CF_2 groups in the repeat unit are the same as those above, as far as the number of active vibrations and their polarization are concerned. This makes the analysis for the room temperature form given by Krimm and Liang[4] accidentally correct.

Band Assignments.—The 3000-270 cm.$^{-1}$ infrared spectrum of a typical polytetrafluoroethylene sample is given in Fig. 3. The observed bands are listed in Table III. The data of Krimm and Laing,[4] which extend to 70 cm.$^{-1}$, also are included in the table.

Three strong parallel bands (A_2) are expected in the infrared spectrum from the group theory analysis. Two are definitely located—the doublet at 638, 625 cm.$^{-1}$ and the broad band at 516 cm.$^{-1}$. The remaining A_2 fundamental is, approximately, a C–F stretching mode and should appear near 1200 cm.$^{-1}$. The very strong 1152 cm.$^{-1}$ band is definitely a perpendicular band and can be eliminated on this basis. Bands are present at 1242 and 1213 cm.$^{-1}$ in spectra obtained by pressing fine powders in KBr or pressing molding powder particles between AgCl plates. Reflection spectra and those of thin oriented films obtained with parallel polarized infrared radiation show only a band near 1213-1210 cm.$^{-1}$. Spectra obtained with diluted water dispersions show only a band at 1225 cm.$^{-1}$. The study of thin films is affected somewhat by the strong reflection maxima in this region. The spectra obtained with parallel polarized radiation would

TABLE III

INFRARED ABSORPTION SPECTRUM OF POLYTETRAFLUOROETHYLENE

This study					Liang and Krimm	
Cm.^{-1}		Int.	Assignment		Cm.^{-1}	
3670		vw				
3570		vw				
3450		vw				
3090		vw				
2925		vw			2905	
					2850	
2620		vw	1380 + 1242 = 2622	E_1		
2590		vw	1380 + 1213 = 2593	A_2		
2530		vw	1380 + 1152 = 2532	E_1		
2450		vw	1213 + 1252 = 2455	E_1		
2367	$\perp$	m	1152 + 1213 = 2365	E_1	2350	
2300		vw	2(1152) = 2300	E_1		
1974	$\perp$	vw	730 + 1242 = 1972	E_1		
1935	$\perp$	w	553 + 1380 = 1933	E_1		
1883	$\perp$	w	730 + 1152 = 1882 638 + 1242 = 1880			
1859	$\perp$	w				
1792	$\perp$	m	638 + 1152 = 1790	E_1		
1703		w	1152 + 553 = 1705	A_2		
1545	$\perp$	m			1545	
1451	$\parallel$	m	203 + 1242 = 1445	A_2	1450	A_2
1420	$\perp$	m	203 + 1213 = 1416	E_1	1410	
1242		vs	σ C–F	E_1		
1213		vs	σ C–F	A_2		E_1
1152	$\perp$	vs	σ C–F	E_1		E_1
932	$\perp$	m	203 + 730 = 932	E_1		
850			Amorphous			
778			Amorphous		780	
738			Amorphous		742	
718			Amorphous		720	
703			Amorphous			
638	$\parallel$	s	CF_2 wag	A_2	636	A_2
625	$\parallel$	s			620	
553	$\perp$	s	δCF_2	E_1	555	E_1
516	$\parallel$	vs	CF_2 rock	A_2	520	A_2
384			Amorphous		384	
					321	E_1
					277	E_1
					203	E_1
					149	
					124	
					102	

favor the 1213 cm.$^{-1}$ band if this is the A_2 fundamental. The 1213 cm.$^{-1}$ band is assigned here to the A_2 fundamental principally on the basis of the polarization of its combination bands. An alternate assignment to the 1450 cm.$^{-1}$ band is also possible.[4]

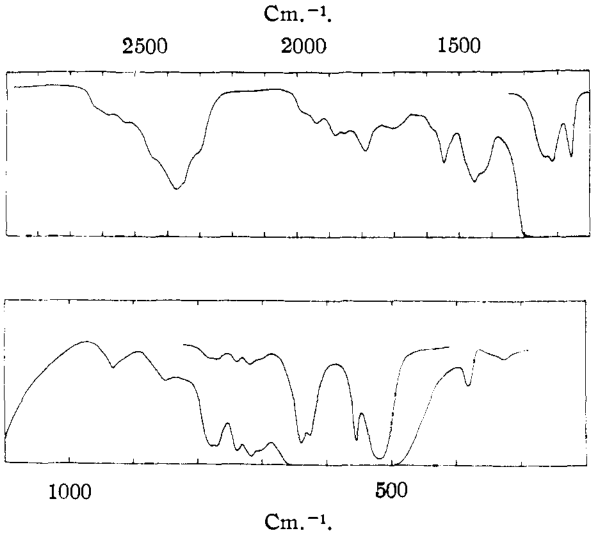


Fig. 3.—Infrared absorption spectra of polytetrafluoroethylene.

The number of E_1 fundamentals predicted more than accounts for the strong perpendicular bands observed. It is expected from the nature of some of the E_1 vibrations that they would have frequencies below the range covered in this study. All of them are not accounted for even when the spectrum is extended to 70 cm.$^{-14}$. The 1242 and 1152 cm.$^{-1}$ bands are assigned to the E_1 C–F stretching modes and the 555 cm.$^{-1}$ band to the CF_2 deformation. It is remarkable that the E_1, CF_2 bending mode falls considerably below the A_2, CF_2 wagging mode. This may be due to the tight structure of the helix and the existence of fairly strong forces between the non-bonded atoms.

The combination bands can be assigned quite successfully on the basis of the factor group selection rules. The existence of inactive (A_1) fundamentals at 1380 and 730 cm.$^{-1}$ can be inferred from their appearance in combination bands.

19° Transition.—The 625 cm.$^{-1}$ component of the doublet at 638, 625 cm.$^{-1}$ has been reported to be absent at 0° and nearly equal in intensity to the 638 cm.$^{-1}$ band at 50°.[3] Our study shows the changes in the 625 and 638 cm.$^{-1}$ bands to be associated with the first-order transition that occurs

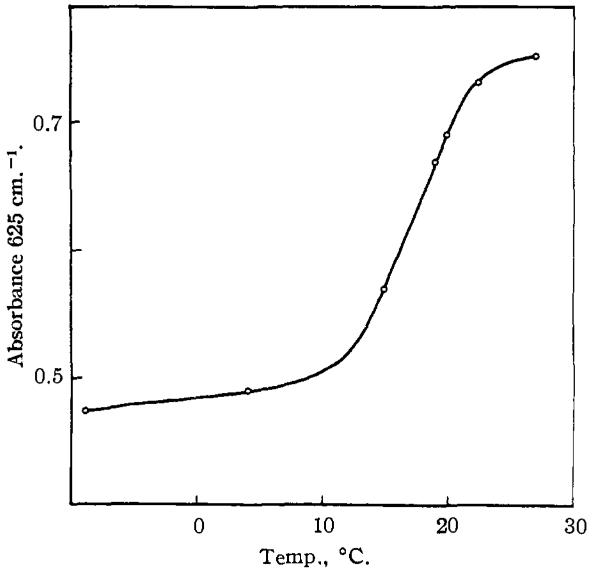


Fig. 4.—Influence of 19° transition on absorption in the 650 cm.$^{-1}$ region.

at 19°. The 625 cm.$^{-1}$ band appears and disappears sharply when passing through the transition temperatures and the 638 cm.$^{-1}$ band changes correspondingly, Fig. 4.

Two explanations suggest themselves. The first attributes this effect to a shift in the wagging frequency with the relaxation of the spiral. This would require the 638 cm.$^{-1}$ band to be absent above 20°. Since, in addition to the crystalline component, there is an amorphous contribution to the 638 cm.$^{-1}$ band, the persistence of this band above 20° is not immediate proof that this explanation is wrong. The second explanation relates the splitting to the change from triclinic to hexagonal packing. In the hexagonal crystal, the 15 CF_2 groups in the unit cell are divided into 5 sets of 3 identical CF_2 groups. This regular perturbation, not present in the triclinic form, may be responsible for the splitting. Further studies are in progress to determine the cause of these variations and the temperature dependence of the infrared spectrum in general.

Acknowledgments.—The author wishes to thank Miss A. L. Ryland and J. F. Whitney for the crystallinity determinations and J. E. Eldridge for supplying the samples for which he had measured densities.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Acid Ionization Constants of Alcohols. I. Trifluoroethanol in the Solvents H_2O and D_2O[1]

BY P. BALLINGER AND F. A. LONG

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The equilibrium constants for the reaction of trifluoroethanol with hydroxide and deuteroxide ion in water and in deuterium oxide, respectively, have been determined by a conductivity method. Combination of the results with data on the ion products for the solvents leads to values of the thermodynamic ionization constants of the acids. The values for 25° are $K_a(H_2O) = 4.3 \times 10^{-13}$ and $K_a(D_2O) = 0.95 \times 10^{-13}$. The method should have general utility for uncharged acids with pK_a values in the range of from 10 to 15 and experimental details are given.

The ordinary aliphatic alcohols are well known to be very weak acids in aqueous solution. However, only a few quantitative measurements of their ionization constants have been reported, although the problem has been discussed and some useful relative data are available. For example, a recent study by Hine and Hine[2] gives relative data on the acidities of a number of alcohols in the solvent isopropyl alcohol. Although the relative strengths in this solvent will probably not be quantitatively the same as for the solvent water, there very probably will be a qualitative correlation. Hence the conclusions that water and ethanol are of very similar acid strength but that most glycols are much more acidic are of considerable interest.

The only quantitative data for the acidities of alcohols in water appear to be those for halogen derivatives, particularly for the highly fluorinated alcohols. Table I lists representative data. The pK_a values of this table clearly indicate the weakness of these acids. However it seems safe to conclude that the actual ionization constants are known only very approximately. There are several reasons for this. All of the data of Table I have been obtained by pH measurements with a glass electrode, usually of a "half-neutralized" solution of the alcohol. The difficulties of accurate measurement of pH values as high as 11 are well known. Furthermore, all of these acids are so weak that there is real doubt about the adequacy of the method itself. Finally, except for the studies of Roberts, McBee and Hathaway,[4] no attempt has been made to correct for ionic strength effects, etc.[7]

TABLE I

Alcohol	Solvent	pK_a	Ref.
CF_3CH_2OH	Water	11.4	3
CF_3CH_2OH	Water	12.43	4
CF_3CH_2OH	50% aq. ethanol	11.3	5
$CF_3CH(OH)CH_3$	Water	11.8	3
$C_3F_7CH_2OH$	50% aq. methanol	11.4	6
$(C_3F_7)_2CHOH$	50% aq. methanol	10.6	6
CCl_3CH_2OH	50% aq. ethanol	11.8	5

An analysis of these various difficulties has made it evident that measurement of the conductivity of aqueous solutions which contain the alcohol together with some alkali offers several advantages.[8] Consider for example an alcohol (abbreviated as SH) with $K_{SH} = 1 \times 10^{-12}$. In an aqueous solution which contains some sodium hydroxide and an excess of SH there will be transformation of NaOH to NaS by the reaction

$$SH + OH^- = S^- + H_2O \qquad (1)$$

The equilibrium constant for this reaction is $K = K_{SH}/K_w$ and for our example $K = 100$ at 25°. With stoichiometric concentrations of 0.01 M

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(1) Work supported by a grant from the Atomic Energy Commission.

(2) J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).

(3) A. L. Henne and R. L. Pelley, *ibid.*, **74**, 1426 (1952).

(4) C. W. Roberts, E. T. McBee and C. E. Hathaway, *J. Org. Chem.*, **21**, 1369 (1956); see also E. T. McBee, W. F. Marzluff and O. R. Pierce, THIS JOURNAL, **74**, 444 (1952).

(5) R. N. Haszeldine, *J. Chem. Soc.*, 1757 (1953).

(6) A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 991 (1953).

(7) The basic difficulty of applying this method to very weak acids is well illustrated by the report in ref. 4 that the pK_a for ethanol in water is 12.70, only 0.3 unit larger than the value for trifluoroethanol. Preliminary conductivity studies indicate that the pK for ethanol is at least two units larger than that for the fluoroalcohol and on general grounds it is likely that the difference is in the order of four units. Evidently the pH method becomes quite inadequate for very weak acids.

(8) *Cf.* G. H. Twigg, W. S. Wise, H. J. Lichtenstein and A. R. Philpotts, *Trans. Faraday Soc.*, **48**, 699 (1952).