Vibrational Analysis as a Tool for Detecting Electronic Mobility. The Case of the Alternating Ethylene–Tetrafluoroethylene Copolymers

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ABSTRACT: Frequency and intensity spectroscopies have been used in the reanalysis of the vibrational spectrum (IR and Raman) of alternate copolymers of ethylene and tetrafluoroethylene. A new assignment of the CH stretching fundamental is proposed. The seeming anomalies of the infrared spectrum in the CH stretching range are accounted for in terms of equilibrium atomic charges and charge fluxes. In particular, the analysis of the dichroic ratios shows that there exists a relevant mobility of the electronic charge along the C–C bonds.

1. Introduction

In the effort to develop a new class of high-performance polymers, detailed studies of ethylene–tetrafluoroethylene copolymers (ETFE) have been made in the past few years. The main object of these studies was the characterization of the chemical and mechanical properties of these products. These classes of copolymers show good mechanical and dielectric properties, good resistance to chemical agents and good processability.[1]

The copolymer with equimolar composition, which is the subject to the present work, shows a highly alternate structure, due to the low value of the products of the reactivity ratios r_1r_2 (on the order of 10^{-2}).[2] The degree of alternation is generally 90% or more depending on polymerization conditions.

Tanigami et al.[3-5] found the crystal structure of ETFE to be orthorhombic with four planar zigzag chains in the unit cell. Conformational energy calculations by Farmer and Lando[6] indicate that the most stable conformation for an isolated ETFE chain is a 3/2 helix, but when the chains are packed in the crystal, the planar zigzag structure becomes energetically favored. Also polarized Raman studies on oriented samples by Zabel et al.[7] confirm the planar zigzag conformation.

In this work we focus our attention on the vibrational spectra of ETFE copolymers: our aim is to characterize the CH_2 units which are close to the CF_2 groups. Intensity analysis of the infrared bands in the CH stretching region will be used as a tool for the study of the charge distribution (and charge mobility) in CH bonds. Also spectra recorded in polarized light will be used to reveal peculiar characteristics of the electronic charge in the C–C bonds.

2. Experimental Section

The materials studied, synthesized in our laboratories, have different molar compositions ranging from 20/80 (E–TFE) to 60/40. Homogeneous films of about 30–40-μ thickness were obtained from ETFE powders under pressure at 300 °C.

Infrared spectra were taken with a Nicolet 20 SXB FT-IR instrument; the spectra reported are the result of a coaddition of 500 scans with a resolution of 2 cm^{-1}. Spectra in polarized light on stretched films using a Ge polarizer have also been recorded.

Raman spectra were obtained with a Dilor XY spectrometer with a 1024-channel diode detector. The spectra were taken on the powders under the microscope.

The numerical treatment of the data has been made on a PC with Lab Calc software (Galactic Industries).

3. Methods of Analysis: Infrared Intensities. Some General Concepts

3.1. Infrared Intensities and Charge Distribution in Molecules. The analysis of the infrared band intensities is a useful tool to obtain information on the electronic charge distribution and charge mobility in molecules and is regrettably seldom used in polymer spectroscopy.

In the last 25 years a number of models have been proposed to obtain, from measured intensity data, sets of parameters useful in describing the electrical properties of different compounds.[8,9] Relevant results have been obtained with the use of two (practically equivalent) models: EOP (electrooptical parameters)[10] and ECCF (equilibrium charges and charge fluxes)[11] models. The EOP model describes the charge distribution in a molecule in terms of bond dipole moments (directed along the chemical bonds). Bond dipoles change in value and direction during molecular vibrations. Thus EOP may be obtained from infrared intensities which can be expressed as a function of a few parameters, namely, μ°_k and $\partial\mu_k/\partial R_t$ (μ°_k are the equilibrium bond dipoles and $\partial\mu_k/\partial R_t$ their variation with the vibrational coordinates).

The ECCF model starts from the hypothesis that the charge distribution in a molecule may be described in terms of point charges located on the nuclei. These charges have "equilibrium" values (q°_α) which represent the charge distribution in the molecule in its equilibrium position and may change during molecular vibrations. Such charge variations are represented by the "charge fluxes" ($\partial q_\alpha/\partial R_t$). In the ECCF model the intensities of the infrared bands may be related to a set of q_α, $\partial q_\alpha/\partial R_t$. ECCF may be directly obtained from EOP and vice versa: each bond dipole may be indeed represented as a pair of point charges of opposite sign placed on the two nuclei defining the bond. In the discussion presented in this paper we will refer both to ECCF and EOP parameters.

Since ECCF (and EOP) are very localized parameters, they may be transferred with success from small model molecules to larger ones for predicting infrared spectra;

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comparison of ECCF (EOP) of a given chemical group in different chemical environments may be useful in evaluating the effect of the substituents on the charge distribution.[12] Infrared equilibrium charges have also been used for a *quantitative* description of the electrostatic potential around a molecule and for an estimate of the reactivity of specific molecular sites.[13]

Infrared intensities of a number of small gaseous molecules have been previously measured and analyzed and sets of ECCF have been obtained. However, the accurate calculation of ECCF (EOP) is not a straightforward procedure. It requires very precise *absolute* intensity data for *all*, well-separated, infrared active bands. A very reliable force field is needed for a correct assignment of bands and for a correct description of the normal modes; finally the numerical values for eigenvectors **L**, are essential in the ECCF treatment. It becomes then apparent from this discussion that the possibility to obtain ECCF is necessarily limited to a class of small and structurally simple compounds for which experimental and theoretical difficulties may be overcome.

On the other hand, a description of the charge distribution is often more interesting in the case of large and complex molecules for which other approaches (e.g., quantum chemical calculations) are impractical. In spite of the difficulties discussed above, we have recently shown[14,15] that it is still possible to obtain "semiquantitative" estimates of some charge parameters also from less sophisticated intensity data, without a detailed dynamical analysis, at least in the case of molecules containing C–H bonds. Characteristic intensity patterns have been observed for vibrations which involve C–H bonds, thus suggesting the occurrence of a characteristic charge distribution (and/or of charge mobility) in C–H bonds.

In this paper we discuss the case of ETFE copolymer; in this case "intensity pattern"/"charge" correlation has been used with success to derive a sufficiently detailed picture of the charge distribution from a rather complicated infrared spectrum.

3.2. Correlation between "Intensity Pattern" and "Charges". For a number of organic compounds, with the only exception of those which contain acetylenic C–H bonds, two very simple rules have always been verified:

(i) Stretching of apolar C–H bonds (q°_{H} practically vanishing) gives rise to very intense CH stretching bands in the IR spectrum. When the polarity of C–H bonds increases, a rapid decrease of CH stretching intensities is observed.

(ii) Correspondingly, the intensities in the CH deformation region are very small if hydrogen atoms carry small equilibrium charges but increase appreciably when the polarity of the C–H bond increases.

From observations (i) and (ii) it follows that compounds with "neutral" C–H bonds show spectra dominated by CH stretching bands. On the contrary compounds with "acidic" C–H bonds show spectra dominated by bands in the deformation region. Moreover, according to (i) and (ii), also relative intensities (the ratio between absorption intensities in the CH stretching region and absorption intensities in the deformation region, A^{str}/A^{def}) may be used to quickly obtain an estimate of the polarity of C–H bonds. This is useful in all those cases where the determination of absolute intensities is difficult as in the case of compounds in the solid state.

The application of the above concepts is immediate in the case of compounds which contain only C–H bonds. In this case the ratio A^{str}/A^{def} is obtained from integration over two, well-separated spectral regions. When the molecule contains other atoms (e.g., C=O, O–H, C–F, C–Cl bonds), it is impossible to measure the integrated intensity over the whole "CH deformation region". Deformation bands may be overlapped with other bands associated with the motions of the substituents. More important is the fact that sometimes the CH deformation mode may couple with the vibrations of the substituents. However, also in this case the analysis of the intensity ratios of some selected bands may be used as a marker for equilibrium charges in C–H bonds. In the application discussed in this paper on ETFE the very intense CH_2 scissoring band, well separated from the absorptions of CF_2, will be compared with CH_2 stretching bands to provide an experimental estimate of the charge of the hydrogen atoms.

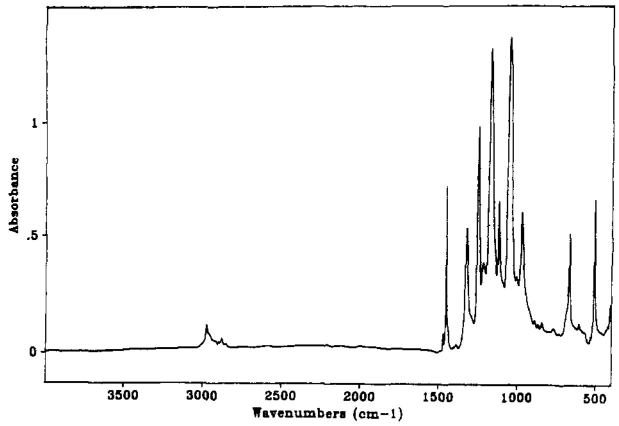


Figure 1. Survey infrared spectrum of ethylene–tetrafluoroethylene (ETFE) (equimolar composition).

Additional information may be obtained from IR spectra recorded in polarized light: in the case presented in this work, the analysis in polarized light of the CH_2 stretching intensities of stretch-oriented samples gives a precise indication of the occurrence of an appreciable charge flux along the CC skeleton and allows a *quantitative* estimation of such flux.

In conclusion, due to the fact that CH modes are very localized vibrations, much information on the electrical behavior of C–H bonds can be directly obtained from the intensity of only CH stretching vibrations also in the case of chemically complex polymers such as the polymer analyzed in this work.

4. Infrared Intensities of ETFE: A Preliminary Analysis

In Figure 1 we report the infrared spectrum of ethylene–tetrafluoroethylene copolymer. The sample is a copolymer of equimolar composition consisting mostly of a highly alternating structure. Ideally, it may be described as a regular alternate sequence of ethylene–tetrafluoroethylene monomers, $(CH_2CH_2CF_2CF_2)_n$. As discussed in the introduction, we assume a planar zigzag conformation for the chains.

From Figure 1, one can immediately notice that the CH_2 stretching bands (3010–2850 cm^{-1}) have negligible intensity if compared with the very strong bands below 1500 cm^{-1}.

A comparison of the IR spectrum of ETFE with that of polyethylene (PE) (Figure 2) shows the opposite intensity pattern. According to (i) and (ii) of section 2.2, we can conclude that the hydrogens of ETFE are much more positive than those of PE (from a complete infrared intensity analysis in terms of ECCF, it is known that the H atoms in PE carry a very small charge, $q^{\circ}_{H}(PE) = 0.05e$). This conclusion must be accurately checked: indeed, in the case of ETFE, it is, in principle, possible that the very large intensity in the 1500–400-cm^{-1} region is essentially due to large dynamical coupling between the strong CF_2 stretchings and CH_2 deformations. In our case a well-

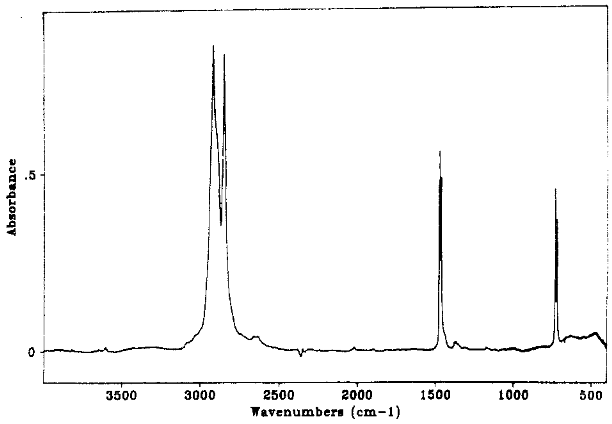


Figure 2. Infrared spectrum of solid polyethylene.

separated, strong band at 1453 cm^{-1} has been assigned to a practically pure CH_2 scissoring mode (δ_{CH_2}): the intensity of this band may be used as an internal "reference".

Let us measure the ratio R between the intensity of CH_2 scissoring and CH_2 stretchings (measured by integration over the all CH_2 stretchings region) of ETFE and compare it with the same kind of ratio obtained from the intensities in polyethylene: it turns out that R = 0.11 for PE and R = 1.11 for ETFE. The observed increase certainly implies an appreciable increase of the charge on the hydrogen atoms of ETFE. A quantitative estimate of the value of this hydrogen charge of ETFE will be made in section 5.2.

5. The CH_2 Stretching Vibrations of ETFE. Infrared Intensities and Dichroism

5.1. Assignments. In this section we present a detailed analysis of the infrared CH stretching region of ETFE based also on spectra in polarized light recorded on stretch-oriented samples (Figure 3). The symmetry group of the regular (alternate, transplanar) polymer is C_{2h}, and we base our study on this model. Any distortion from the regular structure (e.g., occurrence of defects) will be considered only if specific spectral indications are found.

For a C_{2h} model two infrared bands are expected in the high-frequency region of the infrared spectrum (d^+, symmetric CH_2 stretching, and d^-, antisymmetric CH_2 stretching).

The presence of a rather complex spectral pattern in the CH stretching region (Figure 3), immediately suggests that the "real" structure of the polymer must be considered. The copolymer is only ideally a regular chain of alternating ethylene–fluoroethylene units: error in the chemical linking may indeed produce "long" CH_2 sequences of the type $(CH_2)_N$ (N = 4, 6, ...). It is known that CH stretching frequencies are very sensitive to the bond properties of the vibrating CH group: correlations between CH stretching frequencies, interatomic C–H distances, and C–H bond formation energies are clearly shown and discussed by McKean in a series of works.[16] In the case of ETFE, the stretching frequencies of those CH_2 which belong to long sequences and are not adjacent to CF_2 units are expected to be different from that of CH_2 adjacent to a CF_2. The inductive effect of fluorines certainly decreases with the distance along the chain: as a result the "ionic character" of the CH_2 group in the long sequences should decrease by moving away from CF_2. In terms of bond properties, the CH_2 groups in these "defect" domains have lower bond energies and lower CH stretching frequencies than those of the CH_2 in the perfectly alternating chains. It follows that additional CH_2 stretching bonds at lower frequencies should be observed in the infrared spectra. Moreover, since apolar C–H bonds have intrinsic CH stretching absorption intensities larger than the polar ones, even a small population of errors in the linking should give rise to IR bands of appreciable intensity in the CH stretching region. These predictions are confirmed by the analysis of the IR spectra of copolymers with different E–TFE ratios (Figure 4). One can thus distinguish bands due to regular alternating sequences from bands due to defects.

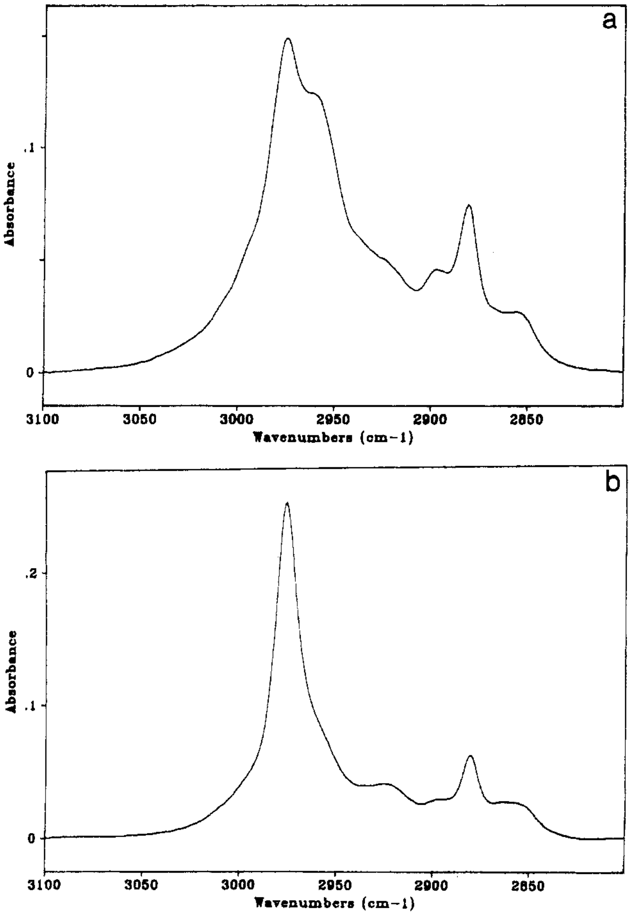


Figure 3. Infrared spectrum of a stretch-oriented sample of ETFE in the CH stretching region: (a) Electrical vector perpendicular to the draw axis. (b) Electrical vector parallel to the draw axis.

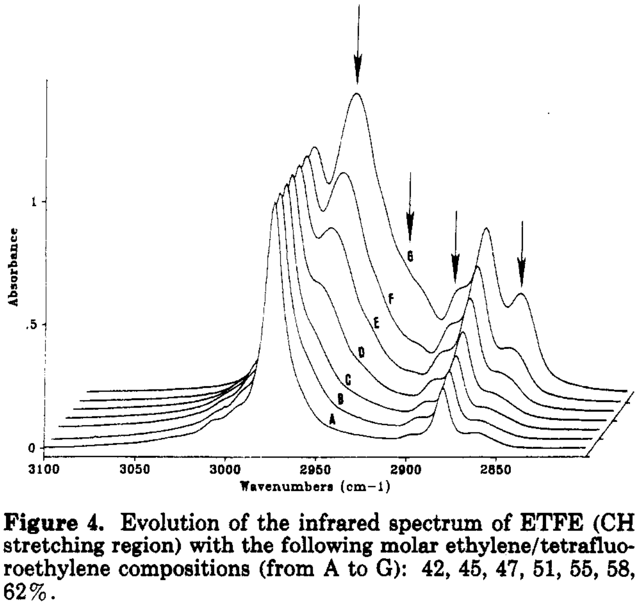


Figure 4. Evolution of the infrared spectrum of ETFE (CH stretching region) with the following molar ethylene/tetrafluoroethylene compositions (from A to G): 42, 45, 47, 51, 55, 58, 62%.

In Figure 4 we identify at least four bands which markedly increase in intensity when the concentration of ethylene increases in the copolymer. These bands at 2958, 2925, 2899, and 2856 cm^{-1} are indicated with arrows in Figure 4.

On the contrary, the strongest CH_2 stretching band at

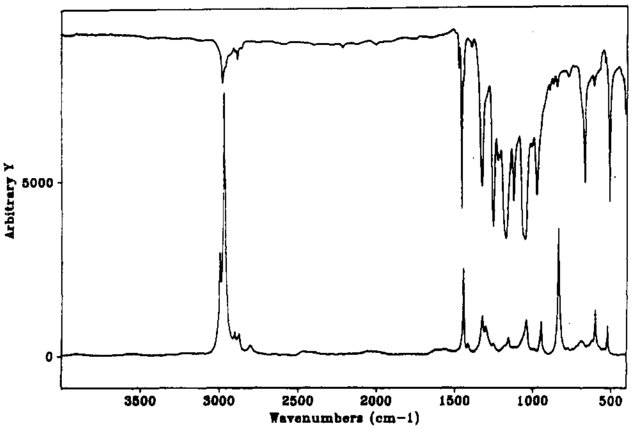


Figure 5. Infrared (upper) and Raman (lower) spectra of ETFE.

2976 cm^{-1} does not increase with the content of ethylene in the copolymer. It follows that the 2976-cm^{-1} band can be assigned to the stretching of the CH_2 in the regular (alternating) domains. The polarization properties of this band (Figure 3) clearly indicate that it is due to the symmetric CH_2 stretching (d^+, B_u species). Notice that, for C_{2h} symmetry, normal modes of A_u species (like d^-) induce dipole moment change in a direction orthogonal to the chain axis. B_u modes induce dipole change *in the molecular plane*: no more restrictions on the direction of the dipole variation are imposed by the symmetry. Thus, in principle, d^+ vibrations (B_u) may induce a dipole variation with nonvanishing component in the directions both parallel and perpendicular to the chain axis. Correspondingly, the infrared band may show appreciable intensity in both parallel and perpendicular spectra. This is indeed the case of the 2976-cm^{-1} band, which shows a parallel component larger than the perpendicular one. Our assignment for the d^+ band is in agreement with that of ref 17.

The assignment of the d^- band of the regular alternating sequences is not straightforward: Kobayashi et al.[17] assign this vibration to the very weak band at about 2856 cm^{-1}. We disagree with this choice since to our knowledge no compounds containing CH_2 groups show d^- modes at a frequency lower than d^+. Also normal-mode calculation gives $\nu(d^-) > \nu(d^+)$:[17] the inversion of this trend would imply changes in the interaction force constants which have not yet been reported with reasonable evidence. On the other hand, the behavior of the intensity of this band as observed in Figure 4 as a function of ethylene concentration in the copolymer composition is an even more convincing piece of evidence for disclaiming the assignment of ref 17.

If the hypothesis of a strong polarization of the C–H bonds is correct, an *appreciable* frequency shift of the center of gravity of CH_2 stretching bands (d^+ and d^-) toward higher frequencies is expected. (The reference values for frequencies of "unperturbed" CH_2 groups may be the d^- and d^+ frequencies of PE, at 2924 and 2842 cm^{-1}, respectively.)

For the above reasons, we need to look for the stretching d^- at frequencies higher than 2976 cm^{-1}. A very weak shoulder in the high-frequency side of the d^+ band (3010 cm^{-1}) is proposed as the d^- band. Notice that the d^- may be extremely weak due to the polar character of the C–H bonds of the "regular" sequences (see (i) and (ii) in section 2.2). Support of the choice of the infrared band at 3010 and 2976 cm^{-1} as d^- and d^+, respectively, comes from the Raman spectra of the same ETFE sample (Figure 5) where two very strong lines are observed at 2996 and 2969 cm^{-1}.

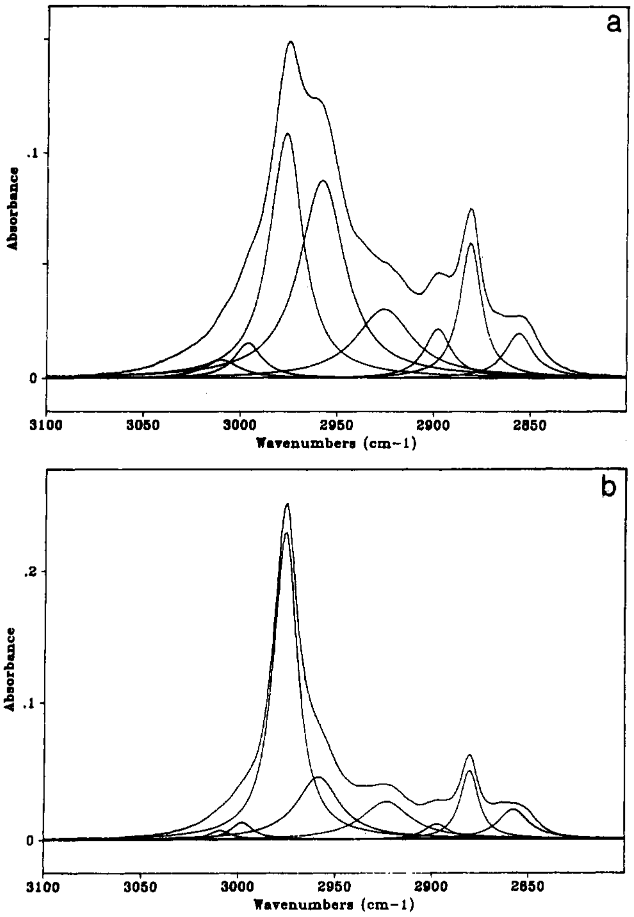


Figure 6. Curve fitting of the IR spectra of stretch-oriented ETFE (CH stretching region): (a) E vector perpendicular (⊥) to the draw axis (b) E vector parallel (‖) to the draw axis.

Table 1. Frequencies, Relative Intensities, and Dichroic Ratios of the Eight Infrared CH Stretching Bands Obtained by "Curve Fitting" of the IR Spectrum of a Sample of Stretch-Oriented ETFE Copolymer (of Equimolar Composition)

	ν (cm^{-1})	$A_\perp$	$A_\parallel$	$R_\perp/R_\parallel$
d^-	3010	0.274	0.136	2.02
	2996	0.409	0.268	1.53
d^+	2976	3.280	5.090	0.65
$d^-[(CH_2)_4]$	2958	3.610	1.840	1.97
$d^-[(CH_2)_n]$	2925	1.570	1.240	1.27
$d^+[(CH_2)_4]$	2897	0.550	0.270	2.02
	2881	1.190	0.890	1.34
$d^+[(CH_2)_n]$	2856	0.520	0.630	1.83

A detailed analysis of the intensity behavior of d^- and d^+ bands (in particular with respect to the dichroism) may provide useful information on the charge mobility in ETFE. However, because of the large band overlap in the CH stretching region, it is practically impossible from the spectra like those of Figure 3 to obtain intensity data relative to single bands. To overcome this difficulty, we have adopted a "curve fitting" procedure.

The results obtained are described in Table 1 and Figure 6. According to Table 1, eight components have been identified. Intensities and dicroic ratios for the eight bands are reported in Table 1 where the assignments are also proposed. As discussed above the 3010- and 2976-cm^{-1} bands are assigned respectively to d^- and d^+ of the regular sequences. Notice that the d^- band shows perpendicular polarization, as required by symmetry. Sequences of the type $(CH_2)_n$ ($n > 2$) are responsible for extra bands in the stretching region. If the inductive effect of fluorine on C–H bonds depends on the distance, we expect different bond properties and frequencies for CH_2 in long sequences.

Bands at 2958 and 2897 cm^{-1} must be certainly assigned to d^- and d^+ vibrations of "internal" CH_2 of $(CH_2)_4$ sequences; these bands are very sensitive to the ethylene

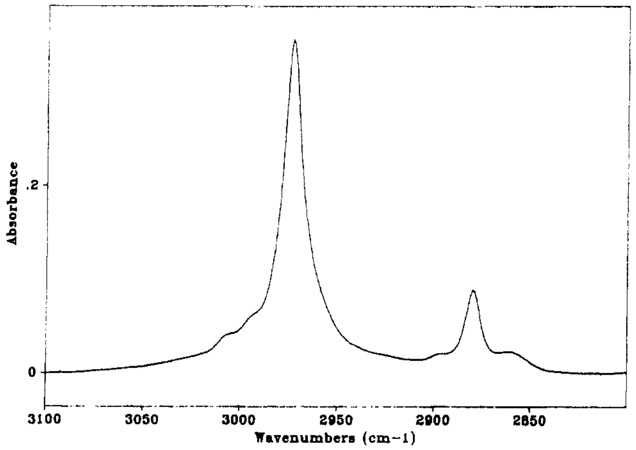


Figure 7. CH stretching region in the IR spectrum of an ETFE sample with a low ethylene content (40%).

content in the copolymer and may be observed even at low ethylene concentration (see Figure 4). The weak components at 2925 and 2856 cm^{-1} (which are clearly identified only in spectra E and F of Figure 4) may be assigned to CH_2 belonging to longer sequences $(CH_2)_n$ ($n > 4$). These bands become stronger when the content of ethylene in the copolymer increases above 50%; notice, moreover, that they show frequencies very close to those of polyethylene (2924 and 2852 cm^{-1}). In other words, these bands are characteristic of CH_2 groups which are not perturbed by fluorine.

In conclusion, from the viewpoint of the frequency analysis, we have identified three kinds of C–H bonds: (i) C–H bonds of CH_2 α to the CF_2 group (they are found either in the CH_2–CH_2 units of the regular alternating copolymer or in longer CH_2 sequences; they absorb at 3010 and 2976 cm^{-1}); (ii) C–H bonds of CH_2 β to CF_2, with bands at 2958 and 2897 cm^{-1}; (iii) C–H bonds of CH_2, third neighbors (γ) or at a further distance from the CF_2 group (they are practically unperturbed by the presence of fluorine and absorb at 2925 and 2856 cm^{-1}).

Two more components in the spectrum need to be assigned, namely, (i) a very weak peak in the high-frequency side (2996 cm^{-1}) at exactly the same frequency as the Raman d$^-$ line (this may be a Raman-active mode, activated by conformational distortions) and (ii) the relatively intense band at 2881 cm^{-1}, which is sensitive to the ethylene amount in the copolymer composition and is still observed at very low ethylene content (Figure 7); the origin of this band is a puzzle and may find various explanations.

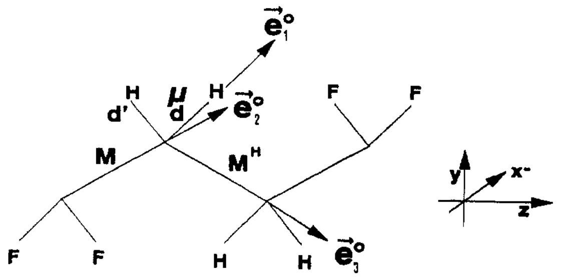
5.2. Charge Distribution in ETFE. Let us focus on the bands related to the perfectly alternating sequences in the ETFE copolymer. The first important problem to be understood is the anomalous dichroism observed for the d^+ band in the stretch-oriented sample. According to the symmetry, this band should arise from a dipole variation $\partial \mathbf{M}/\partial Q$ which lies in the plane of the chain, but with any possible orientation in this plane. From the theoretical viewpoint the fact that the d^+ band shows an appreciable intensity in both spectra recorded in parallel and perpendicular light is well understood. However, d^+ vibration takes place in a direction which is perpendicular to the chain axis. If during the vibration of the CH group charge fluctuations take place along the vibrating C–H bonds (perpendicular to the chain), no parallel component of $\partial \mathbf{M}/\partial Q$ should appear. In other words, to justify the dominating parallel component of the d^+ band, **large charge fluxes which take place along the CC backbone**, induced by CH stretching vibrations, **must exist**. The situation described here may be better clarified if one expresses the two components of $\partial \mathbf{M}/\partial d^+$ in terms of electrooptical parameters. This is done in Table 2, where also the EOP expression for the only $\partial M^x/\partial d^-$ component is reported.

Table 2. Molecular Dipole Moment Changes with d^+ (Symmetric CH_2 Stretching) and d^- (Antisymmetric CH_2 Stretching) as a Function of EOP (For Definition of the Symbols, See Figure Below)

$$\frac{\partial M^y}{\partial d^+} = \frac{2}{\sqrt{3}} \left\{ \frac{\partial \mu}{\partial d} + \frac{\partial \mu}{\partial d'} - \left(\frac{\partial M}{\partial d} + \frac{\partial M^H}{\partial d} \right) \right\}$$

$$\frac{\partial M^z}{\partial d^+} = \frac{2\sqrt{2}}{\sqrt{3}} \left(\frac{\partial M^H}{\partial d} - \frac{\partial M}{\partial d} \right)$$

$$\frac{\partial M^x}{\partial d^-} = \frac{2\sqrt{2}}{\sqrt{3}} \left(\frac{\partial \mu}{\partial d} - \frac{\partial \mu}{\partial d'} \right)$$



Both y and z components of $\partial \mathbf{M}/\partial d^+$ contain parameters which represent the variation of the C–C bond dipoles. $\partial M^H/\partial d$ and $\partial M/\partial d$ may be large if, during the stretching of CH, fluxes of electronic charge take place along the CC backbone. Notice that the z component (the only one responsible of the absorption of light polarized in the direction of the chain axis) depends only on CC dipoles; thus, the observed large parallel component of the d^+ band directly proves that an appreciable charge fluctuation takes place along the CC backbone in ETFE.

The situation discussed here is very similar to that observed in the polarized infrared spectra of stretch-oriented polyacetylene. Also in polyacetylene the CH stretching band shows a dominating parallel component. Using EOP,[18] it has been shown that very large charge fluxes takes place along the CC backbone, induced by the CH stretching of the C–H bond. However, in the case of polyacetylene, we deal with easily polarizable conjugated systems of π electrons; on the contrary, in the case under study we learn that an appreciable charge mobility along σ-bonded carbon atoms does occur. An indication of a certain charge mobility in σ-bonded carbon skeletons has been recently reported from the analysis (in terms of EOP) of the CH_2 wagging infrared intensity in polymethylenic chains.[19]

For the case under study using measured intensities data, it is possible to give an estimate of the EOP involved in the expressions reported in Table 2.

We briefly describe the steps we have taken:

(i) From the dichroic ratios of bands belonging to A_u species (perpendicular polarization), we have obtained a "rough" estimate of the degree of orientational disorder. Since, unfortunately, all bands of A_u species are strongly overlapped with other bands, the measured dichroic ratios are affected by large uncertainties.

(ii) The dichroic ratio of the d^+ band (2976 cm^{-1}), corrected for the amount of orientational disorder,[20] allows calculation of the ratio $|\partial M^y/\partial d^+|/|\partial M^z/\partial d^+|$. This ratio may be expressed in terms of EOP using the expressions of Table 2.

In the hypothesis of partial axial orientation the dichroic ratio is given[20] by:

$$R_{X,Z} = (\sin^2\theta + S)/(2\cos^2\theta + S) \qquad (1)$$

where Z is the draw direction, θ is the angle between the dipole variation and the chain axis, and S is the orientation parameter, which depends only on the distribution function of the chains around the draw axis.

For A_u bands $R_{X,Z} = (1 + S)/S$, since $\theta = 90°$ for symmetry reasons. In the case of our sample we estimate $S \approx 1.28$. From this value and $R_{X,Z}$ of the d^+ band, we find (with eq 1) the ratio $(\partial M^y/\partial d^+)/(\partial M^z/\partial d^+) = \tan\theta = 0.766$.

The orientation parameter S obtained may be interpreted according to different models which describe the kind of orientational disorder in the sample. If we assume that the sample consists of two fractions, one random and one fully oriented, we obtain that about 65% of the chains are randomly oriented.

(iii) The intensity ratio between the d^- and d^+ bands (in the perpendicular spectrum) gives the value of $|\partial M^x/\partial d^-|/|\partial M^y/\partial d^+|$, which can be expressed in terms of EOP, using the formulas of Table 2.

(iv) In this way we obtain a system with four unknowns (see Table 1) to be associated with the two experimental data (ii) and (iii). Since, in general, the nonprincipal parameters in the CH_2 groups are small, we make the approximation that $\partial\mu/\partial d' = 0$.

(v) We can then calculate the two parameters $\partial M/\partial d$ and $\partial M^H/\partial d$ **relative** to the "principal" parameter $\partial\mu/\partial d$. Because of the arbitrariness in the choice of signs for the component of the dipole derivatives, different solutions are possible for the system obtained. A solution compatible with the data obtained is the following:

$$\partial M/\partial d = -4.9\,\partial\mu/\partial d; \qquad \partial M^H/\partial d = \partial\mu/\partial d \qquad (2)$$

This solution indicates that an appreciable charge fluctuation induced by CH stretchings takes place along the C–C bond which links the two units CH_2 and CF_2. From our results it follows that the $\partial M/\partial d$ parameter, which is a nonprincipal EOP (in the sense that it involves a bond dipole variation of a bond (C–C) with respect to the variation (d) of a "different" bond (CH)), has a value about 5 times larger than the principal parameter $\partial\mu/\partial d$. The "numerical" estimate of the value of $\partial\mu/\partial d$ can be made in the following way: $\partial\mu/\partial d$ may be expressed in terms of ECCF as:

$$\partial\mu/\partial d = q°_H + (\partial q_H/\partial d)d°_{CH} \qquad (3)$$

The charge flux $\partial q_H/\partial d$ in the above equation may be transferred from other molecules since it has been found[12] that this parameter has about the same value (−0.20 e/A) for all CH bonds in sp^3 or sp^2 hybridization, independent of the chemical environment.

An approximate value for the equilibrium charge $q°_H$ can be obtained from the intensity ratios of the scissoring and of the antisymmetric CH stretching band. In this way from the measured intensity ratio we obtain a value of $q°_H = 0.19e$. This value indicates a strong polarization of CH_2 in ETFE, comparable to that of acetylenic C–H bonds ($q°_H$(acetylene) = 0.208e).

Using this value for $q°_H$, one obtains from eqs 2 and 3:

$$\partial\mu/\partial d = 0.03e; \quad \partial M^H/\partial d = 0.03e; \quad \partial M/\partial d = -0.142e \qquad (4)$$

The value calculated for $\partial M/\partial d$ is large but reasonable if compared with nonprincipal EOP of other molecules.

6. Conclusions

We have shown in this paper how it is possible to use **relative intensities** of some selected infrared bands to obtain a "semiquantitative" estimation of the charge distribution in a rather complex molecule like ETFE copolymer.

The use of intensity pattern/charge correlations provides unquestionable experimental proof that fluorine atoms strongly polarize (by the inductive effect) the C–H bonds of the CH_2 groups which are first neighbors of the CF_2 units. CH_2 stretchings also show that the inductive effect by the F atom on the adjacent CH_2 groups decreases with distance and practically dies off at the fourth CH_2 neighbors.

The analysis of the behavior of the CH stretching band intensities in the spectra recorded in polarized light on stretch-oriented samples indicates that the backbone of σ-bonded carbon atoms carries rather mobile electrons, sensitive to the vibrations of C–H bonds.

A quantitative estimate of the charge and flux parameters is also attempted; even if these parameters have been obtained under severe approximations, they could be useful for a simple comparison among the ETFE copolymer and other different compounds.

A possible application of these reasonings may be the definition of empirical acidity scales for C–H bonds in different (polymeric) environments.[21]

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