Infra-red optical absorption of oriented polyacetylene

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In this paper we report on polarized infra-red absorption spectra of polyacetylene and deuterated polyacetylene, oriented by rolling. This allows for a complete description of the optically active normal modes, and evidence of some defect modes. Far infra-red measurements lead to the determination of the dielectric constant parallel and perpendicular to the chain.

(Keywords: polyacetylene; optical anisotropy; infra-red spectra; normal modes; dielectric constant)

INTRODUCTION

The vibrational properties of polyacetylene are of much interest as this polymer is the simplest example of highly conjugated double bonds in a one dimensional chain. At the present time, a great number of theoretical papers have tried to account for experimental results from Raman scattering and infra-red absorption. Concerning undoped material, most papers refer to the pioneering work of Shirakawa et al.[1] which gave the first assignments of i.r. peaks. Unfortunately the experimental results used in that work were obtained with unoriented samples so that some of the conclusions must be considered as somewhat hypothetical.

In the present paper we report on i.r. absorption results on oriented *cis* and *trans* polyacetylene and propose assignments for the observed absorption frequencies.

EXPERIMENTAL

Cis polyacetylene and deuterated polyacetylene were prepared in our laboratory by Shirakawa's technique, using the catalytic system $AL(Et)_3$, $Ti(OBu)_4$ in toluene at $-78°C$. Films from twenty to hundred microns thick were used.

Rolling is performed in the atmosphere, holding the film between aluminium sheets in order to smooth the stress. The stretching is achieved by a number of passes, with l/l_0 ratio of about 3.

X-ray diffraction provides a simple method of checking the anisotropy of stretched films. *Figure 1* reports diffraction patterns of *cis* $(CH)_x$ before and after rolling, which indicates the orientation of the polyacetylene chain along the stretching direction. These results are similar to those obtained when the film is oriented by pulling[2].

We should point out that e.p.r. measurements on such samples reveal no change associated with rolling. This differs from the result published by Vancso[3] who found a decrease of the linewidth.

Transmission infra-red spectra with polarized light have been recorded on a fast Fourier transform Bruker spectrometer. During the measurements, samples were
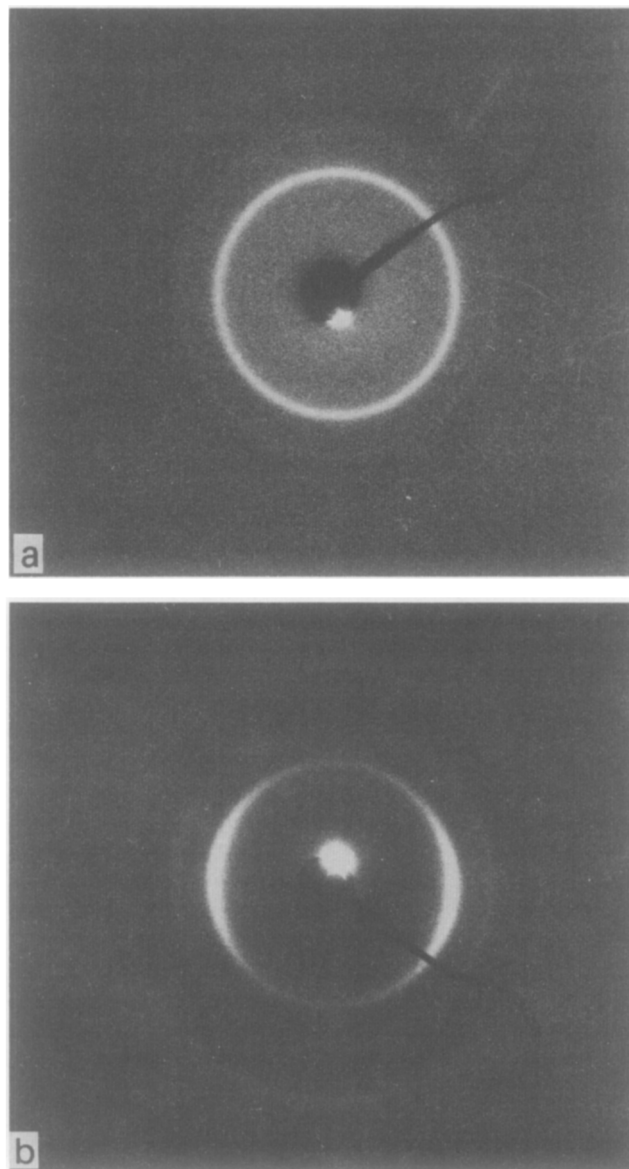

Figure 1 Diffraction patterns of: (a) pristine *cis* polyacetylene; (b) rolled *cis* polyacetylene

kept under vacuum to avoid oxidization. *Cis* $(CH)_x$ absorption spectra with the electric field parallel and perpendicular to the rolling direction are reported in *Figure 2*. Both spectra exhibit the same absorption frequencies but with differing intensities according to the polarization direction. This confirms the preferential orientation of the chain along the rolling direction. An attempt has been made to look for a preferential orientation of the plane of the chains with respect to the plane of the film, by absorption measurement with oblique incidence. No effect was detected.

ANALYSIS OF OPTICAL MEASUREMENTS

Absorption spectra such as those reported in *Figure 2* come from samples which are only partially oriented. The aim is to obtain the pure absorption spectra parallel and perpendicular to the direction of the chain. This will allow us to obtain the separation between parallel and perpendicular absorption peaks as well as the determination of the longitudinal and transverse portions of the dielectric constant. With these aims in mind we can solve the problem with a second rank tensor formalism, neglecting interchain coupling.

Under this hypothesis, the point group of a *cis* chain is D_{2h}, so that a tensor associated to this chain can be written

$$A = \begin{bmatrix} A_X & 0 & 0 \\ 0 & A_Y & 0 \\ 0 & 0 & A_Z \end{bmatrix}$$

in the coordinate system $(0, X, Y, Z)$ bounded to the chain.

In the coordinate system $(0, x, y, z)$ bounded to the film the components are:

$$A' = R^{-1}AR$$

where R is the matrix of the rotation which exchanges the two systems. In the following we chose $0Z$ parallel to a chain and $0z$ parallel to the rolling direction.

For a statistical distribution of chain orientations, the observed value of A is the average of A' for all the values of
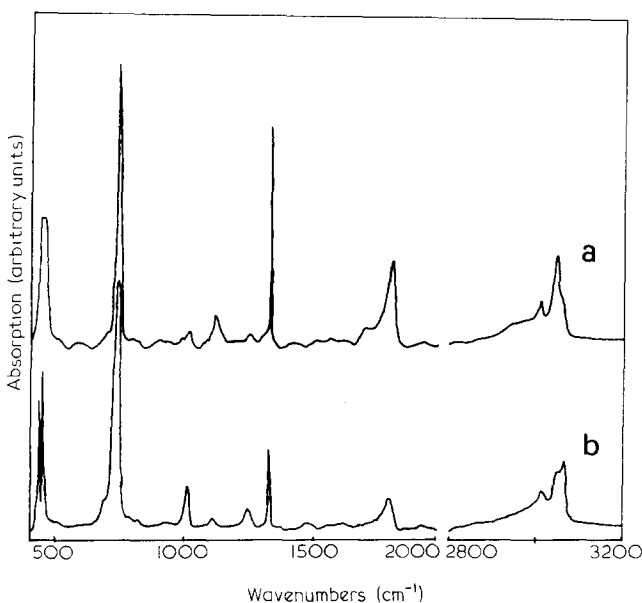

Figure 2 Absorption spectra of *cis* polyacetylene: (a) electric field ‖ rolling direction; (b) electrical field ⊥ rolling direction

R, that is to say for all possible orientations of the chain. According to the previous section, we need only one statistical parameter to describe the set of rotations: the angle $\theta = (0z, 0Z)$ of one chain with respect to the rolling direction.

Under these conditions, the mean value of A' can be written

$$A_{obs} = \begin{bmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{bmatrix}$$

with

$$A_x = A_y = \frac{A_X + A_Y}{4}(1 + \overline{\cos^2\theta}) + \frac{A_Z}{2}\overline{\sin^2\theta}$$

$$A_z = \frac{A_X + A_Y}{2}\overline{\sin^2\theta} + A_Z\overline{\cos^2\theta}$$

and $\overline{\cos^2\theta} = 1 - \overline{\sin^2\theta}$ is the average of $\cos^2\theta$.

Conversely it is easy to express $\frac{A_X + A_Y}{2}$ and A_Z as a function of A_x and A_z:

$$A_\perp = \frac{A_X + A_Y}{2} = \frac{2\overline{\cos^2\theta}\,A_x - \overline{\sin^2\theta}\,A_z}{3\overline{\cos^2\theta} - 1} \quad (1)$$

$$A_\parallel = A_Z = \frac{-2\overline{\sin^2\theta}\,A_x + (1 + \overline{\cos^2\theta})A_z}{3\overline{\cos^2\theta} - 1} \quad (2)$$

(the symbols $\perp$ and $\parallel$ refer to the chain).

For a *trans* chain, the point group is C_{2h} so that the tensor A has the form

$$\begin{bmatrix} A_X & 0 & A_{XZ} \\ 0 & A_Y & 0 \\ A_{XZ} & 0 & A_Z \end{bmatrix}$$

The same calculation, gives exactly the same results for A_{obs}, $A_\parallel$ and $A_\perp$, the of-diagonal term A_{XZ} being unobservable.

We can see that the determination of $\overline{\cos^2\theta}$ is sufficient to calculate $A_\perp$ and $A_\parallel$ from the known spectra A_x and A_z. In practice we determine $\overline{\cos^2\theta}$ in the following way: we chose one absorption line which can be unambiguously assigned to one spectrum ($A_\parallel$ for instance) and we fit the value of $\overline{\cos^2\theta}$ in equation (1) so that the resulting linear combination contains no absorption contribution for that frequency. In *cis*-$(CH)_x$ for instance the most convenient frequency line for this process is the CH in plane mode at $1330\,cm^{-1}$ which belongs to the parallel (‖) spectrum (1049 for CD_x).

The $A_\parallel$ and $A_\perp$ spectra of $(CH)_x$ and $(CD)_x$ are presented in *Figures 3* and *4* respectively. In both cases a good separation of the absorption peaks into two distinct sets can be seen which justifies the analysis process.

RESULTS AND DISCUSSION

Assignment of absorption lines

The assignment of i.r. absorption peaks has been discussed by Shirakawa[1] on the basis of group theory predictions for an infinitely long chain. However, our
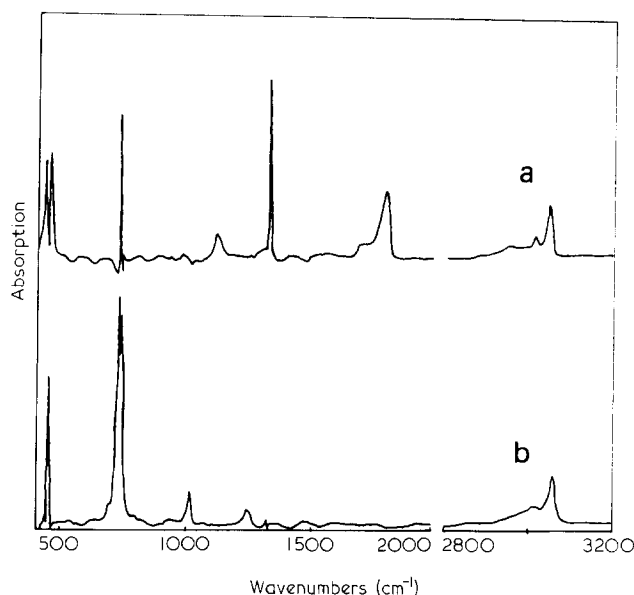
Figure 3 (a) Purely parallel absorption spectra of *cis* CH$_x$; (b) purely perpendicular absorption spectra of *cis* CH$_x$
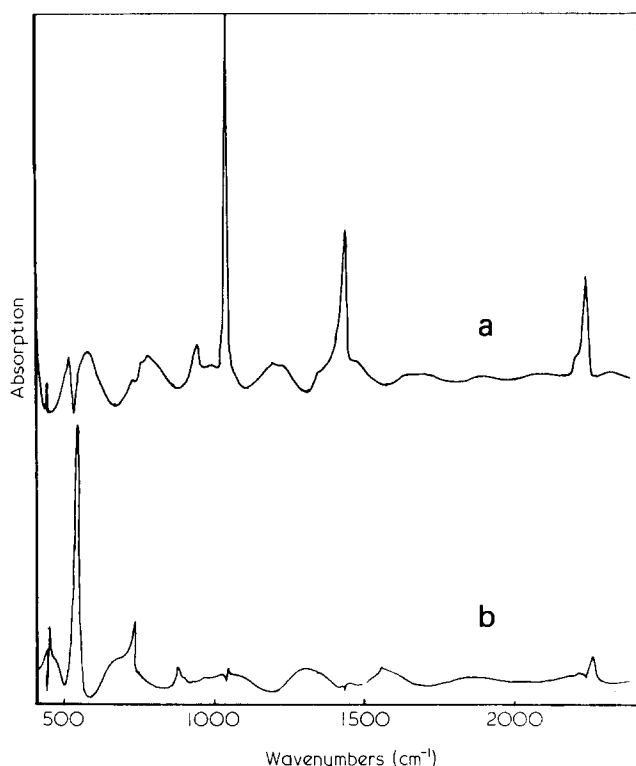

Figure 4 Absorption spectra of *cis* CD$_x$: (a) purely parallel to the chain direction; (b) purely perpendicular to the chain direction

measurements are in some disagreement with his results and therefore, we will have to come back to these differences in the discussion below.

Cis *isomer.* Group theory predictions for this isomer (see *Table 1*) leads to 7 i.r. active one phonon modes, 3 parallel to the chain (T_z), 3 in plane modes perpendicular to the chain (T_x), and 1 out-of-plane mode perpendicular to the chain (T_y). From our measurements we can only separate parallel modes (T_z) from perpendicular modes (T_x or T_y). The point being that we observe for (CH)$_x$, 6 peaks in the parallel spectrum instead of 3 and 3 in the

perpendicular spectrum instead of 4 while we find for (CD)$_x$, 8 peaks in the parallel spectrum and 3 in the perpendicular spectrum. These frequencies are labelled in *Table 2*, together with Shirakawa's results.

If we try to classify the fundamental modes from the point of view of the involved deformations, we expect two C–H stretching modes (T_x and T_z), two C–H in-plane angular deformation modes (T_x and T_z), one C–H out-of-plane mode (T_y) and two chain modes (T_x and T_z). In the set of observed frequencies, some can be assigned without any problem to some modes because of their values.

The frequencies 3058 and 3045 cm^{-1} (2265 and 2248 respectively for (CD)$_x$) are the C–H stretching modes, the 745 cm^{-1} peak (resp. 546) is the out-of-plane C–H mode, 450 cm^{-1} (resp. 402) is the frequency of angular deformation of the chain, lastly 1798 and 1690 (1446 and 1359 respectively) are not fundamental frequencies but combination frequencies[4].

Table 1 Group theory analysis of normal modes

Cis (CH)$_x$ group D$_{2h}$			N	n	n$_H$	n$_C$
A$_g$		Raman	4	4	2	2
B$_{1g}$	R$_z$	Raman	2	1	1	0
B$_{2g}$		Raman	4	4	2	2
B$_{3g}$		Raman	2	2	1	1
B$_u$		Inactive	2	2	1	1
B$_{1u}$	T$_z$	i.r.	4	3	2	1
B$_{2u}$	T$_y$	i.r.	2	1	1	0
B$_{3u}$	T$_x$	i.r.	4	3	2	1

Trans (CH)$_x$ group C$_{2h}$			N	n	n$_H$	n$_C$
A$_g$		Raman	4	4	2	2
B$_g$	R$_z$	Raman	2	1	1	0
A$_u$	T$_y$	i.r.	2	1	1	0
B$_u$	T$_x$T$_z$	i.r.	4	2	2	0

N: number of normal modes
n: number of internal vibrations
n$_H$: number of hydrogen modes
n$_C$: number of chain internal vibrations

Table 2 Experimental frequencies and assignments

(CH)$_x$[a]	(CD)$_x$[a]	(CH)$_x$[b]	(CD)$_x$[b]	Symmetry and assignment[b]
3057	2275	3058⊥	2265⊥	B$_{3u}$ C–H stretching
3044	2255	3045//	2248//	B$_{1u}$ C–H stretching
1800		1798//		⎫
	1448		1446//	⎬ Combinations
1690	1360	1690//	1359//	⎭
1329	1050	1330//	1049//	B$_{1u}$ C–H in plane
	975		975//	
	947		947//	
1249	892	1248⊥	892⊥	B$_{3u}$ C–H in plane
1118	800	1118//	798//	Defect
740	548	745⊥	546⊥	B$_{2u}$ C–H out of plane
446	402	450//	402//	B$_{1u}$ chain angular deformation

Trans (CH)$_x$ and (CD)$_x$				
3013	2231	3011	2225	B$_u$ C–H stretching
1292		1292		Defect
	916	1253	910	B$_u$ C–H in plane
1015	752	1015⊥	750⊥	A$_u$ C–H out of plane

[a] Ref. 1
[b] This work

The in-plane deformation modes of C–H have been assigned by Shirakawa to the peaks observed at 1330 and 1248 cm^{-1}. This is in agreement with our results since they have the expected polarization. 1330 is the T_z mode and 1248 the T_x mode. The corresponding frequencies for (CD)$_x$ are clearly 1049 (T_z) and 892 cm^{-1} (T_x).

Two remaining problems are the determination of the frequency of the second chain mode (T_x), and gaining an understanding of the origin of the unassigned frequencies. It is clear that no experimental value can be assigned to the chain mode frequency. This frequency is expected in the range 1000–1200 cm^{-1} for (CH)$_x$ as well as (CD)$_x$, with polarization perpendicular to the chain. For this mode Shirakawa proposed the peak at 1118. This cannot be so since we found that 1118 is polarized parallel to the chain. Indeed, there is no experimental frequency in the expected range with the expected polarization. We must therefore conclude that the chain mode is too weak to be observed experimentally.

The validity of our assignments can be tested by the Teller–Redlich products rule. *Table 3* shows the experimental and theoretical products in excellent agreement.

Let us now come back to the unassigned experimental frequencies and especially at 1118 cm^{-1}. We pointed out the peculiar behaviour of the intensity of this peak during the isomerization process. During thermal treatment this intensity does not decrease regularly, but remains virtually unaffected until the last step of isomerization and then it decreases to zero. We believe that this frequency comes from localized modes at junctions between *cis* and *trans* sequences. We report in *Figure 5* a possible configuration of such a junction. In this hypothesis the localized mode would be a C–H deformation. This accounts for the observed frequency which is lower than C–H in-plane frequencies and higher than C–H out-of-plane frequencies. The existence of a corresponding line at 798 cm^{-1} for (CD)$_x$ exhibiting the same behaviour during isomerization supports this interpretation since the ratio of frequencies (1,39) is close to the theoretical value for a perfectly localized mode on a rigid chain (1,414). A comparison of the intensity of the peak at 1118 cm^{-1} with the intensities of other C–H deformation peaks gives an order of magnitude of the number of *cis–trans* junctions. Using this method we found the average length of *cis* sequences to be equal to 30 C–H units.

Trans *isomer.* In the case of *trans* (CH)$_x$ or (CD)$_x$ the symmetry point group is C_{2h} and the i.r. active modes can be separated into one in-plane and two out-of-plane modes. This distinction is not the same as the experimental one which is perpendicular or parallel to the chain. The out-of-plane modes are clearly perpendicular to the chain but the in-plane modes contribute to both absorption spectra.

A second difficulty arises from the isomerization process. We found that it is possible to stretch *trans* films by rolling, but the resulting film has no optical anisotropy. In the same way the complete thermal isomerization of oriented *cis* films (150°C during 1 h) leads to unoriented *trans* films.

The best method of obtaining anisotropic *trans* films was to use partially isomerized films, obtained by heating oriented *cis* films at 60°C, over three months. The resulting spectra naturally exhibit *cis* and *trans* lines but the method described above applies and we have in this way separated the *trans* frequencies into in-plane and out-of-plane modes (see *Table 2*). Indeed the assignments of the *trans* modes is not at all difficult: 1015 cm^{-1} (750 for CD$_x$) is the out-of-plane mode, 3011 (resp. 2225) is the C–H (resp. C–D) stretching mode. The only problem is assigning the remaining frequencies. Two lines are observed in (CH)$_x$ at 1292 and 1253 cm^{-1} and one at 910 cm^{-1} for (CH)$_x$. A Raman frequency has already been pointed out at 1290 cm^{-1}.[5,6] In the infra-red spectrum, the intensity of this mode is known to be strongly dependent upon dopant concentration[6–9]. We therefore conclude that the 1292 cm^{-1} mode is not a fundamental mode of the chain but is associated with some defect capable of carrying some charge after doping. The fundamental (CH)$_x$ mode is thus 1253 cm^{-1} (910 cm^{-1} for CD$_x$).

The Teller–Redlich product rule is a good test to confirm the validity of this assignment (see *Table 3*).

Far infra-red spectra. Far i.r. transmission has been measured for the *cis* film. *Figure 6* shows spectra which exhibit the periodical dependence of the transmittance with respect to the wavenumber due to interference effects. Fitting of these curves by calculated transmittances of thin films allows determination of the optical index or dielectric constant. Using the formulae discussed earlier and the values of $\overline{\cos^2\theta}$ deduced from middle infra-red analysis, it is natural to calculate the dielectric constant parallel to the chain

$$(\varepsilon_\parallel = \varepsilon_z)$$

and perpendicular to the chain

$$\left(\varepsilon_\perp = \frac{\varepsilon_x + \varepsilon_y}{2}\right)$$

The results are $\varepsilon_\parallel = 15 \pm 2$ and $\varepsilon_\perp = 2.3 + 0.5$.

Clearly the accuracy is not very high because of the inaccuracy in the determination of $\overline{\cos^2\theta}$. The errors indicated represent the spread of the values obtained for different samples. For *trans* (CH)$_x$ such a determination of ε was not possible.

These values of $\varepsilon_\perp$ and $\varepsilon_\parallel$ can be compared to previous determinations of ε.

Table 3 Teller–Redlich product rule: (ω_H/ω_D)

	Cis (CH)$_x$			Trans (CH)$_x$	
	B$_{1u}$	B$_{2u}$	B$_{3u}$	B$_u$	A$_u$
Theoretical	1.927	1.363	1.927	1.858	1.363
Experimental	1.922	1.364	1.889*	1.863	1.353

* Value deduced from only two experimental modes

Figure 5 Possible configuration of *cis–trans* junction

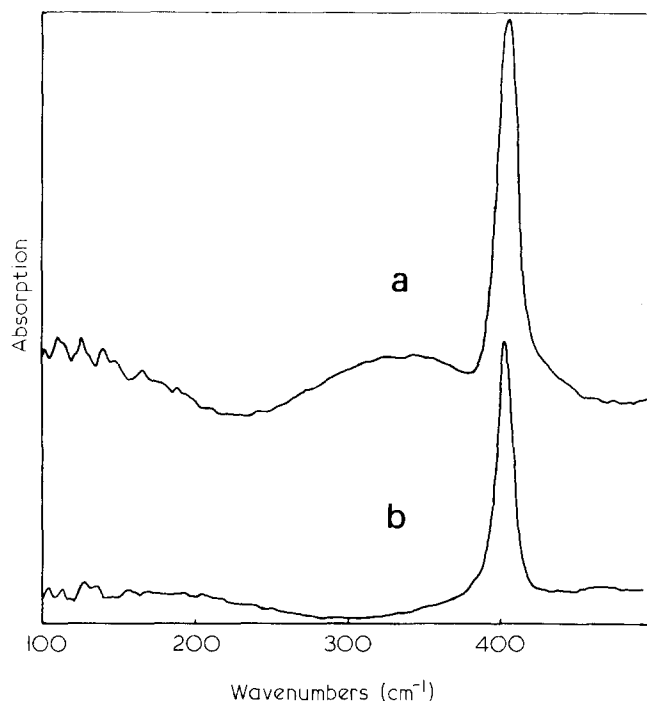**Figure 6** Far infra-red absorption spectra of *cis* CH_x: (a) electrical field ‖ rolling direction; (b) electric field ⊥ rolling direction

Fincher *et al.* found a value of $\varepsilon_\parallel = 11 \pm 1$ both by microwave cavity perturbation at 10 GHz[7] and infra-red reflexion[10]. In both cases, nevertheless, the orientation of the films is more estimated than measured so that our result is consistent with theirs. It is also consistent with previous measurements of Montaner *et al.*[11] on un-oriented films leading to $\varepsilon_m = 7.8 \pm 0.5$ while the present work leads to $\varepsilon_m = \frac{1}{3}\varepsilon_\parallel + \frac{2}{3}\varepsilon_\perp = 6.7 \pm 0.9$.

Other microwave measurements at 9.1 GHz by Mihaly[12] on unoriented films and Devreux[13] on oriented films report a lower value for $\varepsilon_m = 3.7 \pm 0.2$. Such a discrepancy is probably related to a difference in film quality.

CONCLUSION

In this paper we have presented a description of the infra-red absorption of polyacetylene in terms of fundamental modes or defect modes. We expect that the results concerning fundamental modes are a useful tool for all theoretical investigations of chain dynamics.

Conversely theoretical calculation of defect mode frequencies and optical activity are necessary to conform the validity of our assignments and give a description of the motions involved.

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