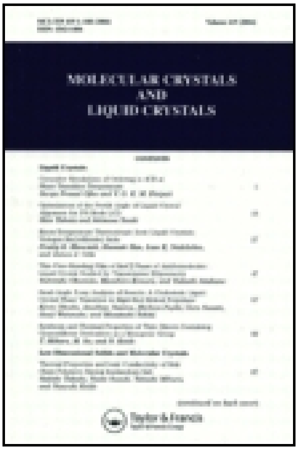

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Optical Modes of Cis and Trans Polyacetylene

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OPTICAL MODES OF CIS AND TRANS POLYACETYLENE

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ABSTRACT Partially oriented $(CH)_x$ and $(CD)_x$ films were obtained by rolling in the cis and trans form. This orientation is evidenced by X ray and polarized infrared spectroscopy. A quantitative analysis of these spectra leads to a separation between the purely parallel and purely perpendicular contributions to absorption. A check with group theoretical predictions allows then a complete assignment of the observed peaks to normal modes of the chain.

INTRODUCTION

In the recent few years, extensive studies of the dynamical properties of polyacetylene have been made, mainly in the lone chain approximation. Normal modes of the pure chain, defect modes, soliton modes, have been investigated theoretically in many details. However, the experimental frequencies to be compared with the theoretical ones are not always assigned with enough confidence. In this paper we report I.R. optical modes and propose assignments for some of them in terms of normal modes or defect modes for cis and trans polyacetylene and deuterated polyacetylene.

EXPERIMENTAL

The experimental aspects of this work and the analysis procedure of the I.R. spectra have been published elsewhere, (M.Galtier et al[1]), so that we just summarize the main points.

Polyacetylene and deuterated polyacetylene were synthesized by Shirakawa's method. Partially oriented films were obtained by rolling. From polarized I.R. absorption spectra, purely parallel and perpendicular absorption were obtained by suitable linear combinations. The discussion and assignment of normal modes were done in the lone chain approximation on the basis of group theory prediction for D_{2h}(cis) and C_{2n}(trans) point group.

NORMAL MODE ASSIGNMENT

Tables 1 and 2 give the frequencies of the I.R active normal modes for trans and cis polyacetylene and deuterated polyacetylene. These results, already published (ref[1]) have been confirmed by R.Turbino[2] with a different experimental technique. One of the expected modes (C-C valence bond in cis) is missing in Table 1 because no absorption line with polarisation perpendicular to the chain could be detected in the expected frequency range. Several combination modes have been also found in the range 1600-1800 cm^{61} in agreement with previously published results by Shirakawa et al[3].

TABLE I Trans$(CH)_x$and $(CD)_x$normal modes

Frequencies (cm^{-1}) $(CH)_x$	$(CD)_x$	Assignment	
3011	2225	B_u	C-H stretching
1253	910	B_u	C-H in plane
1015	750	A_u	C-H out of plane

TABLE II Cis$(CH)_x$and $(CD)_x$ normal modes

Frequencies $(CH)_x$	(cm^{-1}) $(CD)x$	Assignment
3058	2265	B_{3u} CH stretching
3045	2248	B_{1u} CH stretching
1330	1049	B_{1u} CH in plane
1248	892	B_{3u} CH in plane
745	546	B_{2u} CH out of plane
450	402	B_{1u} C-C=C angular deformation

Defect modes

In cis $(CH)_x$ one absorption band appears at 1118 cm^{-1} (798 in $(CD)_x$) with polarization parallel to the chain. This mode has a peculiar behaviour during isomerization (see Fig 1) compared to other cis modes. Its intensity remains important untill the last step of isomerization. We assign it to bending vibration of C-H or C-D group in cis trans junction. This result is supported by the frequency ratio 1118/798 = 1.40, very close to $(M_D/M_H)^{\frac{1}{2}}$

Another defect mode appears in trans$(CH)_x$ at 1292 cm^{-1}. The $(CD)_x$ corresponding frequency seems to be missing. Let us point however that in doped samples, this mode is greatly enhanced with no frequency shift. On the other hand, in doped $(CD)_x$ a weak band appears at 1220 cm^{-1}, increasing with doping level without frequency shift. We thus consider it as the corresponding one.

The origin of these modes is not obvious. A possible explanation is suggested by M.W.Gibson et al[4],which pointed the fact that cis bond in trans polyacetylene are able to confine solitons. The behaviour of the 1292cm^{-1} absorption band under doping is consistent with this idea so that we tentatively assign it to a carbon carbon motion of remainning cis bonds in trans polyacetylene.

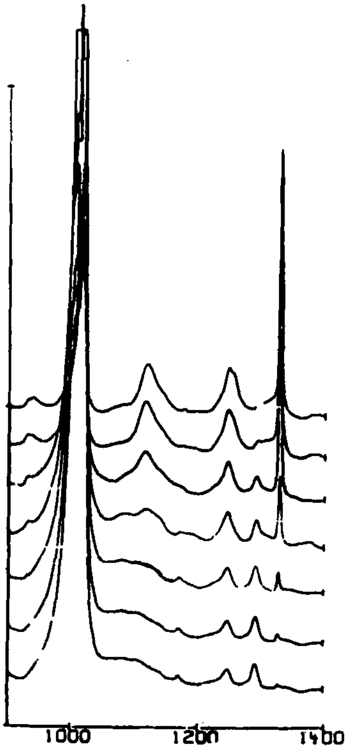

FIGURE 1 I.R absorption during isomerization.

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