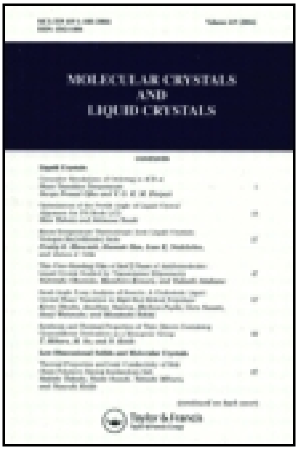

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Vibrational study of polyacetylene

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To cite this article: M. Galtier , C. Benoit & A. Montaner (1982): Vibrational study of polyacetylene, Molecular Crystals and Liquid Crystals, 83:1, 109-115

To link to this article: http://dx.doi.org/10.1080/00268948208072160

Mol. Cryst. Liq. Cryst., 1982, Vol. 83, pp. 109–115
0026-8941/82/8301-0109$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

VIBRATIONAL STUDY OF POLYACETYLENE

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Received for publication August 31, 1981

ABSTRACT : Using spectroscopic data (I.R., Raman), we have built a dynamical model for an infinite cis polyacetylene chain. This model allows an assignement of Raman frequencies and discussion of experimental results.

I. INTRODUCTION

Many experimental informations about polyacetylene vibrational properties are difficult to understand for lack of a dynamical model for the infinite and finite chain. Several attempts have been made for trans isomer (1) (2). We give here the first results concerning cis form.

II. DESCRIPTION OF THE MODEL

Though polyacetylene has a crystalline stucture, the interchain coupling dont seem to play an important role in its vibrational properties. In this work we consider it as a 1d crystal.

Several models are commonly used to describe intramolecular interactions. They differ from each other by the a priori properties expected for the different bonds or interatomic interactions. In the case of trans polyacetylene, Inagaki results (1975), show that these models fail to describe conjugation efforts. For instance Urey-Bradley force field must be completed with off diagonal terms. So we started with a very general expansion of potential energy in terms of internal coordinates of the chain and used the fitting process to reduce as much as possible the number of force constants. Table 1 describes the internal coordinates used in the expansion and table 2 gives the values of force constants deduced from fit. The values given in this table are only the ones corresponding to in plane deformations of the chain. For out of plane vibrations, the number of experimental results available is too small to allow a good fit of parameters.

TABLE 1 :

INTERNAL COORDINATES

C = C double bond length	$(C = C)_{eq} = 1.35$ Å
C - C single bond length	$(C - C)_{eq} = 1.46$ Å
C - H carbon hydrogen distance	$(C - H)_{eq} = 1.09$ Å
φ angle between a single and a double bond	$\varphi_{eq} = 127.3°$
α angle between C_iH_i and the bissector of $C_{i-1}C_iC_{i+1}$	$(C{=}C{-}H)_{eq} = 120°$

III. FITTING PROCESS

Cis polyacetylene contains 8 atoms per unit cell, so that its phonon spectra consists of 24 branches. In the center of Brillouin zone 3 translations modes and one rotation around the chain direction have vanishing frequency. The twenty remaining modes can be easyly classified by group theoretical analysis : 7 modes are Infrared active.

- 3 modes polarized paralled to the chain (B_{1u})
- 3 modes polarized perpendicular to the chain (B_{3u})
- 1 mode out of plane

11 modes are Raman active

- 4 totally symetric (Ag)
- 4 modes B_{2g}

- 2 modes B_{3g} out of plane
- 1 mode B_{1g} out of plane

The two remaining modes are Raman and Infrared inactive (Au).

TABLE 2 :

Force constants : Units are md $Å^{-1}$, md, md Å

$(C=C)^2$	6.70	φ^2	0.80
$(C-C)^2$	3.87	$\varphi_1(C_1=C_2)$	- 0.51
$(C_1=C_2)(C_2-C_3)$	0.95	$\varphi_2(C_2-C_3)$	- 0.29
$(C_1=C_2)(C_3=C_4)$	0.63	α^2	1.00
$(C_2-C_3)(C_4-C_5)$	0.18	$\alpha_1 \ \alpha_2$ *	0.06
$(C-H)^2$	5.05	$\alpha_2 \ \alpha_5$ *	0.06
$(C_1-H_1)(C_2-H_2)$ *	0.02	$\alpha_1(C_1=C_2)$	0.59
$(C_2-H_2)(C_5-H_5)$ *	0.02	$\alpha_2(C_2-C_3)$	0.27

* These force constants cannot be separated by center zone analysis. They have been put equal for simplicity.

Several authors have published experimental results for polyacetylene and deuterated polyacetylene. I.R. results have been quite completely given by Shirakawa et al. (3) and corroborated later by Fincher (4) and RABOLT (5).

Raman measurements are more difficult because of isomerisation process and no result concerns polarized scattering by streched films, so that the assignement of the observed frequencies to the various irreducible representation is doubtful. Moreover, if the different experimentalists are in good agreement for the frequencies of the most intense modes (908, 1247, 1541 cm^{-1} for $(CH)_x$, 976, 1470 for $(CD)_x$) they disagree for the lower ones. (6), (7), (8), (9).

The fitting procedure was the following : starting from one hypothesis on frequencies assignements of the well known modes, we tried to fit the model with a few number of force constants. The purpose of this step is to check the hypothesis by looking for a rough agreement with likely values of force constants. A better fit is then performed using more force constants. Only the ones which give a significant improvement have been retained, so as to keep the model as simple as possible.

This process was applied only to in plane modes, since it does not seem possible to trust any Raman result concerning out of plane modes.

IV. RESULTS

Table 3 compares experimental and calculated frequencies. It is clear that the agreement is good for I.R. active modes excepted for a permutation of the two C-H stretching modes assignements. In contrast, the agreement for Raman active modes is restricted to the most intense ones (Underlined in the table), according to the fitting procedure. In any case we must say that we are in disagreement from Kuzmany's assignements.

In this state this model is certainly crude but we expect that the order of magnitude of force constants are the good ones, so that we used them to calculate the dispersion curves of $(CH)_x$ and $(CD)_x$ reported in fig. 1.

The most striking point to note in the force constants is the high values of coupling constants between the different carbon-carbon bonds. This is the result of the delocalisation of electrons among the chain, as already pointed by Mele an Rice (IO). This long range coupling produces a strong dispersion in phonon branches with a surprising enhancement for $(CD)_x$.

TABLE 3

Calculated and experimental frequencies

RAMAN

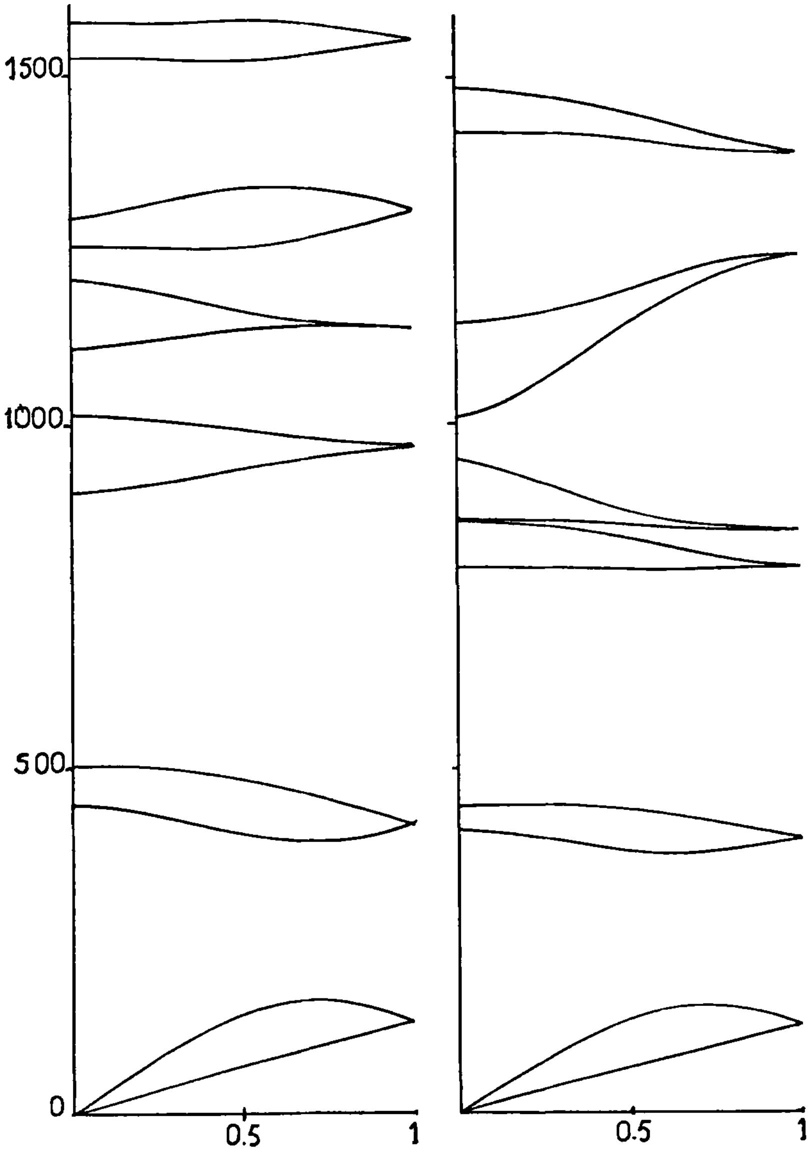
(CH)$_x$			(CD)$_x$		
a	b	c	a	b	d
3090	3090		2301	2315	
1527	1544	1541	1486	1460	1470
1209	1292	1247	951	1205	976
906	1252	908	791	978	765
3049	3030		2272	2260	
1575	1170		1423	1170	
1013	915		858	960	835
508	445		445	406	403

Infra red

a	e	a	e
3063	3044	2260	2255
1261	1249	1146	947
1111	1115	860	892
3037	3055	2235	2275
1302	1329	1008	1050
450	446	410	402

a : present work
b : réf (7), c : ref (8), d : ref (9), e : ref (3).

FIGURE 1



Dispersion curves of $(CH)_x$ and $(CD)_x$

V. CONCLUSION :

We think highly desirable, in order to improve the quality of models that polarized Raman measurements on streched films become available.

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