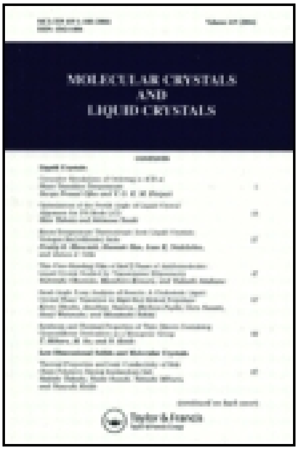

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Molecular Aspects, Vibrational Spectroscopy and Dynamics of Polyacetylene

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Version of record first published: 17 Oct 2011.

To cite this article: G. Zerbi, G. Zannoni, M. Gussoniand & C. Castiglioni (1985): Molecular Aspects, Vibrational Spectroscopy and Dynamics of Polyacetylene, Molecular Crystals and Liquid Crystals, 117:1, 287-294

To link to this article: http://dx.doi.org/10.1080/00268948508074638

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 287-294
0026-8941/85/1174-0287/$15.00/0

Printed in the United States of America

MOLECULAR ASPECTS,VIBRATIONAL SPECTROSCOPY AND DYNAMICS OF POLYACETYLENE.

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Abstract The study of vibrational infrared intensities provides information on the electronic properties of pristine cis and trans and doped Polyacetylene. The extent of Π-electron delocalization turns out to be different in the two pristine isomers. In the case of the doped material a very large charge flux is derived from the spectrum. It is shown that the doped induced infrared spectrum is independent on the kind of dopant, but is only related to the polarization of the lattice and to a large charge flux during vibration.

In this paper we wish to proceed in the interpretation of the vibrational infrared and Raman spectra of pristine and doped Polyacetylene based on a simple vibrational concept. Our attempt is to see how far can one consider pristine and doped Polyacetylene as "normal molecular system" and at which stage of the analysis one may be forced to introduce additional concepts to account for unusual properties acquired by the material because of the delocalization of Π-electrons along the chain or because the electronic structure is perturbed by electron donor or acceptor doping.

In such an analysis we have to account for both absorption frequencies and intensities. Frequencies are related to the dynamics of the system while intensities are related to the electronic structure and to its fluctuations during normal modes.

Following the classical procedure of dynamics of one-dimensional lattices[1,2] we have described the normal modes in terms of a quadratic valence force field.[3] The parameters of the potential were fitted by least squares on the q=0 modes of pristine $(CH)_x$,$(CD)_x$ and $(^{13}CH)_x$.[4] Conjugation is accounted for by interaction terms in the potential up to the second neighbour and the signs of the interaction satisfy the alternation rules already proposed for benzene[5] and represented later by Kakitani et al.[6] The obtained quadratic force constants agree with those obtained from "ab initio" methods on simpler polyenes.[7] q=0 phonon frequencies are well accounted for together with the corresponding vibrational displacements.

The vibrational intensities both of the pristine and of the doped material are treated on the basis of the ECCF (Equilibrium Charges and Charge Fluxes) model which has been successfully used for many other organic molecules.[8-12] The details of the method are fully described elsewhere.[8] In another paper of this volume[13] the relevant aspects of the calculations in the case of pristine and doped Polyacetylene are reported in detail.

In the case of pristine trans Polyacetylene, nice model molecules of this compound are the shorter polyenes such as butadiene (well studied spectroscopically), β-carotene etc. A property which varies with the length of the polyene molecule is the delocalization of Π-electrons along the chain. This is a property which can be measured from infrared intensities.

Indeed it can be shown[13] that: i) the ratio of the intensity of the out of plane deformation mode near 1000 cm^{-1} to the intensity of the CH stretching near 3000 cm^{-1} measures the equilibrium charge on the Hydrogen atoms; ii) the ratio of the intensity of the in plane deformation to the intensity of the out of plane deformation mode (I_{inpla}/I_{opla}) gives the magnitude of $\partial q_C/\partial\phi$, i.e. the flux of the charge on the Carbon when the CCH angle is changing. The same kind of concepts apply also to the case of cis polyacetylene. In ref.13 it is shown that the analysis of the infrared intensities gives quantitative indications that conjugation in trans polyacetylene is much larger than in trans butadiene. Moreover, cis polyacetylene shows a very limited conjugation with π-electrons largely localized within each double bond.

It can be easily guessed that, upon doping, at the site of the doping, the electronic structure of the Polyacetylene chain becomes strongly perturbed. The transferring of the charge from(to) the molecule to(from) the doping agent certainly drastically alters the electronic distribution; the CC lattice then relaxes, at least locally at the site of doping, into a new minimum geometry. These localized geometry changes generate a DEFECT embedded in an otherwise unperturbed lattice when the doping concentration is relatively small. The resulting electronic distribution in terms of equilibrium charges and charge fluxes should be substantially modified if compared with the pristine undoped material.

Lattice dynamical calculations of defect containing Polyacetylene chains account for the spectral observation in terms of centrosymmetrical structural defects, substancially short ($\simeq$4-5 double bonds), where bond alternation is almost completely removed. The centrosymmetrical defect may well be represented by a polaron or a bipolaron. In dynamical calculations we have assumed a bipolaron like defect. The observed absorption bands in infrared (900, 1280 and 1390 cm^{-1}) are then accounted for as originating from DEFECT MODES (FIGURE 1). From the calculated atomic displacements these defect modes show an optical anisotropy along the chain axis as observed in stretch-oriented samples studied with polarized light. From this work we assign the broad band near 900 cm^{-1}(by some authors[14] assigned to a pinning mode) to a coupled in-plane CH deformation and skeletal stretching of ungerade symmetry,hence infrared active.

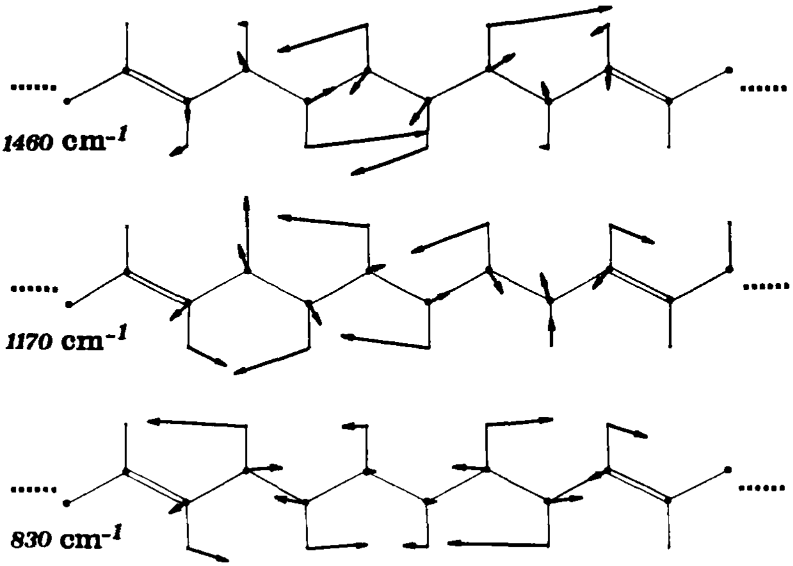

FIGURE 1 Defect modes for doped Polyacetylene.

The important spectroscopic features to be accounted for are the following. Upon doping,even at very light doping regime, a characteristic doped induced spectrum is generated. Such a doped induced spectrum: a) is extremely strong,i.e. each doped site has a very large intrinsic absorption coefficient; b) remains practically unchanged even in the high doping regime when Polyacetylene behaves like a metal; c) is practically independent on whether doping is p or n; d) the intensity is linearly proportional to the concentration of dopant; e) the mode near 900 is very broad; f) the same spectral pattern is found in the case of neutral defects induced by photoexcitation, even if some of the vibrational frequencies are shifted downwards.

Our analysis of the infrared intensities make use of the dynamics of the centrosymmetric defect discussed above. It will be seen later,however, that the conclusions are not strictly related to the model adopted for the defect,but have some general validity.On the basis of the centrosymmetrical defect the infrared intensities of the doped-induced bands can be very well represented, as shown in FIGURE 2.

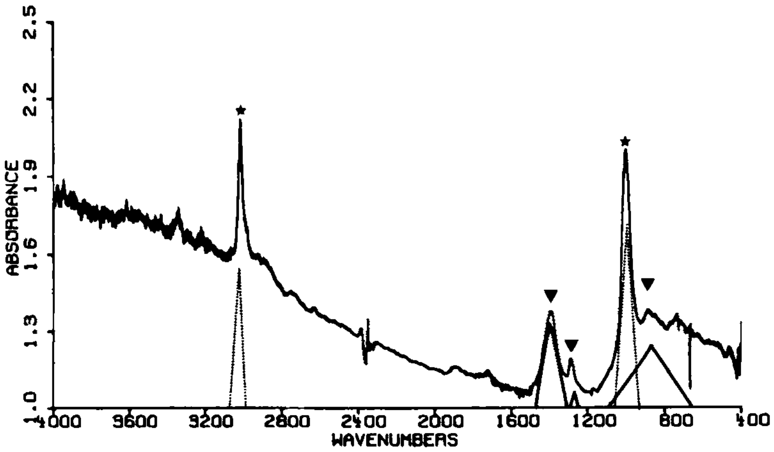

FIGURE 2 Observed and calculated specrum of lightly (0.17%) Iodine doped trans Polyacetylene. Dotted triangle refer to calculated bands of pristine trans PA; full line triangles to bands of doped PA (see ref.13)

The following conclusions can be reached from the analysis of the vibrational intensities of the doping induced spectrum of trans PA:

- upon doping the site where doping occurs becomes strongly polarized,i.e. double and single bonds are not any more apolar,but because of redistribution of charges each CC bond acquires some polarity. The lattice polarization occurs every time electrons are either donated or acquired by doping, but it also occurs when electrons are only redistributed within the defect as it should be the case of the photon induced defect. In other words,singly charged polarons or doubly charged bipolarons as well as neutral defects do induce a polarization of the CC lattice. Such a polarization contributes to the enhancement of the intensity of the doped induced infrared spectrum much more than the transferred spectrum itself.
- the largest contribution to the intensity enhancement is given by the existence of a very large charge flux which accompanies the stretching of the CC skeletal bonds. The value of the charge flux ($\partial q_C/\partial R_{CC}$= 3.5 eA^{-1}) which can be derived from infrared spectra of doped species is by far the largest ever measured in the case of the organic molecules so far studied.
- it is clear that the above properties are independent on the kind of doping or on the kind of electronic defect which is generated within the chain of Polyacetylene.
- the measured large charge fluctuation which follows the stretching of the CC bonds is an experimental indication from infrared that,as a consequence of doping (or photoexcitation), the electronic charge reasonably ascribed to Π-electrons becomes highly mobile thus laying the grounds for further mobility through whichever kind of tunnelling or hopping phenomena the material can allow un-

der the influence of an electric field.

- in the model of doped induced defect modes adopted in our work the unusual breadth of the 900 cm^{-1} band can find the following explanations: a) as shown by calculations, several other defect modes occur in this frequency range but are not selectively enhanced as the one centered near 900 cm^{-1}(see ref.13 for details). b) as already pointed out, the inhomogeneous doping may produce an envelope of several bands slightly shifted one from the other since charge transfer bond differs from site to site. c) even with identical defect the single strongly enhanced defect mode near 900 cm^{-1} can be very broad if the vibrational lifetime is short. The measured width gives a mean vibrational lifetime of $\simeq 10^{-13}$sec,much shorter than for the other modes. The short lifetime of the normal mode which carries so much mobile electronic charge is reasonable since it is certainly strongly damped because of strong interactions with the surrounding medium.

- another feature yet to be accounted for by the model of defect modes is the downwards shift of the $\simeq$900 cm^{-1} band to $\simeq$500 cm^{-1} by photoexcitation. More work is in progress.

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