OPTICAL PROPERTIES OF HEAVILY DOPED POLYACETYLENE FILMS

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OPTICAL PROPERTIES OF HEAVILY DOPED POLYACETYLENE FILMS

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Résumé - Nous avons mesuré le spectre de transmission infrarouge de films minces de polyacétylène pour plusieurs taux de dopage compris entre 0 et 7%. L'analyse du comportement des bandes ω_1 (1400cm^{-1}) et ω_2(900cm^{-1}) avec le taux de dopage montre que celles-ci restent stables au delà de 2% et qu'elles persistent dans l'état métallique. Enfin nous montrons que le mode ω_2 ne peut pas être le mode d'oscillation collectif.

Abstract - The infrared transmission of thin films of polyacetylene has been measured for various doping levels ($0 \leqslant Y \leqslant 7\%$). The analysis of results shows that modes ω_1 (1400cm^{-1}) and ω_2 (900cm^{-1}) arising from structural defects are stable for $Y > 2\%$, and they persist in metallic state. Lastly we showed that ω_2 mode cannot be the pinned mode.

The existence of structural defects in trans polyacetylene is now usually accepted. Many experiments have been interpreted in the context of the soliton or polaron schemes. In a series of experiments with various doping Fincher and al/1/ found that for dilute doping ($Y < 0.1\%$) two new absorption modes appear at 900 cm^{-1} and at 1370cm^{-1}. This I.R. activity is quite independent of the dopant type. This observed generality suggests that I.R modes are intrinsic features of the doped $(CH)_x$ chain. These results have been interpreted by Fincher and Mele/2/ in term of localized modes created by charged defects as solitons. Zannoni and Zerbi/3/ interpreted the infrared and Raman spectra by means of a model of an one dimensional crystal containing a structural disorder. Rabolt and al/4/ by comparison with charge transfer salts, decided in favour of vibronic activations of Raman active Ag modes. Recently Horowitz/5/ showed that this behavior is a universal result arising from the added charge independent of its configuration.
However all these results concern samples with light doping level.
We report here measurements of the transmission coefficient of very heavily doped free standing films of $(CH)_x$.
The film thickness is 2.5 μm. The film is synthetized from Shirakawa techniques and the doping level is performed in liquid phase using pentane solution of iodine. The doping level Y in $[CH(I_3)_Y^-]_x$ is measured by the increase in weight.
For low doping levels, the transmission measurements were performed with à Perkin - Elmer 577 spectrometer, while for high doping levels we used a N_2 cooled grating spectrometer followed by a H_2 cooled Ge:Cu detector/6/. Results are shown in Fig 1.
The behavior of the 1400cm^{-1} and 900cm^{-1} bands and the behavior of the background with doping level are shown in Fig 2,3 and 4 . The transmission spectra have been analy ed with the classical oscillation dispersion by least square fit.
When $Y > 2\%$, the frequency, width and intensity of bands begin to saturate while the background continues to increase.

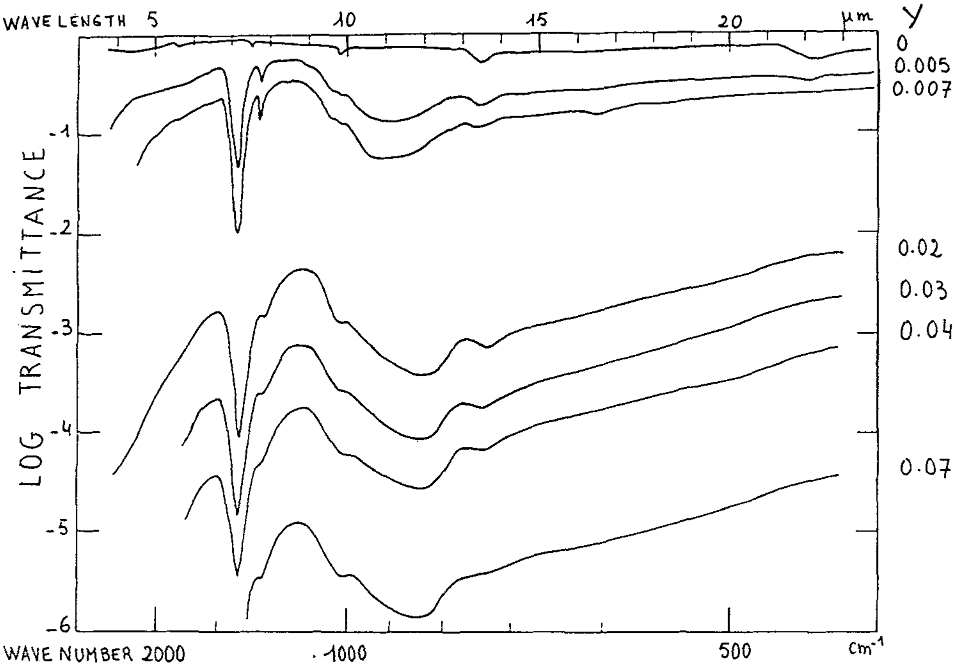

Fig 1 : Transmission of $[CH(I_3)^-{}_Y]_X$ versus doping level Y. Resolution of cooled spectrometer is about 7 cm^{-1} at 1000 cm^{-1}.

According to Horowitz /5/ the conductivity is given by

$$\sigma(\omega) \sim i\, D_0 [\, 1 + (1 - \alpha)\, D_0 \,]^{-1}$$

with $$D_o = \frac{1}{\lambda} \sum_n \lambda_n \omega_n^{\circ 2} (\omega^2 - \omega_n^{\circ 2} - i\, \delta_n \omega)^{-1}$$

ω_n°, δ_n are the bare frequency and the width of phonons respectively; λ_n is the electron - phonon coupling constant ($\lambda = \sum_n \lambda_n$).
α is the coupling with the pinning potential of impurity $\alpha \sim \int \rho(x) V''(x)\, dx$
$\rho(x)$ is the charge density and $V(x)$ the potential of impurity
$V(x) = \varepsilon_o^{-1} (x^2 + d^2)^{-1/2}$

d is the distance impurity_chain, ε_o is the dielectric constant.
Using common values for parameters./7/8/

$\varepsilon_o = 14$, $d = 4$ Å, $\rho(x) \sim [\frac{1}{l} \operatorname{sech} (\frac{n}{l}) \cos (\pi\, n/2\,)]^2$, $l \sim 6$

we obtain a value of α in accord with Horowitz for small values of doping ($\alpha \sim 0.23$). However it is clear that if we increase the doping level the value of α must decrease : *invariance by translation will be restored in the limit* of a continuous distribution of impority charge ($\alpha \Rightarrow 0$) which gives rise to a pole for $\omega = 0$ and a Fröhlich type conductivity. In our calculation we have taken into account the structure of I_3^- oriented parallel to the chain /8/.

The parameter α and the frequencies of infrared modes depend on the doping level, shown in figure 5.

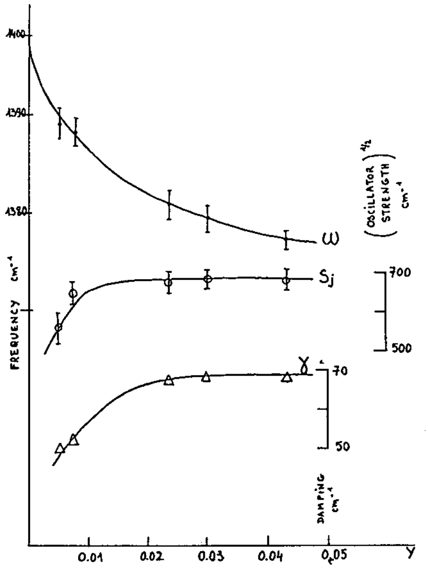

Fig 2 : variation of frequency,width and intensity of ω_1 line(1400cm $^{-1}$) versus doping level.

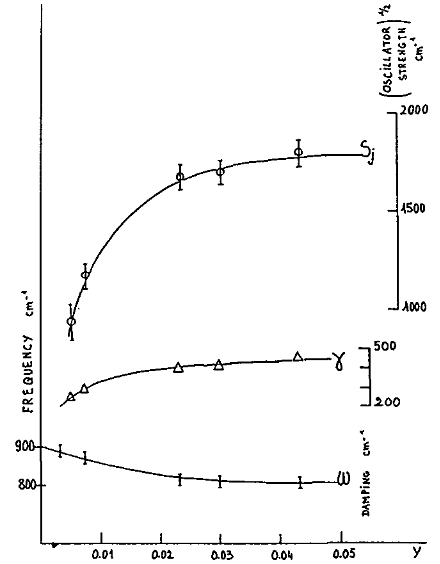

Fig 3 : variation of frequency, width and intensity of ω_2 line (900cm^{-1}) versus doping level. Point Y=0.07 is not plotted in this figure.

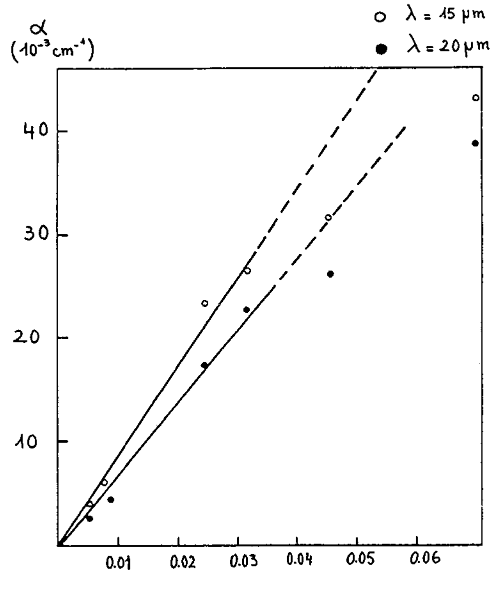

Fig 4 : Variation of background versus doping level.

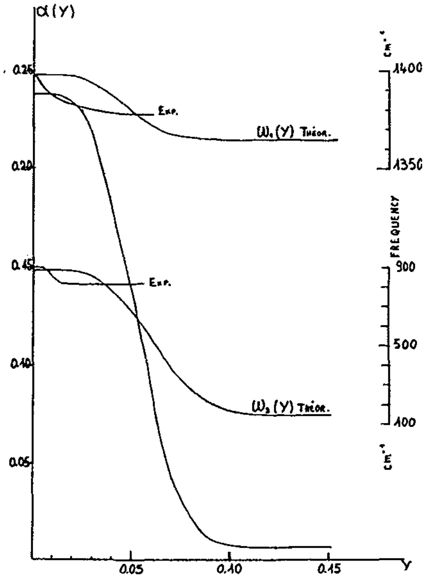

Fig 5 : Variation of the coupling with the pinning potential of impurities, and frequencies of infrared active modes with doping level.

If we suppose that doping of fibrils are not uniform, the behavior of ω_1 line may well be explained by the Horowitz model. However the ω_2 line cannot be the pinned mode : it is clear that, in a long perfect chain, the frequency of the pinned mode must present a very strong dependence on the doping level. Width of $\omega_1$line (ω_2 line ?) is attributed to oscillations of the solitons. We anticipate that, as α decreases, the amplitude of motion of the soliton increases and the width will increase.
The weight of ω_1, ω_2 lines is saturated at about 2%. The relative weight is not a constant, but increases from 2.25 to 6.62 with doping.

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