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Infrared transmission of heavily doped polyacetylene

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Résumé. — Dans ce travail nous présentons des résultats de mesures de transmission et réflexion dans le domaine infrarouge (4 μm -25 μm) effectuées sur des films de polyacétylène. Les mesures ont été faites sur des échantillons de polyacétylène $[\text{CH}(\text{I}_3^-)_Y]_x$ de diverses épaisseurs pour des taux Y de dopage à l'iode allant de 0 à 7 %. La méthode utilisée permet d'obtenir des spectres sur des films libres de tout support. De plus contrairement aux techniques usuelles elle permet de travailler, à fort dopage sur des échantillons assez épais, pour lesquels il est possible de déterminer l'épaisseur avec précision et également le taux de dopage par pesée. Les résultats confirment que, bien que le dopage à l'intérieur des fibrilles ne soit pas uniforme, le système est complètement isomérisé. De plus notre analyse prouve que le mode ω_2 à 900 cm^{-1} qui apparaît sous l'action du dopage ne peut pas être le mode d'ancrage.

Abstract. — This report presents the results of measurements of transmission and reflexion spectra of polyacetylene films in the infrared range 4-25 μm . $[\text{CH}(\text{I}_3^-)_Y]_x$ samples were used with various thickness for iodine doping level Y up to 0.07. We used a high detectivity spectrometer which permitted us to obtain spectra with very highly doped free-standing films. In this way, we could measure both the relatively large thicknesses of samples with accuracy and also directly measure the doping level by weight uptake. The results show that, although intrafibril doping is nonuniform, the material is quite isomerized. In addition, our analysis demonstrates that the ω_2 band (900 cm^{-1}) induced upon doping cannot be the pinned mode.

1. Introduction.

A considerable amount of work has been done on the physical properties of undoped and doped polyacetylene film in the past few years [1]. Such interest was

enhanced by the potential applications of semiconducting or conducting $(\text{CH})_x$ as an electronic material. The essential characteristic of this polymer is the existence of two isomeric forms : the *cis* and the *trans* (Fig. 1a, b), the first being unstable, while the second

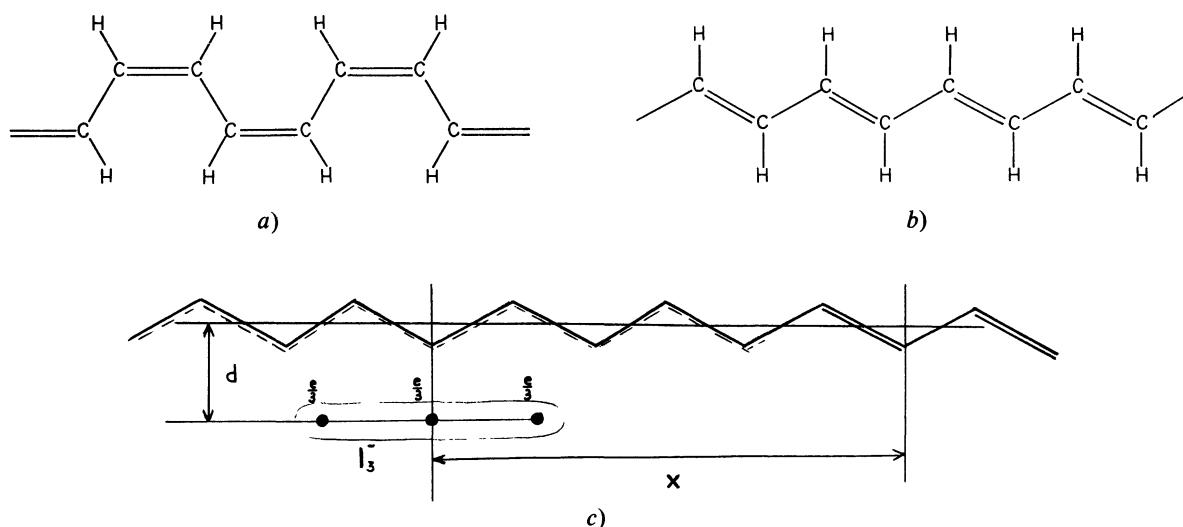


Fig. 1. — (a) Chemical structure of *cis* polyacetylene; (b) Chemical structure of *trans* polyacetylene; (c) Schematic pattern of the pinning potential $V(x)$ due to a charged impurity.

is stable. Furthermore the *trans* isomer has a ground state twofold degenerate : two different senses of isomerization are possible, one in which even numbered atoms move to the right (A phase), the other in which they move left (B phase). A soliton is the boundary between a region of A phase and B phase. In undoped or lightly doped polyacetylene there is a small number of neutral solitons. Upon doping, the charge is transferred from the dopant to the polyacetylene chain either by changing the occupancy of a preexisting soliton, or by the induced creation of a new charged soliton. Recently the possibility of the creation of a pair of solitons (polaron) has been evoked for light doping. Experimental results of magnetic [2, 3] infrared [4, 5] optical [6] and transport [7, 8] measurements on doped $(\text{CH})_x$ support the soliton mechanism for doping, while photoconductivity, light scattering and modulation spectroscopy experiments are consistent with a decay or the creation of soliton pairs [9, 10]. In the series of experiments with various dopants, Fincher *et al.* [11] found that upon dilute doping two new absorption modes appeared in the IR region at 1370 and 900 cm^{-1} . Their intensity is very strong and increases in proportion to the dopant level. These modes were observed for iodine, AsF_5 [11], SbF_5 [12], MoCl_5 , WCl_6 [13, 14] (p-type doping) and for Na [11] (n-type doping). The same kind of behaviour has been observed with $(\text{CD})_x$ [4, 15].

Thus these intense absorptions are not due to specific vibrations of dopant molecules but are intrinsic features of the doped $(\text{CH})_x$ chain. A theory was developed by Mele and Rice [16] concerning the lattice dynamics of solitons in $(\text{CH})_x$. The presence of the defect alters significantly the character of normal modes of vibration of the chain and induces localized modes. With a charged soliton, two of these modes were found to be strongly infrared active, deriving their oscillator strength from interaction with π -electrons. In addition, the oscillation of the charged soliton bound to an ionized impurity should be associated with its own characteristic infrared activity. Zannoni and Zerbi [17] interpreted the infrared spectra with a model of a one dimensional crystal containing a structural disorder. Rabolt *et al.* concluded, by comparison with infrared spectra of charge transfer salts, that these new modes are due to the vibronic activation of Raman active Ag modes [18]. Recently Horowitz [19] and Maki [20] showed that, in continuum model, phase fluctuations of order parameter give rise to new localized modes which are infrared active [19] or Raman active [20]. In the Horowitz model the infrared absorption is independent, of the charge configuration when the doping is light. In this model one of the strong IR active modes, is the pinned mode.

Many of these results concern only models or samples with light doping. On the other hand, theoretical calculations of the stability of chain [21] show

that, up to a small percentage of doping level solitons are not stable.

It was very interesting to measure, with great accuracy the behaviour of the infrared spectra with the doping level, from undoped material to material in metallic regime. Our aim, in this paper is to determine the behaviour of the background and infrared active bands with various doping level and discuss the results.

2. Experimental techniques.

2.1 SAMPLE PREPARATION AND DOPING. — Polyacetylene films were obtained by the method described by Ito *et al.* [22]. The solvent is pentane, the molar ratio Al/Ti = 4 with a Ti concentration of 0.4 mole/litre, at -78°C and the acetylene pressure 0.1 atmosphere. The iodine doping was performed in liquid phase using pentane solutions of iodine at various concentrations. The dopant content was measured by film weight uptake and is always given in I_3/CH percent.

2.2 APPARATUS. — We used two types of spectrometers :

— a Perkin Elmer 577 down to a 10^{-2} transmission level;

— an infrared compact grating spectrometer especially built in order to measure transmission as low as 10^{-6} . This apparatus is extensively described elsewhere [23] so we only report here its essential characteristics. In the middle infrared range, the 300 K background emission is often the greatest limitation of photoconductive detectors. To reduce this effect, a grating spectrometer was built, cooled with liquid nitrogen, incorporating a Ge : Cu detector cooled with liquid helium. The main characteristic of this spectrometer is the noise equivalent power corresponding to the total radiation noise evaluated as $10^{-12} \text{ W} \cdot \text{Hz}^{-1/2}$, which is approximately 2 orders of magnitude lower than the Golay detector. This apparatus works in the range of 400 to 2500 cm^{-1} and allows an ultimate transmittance measurement of 5×10^{-7} near 1500 cm^{-1} . The spectrometer resolution is 7×10^{-3} at 1000 cm^{-1} . It was essentially used to determine the transmittance of highly doped $(\text{CH})_x$ films.

Utilization of free-standing films allows elimination of dispersion effects of substrates and thus an easier quantitative interpretation of the spectra. Measurements using commercial spectrometers require extremely thin doped films, because the transmission decreases exponentially with thickness. In this case, it is very difficult to know the exact thickness of films and whether or not it is constant.

On the other hand, the doping level cannot be directly measured within accuracy by weight uptake.

Therefore it is necessary to employ indirect qualitative methods using measurements of conductivity.

Unfortunately these methods are useless when the I_3^- doping level is greater than 0.01 because the conductivity slowly changes.

Techniques as Tanaka's [24] make it possible to obtain excellent qualitative results, but cannot, in any case, allow a quantitative interpretation of the results.

The utilization of films thick enough to be easily manipulated that still give a measurable transmission even for high doping levels, permits better analysis of results.

In this work, three thicknesses of films were used : 1.3, 2.5 and 6.5 μm .

3. Experimental results.

3.1 *Cis-trans* ISOMERIZATION. — Logarithm of absorption and reflection curves are shown in figures 2 and 3 for 2.5 μm thickness films, with different doping levels. *Cis-trans* isomerization can be induced by heating or doping. Detailed study of the behaviour of the *cis*-bands thermally isomerized has shown that it was not possible to interpret the isomerization processes with a single time constant, but it was necessary to discuss in detail the behaviour of each *cis*-band [25]. We observe a similar behaviour with isomerization induced upon doping.

The 740 cm^{-1} band associated with C-H out of plane deformation [26] depends mainly on the interaction of its nearest neighbours, while the 446 cm^{-1}

band associated with angular deformation of the carbon chain, involves long range interaction. So for short *cis*-sequences the first band persists while the second disappears. With thermally induced isomerization 446 cm^{-1} (and 1 329 cm^{-1}) bands disappear very quickly, while 740 cm^{-1} (and 1 249 cm^{-1}) bands persist. With isomerization induced by doping the 446 cm^{-1} band disappears when the dopant concentration reaches $Y \sim 0.007$ while 740 cm^{-1} disappears when $Y > 0.04$ (Fig. 2). These Y values depend on the thickness of the film, and to obtain total isomerization the required doping level increases with the thickness value [27].

The spectrometer resolution is too low to permit a study of the behaviour of 1 329 and 1 249 cm^{-1} bands.

The relative sensibility of « lattice » mode (446 cm^{-1}) and « local » mode (740 cm^{-1}) is well explained by dynamical model [28, 29]. Calculations demonstrate that the 446 cm^{-1} *cis*-band disappears when the length of *cis*-sequences of the chain becomes shorter than 12-16 (CH-CH) units.

The disappearance of 446 cm^{-1} when the dopant concentration reaches 0.007 signifies that *cis*-sequences no longer exist in any part of the polymer. Recent T.E.M. studies of doping mechanisms in films [30, 33] have shown that dopant nonuniformity is significant. Moses *et al.* [34] have shown the importance of macroscopic nonuniform doping on physical properties. Nonuniform doping has also been studied by Rolland [31], Janossy [33], Epstein [35], Montaner [12]. The origin of the concentration gradients through the film, has been discussed by Benoit *et al.* [32].

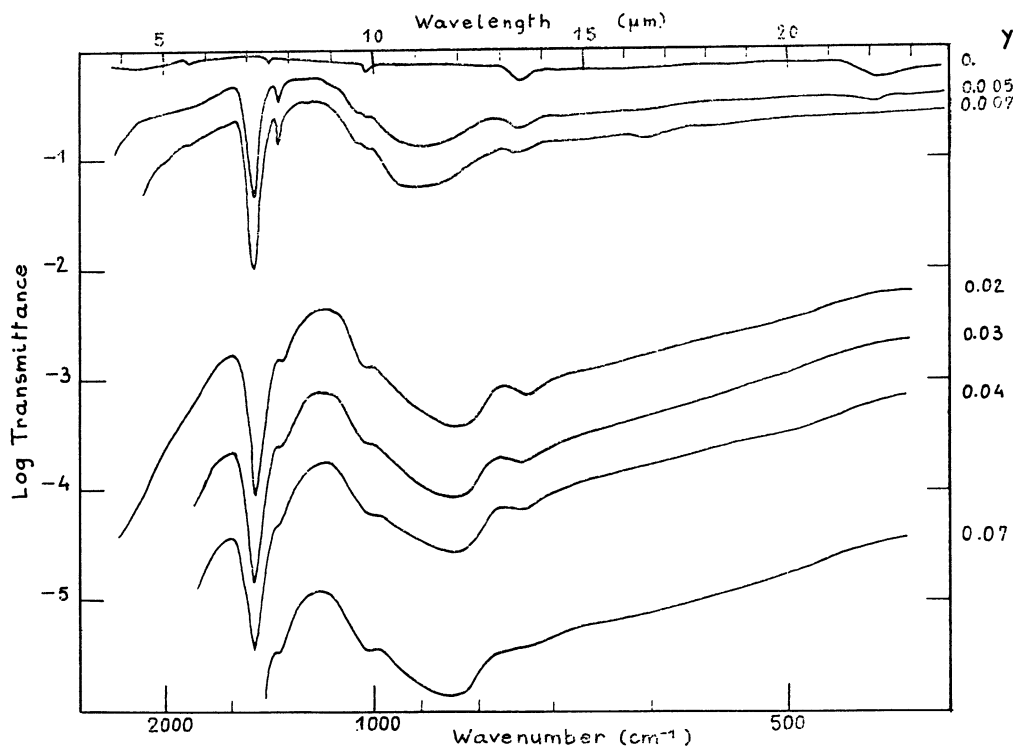


Fig. 2. — Infrared transmission spectra of a 2.5 μm thick *cis* (CH)_x film iodine doped up to $Y = 0.07$.

Using dopant in liquid phase does not greatly change the mechanisms.

Calculations show that the diffusion constant D is of the order $10^{-8} \text{ cm}^2 \text{ s}^{-1}$. Thus, for the thin samples used here the macroscopic doping rapidly becomes uniform. This does not mean that the material properties are uniform, because it is well known that the density and the texture vary from one side to the other. With thin materials it is not necessary to use a slow doping technique to obtain a macroscopic uniform doping, however there is no indication as to whether or not the fibrils are uniformly doped. Recent X-ray diffraction measurements [36] show that, although the fibrils are not uniformly doped, the isomerization is practically total.

The results are interpreted using a model in which the fibrils are only doped on the surface. The doping induces a *cis-trans* isomerization. *Trans*-chains being longer than *cis*-chains ($\sim 10\%$ longer) a strain is induced that produces the isomerization of chains deeper in the fibril.

Our infrared results are not contradictory to such a model as they confirm that the isomerization can be total. But in order to be quite isomerized thick samples must be doped more heavily than thinner ones. This result can be explained by supposing that the stress exercised by external doped *trans*-layers of the fibrils has a limited extent. An elementary estimation can be made, of *trans/cis* ratio $n(r)$ at the distance r from the deeper quite isomerized layer. Supposing that $n(r)$ is a linear function of stress, and stress a linear function of strain, $n(r)$ is then an exponential function of r , with

the exponential coefficient depending on the material morphology. An increase in the doping induces total isomerization of the inner layers and propels the isomerization to penetrate deeper.

Total isomerization will be obtained easier for small diameter fibrils than large diameter fibrils.

3.2 BACKGROUND. — It is noted that the background augments regularly with the doping level (Fig. 4) and begins to become saturated at approximately 6-7%. This comportment is similar to that of the dc conductivity [34]. The analysis of spectra shows that, at low doping levels the background transmission decreases as the frequency decreases, whereas, with high doping levels, it is the opposite: the background transmission increases as the frequency decreases.

Such a result for high doped samples completely agrees with the experimental results of Fincher *et al.* [11] and with Galtier's results in far infrared [37] showing a frequency linearly dependent conductivity in doped $(\text{CH})_x$.

The behaviour of the conductivity disagrees with a single Drude model. Fincher *et al.* interpret their data by hypothesizing that doped $(\text{CH})_x$ is a composite medium with semi-conducting islands separated by interfibril contacts. However, other authors: Grant [38] and Epstein [39] found that the conductivity was frequency independent down to 500 MHz, Moses *et al.* [34] concluded that the proposed metallic islands do not exist in *trans* $(\text{CH})_x$.

Possibilities of interpreting an infrared spectra

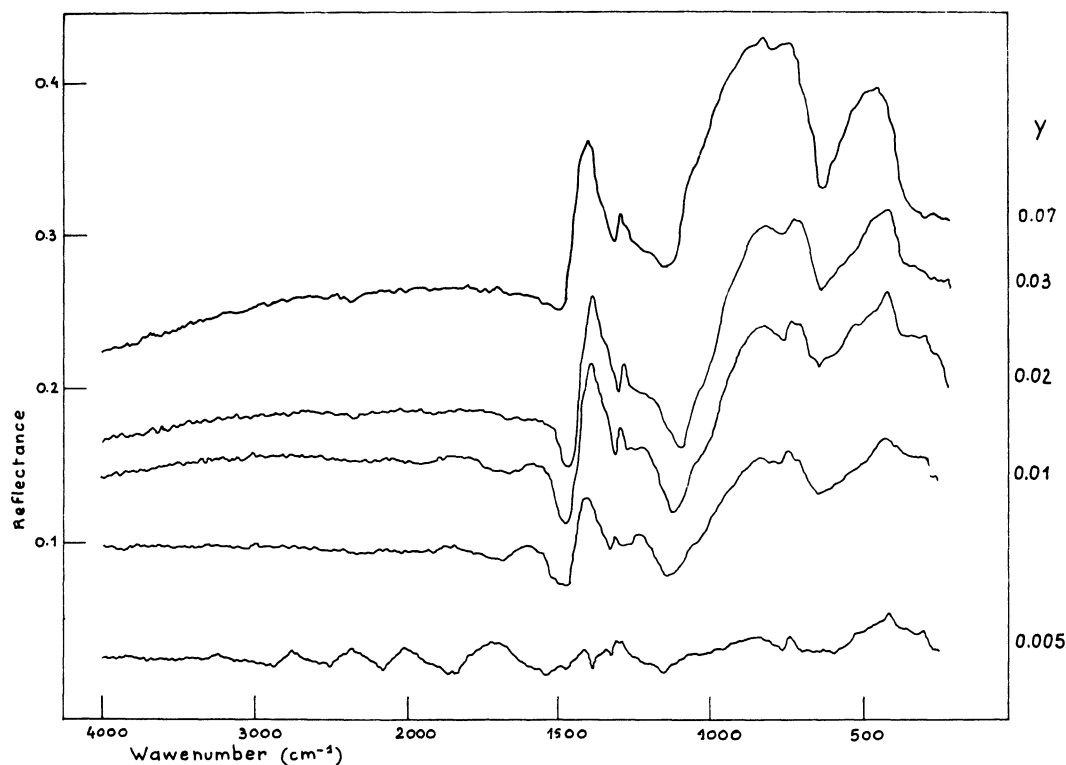


Fig. 3. — Infrared reflection spectra of a *cis* $(\text{CH})_x$ film iodine doped up to $Y = 0.07$.

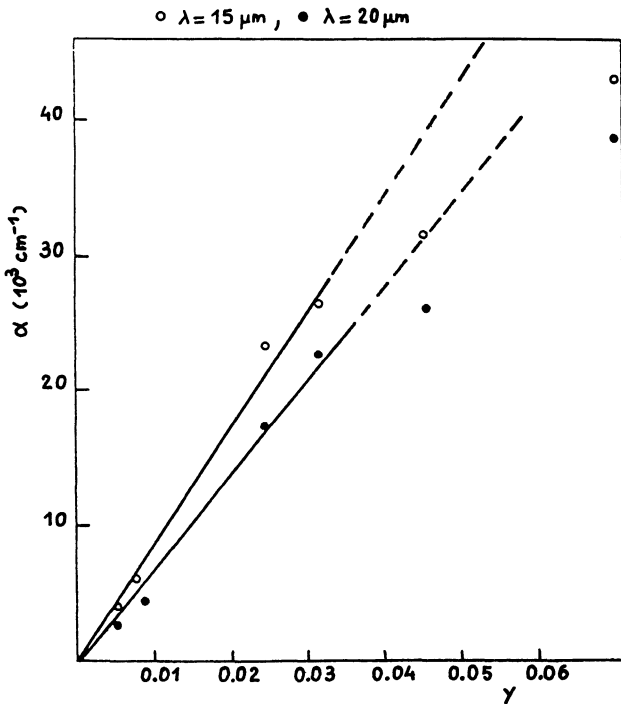


Fig. 4. — Variation of background of a 2.5 micrometer thick film versus doping level Y at lambda = 15 micrometers and lambda = 20 micrometers.

include either an analysis by the Kramers-Kronig method, or an analytic expression for $\epsilon(\omega)$ from which the parameters are determined by a least square fit method. The Kramers-Kronig transform requires information from a very large range of spectra which is not available here. In order to use the second method, it is necessary to make hypotheses concerning the form of $\epsilon(\omega)$. We assume that two terms contribute to the dielectric constant : the first one arising from free carriers $\epsilon_1(\omega)$, the second arising from oscillators $\epsilon_2(\omega)$ (or phase fluctuations of the order parameter) [19, 20].

It is well known that the determination of the complex index, from either the transmission spectra or the reflection spectra does not have a unique solution. In order to interpret correctly the spectrum by this method it is not only necessary to give a good value for the transmission spectra, but also for the reflection spectra.

So, in the first step, we have employed a Drude model for $\epsilon_1(\omega)$ and an oscillator dispersion formula for $\epsilon_2(\omega)$.

We could not obtain a good fit of experimental data, especially background data. Then, we used the expression $\epsilon_1(\omega)$ given by Fincher [11] for a composite medium of anisotropic metallic islands separated by interfibril contacts : the filling factor, fractional alignment factor and depolarization being free parameters with values not differing greatly from those of Fincher [11].

By using the multilayer model of Montaner *et al.* [12] we took into account, that the film surfaces are not

equivalent. We could not obtain a good fit of transmission and reflection data with physically acceptable parameters, for several values of the doping level.

Since a great part of radiation is nonspecularly reflected we tried to correct the reflectivity by using the results obtained by other authors [11]. We obtained no improvement.

In any case, the hypothesis of spheric (ellipsoidal) metallic islands in an insulating (a vacuum) is certainly not elaborated enough. In fact we deal with three mediums : heavily doped regions, undoped regions and a vacuum.

Finally, and this is certainly the most plausible assumption, the observed behaviour results from an evolution of the dielectric states (closing gap, disorder, impurity effect) upon doping. The interpretation is complicated owing to the fact that the medium is a type of an anisotropic conducting network made of wires conducting on the surface and insulating at the centre.

3.3 SOLITON BANDS. — With a very complex conformation the determination of the depolarization field is almost impossible, nor can we calculate the average dielectric constant of the medium.

So we will discuss only the additional absorption due to defects; The absorption coefficient $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{2\omega k(\omega)}{c},$$

with $\sqrt{\epsilon} = n + ik$; $\sqrt{\epsilon}$ is the complex refractive index, c the speed of the light and ω the frequency.

The dielectric constant $\epsilon(\omega)$ is given by a classical dispersion oscillator

$$\epsilon(\omega) = \epsilon(\infty) + \sum_j \frac{S_j}{\omega_j^2 - \omega^2 - i\gamma_j \omega}.$$

The background is taken as a linear function of ω . Such a method does not give good results for the oscillator strengths but is correct for the determination of frequencies and widths. Results are shown in figures 5, 6 for ω_1 and ω_2 modes; figure 7 shows an example of the fit of experimental spectra. We notice that upon $Y \sim 2\%$ the widths and intensities of bands of measured spectra start to become saturated (Figs. 5-6) in agreement with results obtained previously by Kiess [40], while the background continues to increase (Fig. 2). For a film thickness of 2.5 micrometers the intensity ratio varies from 2.26 ($Y = 0.005$) to 6.62 ($Y = 0.04$). On the other hand using a continuum model Horowitz [19] showed that the electron-phonon coupling gives rise to infrared active modes corresponding with fluctuations of the order parameter $\Delta(x)$. Horowitz gives an expression for the conductivity $\sigma(\omega)$ of a linear chain, with a charge density $\rho(x)$ put in a potential $V(x)$ due to charged impurities (dopant). It was interesting to use this expression to verify that it was able to describe the spectra.

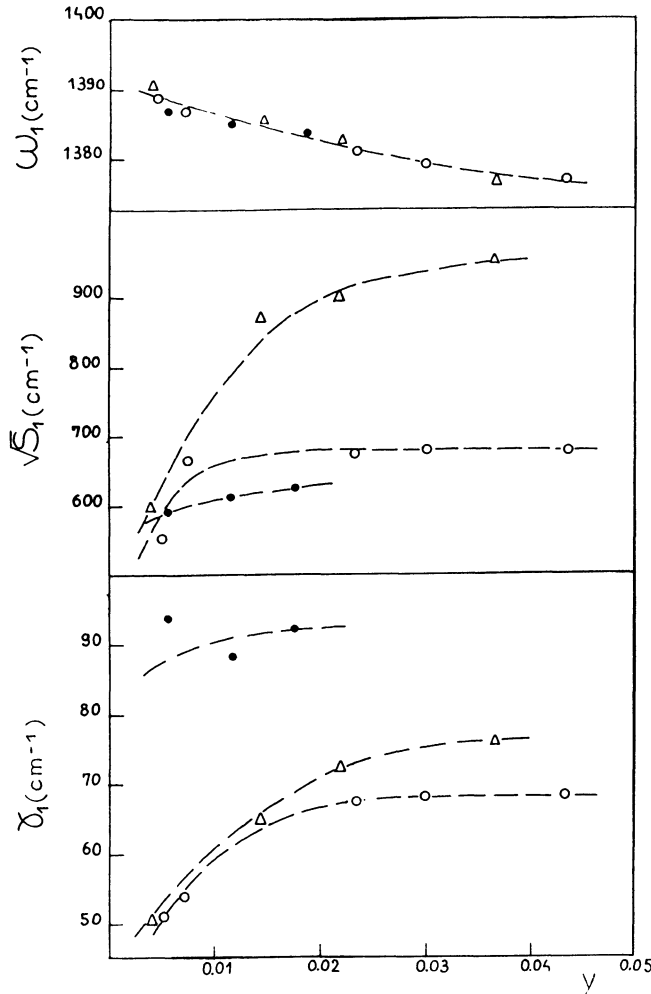


Fig. 5. — Variation of frequency, intensity and width of ω_1 line versus doping level Y for three thicknesses of film : Δ : $e = 1.3 \mu\text{m}$, \circ : $e = 2.5 \mu\text{m}$, \bullet : $e = 6.5 \mu\text{m}$.

According to Horowitz, the conductivity is given by

$$\sigma(\omega) = \frac{i\omega S D_0(\omega)}{1 + (1 - \alpha) D_0(\omega)} \quad (1)$$

$$D_0(\omega) = \sum_n \frac{\lambda_n}{\lambda} \frac{\omega_n^{02}}{\omega^2 - \omega_n^{02} - i\gamma_n \omega} \quad (2)$$

$\lambda = \sum_n \lambda_n$; ω_n^0 is the bare frequency, γ_n the width and λ_n the electron-phonon coupling constant of phonon « n », S is a constant dependent on the charge transfer, the Fröhlich mass, the coupling constants and the phonon frequencies [19]. α is a coupling of the charge with the pinning potential of impurity

$$\alpha \sim \int V''(x) \rho(x) dx \quad (3)$$

with $V(x) = (\epsilon_0 \sqrt{x^2 + d^2})^{-1}$ where ϵ_0 is the dielectric constant, d the distance of impurity to the chain (Fig. 1C) and $\rho(x)$ is the charge distribution.

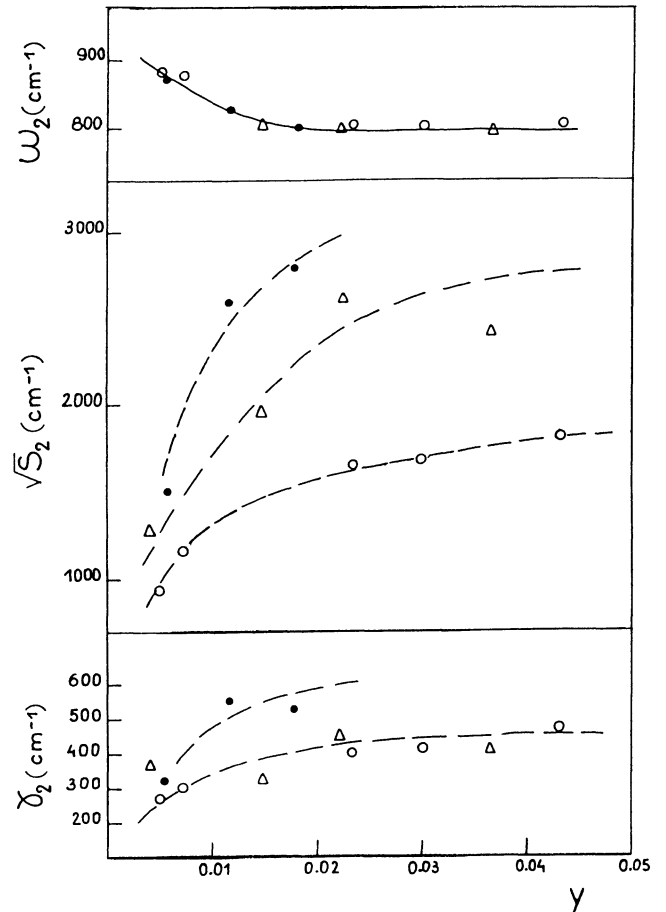


Fig. 6. — Variation of frequency, intensity and width of ω_2 line versus doping level Y for three thicknesses of film : Δ : $e = 1.3 \mu\text{m}$, \circ : $e = 2.5 \mu\text{m}$, \bullet : $e = 6.5 \mu\text{m}$.

The λ parameter, strongly related to the electronic gap and to the band width, is not a free parameter ($\lambda = 1.9$).

If we directly use the Horowitz values for λ_1 , λ_2 , ω_1^0 and ω_2^0 we do not obtain a spectrum close to the experimental one. This is hardly surprising because Horowitz used undamped phonons.

The direct calculation of α shows that this parameter is strongly dependent on the distance « d », the soliton extent, the dielectric constant and the impurity structure.

The experimental spectra can be presented, as Horowitz pointed out [19] under the assumption that a rather large distribution of α values exists and that the phonons are slightly damped. However, if these modes are strongly localized, and chiefly strongly coupled with solitons, they can be very damped.

So, we tried to fit the experimental spectra using 5 parameters ω_1^0 , ω_2^0 , λ_1 , λ_2 and α , and we did not take into account relations for Raman mode. We also obtained a very good description of the experimental spectra (Fig. 8). However, Mele and Rice [41] taking into account the anharmonicity of C-C bond [42]

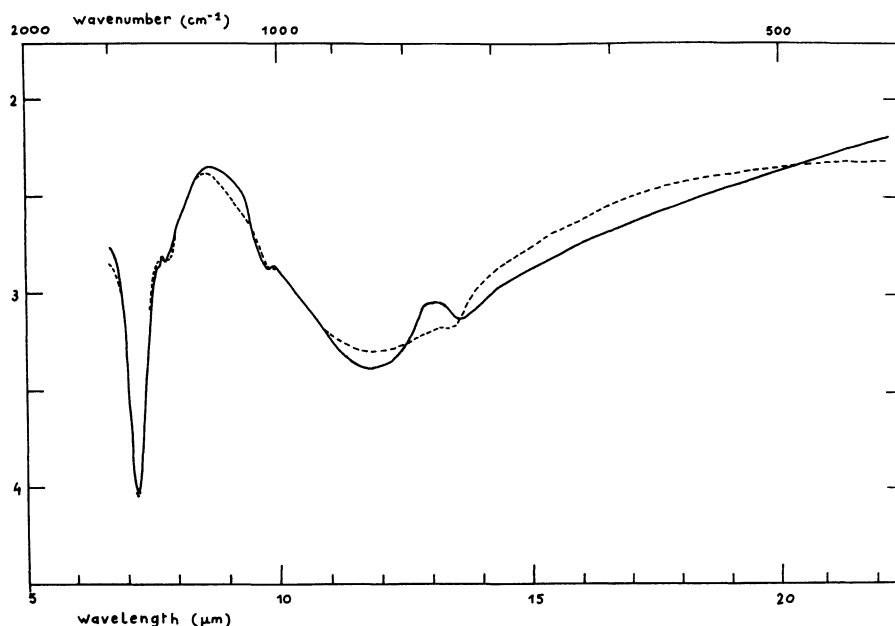


Fig. 7. — Infrared transmission spectra of a 2.5 μm thick film for $Y = 0.023$. Full curve : experimental spectra. Dashed curve : calculated spectra using a classical oscillator model with following values. $\omega_1 = 1\,382\text{ cm}^{-1}$; $\sqrt{S_1} = 703\text{ cm}^{-1}$; $\gamma_1 = 71\text{ cm}^{-1}$; $\omega_2 = 819\text{ cm}^{-1}$; $\sqrt{S_2} = 1\,800\text{ cm}^{-1}$; $\gamma_2 = 436\text{ cm}^{-1}$. Extra bands at 730, 1 050 and 1 250 cm^{-1} have been taken into account by classical dispersion oscillator.

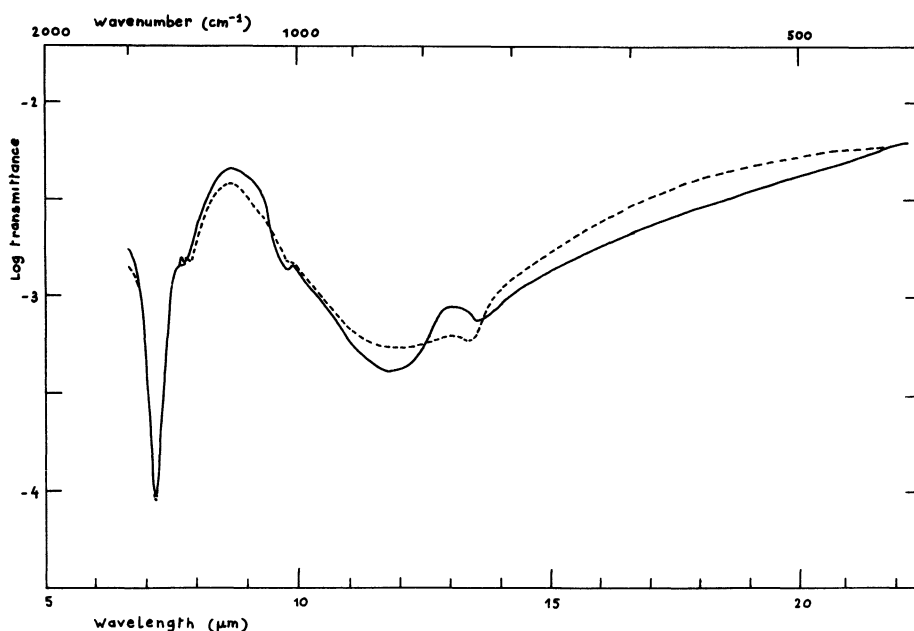


Fig. 8. — Infrared transmission spectra of a 2.5 μm thick film for $Y = 0.023$. Full curve : experimental spectra. Dashed curve : calculated spectra using the Horowitz model with following values. $\omega_1^0 = 1\,381\text{ cm}^{-1}$; $\lambda_1 = 0.037\lambda$; $\gamma_1 = 67\text{ cm}^{-1}$; $\omega_2^0 = 782\text{ cm}^{-1}$; $\lambda_2 = 0.963\lambda$; $\gamma_2 = 489\text{ cm}^{-1}$; $\alpha = 1.29$; $\lambda = 0.19$. Extra bands at 730, 1 050 and 1 250 cm^{-1} have been taken into account by classical dispersion oscillator.

introduce a linear dependence of C-C force constant with the bond lengths.

The presence of a defect modifies the distance of C-C bonds, so, even without electron-phonon coupling, there exist localized modes, for which the bare frequency would be found lower than 900 cm^{-1} .

Simple calculations show that, if a soliton type defect is present in a linear chain with a « great extension », l , a localized mode is obtained with a frequency close to $\omega_1 = \frac{1}{\sqrt{2}}\omega_{\max}$, where ω_{\max} is the frequency of optical mode of the perfectly dimerized chain [43].

Therefore, in the case of a *trans*-chain it would be likely to obtain, one or more localized modes whose frequency is lower than 900 cm^{-1} . These modes are also coupled with electrons and it would be necessary to consider them in the calculations of the response of the system to the electric field.

Horowitz, taking into account the Raman frequencies, found a value for α equaling 0.24.

Since, the lowest frequency lattice mode found by Mele and Rice has a frequency value of $1\,100\text{ cm}^{-1}$, Horowitz deduced that the 900 cm^{-1} mode (ω_2) could only be the pinned mode.

Indeed, in his model the lowest frequency infrared mode approaches zero when $\alpha \rightarrow 0$, as it can directly be seen in expression 1.

In fact, the strong α dependence of ω_2 permits to test that this mode is either a pinned mode or not. Indeed, it is easy to predict that, with increasing dopant concentration, the dopant distribution will become more and more uniform along the chain, $V''(x)$ will approach zero for all values x and then the ω_2 frequency will also approach zero. To estimate this variation we can calculate α by a discret summation on sites.

From Su *et al.* [45] the charge distribution ρ is given by

$$\rho(n) \sim \left[\frac{1}{l} \operatorname{sech} \left(\frac{n}{l} \right) \cos \left(\frac{2\pi n}{l} \right) \right]^2. \quad (4)$$

Taking $\varepsilon_0 = 14$ [11]; $d = 4\text{ \AA}$ [44]; $l = 6$ [45] and evenly distributed I_3^- molecules, parallel to the chain, as impurities, we obtain for α a value of 0.24 consistent with the value obtained by Horowitz [19].

We have done calculations with a chain with 1 000 (C-H) units from $Y = 0.001$ to $Y = 0.15$. Results are shown in figure 9. α is constant for low doping, then decreases rapidly as doping increases. This behaviour is easy to understand : invariance by translation will be restored in the limit of a continue distribution of charged impurities, then $V''(x) = 0$ for all values x , thus $\alpha = 0$ and $\omega_2 = 0$ giving rise to a Fröhlich type of conductivity. Figure 9 shows that as the doping level increases, the frequency of ω_2 mode decreases drastically, which is inconsistent with experimental data. So the ω_2 mode cannot be the pinned mode. Recent results obtained by Tanaka [24] show that, at low temperature, some other absorption bands appear in the low frequency range. It is possible that one of these bands correspond to the pinned mode, this, however, remains to be verified.

Finally, we note that, according to the theory, the ω_1 mode frequency should only begin to vary for high doping levels. In the other models, also, the varying frequencies of the localized modes becomes important, only at high doping level at which the soliton-soliton interaction is strong. The fact that a rapid variation of the soliton frequencies is experimentally found from low doping levels, shows that the doping is extremely inhomogeneous. It also shows that, when

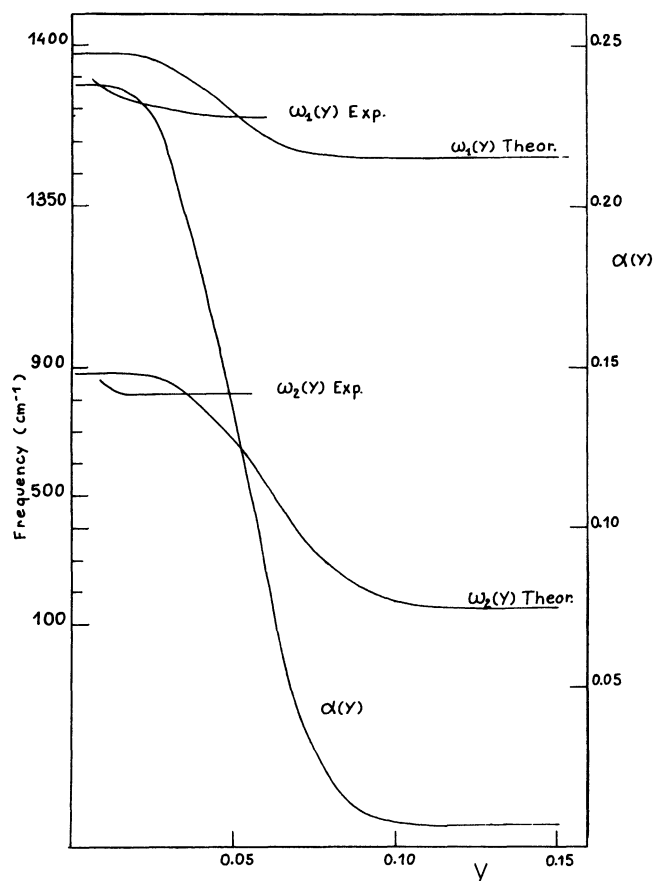


Fig. 9. — Variation of the coupling α with the pinning potential of impurities, and frequencies of infrared active modes ω_1 and ω_2 versus doping level Y .

we determine an average doping level from 0.5 % to 1 % there are, in fact, much more heavily doped regions (two or three times heavier) as well as undoped regions. The simplest model is one in which fibrils are doped on the surface and lightly doped on the inside.

The width of the 900 cm^{-1} and $1\,370\text{ cm}^{-1}$ is very large and increases with doping. The most elementary explanation is to assume that there is disorder due to a distribution of defects having slightly different characteristics (soliton position and extent, dopant position) Zerbi [17] Horowitz [46]. In another hypothesis, already mentioned by Mele and Rice [16] the width would arise from the coupling of the localized mode with the soliton. It is evident that a strong coupling must exist and produce a rather strong diminution of the localized modes. Lastly, when the doping increases, the frequency decreases and the damping increases. Measurements of the widths of these modes with decreasing temperature should make it possible to choose from the different assumptions.

4. Conclusion.

Our measurements show :

That even in metallic state ($Y > 0.06$) the soliton bands persist (Fig. 2) and the chains with defects are

stable, which is not in accordance with Bulka's results [21].

That the doping is certainly not uniform in the fibrils and it is difficult to interpret the results under the assumption of a composite medium made by metallic islands in an insulating medium.

That the pinned mode frequency depends greatly on the α coupling coefficient, which also depends greatly on the dopant charge localization, the polarizability and the size of the ion, the electronic delocalization on the ion (I_3^- , I_5^-), therefore, we do not understand why, experimentally this frequency always has the same value whatever the dopant species. So, the ω_2 mode cannot be the pinned mode. The ω_1 and ω_2 bands are certainly localized excitations.

That the Horowitz model clearly exhibits the system's properties, hypothesizing that ω_1 and ω_2 are localized modes. Nevertheless, it is evident that it will be necessary, in such a model, to introduce a third mode corresponding to a pinned mode, the frequency of which approaches zero when the doping increases. The introduction of such a mode is necessary to recognize the weak dependence of the ω_2 mode on the doping. It will also be necessary to take into account the anharmonicity of σ -bond which will give rise to localized excitation with bare frequencies

< 900 cm^{-1} . It is difficult to explain the saturation of intensity values of the 900 cm^{-1} and 1370 cm^{-1} bands. The presented calculations give only a relative value but it is obvious that beginning at a certain value, the intensity becomes practically constant while the background continues to increase.

It would seem that above a certain doping level, new soliton type defects no longer occur. This would imply that above 2% the species no longer dopes new regions, which is in accordance with Robin's X-ray diffraction measurements.

Besides, the method of analysis used, does not give good absolute values for oscillator strength. We only interpreted the spectra with the additional absorption due to defects. In order to interpret them it would be necessary to precisely take into account the absorption due to free carriers and the absorption due to defects.

Lastly, it will be necessary to remake experiments with much more accuracy especially as a function of the doping level, for Y values up to 0.01. Our work, only reports results concerning iodine doping and cannot be extended without care, to other dopants. However recent infrared experiments dealing with MoCl_5 dopant exhibit similar behaviour.

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