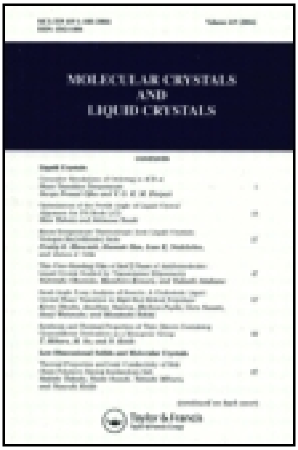

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# RAMAN INVESTIGATION OF ALKALI-DOPED $(CH)_x$ FILMS

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Abstract Resonance Raman spectra induced by $(CH)_x$ films chemically or electrochemically doped with alkali metals are reported. At low doping levels, Raman bands characteristic of the trans isomer are observed. The Raman spectra can be well fitted using the theory developped by Mulazzi based on a bimodal distribution of long and short trans segments respectively. At the same time, typical results obtained for a cis-rich $(CH)_x$ sample, as well as its behavior during a thermal isomerization, are recalled in the frame of the Mulazzi model. When the polymer is highly doped with Li (or Na) atoms, new features at ≃ 1600 $cm^{-1}$ and 1270 $cm^{-1}$ appear and could be an indication that n-doped films are less disordered than p-doped systems.

## INTRODUCTION

The Raman spectroscopy has proved to be a very powerful technique to study the morphology of trans-polyacetylene (1, 2, 3). In particular, the characteristic features observed in the Raman spectra when the exciting wavelength is tuned in the high energy range lead to a determination of the relative concentration of long and short chains. This is done with the use of a theory based on a bimodal distribution proposed by Mulazzi (4, 5). As a matter of fact, this model can be applied successfully to any situation in trans-polyacetylene and in this paper, some of the previous experiments as well as significant theoretical results will be recalled.

When the polymer is doped, its morphology and structure can be drastically changed and a great deal of information can be gained from the vibrational properties. The results obtained in alkali-doped polyacetylene, either chemically or electrochemically doped, will be presented. General conclusions as well as specific ones more specifically associated with alkali-doped samples will be given.

## I - GENERAL FEATURES OF RAMAN SPECTRA OF TRANS-$(CH)_x$

Raman spectra of trans-$(CH)_x$ have been described in details by many authors and the appearance of side-bands (at 1130 $cm^{-1}$ and 1540 $cm^{-1}$ for $\lambda_L$ = 457.9 nm) in addition to the main Raman bands peaked at 1064 and 1458 $cm^{-1}$ has been the subject of controversy. In particular, a hot luminescence process was introduced to explain this phenomenon (6), but both Raman spectra recorded with u.v. excitations (7) as well as anti-stokes Raman scattering experiments (8) turned out to be inconsistent with this model. More recently, Horovitz et al. (9) introduced a theory interpreting Raman spectra from amplitude modes together with a narrow distribution in the effective electron-phonon coupling. Nevertheless, the existence of short conjugated segments in trans-polyacetylene seems to us proved by the u.v. Raman experiments and as a consequence, long and short trans-$(CH)_x$ chains are expected in the polymer, so that a bimodal distribution of chain length was introduced by Brivio et Mulazzi (10) to fit both absorption and Resonance Raman Spectra (RRS) induced by $(CH)_x$. The model gives a remarquable agreement with the experiments in the case of a 100 % trans-$(CH)_x$ sample (4), but can be applied with success to other cases.

For example, in Figure 1 are presented the Raman spectra of a cis-rich $(CH)_x$ sample for $\lambda_L$ = 676.4 nm and 752.5 nm. The double peak structure observed (for $\lambda_L$ = 676.4 nm) on the two main bands are due to "trans" parts remaining in the polymer. When $\lambda_L$ = 752.5 nm, only the low frequency peaks are observed and this rather sharp resonance behavior was unexplained before. Using the parameters given in part C of Figure 1, and whose signification is given else-

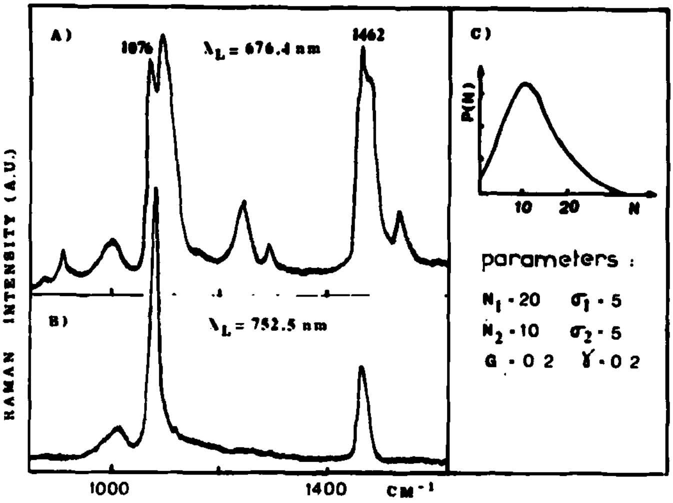

FIGURE 1 Raman spectra of a cis-rich $(CH)_x$ sample : A) $\lambda_L$ = 676.4 nm ; B) $\lambda_L$ = 752.5 nm ; C) distributions curve fitting these spectra (from réf. 5)

where(10), a good fit is obtained. The distributions curve P(N) versus N, where N is the number of C=C double bonds, is also shown in Figure 1.

A thermal treatment at 140° C for example converts gradually the cis-$(CH)_x$ into trans-$(CH)_x$. In the Raman spectrum, the shapes of the Raman bands due to the trans part change, respect to the trans content in the film. When $\lambda_L$ = 752.5 nm, one observes for example the two peaks at 1076 and 1468 $cm^{-1}$ for a 10-20 % trans content (so-called cis-rich sample) while the final spectrum for a 100 % trans-$(CH)_x$ shows the peaks at 1064 and 1462 $cm^{-1}$. A fit of these spectra according to the Mulazzi model leads to changes in the two calculated distributions. One goes from $N_1$ = 20, $N_2$ = 10 for a cis-rich sample to $N_1$ = 100 and $N_2$ = 15 for a 100 % trans-sample. Details concerning these parameters are given elsewhere (11, 5) and the distributions curves are shown in Figure 2. The evolution of the chain length distributions during a thermal treat-

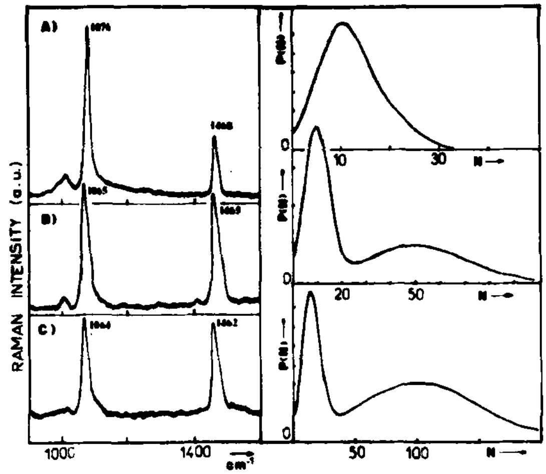

FIGURE 2 Raman spectra at 78 K of $(CH)_x$ thermally isomerized at 140° C. A) 10-20 % trans-$(CH)_x$ ; B) 80 % trans-$(CH)_x$ ; C) 100 % trans-$(CH)_x$
The corresponding distributions curve are shown in the right side of the Figure.

ment is clearly evidenced and the model appears really appropriate to describe quantitatively the morphology of a polyacetylene sample.

## II - N-DOPING OF $(CH)_x$ FILMS

Upon doping, $(CH)_x$ undergoes strong modifications and has been the subject of several investigations. P-type dopants have been mainly used, but n-type dopants have also shown interesting properties. With respect to Raman Spectroscopy, a study of Li-doped $(CH)_x$, doped chemically, has already been done (12) and our purpose is to compare the results obtained with different alkali metals and with different doping procedures.

On Figure 3 are shown the Raman spectra obtained at room temperature for different systems. At low doping concentrations, besides the cis-trans isomerization, the general results obtained in all doped $(CH)_x$ systems is observed, i.e. a shift of the "trans"

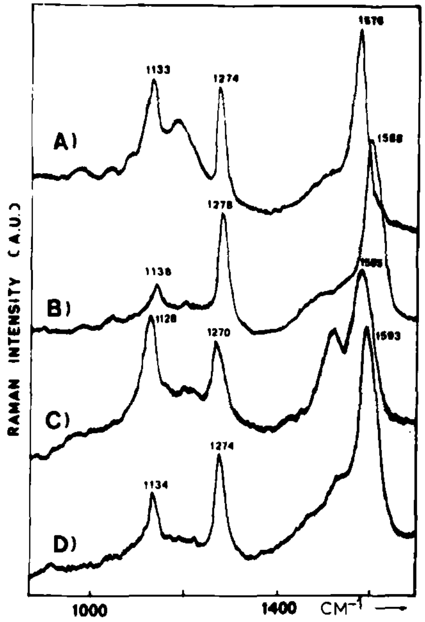

FIGURE 3 Raman spectra of (CH)$_x$ doped with alkali metals at RT.

A) Chemically doped with Li ; $\lambda_L$ = 676.4 nm
B) Chemically doped with Li ; $\lambda_L$ = 457.9 nm
C) Electrochemically doped with Li ; $\lambda_L$ = 514.5 nm
D) Electrochemically doped with Na ; $\lambda_L$ = 514.5 nm

Raman bands towards higher frequencies. When $\lambda_L$ = 457.9 nm, the low frequency peaks which characterize the long chains in high quality samples are never observed.

The most significant results are seen for typical doping concentrations of about 3-4 %. New features appear in the Raman spectra and they can be summarized as follow :

i) the usual bands assigned to the trans isomer become very weak and are peaked at approximately 1135 and 1540 cm$^{-1}$ ;

ii) a new mode is observed at ≃ 1270-1274 cm$^{-1}$ ;

iii) an additional band is also very strong at 1570-1600 cm$^{-1}$. This band is dependant on the excitation wavelength and has already been observed in p-doped systems.

As can be seen on Figure 3, these features are similar whatever the procedure used for doping (chemically or electrochemically) and whatever the alkali metal (Li, Na or even K). The electrochemical treatment has the great advantage to allow a dedoping, in controling the charges passed through the polymer film, and therefore the concentration. By dedoping, the reversibility of the doping can be easily checked as done by other techniques like EPR for example (13). The Figure 4 shows the Raman spectra of $(CH)_x$ electrochemically doped with Na (spectrum D in Figure 3) and reversibly dedoped. It is demonstrated that the additional features observed before have completely disappeared and that Raman spectra induced by a trans-$(CH)_x$ sample are restored, in agreement with the previous results of Eckhardt et al. (14).

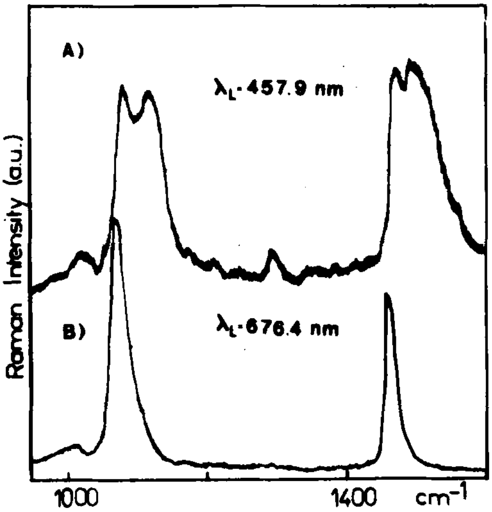

FIGURE 4 Raman spectra of $(CH)_x$ at RT, doped electrochemically with Na and dedoped.
A) $\lambda_L$ = 457.9 nm ; B) $\lambda_L$ = 676.4 nm

## CONCLUSION

At low doping levels, Raman spectra induced by doped $(CH)_x$ films show two main bands characteristic of the trans isomer. These bands shift to high frequencies according to the doping concentration. This result is interpreted as due to a shortening of the trans sequences and the distributions can be calculated using the Mulazzi model. This shows that, at low doping levels, we are observing undoped parts of the polymer, result which is in agreement with X-rays experiments (15). At higher doping levels, the new features observed in the Raman spectra consist of a strong band at ≃ 1570-1600 as already observed in p-doped systems. Since it depends on the excitation wavelength, and does not depend on the dopant, this vibration mode is expected to be associated with the carbon chain. The interpretation could be given by the calculations of Zerbi (16) describing the effects of the formation of centrosymmetrical bipolaron type defects on the density of electronic states. About the mode at 1270 $cm^{-1}$, it is observed in the case of n-doped $(CH)_x$. It has a frequency value very close to that observed in the IR spectrum of doped $(CH)_x$, but it is also in agreement with a frequency mode calculated in (16) for an undimerized chain. In conclusion then, the n-doped systems, for which the reversibility is clearly demonstrated by electrochemical dedoping, seem arranged in more ordered phases. Also, the isomerization occuring by doping turns out to be very good with respect to the conjugation length since the low frequency components associated with long chains are clearly observed in the Raman spectrum for $\lambda_L$ = 457.9 nm.

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