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## PREPARATION AND PROPERTIES OF HIGH QUALITY POLYACETYLENE

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Résumé - Des échantillons de trans-polyacétylène préparés avec beaucoup de soins montrent une composante de haute fréquence de la raie Raman correspondant à un mode vibratoire linéaire  $C = C$  qui est plus faible que d'habitude si elle est excitée avec de la lumière laser de 4579 Å. Ceci est une bonne preuve que l'effet de dispersion est de nature extrinsèque plutôt que provenant d'une luminescence chaude due aux longues conjugaisons non-déformées. Une dégradation de l'échantillon par irradiation ne change pas la forme de la raie mais augmente le fond continu tandis qu'une oxydation augmente la partie à haute fréquence du mode vibratoire  $C = C$ . Un calcul des formes de raies Raman dans le cadre d'une version étendue du modèle des conjugaisons interrompues donne un très bon accord avec les résultats expérimentaux et prouve la validité de la dépendance très importante des éléments de la matrice de transition selon une fonction racine-carrée du nombre des conjugaisons doubles au moins pour des segments courts et de moyenne longueur.

Abstract - By very careful sample preparation a trans-polyacetylene film was grown which showed an unusual weak high frequency component in the  $C = C$  stretch mode Raman line if excited with 4579 Å laser light. This is good evidence that the dispersion effect is of extrinsic origin rather than due to hot luminescence from long undisturbed conjugations. Degradation of the sample by irradiation does hardly change the line shape of the modes but increases the background scattering whereas oxydation enhances the high frequency part of the  $C = C$  stretch mode. A calculation of Raman line shapes within an extended version of the interrupted conjugation model gave very good agreement with experimental results and proved the very strong square root like dependence of the transition matrix elements on the number of double bonds at least for short and medium long segments.

## I - INTRODUCTION

The dispersion of Raman lines has been the subject of many discussions in recent research work on trans-polyacetylene /1-4/. The problem was interpreted in terms of a distribution of defects along the polymer chains which interrupt conjugations statistically. This point of view finally led to a quantitative explanation for the Raman line shapes and scattering intensities /4,5/. On the other hand very recently an alternative explanation of the dispersion effect as a consequence of hot luminescence from uninterrupted and perfect chains was suggested /6/.

## II - PREPARATION AND CHARACTERIZATION OF HIGH QUALITY TRANS-(CH)<sub>x</sub>

A discrimination between the two models suggested for the explanation of the dispersion can be obtained by checking whether it has extrinsic

or intrinsic character. Careful sample preparation was already shown by Lichtmann et al. /7/ to lead to a double peak structure in the Raman lines for the C = C stretch mode if excited with 4579 Å laser light. We have further improved the procedure suggested by Shirakawa et al. /8/ and finally obtained 4579 Å excited Raman spectra, where the high frequency part of the C = C stretch modes are reduced to about 50 % of the low frequency component. A corresponding spectrum is shown in Fig. 1 trace A.

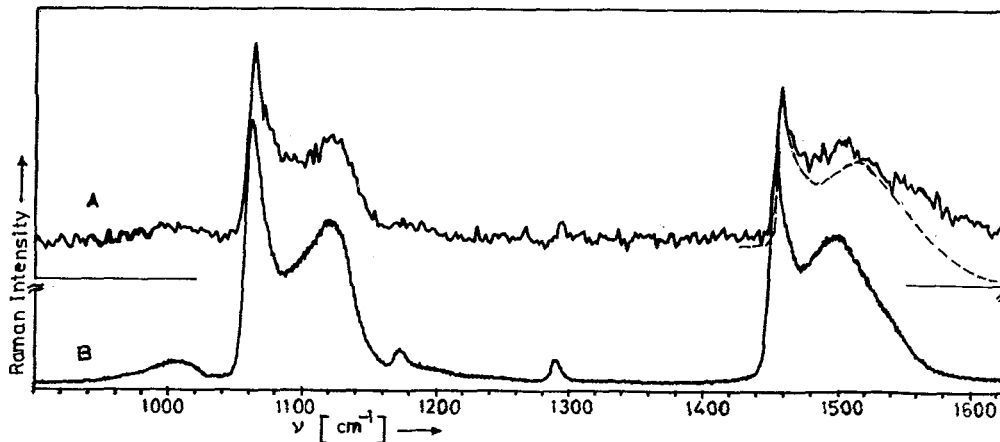


Fig. 1 - Raman spectra of special quality trans-(CH)<sub>x</sub> as excited with 4579 Å laser radiation. A: as grown and isomerized, B: after storage at low temperatures for 6 months.

The major improvements were due to a higher degree of purification of equipment and gases used and an immediate isomerization under optimized condition after the polymerization process (10 minutes, 170°C, very good vacuum). The spectrum of Fig. 1A is striking because of its low scattering intensity around 1490 cm<sup>-1</sup> but also because of its tailing towards high frequencies. It turns out that the spectrum is not stable against long time storage even at low temperature. Trace B in Fig. 1 shows a spectrum of the same batch as A after 6 months storage at dry ice temperature. Though the spectrum is still of high quality the relative scattering intensity around 1490 cm<sup>-1</sup> increased and the tailing decreased. This change may be interpreted as an effect where very short segments anneal towards slightly longer segments.

### III - IRRADIATION AND OXYDATION OF SAMPLES

In order to study the influence of defects on the line shape of the C = C stretch modes we irradiated and oxydized the samples. The polymer was found to be very sensitive to both types of degradation processes but the respons was characteristically different. A 70 minutes irradiation at reduced temperatures with a medium pressure UV-Hg are lamp of 125 W led to a strong increase of the background and to a decreased but otherwise unchanged line pattern. Oxydation hardly increased the background but changed the line pattern. Finally 2.5 hours irradiation with C<sub>60</sub><sup>60</sup> γ rays at room temperature was much less effective than UV-irradiation. Fig. 2 curve A-D shows the corresponding line shapes for the C = C stretch mode around 1500 cm<sup>-1</sup>. We conclude from these results that different types of defects have a completely different influence on the Raman line shapes.

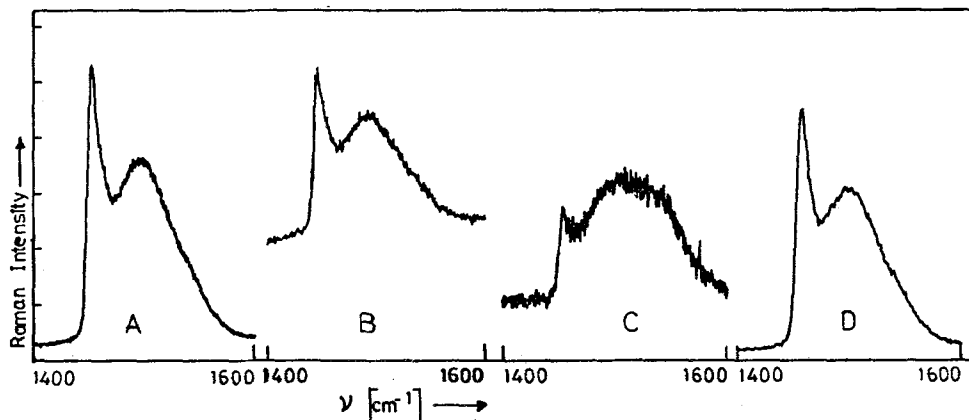


Fig. 2 - Raman lines for the C = C stretch mode of trans-polyacetylene. A: as isomerized, B: after UV-irradiation, C: after oxidation, D: after irradiation with  $\gamma$ -rays.

#### IV - EXTENDED INTERRUPTED CONJUGATION MODEL

In order to obtain a more quantitative physical information a line shape analysis according to the interrupted conjugation model was performed /9/. As compared to previous work the method was improved by evaluating the transition matrix elements  $\rho_{gm}(N, I)$  and the energy eigen values for all allowed transitions from the  $\pi$  to the  $\pi^*$  band explicitly on a Hückel basis.  $\rho_{gm}(N, I)$  was calculated using the zero differential overlap condition

$$\rho_{gm}(N, I) = \langle \psi_g | R | \psi_m \rangle = \sum_{\mu} C_{g\mu} C_{m\mu} R_{\mu} \quad (1)$$

where  $\psi_g$  and  $\psi_m$  are molecular orbitals  $C_{g\mu}$  and  $C_{m\mu}$  are molecular orbital coefficients and  $N$  labels the number of double bonds on the chain and  $I$  the transition number. Fig. 3 shows the behavior of the matrix elements as a function of  $N$  and  $I$ . The full drawn lines are computer fits using the analytic formula

$$\rho_{gm}(N, I) = (A_I N^2 + B_I N) / (C_I + N^3)^{1/2} \quad (2)$$

where  $A_I$ ,  $B_I$  and  $C_I$  are fitting parameters. For small  $N$  the approximation  $\rho \propto \sqrt{N}$  as used in previous work /5/ is quite good. For  $N$  larger than 40  $\rho$  increases with a reduced exponent of  $N$ . For transitions deeper into the band (increasing  $I$ ) the matrix elements decay rapidly. Since they enter the scattering intensity to the fourth power only the lowest few transitions have to be considered. The dashed line in Fig. 1A shows a calculated line profile for the C = C stretch mode Raman line as excited with 4579 Å laser light. From the distribution of undisturbed conjugations used for the fit we found that 65 % of the material is in segments longer than 25 double bonds for the special quality material. Simultaneously to the Raman line dispersion the line shape of the optical absorption could be calculated in very good agreement with experimental results.

#### V - DISCUSSION

The fact that the scattering intensity of the high frequency part of

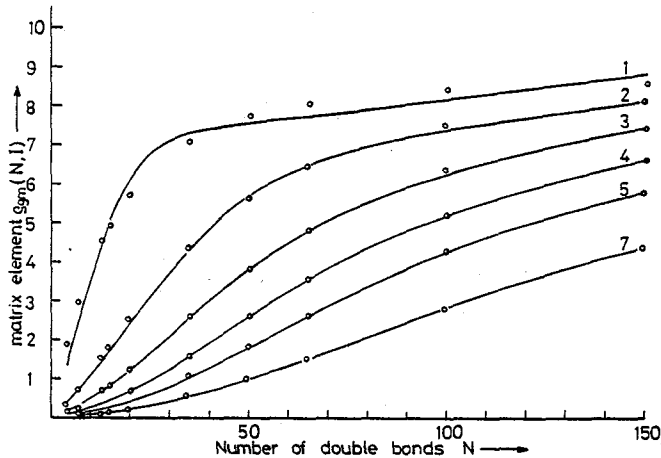


Fig. 3 - Transition matrix elements  $\rho_{gm}(N, I)$  as a function of the number of double bonds  $N$  and transition  $I$ , (o) as calculated numerically and (—) as computerfitted.

the C = C stretch mode can be strongly reduced by careful sample preparation is evidence for its extrinsic nature. Very little is known about the structure of the defects interrupting the conjugations. As shown in this work and also in previous work /3/ oxygen plays a dominant role. Defects induced by irradiation react in a substantially different way to the spectrum. In comparison to previous work /11/ we found a high sensitivity of the polymer to irradiation at low temperatures. One reason for this surprising result could be the fact, that at reduced temperatures no thermal annealing during the irradiation process can take place.

The explicit calculation of the transition matrix elements showed that  $\rho_{gm}(N, I)$  is indeed strongly dependent on  $N$ . The lifetime of the excited electronic state as deduced from the damping constant  $\gamma_e$  for the electronic transition was found to be  $\tau = 1/2\pi\gamma_e = 0.3 \times 10^{-14}$  sec in good agreement with a value expected for a decay of the excited state into a soliton antisoliton pair /12/.

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#### REFERENCES

- /1/ LEFRANT S., LICHTMANN L.S., TEMKIN H., FITCHEN D.B., Solid State Commun. 29(1979)191
- /2/ LICHTMANN L.S., FITCHEN D.B., TEMKIN M., Synth. Met. 1(1979/80)139
- /3/ FITCHEN D.B., Mol. Cryst. Liq. Cryst. 83(1982)1127
- /4/ KUZMANY H., phys. stat. sol. (b) 97(1980)521
- /5/ KUZMANY H., TMHOFF E.A., FITCHEN D.B., SARHANGI A., Phys. Rev. B 26(1982)7109
- /6/ MELE E., Solid State Commun., to be published
- /7/ LICHTMANN L.S., SARHANGI A., FITCHEN D.B., Chem. Soc. 17(1981)1491
- /8/ SHIRAKAWA H., ITO T., IKEDA S., J. Polymer Science 4(1973)460
- /9/ KUZMANY H., SURJAN P., KERTESZ M., unpublished
- /10/ SALEM L., "Molecular orbital theory of conjugated systems" W.A. Benjamin inc. London-Amsterdam-Ontario Sydney-Tokio, 1966
- /11/ YEN S.P., SOMOANO R., KHANNA S.K., REMBAUM A., Solid State Commun. 36(1980)339
- /12/ SU W.P., SCHRIEFFER J.R., Nat. Acad. Sci., NY. 77(1980)5626