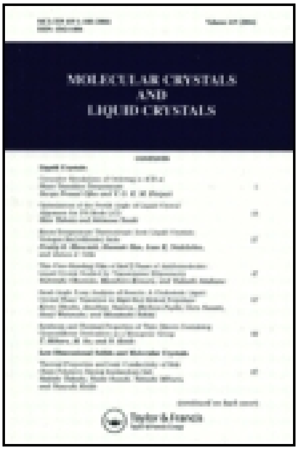

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Resonance Raman Scattering of Undoped Trans-Polyacetylene in the Region of the Absorption Edge

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RESONANCE RAMAN SCATTERING OF UNDOPED TRANS-POLYACETYLENE IN THE REGION OF THE ABSORPTION EDGE

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Abstract : Resonance Raman Scattering of undoped $CH)_x$ was studied for excitation wavelength λ_L between 700 and 1064 nm. Scattering is entirely due to long conjugated chains, but with evidence of disorder. Positions and shapes of the Raman lines are studied as a function of λ_L. The action spectrum shows a maximum near 1.4 eV, with a width > 0.2 eV at 2 K and no other structure.

1 - INTRODUCTION

There has been a large number of experimental and theoretical studies of Resonance Raman Scattering (RRS) in polyacetylene (see for instance the contributions by Lefrant and by Mulazzi in these Proceedings). In the trans isomer, almost all data were obtained using excitation around or above 1.9 eV (647 nm), and a great deal of attention was given to lineshapes rather than to intensities. One of the few attempts in obtaining a RRS excitation spectrum -again above 1.8 eV - is that of Lauchlan et al[1]. The main issue in all these works was to assess the importance of chain distribution length, particularly the role of short conjugated segments, in the RRS lineshapes.

On the other hand, RRS has been used in recent years as a tool to study electronic states and electron-phonon interactions in crystalline solids, especially semiconductors[2]. This seemed worth trying on $CH)_x$. Such a study has been very recently done on cis $CH)_x$[3] - see also the contribution by Fitchen in these Proceedings -. In this paper, we would like to report on our study of RRS in trans $CH)_x$ excited by photons of 1.8 eV and lower energies, down to 1.16 eV ; this range of energies encompasses the absorption edge of trans $CH)_x$, but is less easily accessible than the corresponding region in cis $CH)_x$. Our work is still in progress but we feel that the data obtained up to now, albeit incomplete, are sufficiently new to be of interest. A more detailed account will be published elsewhere.

2 - EXPERIMENTAL PROCEDURES

Two trans $CH)_x$ films were used. The polymer was obtained by the Shirakawa method, isomerized in the cis form by slow chemical K doping, then dedoped by removal of the K^+ ions using a weak electron acceptor. This procedure yields all-trans films of high quality, judging from their spectroscopic properties[4]. The films were continuously kept in an inert atmosphere. The lineshape of Raman lines excited in the blue were indicative of "high quality".

Sample 1 was a thin - about .5 micron thick - film deposited on the inner surface of a quartz cuvette. It was used for study with excitation from 700 to 920 nm at room temperature,but it does not totally absorbs light beyond ca 900 nm. Sample 2 was a ~ 50 microns thick free standing film. It was used for study with excitation from 800 to 960 nm and at 1064 nm, mostly at 2K in superfluid He.

But for one experiment - see § 3.1 -, the excitation light was provided by a Coherent 590 jet dye laser, using appropriate dyes : Rhodamine 700, Oxazine 750, Styryl 9 and 9M (Lambda Physik), and pumped accordingly by a 1 W Krypton laser (Spectra-Physics 165) or a 8 W Argon laser (Coherent CR 15). The corresponding bandwidth was always less than 1 Å. Interference filters were generally used to suppress the dye fluorescence background. The scattered light was dispersed by a Jarrel-Ash double monochromator, and detected by photomultipliers : RCA C31034 up to 850 nm and RCA 7102 up to 1100 nm. Photon counting (Ortec) was used.

The incident power was kept at 10 mW or below in the region of strong absorption, at 20 mW or below at the longest wavelengths. *No photodegradation of the samples was observed.* The whole setup spectral response was calibrated by comparison to calibrated tungsten lamp and interference filters. All data presented here have been corrected for variation of the instrument response, but not for the influence of the sample optical properties ; correcting for the latter is an intricate and quite uncertain procedure, which would require detailed knowledge of the morphology and optical properties of each individual sample. We feel that the procedure adopted here will be more useful to the reader, at the present stage of our work.

3 - EXPERIMENTAL RESULTS

3.1 RR Spectra. A strong RRS response was observed at all excitation wavelengths λ_L, and the spectra were essentially identical at all λ_L and for both samples. Fig.1 shows a spectrum recorded with $\lambda_L = 1064$ nm. It is the only one recorded with a different setup, and is our first attempt to extend the measurements beyond the working range of PMs. Sample 2 was excited at 2K by a Nd-YAG laser and scattered light was detected using a Ge detector and lock-in technique. All spectra show the two, slightly asymmetric, main lines ν_1 and ν_2 , a weak third line ν_3 and a broad asymmetric band peaking around 1020 cm^{-1}. For instance, at 960 nm and 2 K, $\nu_1 = 1060\ cm^{-1}$, $\nu_2 = 1453\ cm^{-1}$, $\nu_3 = 1294\ cm^{-1} \pm 1\ cm^{-1}$. Therefore, the spectra recorded here are always those of long conjugated $CH)_x$ chains; they are not associated to stable or photoexcited defects, some of which are known to absorb in the energy range studied here[5].

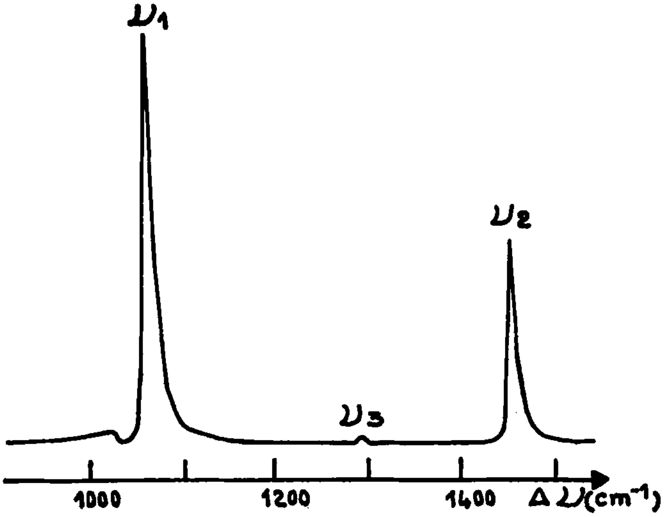
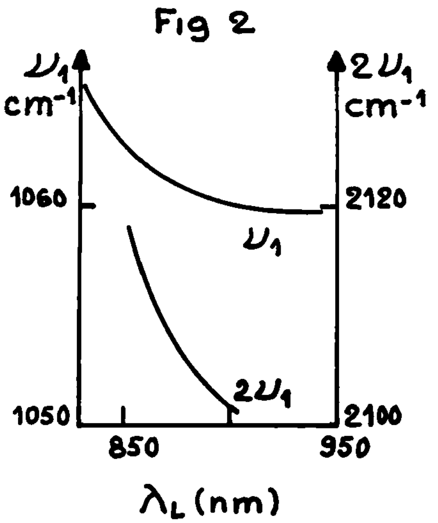


FIGURE 1 RRS spectrum of sample 2 at 2 K for λ_L = 1064 nm (uncorrected intensities).

3.2 Position and shape of the main lines ν_1 and ν_2. These lines are asymmetric at all λ_L. As λ_L increases to 900 nm, there is a slight decrease of their energy: for example, for ν_1, at 2K from 1065 cm^{-1} at λ_L = 800 nm to 1060 cm^{-1} at λ_L = 900 nm. The positions of the maxima then remain constant for λ_L > 900 nm and the same values are found at λ_L = 1064 nm (Fig. 2). The observed frequencies are larger at room temperature. Let Γ_- be the halfwidth of a line towards smaller wavenumbers, and Γ_+ the one towards larger ones. As shown in Fig. 3 at 2 K, $\Gamma_-(\nu_1)$ decreases as λ_L increases and is nearly constant (4 cm^{-1}) for λ_L > 900 nm. $\Gamma_+(\nu_1)$ is always larger than $\Gamma_-(\nu_1)$ and reaches its minimum value (6 cm^{-1}) near λ_L = 900 nm. It seeems to increase again beyond 900 nm but this deserves further study. At room temperature $\Gamma_-(\nu_1)$ and $\Gamma_+(\nu_1)$ are both practically constant (~ 6.5 and ~ 9 cm^{-1} respectively). In



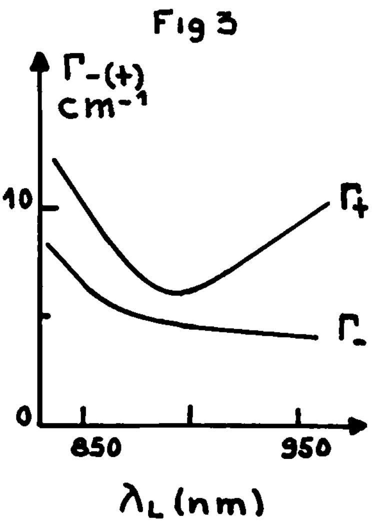


FIGURE 2 Positions of the ν_1 line and of its overtone $2\nu_1$ for sample 2 at 2 K versus excitation wavelength λ_L.

FIGURE 3 Linewidths Γ_+ and Γ_- of the ν_1 line for sample 2 at 2 K versus excitation wavelength λ_L.

addition, the ν_1 line always shows a small wing at large wavenumbers but it never evolves into a shoulder as observed under visible light excitation.

3.3 Relative variation with λ_L of the scattering cross section for ν_1. As mentioned in §2, these data have not been corrected for the change of sample optical properties with wavelength. These properties are very imperfectly known since they vary from sample to sample - especially with sample thickness - [4], so they should be studied in situ ; such measurements are planned for the future. Changes in reflectivity or morphology of the film with depth may have a minor influence, so that only the main features of the RRS action spectra reported here are significant. Incomplete absorption of the incident light may on the other hand be very important : it would decrease the apparent cross section. Such an effect can be seen on sample 1, the thin film, beyond 900 nm. On sample 2, however, light is totally absorbed up to 960 nm at least, and the corresponding action spectrum should be reliable.

Fig. 4 shows the action spectra of ν_1 measured up to now. The most accurate is the one measured on sample 2 at 2K for $\lambda_L > 820$ nm. The cross section is approximately constant up to $\lambda_L = 800$ nm, then increases by more than one order of magnitude up to about $\lambda_L = 900$ nm, and finally decreases again slowly. Therefore, a single peak is observed in the action spectrum with a maximum near 1.4 eV

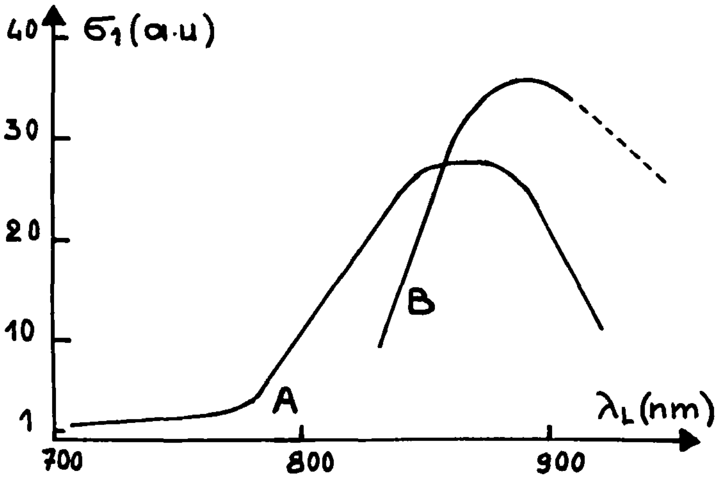


FIGURE 4 Action spectra of the ν_1 line.
Curve A : Sample 1 at room temperature
Curve B : Sample 2 at 2 K.

at 2K and a width of at least .2 eV, probably more. No vibronic replica is observed between 700 and 800 nm ; the reflection spectrum of some thick films at least, prepared as our sample 2, shows some weak structure in that λ range [6], but not enough to smear out vibronic structure- were it present - on the RRS action spectrum.

The action spectrum of ν_2 has been also studied and is very similar. The ratio of the cross sections $\sigma(\nu_1)/\sigma(\nu_2)$ slowly increases, with some structure, from 730 to 960 nm. ν_3 has not be studied in details, but seems to have a similar action spectrum.

3.4 Further observations. Some overtone and combination bands have been observed and their action spectrum is presently under study, with the objective of providing enough data to make possible a theoretical fit as was recently done on cis $CH)_x$[7]. These bands are much more intense at 2 K than at 300 K ; they show large shifts from their harmonic positions (Fig.2), which depend on λ_L and T.

4 - A SHORT QUALITATIVE DISCUSSION

The dependence of the position and width of the Raman lines on λ_L indicates that one is dealing with an inhomogeneous population of scatterers. However, resonant scattering by short chains is not observed. One may possibly be dealing with a distribution of long, but finite, chains of various lengths ; but it seems physically more acceptable to relate the inhomogeneity to the imperfect crystallinity of the crystalline parts of the material : non planarity and bending of the chains, variations of interchain interactions, etc ... generating inhomogeneous broadening of the absorption band edge (which is almost structureless) and of the RRS action spectrum (§ 3.3), as well as a distribution of force constants and electron-phonon couplings. A suitable model for this part of $CH)_x$ films could then be derived from Hosemann's "para-crystal"[8].

The maximum in the RRS action spectra does not correspond to any clear feature in the absorption spectrum, contrary to cis $CH)_x$[3] , but the reflectivity shows a small bump just below 1.5 eV. We shall refrain from any firm attribution here. It seems however impossible to associate it to defect states (since the RRS spectrum is that of trans $CH)_x$ chains). To assign it to band states, one needs a mechanism providing a very large cross-section enhancement at band edge without corresponding increase in absorption . The observed structure of the RRS action spectrum could be related to an intrinsic correlated electronic state. This could be for instance an exciton of large radius with a severely inhomogeneously broadened absorption.

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