

Analysis of resonant Raman scattering spectra of fully oriented undoped and iodine-doped *trans*-polyacetylene: Experiments and theory

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Polarized resonant Raman spectra of oriented *trans*-polyacetylene taken at different excitation wavelengths ($\lambda_L = 647.1$ and 457.9 nm) are presented for undoped and iodine-doped samples together with theoretical calculations based on distributions of conjugated segments. A detailed analysis of the band shapes and peak positions of the Raman bands in the two different cases reveals important differences, in agreement with a modification upon doping of the morphology of the polymer. The proposed model turns out to be appropriate for interpreting all the experimental data.

I. INTRODUCTION

Interpretations of the resonant Raman scattering (RRS) spectra of *trans*-polyacetylene¹⁻³ using essentially two different models⁴⁻⁶ have been recently proposed. The model in Ref. 5 is based on the hypothesis that the properties of *trans*-(CH)_x chains can be described in terms of noninteracting conjugation-length segments, whose electronic and lattice dynamical properties and the electron-vibrational interaction couplings in the excited electronic states can be studied as function of N (the number of double bonds in a noninterrupted conjugated segment). The other model⁶ is based on one-dimensional (1D) Peierls noninteracting chains whose dynamical properties are studied by using three dispersionless harmonic oscillators.

Recently the synthesis of fully oriented *trans*-(CH)_x samples^{7,8} has allowed experiments to perform polarized Raman scattering measurements⁹ which have furnished additional information on the properties of the conjugated segments responsible for the scattering of light. The results turned out to be fairly important in order to test the validity of the bimodal distribution model.⁵ In the framework of this model, the theoretical predictions,¹⁰ based on the properties of conjugated segments with $N < 10$, were found in good agreement with the experimental data,⁹ particularly concerning the dependence of the Raman band shapes and peak position for different polarizations of incident and scattered light versus the excitation wavelength.

In this paper, we present measurements of polarized RRS spectra performed on a new type of oriented *trans*-(CH)_x films ($\Delta l/l = 7$) obtained by using a new catalyst for the synthesis.⁸ We compare these new results with those reported in Ref. 9 and we present, for the first time, polarized RRS spectra of similar highly oriented samples doped with iodine at a concentration level of 2.3%. In this way, it is possible to make a direct comparison of the Raman band shapes and peak positions with those obtained for undoped oriented samples. All the experimental data are interpreted in terms of the bimodal distribution model and the changes in the spectra occurring upon doping are discussed.

II. EXPERIMENTAL RESULTS

The $|||$ and $\perp\perp$ polarized RRS spectra¹¹ of undoped stretched *trans*-(CH)_x for $\lambda_L = 647.1$ nm and $\lambda_L = 457.9$ nm, respectively, are shown in Fig. 1. In the experiments the samples were kept under vacuum and cooled down to liquid-nitrogen temperature (LNT).

In the red frequency region ($\lambda_L = 647$ nm) the experimental spectra are rather similar to those previously reported.⁹ In Figs. 1(a) and 1(b) the main Raman bands peak at 1068 cm^{-1} and 1466 cm^{-1} in the $|||$ configuration while they are shifted to 1090 cm^{-1} and 1485 cm^{-1} in the $\perp\perp$ configuration. In the violet region ($\lambda_L = 457.9$ nm) the $|||$ spectrum presented in Fig. 1(c) exhibits the double-peak structure characteristic of a sample with a reasonable amount of long conjugated segments in the chains. In Fig. 1(d) the $\perp\perp$ spectrum exhibits two bands peaked at 1135 and 1524 cm^{-1} , while the low-frequency components (apparent peaks at 1070 and 1465 cm^{-1}) have negligible intensity. All the $\perp\perp$ spectra are very weak with respect to the $|||$ ones. Although the spectra presented here in Figs. 1(a), 1(b), and 1(c) have some resemblance, at first sight, to the spectra of Fig. 1 in Ref.

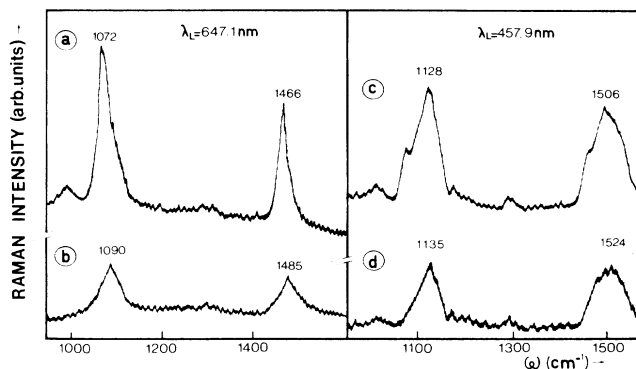


FIG. 1. Experimental spectra of stretched undoped *trans*-(CH)_x at 77 K. (a) and (b) $|||$ and $\perp\perp$ polarized spectra for $\lambda_L = 647.1$ nm, respectively; (c) and (d) $|||$ and $\perp\perp$ polarized spectra for $\lambda_L = 457.9$ nm, respectively.

9, we would like to point out that the peak positions and the shape of the bands are different in the two cases. This is expected since the spectra are recorded from two oriented samples obtained with a different synthesis technique.

Samples produced from the same synthesis (same stretching ratio) were doped with iodine at a concentration of 2.3% and polarized RRS spectra were recorded in condition similar to those reported above. For $\lambda_L = 647.1$ nm, the $|||$ spectrum displays two sharp peaks at 1064 and 1453 cm^{-1} [Fig. 2(a)]. In the $\perp\perp$ spectrum the signal is much lower than for the corresponding case of undoped oriented $\text{trans}-(\text{CH})_x$ and the peaks of the weak bands are shifted to 1102 and 1488 cm^{-1} , respectively. For $\lambda_L = 457.9$ nm the $|||$ spectrum displays two structureless bands at 1140 and 1525 cm^{-1} [Fig. 2(c)]. The $\perp\perp$ spectrum [Fig. 2(d)] shows two weak bands peaked at approximately the same frequencies. The depolarization ratios (defined in Ref. 9) which increase in both cases by going from the red to the violet region, are found to be four times smaller for iodine-doped sample than for the undoped one for $\lambda_L = 647.1$ nm.

In Figs. 3(a) and 3(b), we show the low frequency part of the $|||$ and $\perp\perp$ polarized RRS spectra, respectively, for $\lambda_L = 514.5$ nm. The stretching mode at 108 cm^{-1} of the I_3^- species¹² is clearly detected in the $|||$ spectrum. This mode is highly polarized since in the $\perp\perp$ spectrum, its intensity is very weak. The measured uncorrected depolarization ratio has been determined to be 0.04. In addition, a very weak Raman band is observed at 165 cm^{-1} ; this has been assigned to the I_5^- iodine species which is apparently present in the sample at a very low concentration. Despite the difficulty of the measurements due to the weakness of the signal, it seems that the depolarization ratio is higher than for I_3^- .

III. THEORETICAL RESULTS AND DISCUSSION

We have evaluated for the stretched undoped samples the $|||$ polarized spectra for $\Omega_L = 1.83$ and 2.7 eV and the $\perp\perp$ polarized spectrum for $\Omega_L = 2.7\text{ eV}$ [Figs. 4(a), 4(b), and 4(c)], by using the model based on the distribution of

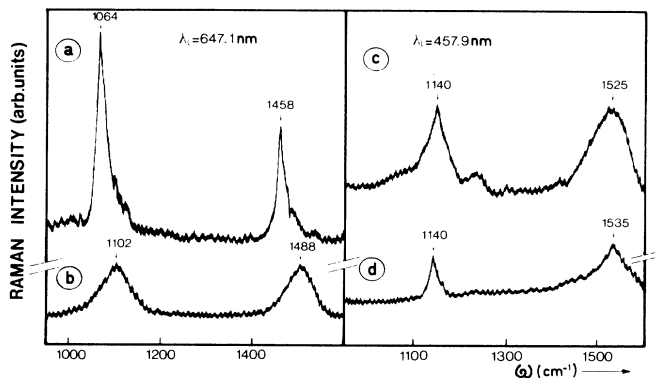


FIG. 2. Experimental spectra of stretched $\text{trans}-(\text{CH})_x$ doped with iodine at 77 K. (a) and (b) $|||$ and $\perp\perp$ polarized spectra for $\lambda_L = 647.1$ nm, respectively; (c) and (d) $|||$ and $\perp\perp$ polarized spectra for $\lambda_L = 457.9$ nm, respectively.

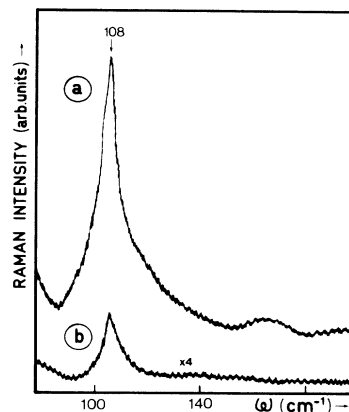


FIG. 3. Low-frequency Raman polarized spectra of $(\text{CHI}_{0.023})_x$; $\lambda_L = 514.5$ nm. $T = 77$ K. (a) $|||$ polarized spectrum; (b) $\perp\perp$ polarized spectrum. Note the different scale in the intensity of the two spectra.

segments of different conjugation length, as proposed in Refs. 5 and 10. Details of the calculations and notations have also been published elsewhere (see Refs. 9 and 10). The evaluations shown in Fig. 4 have been performed with the following parameters: $N_1 = 100$, $\sigma_1 = 50$, $N_2 = 14$, $\sigma_2 = 7$, and $G = 0.5$. (G is the relative weight of the long-segment distribution with respect to the short one.⁵) In the calculations, we have assumed that all the chains are parallel to the stretching axis.

We recall that the $\perp\perp$ polarized spectrum in the violet region is evaluated by taking into account in the RRS cross sections that the electric dipole moments for the electronic transitions of short conjugated segments have components perpendicular to the chain axis, whose intensities increase for N decreasing from 9 to 3. This follows from the analysis of the strong localization of the π and π^* electronic states for $N < 10$. In this way, only the electronic and vibrational contributions of the short conjugat-

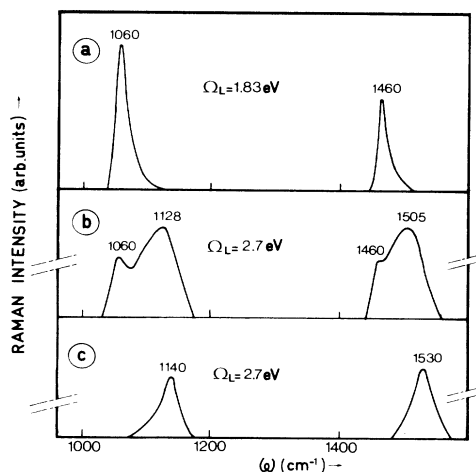


FIG. 4. Calculated spectra of stretched undoped $\text{trans}-(\text{CH})_x$. (a) $|||$ polarized spectrum for $\Omega_L = 1.83\text{ eV}$; (b) and (c) $|||$ and $\perp\perp$ polarized spectra for $\Omega_L = 2.7\text{ eV}$. Parameters are given in the text.

ed segments determine the $\perp\perp$ polarized RRS cross sections.

In Fig. 5 we show the results of similar calculations performed on iodine-doped stretched samples. Experimental Raman spectra were well fitted by using the following parameters: $N_1=100$, $\sigma_1=50$, $N_2=6$, $\sigma_2=3$, and $G=0.4$.

As discussed in Ref. 9, the $\perp\perp$ polarized spectrum observed with $\lambda_L=647$ nm, can be interpreted by considering misaligned segments whose average conjugation length would be of the order of $20N$. Moreover, the presence of short oriented segments can contribute significantly to the RRS cross sections in the high frequency parts of the bands. This may affect the peak positions of the Raman bands in the $\perp\perp$ spectrum and explains the sample-dependent shift observed in the experimental spectra with respect to the $\parallel\parallel$ spectra (see, e.g., the data in Fig. 1(b) and those published in Ref. 9). As suggested in Ref. 10, an additional contribution could come from transitions from the ground to electronic excited states of the conjugated segments which have electric dipole moment components perpendicular to the chain axis and whose frequencies lie near the electronic gap.

In the violet region, the $\perp\perp$ spectrum can be interpreted in terms of the contributions to the scattering of short segments whose electric dipole moments tend to be aligned in the double-bond direction. It has been shown theoretically¹⁰ to be the case when segments have conjugation lengths less than ten double bonds. This is evidenced by the negligible contribution (for $\lambda_L=457.9$ nm) of the long segments to the scattering in the $\perp\perp$ spectrum at 1070 and 1460 cm^{-1} , as observed experimentally [Fig. 1(d)] and theoretically predicted [Fig. 4(c)].

Concerning the doped samples, it appears that upon doping, the distributions of the conjugated segments are strongly modified. First, the mean value of the short-segment distribution has decreased to $N_2=6$. Second, the relative weight of the long-segment distribution with respect to the short-segment distribution has decreased to 0.4. As a consequence, doping with iodine leads to the disappearance of conjugated segments of long and intermediate length in the undoped phase.

In fact, it should be remembered that, for this dopant concentration, RRS is mainly sensitive to the undoped part of the polymer (see Ref. 13). This observation is in very good agreement with (i) the sharp and asymmetric Raman band shapes for $\lambda_L=647.1$ nm [Fig. 2(a)]; (ii) the large shift ($\cong 35$ cm^{-1}) of the peak positions of the Raman bands in the $\perp\perp$ spectrum with respect to those in the $\parallel\parallel$ spectrum [Fig. 2(b)]; (iii) a very small depolarization ratio (four times smaller) as compared to what is measured in the undoped oriented polymer.

In the violet region ($\lambda_L=457.9$ nm), differently from the undoped case, no or very small shift is seen in the peak positions of the bands in the $\perp\perp$ spectrum compared to those of the $\parallel\parallel$ spectrum [see Figs. 2(c) and 2(d) and Figs. 5(b) and 5(c)]. This corroborates our interpretation of the $\perp\perp$ spectrum in terms of short conjugated segments

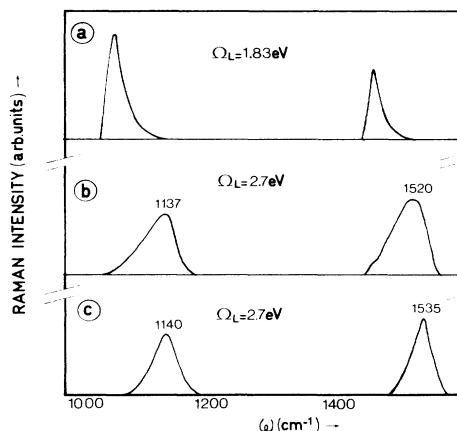


FIG. 5. Calculated spectra of stretched $trans\text{-(CH)}_x$ doped with iodine. (a) $\parallel\parallel$ polarized spectrum for $\Omega_L=1.83$ eV; (b) and (c) $\parallel\parallel$ and $\perp\perp$ polarized spectra for $\Omega_L=2.7$ eV. Parameters are given in the text.

whose electric dipole moments are not parallel to the chain axis.

If we consider that in other samples doped with electron acceptors, the maximum oxidation state has been found to be $\text{CH}^{+0.08}$ (Ref. 14), it is reasonable that in the present case very short conjugated segments (average value $N_2 \cong 6$) remain undoped. For $(\text{CH}_{0.023})_x$, intermediate and long conjugated segments are therefore doped only. Moreover, from the experimental low-frequency polarized spectra shown in Fig. 3, the I_3^- species are found oriented parallel to the stretching axis.

In summary, we have shown that the bimodal distribution model is appropriate, as already published,⁹ to give a consistent interpretation of polarized RRS spectra for oriented undoped and iodine-doped $(\text{CH})_x$ samples. Furthermore a comprehensive and realistic description of the morphology of the $trans\text{-(CH)}_x$ polymer can be derived from the parameters used to fit the experimental RRS spectra.

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