Analysis of the Raman Spectra of Modified trans-(CH)x

S. Lefrant¹, G. Arbuckle², E. Faulques¹, E. Perrin¹, A. Pron³, and E. Mulazzi⁴

¹Université de Nantes, 2 rue de la Houssinière, F-44072 Nantes Cedex 03, France
²Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA
³Technical University of Warsaw, PL-00664 Warsaw, Poland
⁴Dipartimento di Fisica dell’Università di Milano, I-20133 Milano, Italy

1. Introduction

The relationship between the conjugation length in polyacetylene and the maximum d.c. conductivity obtained after doping can be very important in understanding transport properties in this material. In this context, samples with additional defects have recently been prepared and their electrical and optical properties studied. The addition of hydrogen atoms can be achieved in a controlled manner as shown by Soga and Nakamaru /1/. The treatment can be followed even more accurately by using deuterium atoms since the C-D stretching vibration is detected by infrared spectroscopy. As a result, a breaking of the conjugation length of the carbon chain is expected by the creation of carbon atoms in Sp3 orbital configuration.

Vibrational spectroscopy and in particular resonance Raman scattering is very sensitive to the conjugation length in polyacetylene and can therefore be used as a probe for the chain modifications provided by this kind of treatment. A similar study has been reported by Furukawa et al. /2/ and we present in this paper Raman results obtained on deuterated samples of different compositions. All our data are then theoretically investigated by using the bimodal distribution of conjugated segments elaborated by Brivio and Mulazzi /3/. Finally, a comparison is made with samples in which the disruption of the conjugation is achieved by introducing more complicated defects consisting of a carbonyl defect adjacent to an Sp3 one. Results are discussed in view of the recent theoretical results presented by Brédas et al. /4/.

2. Experimental Data and Discussion

In Fig. 1, we report RRS spectra of (CHDy)x with y = 0, y = 0.069, y = 0.11 and y = 0.17 respectively, for the two excitation wavelengths λL = 676.4 nm and λL = 457.9 nm. For λL = 676.4 nm, the two Raman bands peaked at 1073 and 1462 cm⁻¹ for pristine (CH)x (y = 0, Fig. 1a) exhibit small changes when y goes from 0 to 0.17 consisting in a shift in frequency to 1087 and 1472 cm⁻¹ respectively (Fig. 1d). Also, for this concentration, the bands become more symmetrical.

For λL = 457.9 nm, the spectrum of the pristine polymer does not exhibit a well resolved double peak structure and the satellite components are peaked at 1119 cm⁻¹ and 1503 cm⁻¹ (Fig. 1e). By deuteration, significant changes are observed in the profile of the bands leading to peaks at 1131
Fig. 1: Raman spectra of (CHDy)x; T = 20°C

\[ \lambda_L = 676.4 \text{ nm : a) } y = 0, \text{ b) } y = 0.069, \text{ c) } y = 0.11, \text{ d) } y = 0.17 \]

\[ \lambda_L = 457.9 \text{ nm : e) } y = 0, \text{ f) } y = 0.069, \text{ g) } y = 0.11, \text{ h) } y = 0.17 \]

and 1514 cm\(^{-1}\) for \((CHD_{0.17})_x\) (Fig. 1h). Also, it can be mentioned that the low-frequency components due to the contribution from the long conjugated segments can hardly be seen. The spectra are qualitatively identical to those presented in /5/ in the case of hydrolyzed p-doped films. Moreover, it should be noticed that these Raman spectra also show some similarities with those of doped (CH)x at low doping levels /6/.

The different features of the Raman spectra given above can be described in terms of a double distribution of short and long conjugated segments respectively. In this model /3,7/ the electronic and vibrational properties and the electron vibration interaction in the excited electronic states of the conjugated segments are studied as a function of the number of double bonds (N). The Hückel model is used for 3 < N < 30 whereas for N \(\geq 30\), calculations are made with a tight binding model. Details of the parameters are given in /3,7/ and applications of this theoretical approach have been successfully used to fit Raman spectra in many different cases /8/.

In the present case, we have determined the parameters which give a good fit for all the series of Raman spectra. They are reported in Table 1 in which \(N_1\) and \(N_2\) are the two distribution centers, \(S_1\) and \(S_2\) their standard deviations and \(G\) the relative weight of the long segments' distribution.

In this study, it appears that the first stage of deuteration leads to a significant decrease of the conjugation length in the polymer since the two distribution centers are shifted downwards from 60 to 40 and from 20 to 15 double bonds respectively. This is an important effect if we keep in mind that the starting material was not of very good quality with respect to the