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E. Mulazzi^a, G. P. Brivio^a, S. Lefrant^b & E. Faulques^b

^a Dipartimento di Fisica dell'Università di Milano, Via Celoria 16, I-20133, Milano, Italy

^b Laboratoire de Physique Cristalline (ERA CNRS n°13), Université de Nantes, 44072, Nantes, Cédex, France

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INTERPRETATION OF RAMAN SPECTRA INDUCED BY PARTIALLY ISOMERIZED AND DOPED POLYACETHYLENE *

E.MULAZZI¹, G.P. BRIVIO¹, S. LEFRANT² and E.FAULQUES²

¹ Dipartimento di Fisica dell'Università di Milano, Via
Celoria 16- I-20133 Milano, Italy

² Laboratoire de Physique Cristalline (ERA CNRS n°13),
Université de Nantes, 44072 Nantes Cédex, France.

Abstract Experimental data of Resonant Raman Scattering spectra from partially isomerized and doped polyacetylene are presented and interpreted by using a bimodal distribution of conjugation length segments. A good agreement is found between the experimental data and the theoretical evaluations. The Resonant Raman Scattering spectra from doped samples are interpreted in terms of the electronic and vibrational properties of undoped segments in the polyacetylene chain.

Among the different models recently proposed ^{1,2,3} to interpret the Resonant Raman Scattering (RRS) spectra of trans polyacetylene (PA), we have shown that a bimodal distribution of conjugated segments can be used successfully. In particular this model applies to various trans contents in the polymer film. In Fig. 1a the RRS spectra of thermally treated PA at 140°C at different isomerization times, for incident light wavelength $\lambda = 752.5$ nm, are shown. These results refer to the same PA sample from a cis rich sample (10-15% trans) (top spectrum) to a fully isomerized one (100% trans) (spectrum at the bottom). It is seen that the Raman peaks at $\omega \approx 1076$ cm⁻¹ and $\omega \approx 1468$ cm⁻¹ in the spectra taken from the cis rich sample are shifted to 1064 cm⁻¹ and 1462 cm⁻¹ respectively, (spectra at bottom), as recorded usually for a 100% trans PA. The model used to interpret these spectra which takes into account the electronic and dynamical properties of the PA sample, can explain both the absorption curve as well as the RRS spectra recorded at different wavelengths ^{1,4}. Figure 1b represents the computed RRS spectra and the corresponding bimodal distribution used in the calculation, as function of the number of double bonds N in the

segments, is shown in the right insets. The theoretical spectra in Fig. 1b have to be compared to the experimental ones of Fig. 1a. We notice that for the wavelength $\lambda_L = 752.5$ nm, only the longest conjugated segments present in the sample contribute to the RRS cross sections. This model can also account for the resonant behaviour, observed for the same cis rich sample for different excitation wavelengths.

In particular it can explain the double peaked structure observed⁵ when $\lambda_L = 676.4$ nm ($\Omega_L = 1.83$ eV). The bimodal distributions which allow the evaluation of these spectra, can also account for the RRS spectra obtained at the same isomerization times at higher excitation wavelengths^{6,1}, e.g. at $\lambda_L = 457.9$ nm, where the shorter segment contribution is much more relevant. Then following this model the spectra at different isomerization times are explained in terms of different bimodal distribution functions. The mean values of the number of double bonds of the two distributions (N_1 and N_2) increase during the isomerization process (See Table 1).

In order to give a better insight in our calculations of RRS spectra we have collected the parameters of the distributions used in the calculations⁵ in Table 1, for partially and fully isomerized PA films, as well for a Bromine doped PA sample.

TABLE 1

Sample	N_1	σ_1	N_2	σ_2	G
Cis rich PA	20	5	10	5	0,2
80% trans PA	50	20	10	5	0.5
100% trans PA	100	50	15	7	0.75
Br-doped PA (17%)	20	10	7	3	0.4

For a Br-treated PA sample, the experimental spectra shown in Fig. 2 are characteristic of the trans PA isomer as generally observed in doped systems. The two main bands are peaked at $\omega \approx 1084$ cm^{-1} and at $\omega \approx 1462$ cm^{-1} , respectively, for $\lambda_L = 676.4$ nm and shift to 1132 cm^{-1} and 1524 cm^{-1} for $\lambda_L = 4579$ nm. In the same figure we report the evaluations of the RRS spectra obtained by using

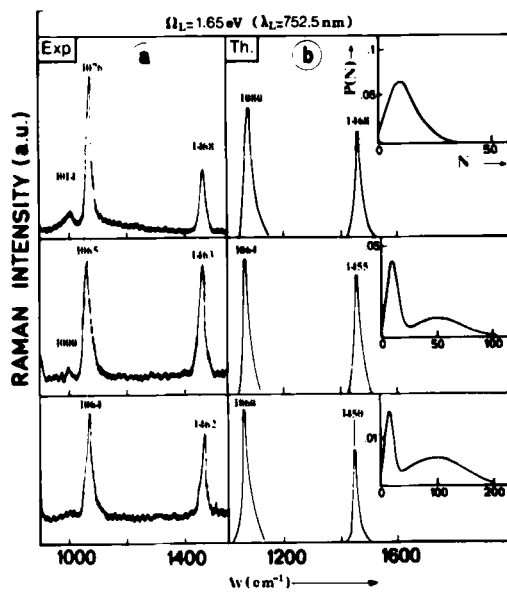


FIGURE 1

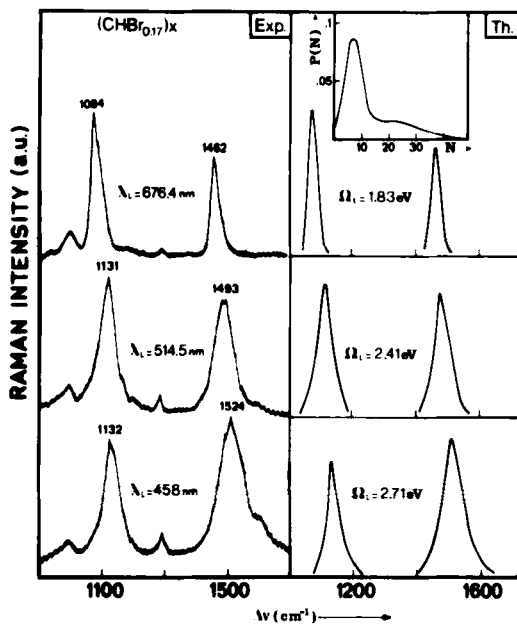


FIGURE 2

the bimodal distribution model. We have obtained good agreement with the RRS data, when the two distributions are respectively peaked on 20 and 7 double bonds (see Table 1 and the drawing of the bimodal distribution in the inset of Fig. 2). We would like to notice that in this case the bimodal distribution is centered on two smaller values of conjugation length segments than those considered in the good quality trans PA simple case^{1,4}. This is in agreement with previous assumption deduced from experimental data⁷.

In conclusion we want to point out that the bimodal distribution model^{1,4} applies successfully to the calculations of RRS spectra taken from PA sample with any trans content. In particular the parameters of the distributions used in order to explain the RRS spectra from partially, fully isomerized and doped PA samples are consistent with the coherence length determined by X-ray diffraction experiments^{8,9,10}. Furthermore this model does not only account for the line shapes of the Raman bands for any excitation wavelength, but also for their relative intensities.

REFERENCES

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1. G.P. Brivio and E. Mulazzi, Chem.Phys.Lett. **95**, 555 (1983); E. Mulazzi and G.P. Brivio, Mol.Cryst.Liq.Cryst., **105**, 233 (1984); G.P. Brivio and E. Mulazzi, Phys.Rev. **B29** (1984).
 2. H.Kuzmany, E.A.Imhoff, D.B.Fitch and A. Sarhangi, Phys. Rev. **B26**, 7109 (1982)
 3. Z. Vardeny, E. Ehrenfreund, O. Brafman and B. Horovitz, Phys. Rev.Lett. **51**, 2326 (1983).
 4. E. Mulazzi, G.P. Brivio, E. Faulques and S. Lefrant, Sol. St. Comm. **46**, 851 (1983).
 5. S. Lefrant, E. Faulques, G.P.Brivio and E. Mulazzi, Sol.St.Comm. (1984) in press.
 6. E.A. Imhoff, Ph.D. Thesis, Cornell University (1983),unpublish.
 7. E. Faulques and S. Lefrant, J.de Phys. **44**, C3-337 (1983).
 8. P. Robin, J.P.Pouget, R. Comes, H.W. Gibson and A.J.Epstein, J. de Phys., **44**, C3-87 (1983).
 9. P. Robin, G.P.Pouget, R. Comes, H.W. Gibson, and A. Epstein, Phys.Rev. **B27**, 3938 (1983).
 10. G.Perego, G.Lugli and U.Pedretti, Proc. of this Conference (1984).