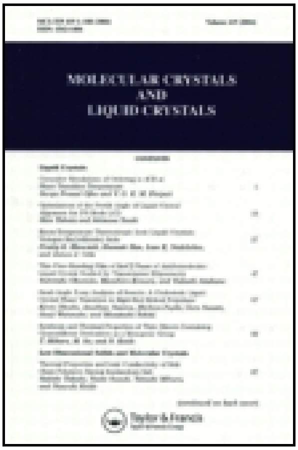

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

An Insight on the Polyacetylene Properties Through Resonant Raman Scattering Spectra Analysis

E. Mulazzi [a] , G. P. Brivio [a] & R. Tiziani [a]
[a] Dipartimento di Fisica, Università di Milano and GNSM of CNR Via Celoria, 16, Milano, Italy

Version of record first published: 17 Oct 2011.

To cite this article: E. Mulazzi , G. P. Brivio & R. Tiziani (1985): An Insight on the Polyacetylene Properties Through Resonant Raman Scattering Spectra Analysis, Molecular Crystals and Liquid Crystals, 117:1, 343-349

To link to this article: http://dx.doi.org/10.1080/00268948508074649

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 343-349
0026-8941/85/1174-0343/$15.00/0

Printed in the United States of America

AN INSIGHT ON THE POLYACETYLENE PROPERTIES THROUGH RESONANT RAMAN SCATTERING SPECTRA ANALYSIS*

E. MULAZZI, G.P. BRIVIO and R. TIZIANI
Dipartimento di Fisica, Università di Milano and GNSM of CNR
Via Celoria, 16, Milano, Italy.

Abstract Resonant Raman Scattering spectra of trans polyacetylene $(CH)_x$ and $(CD)_x$ are interpreted in terms of a model based on a bimodal distribution of conjugation length segments. Such a theory takes into account the electronic and lattice dynamics properties of different conjugation length segments, together with the electronic dipole moments from the transitions and the electron vibration interactions in the excited electronic states. This model accounts also for the Resonant Raman Scattering spectra taken during the isomerization process and from cis rich samples.

It is well known that trans polyacetylene is a disordered system; the origin of this disorder may be attributed to defects, inhomogeneities, crosslinks. This type of disorder determines different dimerization properties along a chain, which can be observed in the Resonant Raman Scattering (RRS) spectra[1,2] taken from fully isomerized trans samples and during the isomerization process from cis to trans $(CH)_x$. In fact RRS technique is a very sensitive and unique tool to point out the peculiar effect of such a disorder on the samples since by changing the resonant incident frequencies one obtains very different spectra[1,2,3]. So the experimental evidence from these results strongly draws to the conclusion that a variable dimerization along a chain is responsible for the peculiarities of the different spectra.

Recently Vardeny et al.[4] have introduced a model based on disorder on long (infinite) chains which are studied in the Peierls approximation. In this model the different dimerization properties are expressed in terms of variable dimensionless electron phonon coupling λ which is related to the Peierls gap Δ and to the lattice dynamics properties of the ground state. A unimodal distribution $P(\lambda)$ weights the contributions to RRS spectra from various chains.

An alternative model[5], previously introduced, takes into account the different dimerization properties of polyacetylene by considering the chain as constituted by different conjugation length segments. This model is based on the hypothesis that in a stable system different dimerization properties correspond to different conjugation length segments with variable N number of double bonds. This implies different electronic and lattice dynamics properties of the different conjugation length segments, which can be studied easily in the Hückel model. The contributions to the RRS cross sections from the different segments are weighted by a bimodal distribution which depends on the number of double bonds N.

We briefly summarize the main points of the model[5].

a) The vibrational Raman active mode frequencies, the resonant electronic transition frequencies, the electric dipole moments, the electron vibration interactions in the excited electronic states, which are the physical quantities defining the RRS cross sections, are all evaluated for dimerized segments of different conjugation length. We start from a total Hamiltonian of the polyacetylene system which is the sum of different Hamiltonians each of them referring to different segments. Interaction Hamiltonians between different segments in the same or in different chains are neglected. The property of alternated single and double carbon bonds in the chain is included in each Hamiltonian, from the very beginning. It is expressed by the two hopping integrals β_1, and β_2 (for the single and double bond, respectively) in the Hückel model, as input parameters. β_1 and β_2 decrease by increasing N. In this way it is possible to evaluate in a consistent model the eigenvalues, the electronic dimerized wave functions, the vibrational properties, the electric dipole moments and the electron vibration couplings in the excited electronic states.
The properties of the segments are studied in the framework of the Born von Karman cyclic condition for $N \geq 30$. In fact the electronic and vibrational properties are almost unaffected by the length of the segments for $N \geq 30$. In the case $3 \leq N < 30$ the physical properites are studied in terms of the Hückel model for finite segments and they are dependent on N.

b) In order to calculate the RRS cross sections we have introduced a bimodal distribution of conjugation length segments. Such a bimodal distribution is needed because the samples are formed by a crystalline and an amorphous part and because we are averaging over N the properties of different conjugation length segments whose contributions define the RRS cross sections. For a fully isomerized and undoped trans sample the bimodal distribution function is formed by two normalized Gaussians $P_1(N)$ and $P_2(N)$ which are centered on $N_1 \cong 100$ N and on $N_2 \cong 15N$, respectively. The weights of the two Gaussians are G and 1-G respectively, where $0 \leq G \leq 1$. The function $P_1(N)$ with its relative weight G gives an estimate of the contribution of the electronic and vibrational densities of states to the optical response. Then the mean value $N_1 \cong 100$ N is only indicative for the number of double bonds of long (infinite) segments, whose electronic and vibrational properties are almost indipendent on N. On the contrary $P_2(N)$ with its relative weight 1-G, is introduced to take into account that the contribution to the RRS cross section from short segments is peaked on a particular mean value N_2. In fact the contribution from the amorphous part of the sample cannot be described by the tail of the long segment distribution. Such an assumption is justified by the experimental RRS spectra taken from trans $(CH)_x$ and $(CD)_x$ during the isomerization process. By examining those spectra it is possible to observe from the line shape changes that the distribution of short segments is modified during the process (N_2 varies) but is characterized by a function centered on a well defined N_2.

In Fig. 1 and 2 we show the calculated RRS spectra of trans $(CH)_x$ for different incident laser frequencies reported therein, determined by the two more intense Raman active modes of trans $(CH)_x$. These results are to be compared with the experimental data in Refs. 2 and 3. The parameters used in the calculations are [5] $N_1=100$, $\sigma_1=50$, $N_2=15$, $\sigma_2=7$, $G=0.75$.
In Figs. 3 and 4 we present the calculated RRS spectra of trans $(CD)_x$ for different incident laser frequencies, as reported. In Fig. 3 the experimental data from Ref.7 are drawn for comparison. The parameters for the distribution functions used in the calculations are[8] $N_1=100$, $\sigma_1=50$, $N_2=15$, $\sigma_2=7$, $G=0.5$. It is interesting to notice that in trans $(CD)_x$ three intense Raman active modes give contributions to the RRS spectra as it follows from lattice dynamics calculations[8] [9]. All the calculated spectra are in good agreement with the experimental RRS data. Fig. 4 shows the calculated spectra from trans $(CD)_x$ for incident laser frequency $\Omega_L=3.4$ eV. At our knowledge there are no experimental data in this U.V. region to be compared with. This model accounts also for the RRS spectra taken from cis rich samples and from samples during the

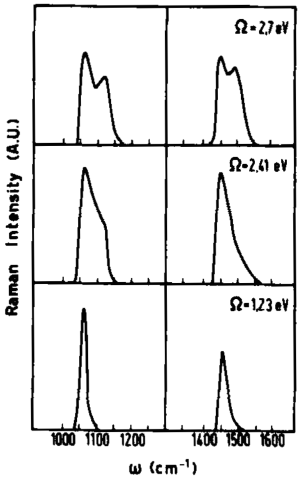

FIGURE 1 Calculated RRS spectra of trans $(CH)_x$ for different light frequencies Ω_L. The parameters are given in the text.

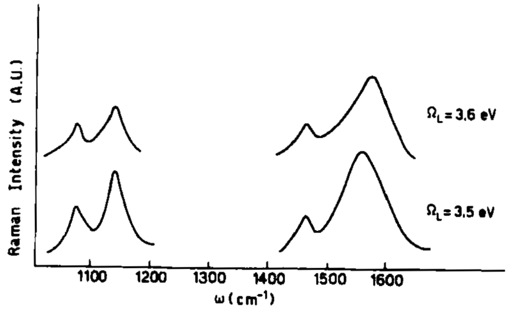

FIGURE 2 Calculated RRS spectra of trans $(CH)_x$ for different light frequencies Ω_L in the UV region. Parameters as in Fig.1.

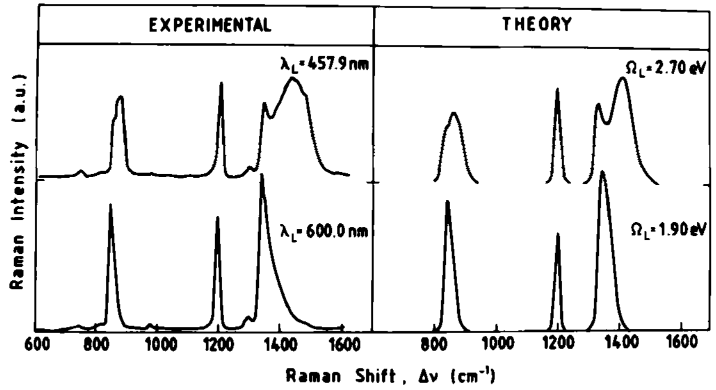

FIGURE 3 Experimental[7] and calculated RRS spectra of trans $(CD)_x$ for different incident light frequencies Ω_L as listed therein. The parameters are given in the text.

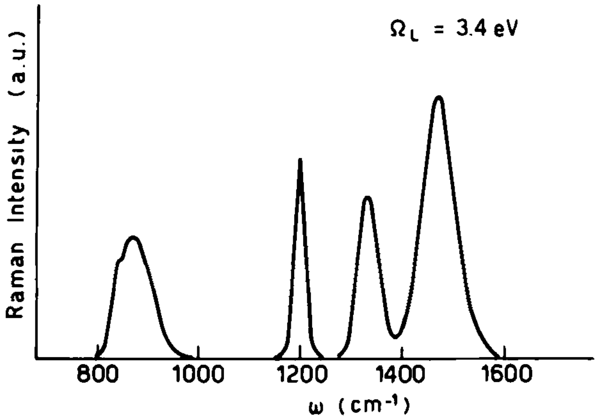

FIGURE 4 Calculated RRS spectrum of trans $(CD)_x$ for incident light frequency Ω_L = 3.4 eV. The parameters are the same as in Fig. 3.

isomerization process[5,8].

It is worthwhile to examine this model (Different Conjugation Length Segments, DCLS) and that proposed in Ref. 4 (VEBH). Both models try to interpret the RRS, by taking into account the effect of the disorder in trans polyacetylene. However the dimerized character of the electronic wavefunctions is not included in the VEBH model when calculating the electric dipole moments. This result is too reducive, since in all the other models (e.g. tight binding approximation for infinite chains[10]) the electric dipole moments, connecting electronic ground and excited states, do depend on the transition energy. In particular the dipole moment for dimerized infinite chains[10] is function of $(1+\nu)/(1-\nu)$, where $\beta_1 = \beta_2$; then by increasing the gap, ν decreases and so does the corresponding dipole moments. Furthermore the electron phonon dimensionless λ parameter they used, is independent of the dimerized electronic state. So no difference is paid between the electron phonon coupling defining the ground state lattice dynamics of the system and that in the excited electronic state weighting the RRS cross sections. So the advantage of the VEBH model to carry on analytical expressions for the response function of the system is reduced by the fact that it neglects all the above mentioned properties which are very important in order to calculate the RRS cross sections. Such properties of trans polyacetylene are all included in the DCLS model. Moreover, since the trans $(CH)_x$ is a semiconductor obtained in the isomerization process from the cis isomer, the DCLS model seems to be more appropriate for this system, as no metal-semiconductor Peierls transition is observed experimentally.

In their model VEBH introduce a distribution function of electron phonon interactions $P(\lambda)$ to take into account the different dimerization properties of the system. Certainly it looks attractive to have only one distribution function with a single adjustable parameter λ. But λ is strongly model dependent and it is easy to see that small variations of λ can induce drastic changes in the gap energies and in the calculated RRS spectra. Also in DCLS model only <u>one</u> distribution depending on the electron vibration coupling in the excited electronic state could be introduced instead of the bimodal distribution depending on N. By using this unimodal distribution it is possible to weight the corresponding electric dipole moments, the electronic transitions and thevibrational frequencies. But we have chosen the bimodal distribution functions $P_1(N)$ and $P_2(N)$, whose meaning has been discussed previously, because they depend on a model indipendent physical property of the system, the number of double bonds in the conjugated length segments. So if it will be possible to improve on the Hückel model, by working out a better description for the electronic and vibrational properties of the system,the physical meaning of $P_1(N)$ and $P_2(N)$ will be preserved.

REFERENCES

*Work partially supported by Progetto Finalizzato Chimica Fine e Secondaria.

1. D.B. Fitchen, Mol. Cryst. Liq. Cryst. 83, 95 (1982).
2. S. Lefrant, J. de Phys. 44, C3, 33 (1983).
3. E. Mulazzi, G.P. Brivio, E. Faulques and S. Lefrant, Sol.St. Comm. 46, 851 (1983).
4. Z. Vardeny, E. Ehrenfreund, O. Brafman and B. Horovitz, Phys. Rev. Lett. 51, 2326 (1983); B. Horovitz, Z. Verdeny, E. Ehrenfreund and O.Brafman, Synth. Met. 9, 215 (1984)
5. 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. B (1984)
6. E.A. Imhoff, Ph. D. Thesis, Cornell University (1983) unpubl.
7. L.S. Lichtmann, A. Sarhangi and D.B. Fitchen, Sol. St. Comm. 36, 869 (1980).
8. R. Tiziani, G.P. Brivio, and E. Mulazzi, Phys. Rev. B, submitted (1984).
9. E. Mulazzi, R. Tiziani, L. Piseri and R. Tubino, to be published (1984).
10. C. Cojan, G.P. Agrawal and C. Flytzanis, Phys. Rev. B15, 347 (1977).