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To cite this version:

HAL Id: jpa-00222717
https://hal.archives-ouvertes.fr/jpa-00222717

Submitted on 1 Jan 1983

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DISPERSION CURVES AND RESONANT RAMAN SPECTRUM OF TRANS POLYACETYLENE

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Résumé
La dynamique du réseau du trans-polyacétyle est présentée et comparée avec les vibrations des liaisons C=C et C-C dans les polyènes courts. Ce modèle nous a aidé à expliquer la forme et la position des bandes Raman. Les résultats obtenus sur le renforcement sélectif de l'effet Raman sont interprétés en fonction du temps de vie de la photoexcitation.

Abstract
The lattice dynamics of trans-polyacetylene is discussed and compared with the vibrational C=C and C-C stretching frequencies of short polyenes. The widths, the shape and the position of the Raman bands and their variation with the laser frequency are interpreted in terms of the lattice dynamical model. Some consideration on the selective resonant enhancement as a function of the lifetime of the photoexcitation are also presented.

Aim of this note is to discuss the implications of the lattice dynamics in the Resonant Raman (RR) Scattering of trans-polyacetylene (pa). In previous papers (1,2) we have shown how to derive bond-bond long range interactions for an infinite trans polyene chain by extending a method proposed by Kakitani (3) for short polyenes and aromatic molecules. In this model the electron-electron correlation is neglected and long range force constants arise from the electron-phonon (e-p) coupling (4). The dynamical matrix can then be expressed in terms of a very limited number of parameters, namely six force constants describing the short range forces which arise from the deformation of the σ electrons and an additional parameter for the bond-bond interactions, coming from the deformation of extended π electronic states. This latter parameter, which describes the e-p coupling, is expressed in the framework of the Hückel’s theory (5) as the first derivative of the transfer integral with respect to the bond length ∂t/∂R. The force field has been determined by a least squares fitting on the experimental frequencies of trans- (CH)X, (CD)X and (C13H)X. By using for ∂t/∂R a value consistent with the experimental energy gap, the frequencies of the most intense Raman active C=C and C-C stretching modes for short polyenes fall on the dispersion curves of the infinite chain at intermediate wavevectors corresponding to q=n/2πa(n+1), where n is the number of double bonds, a the size of unit cell. In Fig.1 the results relevant for the interpretation of the Raman bandshapes (7,8,9) in both (CH)X and (CD)X are summarized. The following remarks can be made i) the widths of the Raman bands are clearly related to the corresponding calculated phonon dispersion ii) the position of the peaks for the two limiting excitations (676 and 350.7 nm) corresponds to the phonon frequencies at the center and at the edge of the Brillouin zone respectively. An interpretation of the Resonant Raman bandshapes can be attempted as follows. During the thermal isomerization of the cis polymer a number of conjugation defects are created which destroy the translational invariance of the chain. This creates an activation of phonons with finite wavevectors which correspond to the most intense Raman modes of segments with short conjugation length. The activation of the whole phonon spectrum in the first order Raman scattering has been already observed in other materials without long range order, such as amorphous 3-d semiconductors, where the shape of the Raman spectrum maps the density of the states g(ν) (10). The expression for the scattering intensity can then be written...
As matter of fact for both C=C and C-C stretchings the low-frequency side of the Raman bands consists of a sharp, asymmetric, exciting frequency independent peak reminiscent of the inverse square root singularity of the density of the states $g(v)$ and of a broad feature which appears with increasing intensity as the laser is tuned towards higher frequencies ($\Omega_L$)\(^2\).\(^2\). This latter feature can be related to the selective resonance enhancement of finite segments (Fig. 2), whose polarizability matrix element $\alpha(v)$ has a maximum which moves towards higher vibrational frequencies as increasingly shorter conjugation lengths are brought into resonance conditions.

A number of authors \(^{8,9,11}\) have proposed theoretical models for the interpretation of the observed spectra, in the attempt of providing a quantitative estimate of the average conjugation length. This quantity is certainly of primary importance in relation to the morphology and the conduction mechanism in this polymer. We feel however that the lack of knowledge of the vibrational and electronic states and their lifetimes as a function of $n$ prevents to reach a definitive answer to this problem. The main difficulty arises in determining whether the contribution to the scattering intensity of short segments comes from their concentration or from resonance effects. A rough estimate of the intensity enhancement due to resonance effects can be obtained as follows. Assuming only two electronic states the first order R.R. cross section for a conjugated segment of length $n$ can be written as \(^{12}\)

$$
\frac{d\Sigma}{d^2} (\Omega_L) = \Omega_L (\Omega_L - \omega_n)^3 |M|^4 \frac{\Delta^2}{2} \cdot \int_{-\infty}^{\infty} \exp(-\Delta^2/2)
$$

$$
= \frac{\omega_n (\Delta^2/2)^k \exp(-\Delta^2/2)}{k! (\Omega_L - \Omega_n - i \gamma/2) (\Omega_L - \Omega_n - i \gamma/2)}
$$
where Ω_L is the laser frequency, M is the electric dipole matrix element, ω_n is the vibrational frequency for a chain of conjugation length n and Ω^2_H is the corresponding purely electronic transition (no phonons created or destroyed), Δ is the dimensionless displacement between the equilibrium position of the ground and the excited state and γ is the inverse lifetime of the excited vibronic state. Within the framework of Hückel's theory of the conjugated systems (5) M is proportional to the square root of the conjugation length n and therefore dΩ^2_H(Ω_L)/dΩ = n^2Ω_H(Ω_L). In the weak coupling limit only the k=0 term is relevant, \( \exp(-\Delta^2/2) + 1 \) and therefore

\[
\sigma_n(\Omega_L) \propto \frac{\omega_n^3(\Omega_L - \omega_n)^3}{\left((\Omega_L - \omega_n^2)^2 + (\gamma/2)^2\right) \left((\Omega_L - \omega_n^2 - \omega_n)^2 + (\gamma/2)^2\right)}
\]  

The ratio \( \sigma_n/\sigma_\infty \) represents the enhancement factor of a double bond in a segment of conjugation length n with respect to a double bond in a very long conjugated sequence. In Table 1 the enhancement factors \( \sigma_n/\sigma_\infty \) for various \( \Omega_L \) are reported as a function of γ. If s denotes the ratio between the areas of the low and the high frequency peak of the Raman band, \( n_s \) and \( n_t \) the number of bonds residing in "short" and "long" conjugation lengths respectively, one has \( (n_s/n_t)^2 = s(\sigma_s/\sigma_\infty) \).

It is apparent from Table 1 that the enhancement factor \( \sigma_n/\sigma_\infty \) depends quite critically on the lifetime of the excited vibronic state. An increasingly larger concentration of short chains is required to fit the spectra as the damping factor becomes larger. In particular the bandshapes exhibited by the spectra taken with \( \Omega_L = 21839 \text{ cm}^{-1} \) (s \( \approx 0.2 \)) are consistent with a percentage of long chains which varies from 93% to 66% as γ is changed from 2000 cm\(^{-1}\) to 6000 cm\(^{-1}\).

It must be noticed that a rather low concentration of short chains is inferred from the spectra taken with the 350.7 nm excitation (9) (see Fig. 1), which still shows the peaks corresponding to the long conjugated lengths (1072 and 1466 cm\(^{-1}\)) even if they are in completely off-resonance conditions.

In conclusion our analysis of the RR Scattering from trans-pa favours a structural model in which short conjugation sequences are present in rather small concentration. The spectra reported in literature and also some preliminary data obtained in our laboratory show drastic changes in the shapes of the RR bands when polymerization and isomerization conditions are changed, as well as in connection with the thermal history of the sample, suggesting that cross links are probably responsible for the breakdown of the conjugation. As a matter of fact the e-p coupling should produce strongly dispersed C=C phonons also in the cis-pa. The sharp and symmetric Raman peaks observed in this case (8) suggest that defects responsible for the activation of phonons with intermediate q vectors are formed by thermal isomerization and not during the polymerization process.

More Raman data taken with excitations in the near UV region are certainly needed. Also an experimental estimate of the lifetime of the photoexcited state could clarify if an appreciable concentration of short chains or resonance effects are responsible for the observed bandshapes of the RR spectra.

### Table 1

Resonance enhancement factors (Eq. 3) as a function of γ for various exciting frequencies.

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>( \Omega_n = 30770 )</th>
<th>( \Omega_n = 21839 )</th>
<th>( \Omega_n = 19436 )</th>
<th>( \Omega_n = 14784 )</th>
</tr>
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<tbody>
<tr>
<td>( \gamma/2 )</td>
<td>( \sigma_n/\sigma_\infty )</td>
<td>( \sigma_s/\sigma_\infty )</td>
<td>( \sigma_{11}/\sigma_\infty )</td>
<td>( \sigma_{11}/\sigma_\infty )</td>
</tr>
<tr>
<td>1000</td>
<td>5141.8</td>
<td>816.8</td>
<td>101.2</td>
<td>0.002</td>
</tr>
<tr>
<td>1500</td>
<td>2645.2</td>
<td>271.1</td>
<td>38.3</td>
<td>0.01</td>
</tr>
<tr>
<td>2000</td>
<td>1425.5</td>
<td>113.1</td>
<td>18.8</td>
<td>0.01</td>
</tr>
<tr>
<td>2500</td>
<td>814.8</td>
<td>56.5</td>
<td>11.0</td>
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</tr>
<tr>
<td>3000</td>
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<td>7.3</td>
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<td>3500</td>
<td>313.6</td>
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<td>5.3</td>
<td>0.07</td>
</tr>
<tr>
<td>4000</td>
<td>208.4</td>
<td>14.1</td>
<td>4.1</td>
<td>0.11</td>
</tr>
</tbody>
</table>
REFERENCES

(2) L. PISERI, R. TUBINO, L. PALTRINIERI and G. DELLEPIANE, Solid State Commun. in press.
(5) L. SALEM, The Molecular Orbital Theory of Conjugated Systems, Benjamin 1972