Electronic and dynamical effects from the unusual features of the Raman spectra of oligo and polythiophenes

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Abstract

A comprehensive search for structure/property correlations in the Raman spectra of oligo and polythiophenes is carried out for many homologous series of oligothiophenes (approximately 50 compounds). The observed spectroscopic features are interpreted, with the help also of ab initio calculations, on the basis of the theories currently adopted for the understanding of the properties of polyconjugated materials. From the analysis of the vibrational spectra the behavior of $\pi$ electrons as function of conjugation length electron–phonon coupling, pinning, effective electronegativity of the heteroatoms, etc. is discussed and frequency and intensity correlations useful in chemical diagnosis are proposed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The characterization of a material at the molecular level is an essential step in the science and technology of polyconjugated molecules which are becoming the center of interest for new technologies [1–3]. The methods for characterization are not as many and as easy as for other classes of organic materials since these molecules (oligomers or polymers) may contain chemical, stereochemical and/or conformational irregularities, they may be crystalline or amorphous and most of the times they are insoluble and intractable.

On the other hand, the peculiar physical properties which make these molecules very appealing to modern technology are determined and modulated by the intramolecular delocalization of $\pi$ electrons along a path defined by the conjugated C=C bonds [1–6]. When conjugation increases the energy gap between occupied and unoccupied electronic levels decreases together with the ionization potential and the redox potential. It is also well known that $\pi$ electron delocalization can also change because of conformational distortions and/or intermolecular interactions. In the study of the properties of these systems it becomes then necessary to consider as a useful structural parameter the effective conjugation length (ECL) whose measure becomes crucial in the science of these kinds of materials.

Since the beginning of the explosive development of science and technology of polyconjugated materials, it has been realized that their vibrational infrared and Raman spectra are very peculiar and unusual [7] and escape the traditional analysis based on spectroscopic correlations which are the common and traditional analytical diagnostic tool used by organic chemists. On the other hand, the understanding of the spectroscopic peculiarities offers a unique tool for the understanding of the structure and electronic properties of polyconjugated materials. It follows that vibrational spectroscopy becomes a useful tool for the determination of ECL and, in general, for the molecular characterization of these materials not only in the chemical laboratory, but also directly on the level of device production.

The basic fact, abundantly presented and discussed in the literature, is that the Raman spectra even of structurally very complex polyconjugated molecules show very few lines selectively enhanced which originate from totally symmetric modes [8–15]. The strong enhancement is asso-
citated to the occurrence of the electron–phonon coupling, e/ ph, when atoms perform one or a few specific vibrational modes. Such coupling takes place because in these normal modes (variously defined as amplitude modes [8–10] or Z modes [11–15]) the extent of modulation of π electron delocalization is the largest.

The theoretical aspects which form the basis of the interpretation of the Raman spectra were first presented by Horovitz [8,9] and Ehrenfreund et al. [10] who estimated the extent of e/ ph coupling with a parameter λ derived from the Raman spectrum. Since this model turned out to be inapplicable to complex polyconjugated materials the model of the effective conjugation coordinate (ECC) was proposed [11–15]. It has been shown that for linear polyconjugated polymers (and oligomers) only one mode exists along which the e/ ph coupling is the largest. It follows that the corresponding totally symmetric normal transition becomes the strongest and dominates the Raman spectrum. If ECC theory is adopted the vibrational coordinate which better describes this vibration is labelled as Z and the frequency of this mode is labeled as νn [11–15].

Theory indicates that νa should show frequency and intensity dispersion with ECL. Experiments on many classes of polyconjugated oligomers and polymers support the theoretical predictions [16–29]. Moreover, from the study of νn additional concepts which are directly related to the electronic properties of these molecule can and have been derived.

The basic concept derived from ECC theory is that in polyconjugated molecules there exists a totally symmetric collective normal mode Qn (with frequency νn) which involves the simultaneous collective stretching of C=C and C–C bonds along a large section of the polyconjugated molecular chain. Such theory was first applied to the case of trans-polyacetylene which allowed to easily define a dimerization parameter u = dC–C − dC–C [8–10] and a dimerization amplitude vibrational mode Δu (which practically corresponds to Z) [11–15] as a mode in which u is involved at the largest extent. It becomes apparent that the e/ ph coupling is the largest along Z since the extent of delocalization of π electrons is the largest.

In the case of polyaromatic or polyheteroaromatic systems the Z coordinate is the totally symmetric linear combination of CC stretching internal coordinates which describes the geometrical path nuclei must follow in going from the lower energy aromatic configuration towards the higher energy ‘quinoid’ configuration [12,13,16–29]. These two extreme structures are two of the most common canonical structures which enter, with different weights (a and b, respectively), the definition of the ground and excited electronic states of such systems:

\[
\Psi = a\psi_a + b\psi_b
\]

For the sake of clearness in the discussion which follows in Fig. 1, we define the CC stretching internal coordinates and define directly the Z coordinate for the case of polythiophene which is the center of our discussion in this paper.

In general, the strong Qa mode (which is described almost uniquely by the Z coordinate) shows frequency and intensity dispersion with ECL [11–15]. Since the shift of νn can span a reasonably large frequency domain Qa may mechanically couple with other totally symmetric normal modes, thus lending intensity to them.

2. The case of oligothiophenes: experiments

The dispersion of νn with ECL of oligo and polythiophenes has been already studied [21], but some corrections need to be presented. We think that with the large number of spectroscopic data presently available it becomes possible to carry out more detailed structure–spectra correlations. This allows us to correct and complete what has been proposed some years ago [21]. We present here the results of our new studies which modify previous conclusions and extend the interpretation of the vibrational spectra to many classes of polyconjugated oligomers and polymers of the class of thiophene derivatives.

The Raman spectrum of 4,4′-dipentoxy-2,2′:5′,2″-tertrathiophene reported in Fig. 2 is prototypical of a very large class of oligo and polythiophenes and we use it as reference in the present discussion. The spectral range 1600–1450 cm⁻¹ has been the center of interest of the previous studies which have used the observed Raman lines for molecular diagnosis. In this work we extend our analysis to a broader spectral range.

Generally, for the class of oligo and polythiophenes one observes in the Raman spectra four characteristic features.

(i) Line A (~1600 cm⁻¹): generally weak, shows unquestionably frequency dispersion with increasing chain length. It is clearly observable from di-thiophene to hexathiophene; along with the downward frequency shift its relative intensity weakens and becomes almost unobservable for oligomers with relatively long chain length (e.g., hexathiophene) [21–23,28,29].
Fig. 2. FT-Raman spectrum of solid 4,4'-dipentoxy-2,2':5',2':5,2'' tetrathiophene (λ_{exc} = 1064 nm) with labeling of the characteristic lines discussed in the text.

(ii) Line B (≈ 1500 cm\(^{-1}\)): it is a common feature of the Raman spectra of aromatic and heteroaromatic systems. It is always very strong and dominates the whole Raman spectrum. While it shifts to lower frequencies in the case of oligopyrroles and oligofurans when chain length increases it is almost independent from chain length in the case of thiophenes. It shows somewhat different frequencies from one chemical series to another within the class of oligo and polythiophenes, but within each class it is almost invariably strong and unshifted.

(iii) Line C: it appears at the lower frequency side of line B only for a few classes of molecules and shows intensity enhancement with increasing chain length.

(iv) Line D: for all the molecules studied (and similarly for many other polyaromatic systems) a sharp line (sometimes a doublet) of medium-strong intensity is observed in

Fig. 3. Ab initio calculated (unscaled) Raman frequencies and intensities (I = 45\(\alpha^2 + 4\gamma^2\)) of a few characteristic normal modes of oligothiophenes Th\(n\) (\(n = 2,3,4,\) and 5). Notice the superlinear increase of the intensity of the B mode.
the Raman spectrum in the range 1050–1080 cm\(^{-1}\). This scattering has always escaped the attention of the researchers who have been mostly interested in the ring stretching region.

The dispersion with chain length of line A has been generally taken as evidence of the delocalization of \(\pi\) electrons along the whole polyconjugated backbone. A question which has been left unsolved for many years consists in the fact that, in spite of its downward frequency shift with increasing chain length, its intensity decreases rapidly, contrary to what expected according to ECC theory, if conjugation takes place. Moreover, the strength combined with the lack of dispersion of line B remained an unsolved puzzle. A recent theoretical work by Negri and Zgierski [30] has shown that line A originates from ring stretching vibrations mostly localized on the thiophene rings at either ends of the chain, somehow coupled with the vibrations of the neighboring units where the coupling dies off quickly with distance.

These observations have driven us to re-consider the vibrational assignment of lines A and B and to find an explanation of lines C and D. The need of a re-analysis of the physical phenomena which are reflected in the Raman spectra necessary follows.

3. The prototypical \(\text{ab initio}\) calculations on oligothiophenes

Several normal coordinate calculations on oligo and polythiophene have been carried out mainly focused on the
description of the $Q_n$ mode [21]. However, such calculations may be biased by the effort in finding a suitable quadratic force field which may better fit the experimental observations. With the use of ab initio calculations we have tried to derive independent information which we take as qualitative messages (and trends) on the electronic and dynamical properties of these systems. At the beginning both 3-21G and 6-31G* basis sets [31] have been used. Since we were aiming at qualitative descriptions of the properties and both sets were giving parallel information we eventually settled on the 3-21G basis set which makes calculations faster for large molecules. Calculations have been carried out for oligothiophenes of general formula Th–(Th)$_n$–Th with $n = 0, 1, 2$ and 3.

In our calculations we have made the reasonable assumption that the oligomers are planar. Vibrational frequencies, vibrational displacements and Raman intensities have been calculated on the optimized geometry. Since no attempts were made to fit ab initio calculated to experimental quantities no arbitrary scaling has been introduced. The calculated vibrational Raman intensities and frequencies of the totally symmetric modes together with the associated vibrational displacements are reported in Fig. 3 and Fig. 4a through d.

Our calculations are substantially in agreement with those of Negri and Zgierski [30] and point out that the strongest Raman line B originates from ring stretching modes mostly localized at either ends of the oligomeric chain. Its frequency does soften with increasing length of the oligomer (Fig. 3). However, the relative intensity $I_{B}/I_{A}$ rapidly decreases with increasing chain length. The experimental pattern nicely agrees with that calculated ab initio.

4. ECC theory

For a comprehensive understanding of the experimental and theoretical results presented in Sections 2 and 3 a few of the basic concepts of ECC theory need to be outlined [11–15]. Two are the spectroscopic observables which, in general, are predicted and are found to change noticeably when ECL changes, namely vibrational frequencies and scattering cross sections (i.e., Raman intensities). When ECC theory is adopted the softening of the $n$ mode is associated to the softening of the corresponding quadratic force constant $F_n$ which is expressed as:

$$F_n = K^s + f^s + \Sigma_i f_i^{\theta_i,s}$$ (2)

where $K^s$ is the combination of diagonal C=C and C–C stretching force constants of the central unit, $f^s$ is a combination of the interaction force constants between CC bonds within the central unit and $f_i^{\theta_i,s}$ is a combination of interaction force constants between the CC bonds of the central unit and the CC bonds of the $s$-th unit along the chain. $s$ in $\Sigma_i$ is, in principle, unknown and defines the distance of interaction between π bonds. It could possibly be estimated if reliable ab initio calculations were available. The term $\Sigma_i$ is related to the e/π coupling which, on its turn, may be associated to the changes of the hopping integral during CC stretching [12,32]. In Ref. [32], Piseri et al. provide an expression for the terms which possibly enter $\Sigma_i$.

$$F_{ij} = F_i \delta_{ij} + \pi_{ij} \left( \partial \beta / \partial R \right)_j^2$$ (3)

where $\pi_{ij}$ are the bond–bond polarizability coefficients, $\partial \beta / \partial R$ is the e/π coupling constant within the frame of the Hückel model and $R_j$ refers to the $j$-th internal coordinate of CC stretching along the polyconjugated chain. As discussed elsewhere [12,13] the last term in Eq. (2) turns out to be negative (softening term) and its absolute value depends on the strength $f$ and the interaction distance $s$. If $s$ is small and $f_i^{\theta_i,s}$ are small $F_s$ is large and does not change much with conjugation, thus producing no or small frequency dispersion.

It has been shown [11,12] that $F_n$ can be related to the parameter $\lambda$ defined by Horovitz in the amplitude mode theory of polyacetylene [8–10], thus the two theories are consistent in describing the electronic phenomena which occur in polyconjugated systems and determine the optical spectra.

As to the scattering intensity, additional terms must be considered [12,15]. The uv element of the Raman scattering tensor associated to the $k$-th normal mode $Q_k$ can be expressed as:

$$[A_{uv}] = \left( 1 / \hbar c \right) \left( \mu_{\mu}^{uv} \mu_{\nu}^{uv} \right)_0 \left( \partial E^s / \partial Q_k \right)_0$$

$$\times \left( v_{eg} - v_L + i \Gamma_o \right)^{-1}$$ (4)

where $(\mu_{\mu}^{uv} \mu_{\nu}^{uv})_0$ are the electronic transition moments, $(\partial E^s / \partial Q_k)_0$ is the derivative of the potential energy curve $E$ of the excited state with respect to $Q_k$, evaluated at the equilibrium geometry of the ground state $g$, $v_{eg}$ and $v_L$ are the frequencies associated to the gap transition and to the exciting laser line respectively; $\Gamma_o$ is a damping factor related to the lifetime of the excited state.

In Eq. (4) the term $(\partial E^s / \partial Q_k)_0$ is related to the e/π coupling [12]. It has been previously shown that $\Lambda$ is a totally symmetric vibrational coordinate which represents $\Delta_x^{\xi \xi \cdots}$, i.e., the change of equilibrium geometry between $g$ and $e$. One can then re-write Eq. (4) in the following way:

$$[A_{uv}] = \left( 1 / \hbar c \right) \left( \mu_{\mu}^{uv} \mu_{\nu}^{uv} \right)_0 \left( \partial E^s / \partial \xi \right)_0$$

$$\times L_{L \xi} \left( v_{eg} - v_L + i \Gamma_o \right)^{-1}$$ (5)

where $L_{L \xi}$ is the eigenvector derived from a classical normal coordinate calculation.
As pointed out in Ref. [12] only those \( Q \) which have nonvanishing \( L_{\alpha k} \) have appreciable Raman intensity and their intensities are proportional to \( |L_{\alpha k}|^2 \) since all other factors in Eq. (4) are independent of \( k \).

We observe that the \( e/\text{ph} \) coupling term occurs in both spectroscopic observables (i.e., frequencies and intensities, Eqs. (2) and (4) or Eq. (5)), but that if, on one hand, it may account for the frequency dispersion it may not be the most important factor in determining the scattering cross section when conjugation length increases.

We can quote as prototypical examples the cases of \( \text{trans} \) polyenes (and \( \text{trans} \) polyacetylene) and oligothiophenes (and polythiophene). In the former case, \( F_a \) spans a large range of values accounting for a large frequency dispersion which indicates a great extent of delocalization (weak pinning of \( \pi \) electrons, i.e., large softening of \( F_a \) ) [16]; on the contrary, in the case of thiophenes \( F_a \) is almost constant and practically no dispersion is observed or calculated, thus suggesting small delocalization and/or strong pinning. On the other hand, the existence of a different from zero \( e/\text{ph} \) coupling in thiophenes is independently shown by the dispersion of the calculated and observed electronic and vibrational hyperpolarizabilities which can be directly related to the Raman scattering cross sections [14, 15, 33]. The superlinear variations of the scattering cross section with ECL can depend significantly also on the increase of the electronic transition moments and the decrease of the HOMO–LUMO energy gap.

5. Classes of molecules studied and experimental data

The theoretical aspects outlined in Sections 3 and 4 form the basis of our studies of the vibrational spectra of a very large variety of classes of oligo and polythiophenes derivatives which have been recorded in our laboratory. While some details of the dynamics and spectra of a few interesting classes of compounds will be reported in a separate paper [34] an attempt is made here to provide an overall and comprehensive interpretation of the observed spectra. Our aim is to understand the physical phenomena which may occur in these systems because of \( \pi \) electron delocalization and to derive structure–property–spectra correlations.

In the choice of the molecules to be studied for an overall understanding of the spectroscopic properties of oligo and polythiophenes, we proceeded logically from the simplest systems to structurally more complex molecules whose chemical structure are well defined. Only for a few alkyl substituted thiophenes the precise position of the substituent on a given ring is not known due to the synthetic route followed.

In this work, approximately 50 molecules were studied. In the discussion which follows molecules are collected in groups and are labeled according to their chemical for-
Group F: Regiospecific alkoxythiophenes: $\alpha$-$\omega$-$4$-$4'$ dipentoxy-oligothiophenes; from Dr. M.C. Gallazzi.

Group G: $\alpha$-$\alpha'$ dimethyl end-capped oligothiophenes DMT$n$ (where $n = j + 2 = 3,4,5,6$ number of thiophene rings and $j = 1,2,3,4$). The vibrational spectra were provided before publication by one of the authors (V.H) and have been recently published [29].

Group H: Methylene bridged dithienyls BT$+M_r$ (where $r = 1–3$ is the number of methylene groups in the bridge); from Dr. F. Sannicolo, University of Milano, (I).

Group I: Oxygen-bridged dithienyl BT$+O_r$ (where $r = 1–3$ is the number of oxygen atoms in the bridge); from Dr. F. Sannicolo.

FT-Raman spectra (with 1064 nm excitation) were recorded first with a Bruker FT-Raman interferometer and later with a Nicolet 910 interferometer with liquid nitrogen Ge detector. Resolution was kept at 4 cm$^{-1}$. Most of the materials were solid. When necessary solutions were examined and sometimes integrated intensities were measured relative to a suitably chosen internal standard. For the sake of completeness the infrared spectra were also recorded, but are not discussed here.

6. Discussion

We start from the seemingly simplest series of oligomers, namely group A (T$n$). The molecular and crystal structures of $n = 1,2,3,4,5$, and 6 have been determined with various techniques.

On the whole, for the systems with $n > 1$ the thiophene units can be reasonably taken as co-planar [35].

Group theory and selection rules both for oligomers and the polymer of the type T$n$ have been discussed in Ref. [13]. Starting from the planar chain of polythiophene we expect seven totally symmetric, $A_g$ Raman active and $B_g$ dependent $k = 0$ phonons. The $A_g$ frequencies have been calculated on the basis of ECC theory as function of $F_z$ (Fig. 5) and found a striking coincidence in the experimental Raman spectra for a given numerical value of $F_z$. Phonon dispersion curves have also been already calculated (Fig. 6) based on the approximation of a force field independent of conjugation length, i.e., with a fixed value of $F_z$. In this paper, usually, we neglect the totally symmetric high frequency C–H stretching mode which occurs with vanishingly small intensity near 3000 cm$^{-1}$. We are then left to consider six totally symmetric modes which have been already considered in the dynamical calculations reported in Ref. [21] and which are the subject of re-analysis and revision in this paper.

First, we are in position to better describe the origin of line A universally observed as chain length dependent line in all the relatively short oligomers (when the length
Fig. 5. Frequency dispersion of the totally symmetric modes of polythiophene as a function of $F_k$ from Ref. [21].

increases its frequency decreases and the intensity weakens. Fig. 4a through d clearly show that line A originates mostly from modes localized at either ends of the oligomer chain and can be taken as originating from an ‘end-group’ mode which is simply mechanically coupled to some extent with the neighboring units. A simple and purely mechanical model (no electronic effects) accounts for the lowering of the frequency with increasing chain length. The fact that line A shows no intensity enhancement is simply justified by application of Eq. (5) where the term $L_{nk}$ is extremely small because mode A does not contain a sizeable contribution by any kind of $\pi$ coordinate. Its intrinsic relatively weak Raman intensity is uniquely associated to the nature of the end groups; it is then expected that its intensity relative to the Raman intensity of the other bulk modes must decrease when $n$ increases. Some small coupling with the $\pi$ mode of the bulk may occur (thus gaining some intensity), but it is irrelevant to the present discussion. Obviously, this line is not expected for an infinite polymer for which cyclic boundary conditions hold and no end modes can exist. The above assignment is in agreement with the results presented by Negri and Zgierski [30].

In the light of the above discussion, we must conclude that in some previous works [21] line A was erroneously taken as $\nu_1$ and its softening was related to delocalization in terms of the ECL of the oligomer. It will be shown that $\nu_1$ must be assigned to line B.

Next comes the justification of the lack of dispersion of line B, of its strength and of its superlinear increase with chain length. Since line B is observed in the Thn series unshifted even starting from the oligomer with $n = 3$ (i.e., with one inner thiophene ring) necessarily the corresponding phonon dispersion curve must be flat, i.e., conjugation length independent. From the calculated eigenvectors of Fig. 4a through d the contribution by the $\pi$ coordinate is certainly very large, and may increase with chain length, thus making the term $L_{nk}$ in Eq. (5) large and dominant, thus possibly yielding large $A_{\nu_1}$. This condition is necessary, but not sufficient since the second $\pi$-dependent term in Eq. (5) (i.e., $\partial E^e/\partial \pi$) has also to be sizeable in order to justify the selective intensity enhancement of the totally symmetric $Q_\pi$ mode which gives rise to the strong line B. As already stated above, this term is different from zero as shown by theoretical and experimental evaluations of both the electronic and vibrational hyperpolarizabilities which can also be related to Raman intensities (for a discussion of these aspects see, for instance, Refs. [14,15,33]).

All the aspects considered above lead to the conclusion that the term $\partial E^e/\partial \pi$ should be fairly large, but almost constant. This carries as a consequence that the distance $s$ of interaction appearing in Eq. (2) must be short, i.e., the electronic interactions in the class of thiophenes, as revealed by quadratic force constants, are limited almost to nearest neighbors and do not feel the increase of conjugation length. In other words, it appears that in the polythiophene chains $\pi$ electrons are strongly pinned within a very restricted domain of the polyconjugated chain.
Spectroscopic experiments [35] and ab initio calculations [36,37] on molecules of group H (bridged dithienyls, BT + Mf) provide enough evidence that some conjugation dependent interaction force constants, which extend at least to the first neighbor, exist (F\textsubscript{0}\textsuperscript{H} in Eq. (2), with s = 1); in these systems by changing the number r of the methylene groups the molecule is twisted of a known torsional angle which modulates the overlapping of the p\textsubscript{z} orbitals across the inter ring CC.

On these bases, the superlinear variations of the scattering cross section with increasing chain length must necessarily be ascribed to the changes of the electronic transition moments (\mu\textsuperscript{\textsubscript{0}}\textsuperscript{\textsubscript{0}}\mu\textsuperscript{\textsubscript{0}}\textsuperscript{\textsubscript{0}}), which appear in Eqs. (4) and (5) and to the decrease of the energy gap.

In reference to the assignment previously proposed for the thiophene oligomers Th\textsubscript{n} (group A) line B becomes \nu\textsubscript{1} in Fig. 5.

The analysis of the spectra of other groups of molecules examined in this work show that the strong line B is found to occur at fixed, but higher frequencies in group B (ECTh\textsubscript{n}) which bear electronically inert substituents at either ends in positions 4 and 5. The upward shift has to be ascribed simply to some kind of dynamical effect which will be discussed in another paper [34]. The same observation can be made for line B in groups F and G where molecule possess end group substituents in positions 4 or 5. The substitution in position 3 (hereafter referred as IN) does not display such dynamical effect.

We then proceed to the assignment of lines C and D. Line C appears in \alpha-\omega substituted oligomers (molecules belonging to the groups B, F and G) and its intensity increases slightly with increasing chain length. Line C occurs at frequencies very close to the strong line B and since both belong to the same symmetry species both modes may be strongly coupled and C may borrow intensity from B. Line C shows a slight upward shift with increasing chain length. Because of the great complexity of the dynamical system there is no clear compelling evidence that line C should originate either from the \nu\textsubscript{2} mode or from another end group mode. No further analysis based on the available data can be proposed.

Line D (near 1100 cm\textsuperscript{-1}) derives directly from the dynamics associated to the \nu\textsubscript{2} mode. The ab initio calculations presented in this paper on Th\textsubscript{n} models show that (i) its frequency is almost independent from chain length while its intensity slightly increases with increasing chain length. The calculated intensity for the three molecules considered is \sim 10\% of the B line.

The situation is very similar to the case of trans polyacetylene which shows two parallel totally symmetric modes strongly ECL dependent namely (i) \nu\textsubscript{1} (\sim 1450–1600 cm\textsuperscript{-1}) and (ii) \nu\textsubscript{1} (\sim 1080–1150 cm\textsuperscript{-1}). \nu\textsubscript{1} corresponds to the CC stretching (\nu\textsubscript{2} mode) necessarily carrying some wagging of the CH groups in which the H atoms recoil opposite to the displacements of the C atoms; \nu\textsubscript{1} consists mainly in C–H wagging coupled with the \nu\textsubscript{2} mode where both H and C atoms move in the same direction [12]. These two modes show softening with ECL and are dynamically coupled, thus allowing intensity borrowing from \nu\textsubscript{1} to \nu\textsubscript{2}. The same situation is found in oligo and polythiophenes and also in many other systems which are capable to sustain the \nu\textsubscript{2} mode and possess C–H groups with a suitable topology to make them available for the motions of the H atoms as mentioned above.

The case of oligo thiophenes is clearly described in Fig. 4a through d where the calculated (ab initio, unscalled) Q\textsubscript{z} mode near 1680 cm\textsuperscript{-1} (assigned in this work to \nu\textsubscript{1}) can be correlated to the mode calculated near 1150 cm\textsuperscript{-1} which shows clearly that there is a sizeable \nu\textsubscript{2} component associated to the C–H wagging.

It has to be noted that for the Th\textsubscript{n} models treated in the calculations line D does not show frequency dispersion consistently with the behaviour of line B. This is not the case of polyacetylene where both lines show dispersion with ECL. While a clarification of the origin the D line has been found its assignment to mode \nu\textsubscript{2} or \nu\textsubscript{4} of Fig. 5 is not unequivocal.

7. Spectra–property correlations

Based on the vibrational analysis limited to the Raman spectra of several classes of oligo and polythiophenes some new information on the dynamical and electronic properties of these systems have been derived.

(i) The role played by the relevant terms in Eq. (4) or Eq. (5) can be clearly disentangled. The e/\textsubscript{ph} coupling is \neq 0 since Raman intensity of the \nu\textsubscript{2} mode is not vanishing, as also shown by the behavior of the calculated and measured electronic and vibrational hyperpolarizabilities. The e/\textsubscript{ph} coupling interaction is, however, practically constant with chain length since \nu\textsubscript{a} does not soften with increasing chain length even starting from the shortest molecule Th3. The constancy of e/\textsubscript{ph} coupling implies the existence of a strong ‘pinning’. The precise origin of such ‘pinning’ has yet to be discovered. Various causes of ‘pinning’ are generally suggested, namely intra-ring electronic effects, conformational distortions and/or intermolecular forces. While all these factors may play different roles in the various classes of molecules considered, it is remarkable that even for the simplest series of molecule, Thn, where quasi-planarity is experimentally found (and has been forced in the calculations) strong ‘pinning’ is calculated ab initio for molecules in vacuo. Intramolecular pinning thus seems to be the main factor. Certainly for other series of substituted oligo and polythiophenes, the conformational distortions due to the bulkiness of the substituents cannot be neglected as additional factor limiting delocalization.

(ii) The role of the electronic transition moments (Eq. 4 and Eq. (5)) and of the energy gap becomes essential in determining the superlinear enhancement of the Raman

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intensity for the class of oligo and polythiophenes. This affects the derived molecular and/or nonlinear optical properties.

(iii) All quantum chemical calculations so far presented indicate that the bond lengths (and bond orders) of the inter-ring C–C bonds do not seem to change substantially with increasing chain length as if the interactions die off quickly almost within the first neighbor. In other words, the distance of interaction \( s \) appearing in Eq. (2) turns out to be extremely small for thiophene systems.

(iv) A new concept of general validity for all organic molecules clearly follows from the above observations. Dynamical interactions and bond properties (frequencies and geometries) reflect more localized molecular phenomena while electrical interactions (dipole moments and polarizabilities) probe phenomena at longer distances. This result carries as an obvious consequence the question of the evaluation of the extent and strength of \( \pi \) electron delocalization generally judged either from the red shift of the electronic spectrum or from the Raman spectrum when ECL increases. More elaborate quantum chemical calculations which take into account electron correlations are certainly needed for the clarification of this important point of general interest in the field of polyconjugated materials.

(v) Because of the lack of frequency dispersion with ECL of the strong line B it would seem that the Raman spectra lose their importance in determining the extent of delocalization. This would be indeed the case if only frequencies were considered. The measure of absolute Raman intensities (or intensities relative to a suitably chosen internal standard) turns out to be an essential tool to judge electronic delocalization. It can be stated in a more general way that the combined use of Raman frequencies and Raman absolute intensities is a way to probe \( \pi \) electron delocalization.

(vi) End effects are sizeable in these kinds of systems and should be kept in mind when the vibrational spectra of polyaromatic oligomers are considered. A typical example is given by the group B (ECTn) where the substituent attached to the ring at either ends are certainly electronically inert, but are capable to shift upward the strong \( \pi \) mode (line B). From the mechanics of simple one-dimensional systems end groups play a relevant role in affecting the collective motions (quasi-phonon-like waves) which take place along the chain [36–40]. The understanding of these observations in terms of dynamics waits for further studies.

(vii) We searched for similar behavior in other polyaromatic systems and pointed our attention to oligofurans [24,25] and oligopyrroles [17–20]. The identification of end group modes in these systems is not straightforward since the observed softening in oligofurans (\( \Delta \nu_n = 59 \text{ cm}^{-1} \)) and oligopyrroles (\( \Delta \nu_n = 45 \text{ cm}^{-1} \)) [16] shows that the term \( \Sigma_n \) (i.e. softening or weaker pinning) is certainly larger than in the case of thiophenes (\( \Delta \nu_n = 0 \text{ cm}^{-1} \)), thus reasonably suggesting for furans and pyrroles an extension of the interactions to a few neighbors.

(viii) In the search for a better understanding of the so-called ‘pinning’ of \( \pi \) electrons in heteroaromatic poly-

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**Fig. 7.** Ring stretching frequencies \( \nu_{\text{ring}} \) (cm\(^{-1}\)) of the heteroaromatic monomers furan, pyrrole, thiophene and selenephene (X = O, N, S and Se, respectively) as function of the effective electronegativity parameter \( h_x \) proposed by Streitwieser [44]. The value for X = Se is obtained by extrapolation of the straight line which includes the observed value of \( \nu_{\text{ring}} \) for selenephene.
mers [16] we focused our attention on the Raman spectra of the monomers. The totally symmetric ring stretching modes \( v_{\text{ring}} \) of furan, pyrrole and thiophene are observed at 1597, 1562 and 1460 cm\(^{-1}\), respectively. It should be interesting to understand the difference in such frequencies by changing the heteroatoms [41]. The heteroatoms (X = O, N and S) differ for their mass and for their electronegativity. Since from dynamical calculations [42,43] X does not seem to move during the above mentioned ring stretching modes the mass effect on \( v_{\text{ring}} \) is certainly negligible. The observed changes of \( v_{\text{ring}} \) must be related to the electronic effects associated to the electronegativity of X. In the quantum treatment of the heteroaromatic molecules Streitwieser [44] has introduced an empirical parameter \( h \) that accounts for the Coulomb integral that is related to the effective electronegativity of the X atom (\( h_\alpha = 2, h_N = 1.5 \) and \( h_S = 0 \)). No data are available for X = Se. The plot of \( h_\alpha \) vs. \( v_{\text{ring}} \) gives a nice straight line which includes also \( v_{\text{ring}} = 1440 \) cm\(^{-1}\) for X = Se providing a value of \( h_\alpha = -0.4 \). Fig. 7. These data show the close relationship between vibrational and electronic properties in conjugated materials where the heteroatoms play the main role in determining dynamics and spectra both electronic and vibrational.

8. Conclusions

In this work we have tried to account in a comprehensive way for many Raman spectra of polyconjugated oligo and polythiophenes. Our work uses information derived from: (i) simple frequency correlations, (ii) ab initio calculations of frequencies, intensities and molecular hyperpolarizabilities, (iii) normal mode calculations on some oligomers and polymers, (iv) ECC theory and (v) experimental intensity spectroscopy.

This study has led to modify the interpretation of some of the observed Raman lines previously reported. The changes of the vibrational assignment carry some relevant conceptual consequences which add some new knowledge on local vs. collective intramolecular coupling in polyconjugated systems.

The work also offers some help in the chemical diagnosis of oligo and polythiophenes based on Raman spectra.

For chemical diagnosis, the following Raman spectroscopic correlations can be suggested. When oligo and polythiophene structures exist in the sample, where delocalization is effective, the following general observations can be made.

(i) A vanishingly weak scattering in the C–H stretching range (3100–2800 cm\(^{-1}\)) is hardly observed even when long alkyl chains exist as substituents (see Fig. 1), (ii) a very strong \( \pi \) mode near 1450 cm\(^{-1}\) accompanied by a cluster of much weaker lines at higher and/or lower frequencies occurs, (iii) the very strong \( \pi \) mode is accompanied by a well-defined and characteristic sharp and medium-strong scattering near 1050 cm\(^{-1}\) associated to the totally symmetric in-plane wag of the C–H groups in the positions \( \beta \) and \( \beta' \), (iv) weaker lines constantly occurring near 729 and 320 cm\(^{-1}\) can, most of the time, appear and correspond to the predicted totally symmetric modes \( v_\pi \) and \( v_\pi' \) in Fig. 5, (v) extra weak lines are observed in the range 1250–1100 cm\(^{-1}\) and have been variously (and empirically) associated in the literature to conformational disorder, (vi) a scattering above 1450 cm\(^{-1}\) is always observed for oligomers, it shifts to lower frequencies and loses its intensity with increasing chain length. This line is associated to mostly ring stretching of the two end rings slightly mechanically coupled with the inner rings. This line becomes then an indication that the oligomer is relatively short. Its length may possibly be estimated and the multimodal character of a mixture of short chains can be studied from the observation of various end group lines.

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