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Vibrational spectroscopy of structural defects in oligothiophenes

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Vibrational spectra of oligothiophenes with structural defects are calculated within the density-functional-theory methodology. The effects of the defective αβ linkages on the infrared (IR) and Raman spectra are characterized from calculations of all isomers up to the hexamer. The signatures of αβ linked monomers can be found in IR spectra from broken symmetry arguments which result in absorptions localized in the defective region. The positions of the absorption peaks in the Raman spectra seem to be unaffected by the presence of such defects; however, strong reductions in the intensities are observed because of the shortening of the conjugation length.

1. Introduction

Traditionally, vibrational spectroscopy has been one of the most powerful tools for the structural analysis of organic compounds from small molecules to polymeric material. In a similar fashion, in the area of conducting polymers, infrared (IR) frequency and intensity spectroscopy and Raman spectroscopy are applied to a large group of conjugated systems and the signatures of the structural changes are reported. In the case of disordered structures such as in conjugated oligomers and polymers, the assignments of the transitions, shifts in the group frequencies and changes in the intensities provide strong insight into the complexity of the problem.

Among the conjugated polymeric material, oligo- and polythiophenes have attracted a great deal of attention because of their high conductivity and optical properties [1–3]. Oligothiophenes have been studied in detail as they can be synthesized with various techniques in crystalline form containing six [4] or even eight monomeric units [5]. On the other hand, polythiophenes suffer from the usual problems of low solubility and low processibility. In addition to these complications, the structures of the polymers strongly depend on the method of preparation and the reaction conditions. Consequently, the resulting material is hardly composed of ideal α–α linked linear chains but contains a large degree of structural defects [6]. These defects can be categorized as the mislinkages involving β carbons, branching, hydrogenation at monomer–monomer

linkages and charge defects such as polarons and bipolarons.

Oligothiophenes have turned out to be a good case study where the electronic structure calculations have provided a great deal of understanding of the intricacies of the structure. The optimized geometry of unsubstituted and substituted small oligomers has been reported using accurate quantum mechanical calculations. Semiempirical methodology has been applied to oligomers containing as much as 20 units. The rotational motion around the monomer–monomer bond has been studied in detail for various bithiophenes in order to understand the transition from the gas-phase twisted structure to the accepted planar structure in the solid phase. The electronic and vibrational spectra have been computed for many systems where the agreement between the theory and experiment was proven to be very good.

For some time we have been involved with the understanding of the structural defects in conjugated polymers. The ideal α–α linked linear chains are hardly realized in thin films or the amorphous material. The growth from β carbons is energetically very feasible, therefore the strong oxidative conditions generally result in a very high degree of linkages involving β carbons and consequently the the degree of conjugation is lowered. The extent of such structural defects is thought to be as large as 20%. We have carried out a thermodynamical stability analysis of the likelihood of various linkage types by accurate quantum chemical calculations. The results of these calculations are utilized to establish a probability function for growth mechanisms which then is used in Monte Carlo simulations of polypyrrole (PPy) [7,8] and polythiophene (PT) [9]. We were able to predict the extent of αβ defects and dependence on temperature

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for PPy and PT. The presence of mislinkages also affects the oxidized structures as polarons and bipolarons. The semiempirical and *ab-initio* calculations show strong charge localization for the oxidized form [10] whereas the density-functional calculations point to delocalized charges [11]. The localization of the charge on a portion of the chain (usually 4–7 units) results in a strong shift in the ordering of the single and double bonds and these shifts can be detected in Hartree Fock (HF) type calculations. However, an αβ linkage both destroys the conjugation and strongly disturbs the extension of the localized charge.

In this study, we employ density-functional-theory (DFT) calculations in order to classify the changes in the vibrational spectroscopy of oligothiophenes. The calculated spectra of linear αα ideal systems are compared to those of system including αβ linkages.

2.   IR spectra of αβ defects

All calculations are carried out with the Gaussian 98 package [12]. We have optimized structures within DFT methodology employing the three-parameter hybrid-functional of Becke [13] and the basis set of 6-31g(d). This combination has been used heavily for the electronic and spectroscopic calculations of conjugated oligomers and shown to give reliable results. The frequencies are scaled with the scaling factor of 0.9613.

There are a great deal of experimental and theoretical results on the structure of oligothiophenes. Both electronic structure calculations and electron diffraction data show that bithiophene is twisted with a torsional angle between the two thiophene rings of l35–150°. The minimum energy configurations of longer oligothiophenes are also nonplanar, where the thiophene monomers are lying in almost *anti* conformations. The only exception to this are the oxidized (polaron and bipolaron) forms of the oligomers where a high degree of planarization is observed along the charge localization. For the neutral structures, we have found the torsional angles to be changing between 158–167°. The chain becomes more planar going from edges to the centre. On the other hand, the high conductivity of poly- and oligothiophenes indicates a large degree of conjugation that favours the planar structures and in fact the crystallographic results point to plant structures.

Our calculated vibrational spectra of regular nT for $n = 2$–6 in planar and twisted forms are indistinguishable within the errors of the computational procedures except for the few imaginary frequencies in the planar form. On the other hand, the defective structures form kinks and at these kinks the deviations from planarity increase. In order to have a meaningful comparative study, we opt to calculate and match spectra of nonplanar, gas-phase-optimized structures. The notation for isomers is such
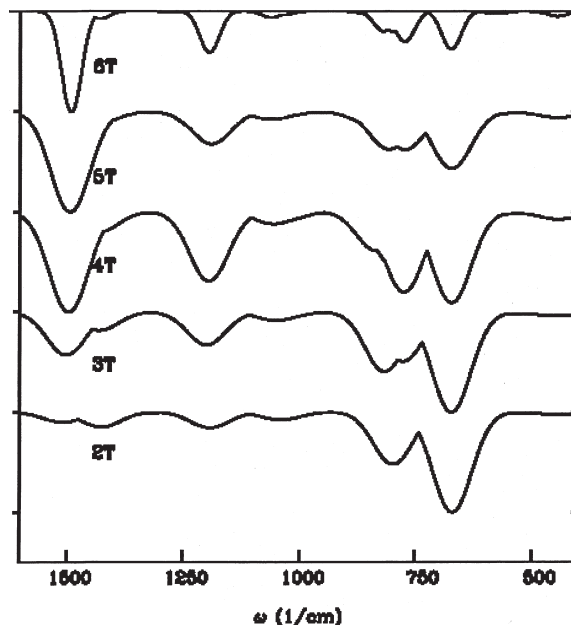

Figure 1.   IR spectra of ideal 2T–6T.

that a given structure is denoted by a sequence of _,_ symbols where each symbol characterizes the sequence of carbon atoms forming the monomer–monomer bonds.

In figure 1, the IR spectra of linear _-_ oligomers from 2T to 6T in the range of 400–1600 cm^{-1} are presented. The absorption around 1490 cm^{-1} is a collective mode composed of essentially asymmetric stretching of C_α-C_β bonds. This absorption becomes stronger as the chain grows. The second group of absorptions around 1200 cm^{-1} is a combination of stretching of the monomer-monomer bonds and the bending of C-C-S. The last group of absorptions is a mixture of the out-of-plane bendings of hydrogens and C-S-C stretching. Both of these are found in the 670–800 cm^{-1} range. The only absorptions outside this region are at around 3000 cm^{-1} and represent C-H stretchings. They are relatively constant for all oligomers studied, hence they are not presented in this figure.

If only a single β linkage in each oligomer is considered, then the total number of possible structures for nT is $(n + l)$, We have shown previously that these defective linkages were thermodynamically very stable and could form up to 20% of all monomer–monomer bonds. In table 1, we present the energy of all possible oligomer types up to 6T. The energy differences between the ideal chains and the most unstable chains are less than 3.0 kcal mol^{-1}.

In figure 2(a-e) the calculated spectra of these structures are given. For the αα dimer (figure 2(a)), the C-H absorption is at 669 cm^{-1} and that of C-S-C is at 798 cm^{-1}. If the linkage is of αβ type, then the basic difference is the splitting of the peaks in the 670–800 cm^{-1}

Table 1. Ground state energy of regular and oligothiophenes (au) and measure of the spectral change upon introducing β linkages.

Oligomer	Ground state energy	Overlap of spectra
2T	−1104.8169927	
2T_ab	−1104.8160988	0.9688
3T	−1656.6317954	
3T_aaab	−1656.6306567	0.9264
3T_aaba	−1656.6298936	0.8733
4T	−2208.4467840	
4T_aaaaab	−2208.4456293	0.9169
4T_aaaaba	−2208.4453584	0.8494
4T_aaabaa	−2208.4451074	0.8067
5T	−2760.2638046	
5T_aaaaaaab	−2760.2608536	0.9277
5T_aaaaaaba	−2760.2607043	0.8583
5T_aaaaabaa	−2760.2594473	0.8049
5T_aaaabaaa	−2760.2602374	0.7799
6T	−3312.0771996	
6T_aaaaaaaaab	−3312.0760857	0.9602
6T_aaaaaaaaba	−3312.0748946	0.8863
6T_aaaaaabaa	−3312.0746819	0.8378
6T_aaaaabaaa	−3312.0755748	0.8041
6T_aaaaabaaaa	−3312.0756063	0.7897

range. Out-of-plane C-H bending vibrations are localized either at the monomer bonded from its _ carbon ($673\,cm^{-1}$) or at the other monomer ($763\,cm^{-1}$). Similarly C-S-C stretchings split into two absorptions.

From 3T to 6T, again the strong splitting of the 670–$800\,cm^{-1}$ region is observed. Both types of vibration active in this region are strongly localized on different monomers. The absorption around $1200\,cm^{-1}$ remains unchanged by the presence of defects except that the intensity decreases to an extent. The vibrations around $1500\,cm^{-1}$ are also affected slightly. The maxima are increased by about $10\,cm^{-1}$ and there is a significant loss of intensity as the defect moves towards the centre. The position of the αβ bond changes the conjugation and hence changes.the spectra.

In order to find the overall change in the spectra upon introducing __ bonds, we introduced a measure of spectral similarity which is based on the overlap of the defective spectra with that of the ideal spectrum. The overlaps are calculated for the normalized spectra numerically and presented in the third column of table 1. For the case of two identical spectra, this measure should be 1.000. From this analysis it is clear that the more the __ linkage moves towards the centre of the chain, the more pronounced the changes in the spectra are . The most important reason behind these changes is the structural kinks forming due to the bonds via _ carbons. Even though deviations from planarity seem to
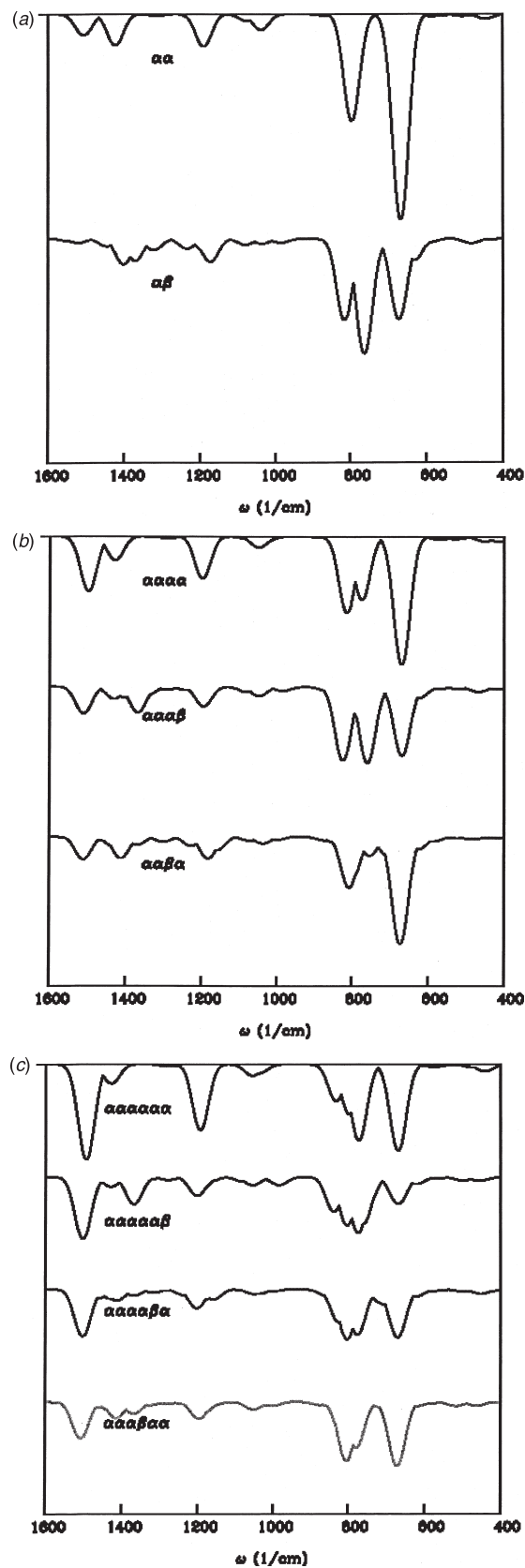

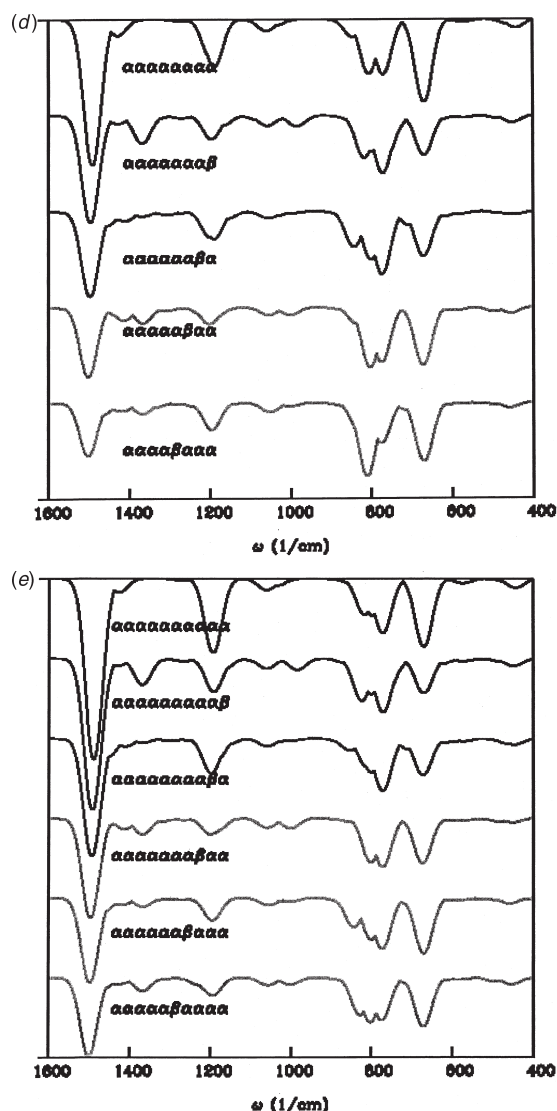Figure 2. IR spectra of regular and defective (*a*) 2T, (*b*) 3T, (*c*) 4T, (*d*) 5T and (*e*) 6T.

Figure 2. Continued.

Table 2. Raman active vibrations and their activity.

Molecule	Harmonic frequency (cm^{-1})	Raman scattering activity (A × 4/amu)
3T	1453	10 726
3T_aaab	1462	6505
3T_aaba	1457	1961
4T	1449	53 789
4T_aaaaab	1458	32 926
4T_aaaaba	1461	12 734
4T_aaabaa	1466	9534
5T	1442	129 251
5T_aaaaaaab	1444	54 577
5T_aaaaaaba	1440	10 994
5T_aaaaabaa	1439	1556
5T_aaaabaaa	1432	768
6T	1438	311 301
6T_aaaaaaaaab	1439	244 406
6T_aaaaaaaaba	1439	75 414
6T_aaaaaaabaa	1444	70 989
6T_aaaaaabaaa	1449	50 244
6T_aaaaabaaaa	1452	23 447
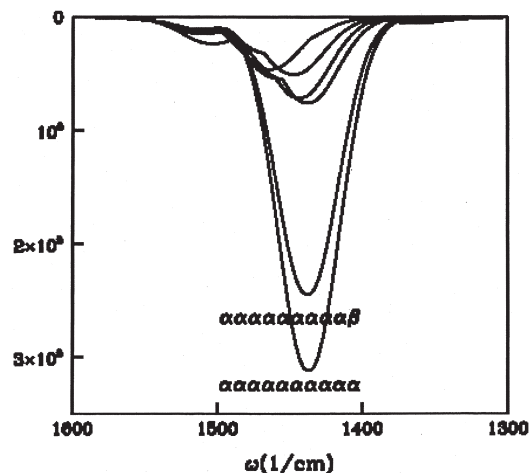
Figure 3. Raman spectra of regular and defective 6T.

have minimal influence on the IR spectra, the linearity of the chain plays a significant role.

3. Raman spectra of αβ defects

Symmetric and antisymmetric collective modes in conjugated polymers are Raman active as described extensively by Zerbi and co-workers [14]. They are reported to be very sensitive to the doping process of the systems. The calculated Raman spectra of nT in both linear and defective forms are very simple and localized mainly around 1445–1500 cm^{-1}. In table 2, we summarize the changes in absorptions as the defective linkages shift from the edge of the oligomer to the centre. The most intense peak is always the symmetric C-S-C bending which is strongly coupled to monomer–monomer and C_β-C_β stretchings. This mode is usually localized at the centre of the oligomer and the contribution from end

monomers is minimal. When the defective bonding is at the end, there is not a significant change. As the defect moves towards the centre, this localization shifts in a way such that the monomer with the β bond remains inactive in the Raman active mode. The intensity of the peak increases with increase in the chain length and decreases with decrease in the distance of the defect to the edge. In figure 3, we present the calculated complete spectra for all isomers of 6T for the region 1300–1600 cm^{-1}. For clarity, not all spectra are identified in the figure but, together with table 2, it is easy to distinguish each isomer. It seems that the Raman spectra of neutral oligothiophenes cannot provide information on the extent of

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αβ defects unless an intensity comparison can be made with the spectra of ideally linked polymers.

4. Conclusion

The calculated IR spectra of defective thiophene oligomers show various deviations from planar, α-α linked ideal chains. The deviation from planarity in these oligomers does not alter the general characteristics of the spectra. On the other hand, αβ linkages disturb the symmetry and hence alter the degeneracy of absorptions. As a result of this broken symmetry, splittings in collective modes and out-of-plane C-H bendings are observed. In the Raman spectra, peak positions remain unaffected by such mislinkages; however, the intensity decreases significantly.

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