Hole-vibronic coupling in oligothiophenes: impact of backbone torsional flexibility on relaxation energies

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Density functional theory calculations together with highly resolved gas-phase ultraviolet photoelectron spectroscopy have been applied to oligothiophene chains with up to eight thiophene rings. One of the important parameters governing the charge transport properties in the condensed phase is the amount of energy relaxation upon ionization. Here, we investigate the impact on this parameter of the backbone flexibility present in oligothiophenes as a result of inter-ring torsional motions. With respect to oligoacenes that are characterized by a coplanar and rigid backbone, the torsional flexibility in oligothiophenes adds to the relaxation energy and leads to the broadening of the first ionization peak, making its analysis more complex.

Keywords: gas-phase ultraviolet photoelectron spectroscopy; reorganization energy; vibronic coupling

1. Introduction

The possibility of using organic semiconductors to produce low-cost, large-area and flexible electronic devices has driven the synthesis and characterization of a large number of organic molecules. The challenge is to design solution-processable air-stable organic semiconductors that perform well with regard to the inorganic materials being currently used and lead to devices produced at a fraction of the cost (Newman et al. 2004).

Thiophene-based oligomers and polymers have been used in a variety of devices, such as liquid crystal displays (Iwanaga et al. 2000), field-effect transistors (Dimitrakopoulos & Malenfant 2002; Merlo & Frisbie 2003), solar...
cells (Roncali 2005), light-emitting devices (Mazzeo et al. 2003, 2005), lasers (Zaveliani-Rossi et al. 2003; Pisignano et al. 2005) or sensors (Torsi et al. 2002). Synthetic flexibility is a key to optimized performance, and functionalized thiophene-based molecules illustrate well how the chemical structure can be tailored to achieve a desired property.

Practical applications of organic molecules as active materials in electronic devices are tied to high charge carrier mobilities. Some of the best carrier mobilities in organics have been measured in polythiophenes and oligothiophenes (Horowitz et al. 1996; Bao et al. 1997; Fichou 1999; Katz et al. 2001; Facchetti et al. 2004a; Ong et al. 2004). Facchetti et al. (2004a, b) showed that oligothiophene substitutions with perfluoroalkyl groups can switch the majority carrier activity from p- to n-type and that regiochemical modifications of these substituent groups alter solid-state packing and film morphology. Ambipolar transport (i.e. encompassing both n- and p-types) was successfully achieved in a thin-film transistor using a quinoid oligothiophene derivative (Casado et al. 2002, 2003; Pappenfus et al. 2002a, b; Chesterfield et al. 2003).

Although pentacene keeps the record in hole mobilities (Jurchescu et al. 2004) measured in organic field-effect transistors, regardless of the method of film deposition and contact configuration, commercial applications of this material are hampered by its environmental instability and low solubility. Recently, a hybrid thiophene–acene semiconductor has been investigated and revealed high mobility and increased air stability, indicating that the properties of the two fragments (acene and thiophene) can be combined to design a material with overall superior performance (Kwon et al. 2004; Heeney et al. 2005; Merlo et al. 2005; Coropceanu et al. 2006).

Despite experimental efforts to synthesize and characterize oligothiophenes and derivatives, most of the theoretical evaluations of the transport parameters have been directed to other organic molecules, such as oligoacenes (Cornil et al. 2001; Haddon et al. 2002; de Wijs et al. 2003) and their derivatives (Kwon et al. 2004; da Silva et al. 2005). The theoretical characterization of oligothiophenes is more challenging than for oligoacenes. Indeed, the flexibility of the oligothiophene backbone, resulting from inter-ring torsional motion, in comparison with the rigid and planar structure of oligoacenes, adds new complexity to the analysis. First, this is due to a significant contribution to reorganization processes of low-energy vibrations along the torsional degrees of freedom. Note that these low-frequency modes, in addition to their effect on the reorganization energy, also lead to a strong modulation of the transfer integrals, and are thus responsible for the temperature dependence of the mobility (Grozema et al. 2002; Bredas et al. 2004). The importance of this inter-ring torsion on the total reorganization energy was evaluated by Hutchison et al. (2005) for a series of heterocycles (including oligothiophenes). Grozema et al. (2002) also studied theoretically the effect of the inter-ring torsion on the hole mobility along polythiophene and polyphenylenevinylene chains. The lower mobilities found experimentally in polythiophene with respect to those in polyphenylenevinylene were attributed to larger deviations from planarity in the former system (Grozema et al. 2002).

Another difficulty in the description of oligothiophenes in comparison with oligoacenes (which is also related to torsional motion) is due to the marked difference between the frequencies of the normal modes (NMs) in the neutral and
cation states; as a result, quadratic vibronic coupling effects are also important in these systems. In addition, the potential energy surface (PES) of the neutral species is complex since it displays two fundamental minima (Rubio et al. 2003) separated by a tiny barrier; as a result, the PES is anharmonic.

In this work, we analyse the intramolecular reorganization energy related to hole charge transport in oligothiophenes, using first-principles correlated quantum mechanical calculations and a multimode vibrational analysis of the highly resolved gas-phase ultraviolet photoelectron spectroscopy (UPS) data.

2. Experimental

The He I gas-phase photoelectron spectra were recorded using an instrument that features a 36 cm radius, 8 cm gap hemispherical analyzer (McPherson) and custom-designed excitation source, sample cells, and detection and control electronics; these have been described in more detail previously (Lichtenberger et al. 1986). The samples sublimed cleanly at the following temperatures (10⁻⁴ torr, temperatures monitored using a ‘K’-type thermocouple passed via a vacuum feed-through and attached directly to the sample cell) with no evidence of decomposition products in the gas phase or as a solid residue for any of the samples: \( T_3 \), 78–90°C; \( T_4 \), 158–175°C; \( T_6 \), 250–275°C; and \( T_8 \), 365–425°C. The argon \( ^2\text{P}_{3/2} \) ionization at 15.759 eV was used as an internal calibration lock of the absolute ionization energy. The difference between the argon \( ^3\text{P}_{3/2} \) ionization and the methyl iodide \( ^2\text{E}_{1/2} \) ionization at 9.538 eV was used to calibrate the ionization energy scale. The instrument resolution (measured using FWHM of the argon \( ^2\text{P}_{3/2} \) peak) was 0.024–0.034 eV during data collection. All data are intensity corrected with an experimentally determined instrument analyzer sensitivity function. Data were fit using asymmetric Gaussians (Lichtenberger & Copenhaver 1990), with positions reproducible to ±0.02 eV (approx. 3σ level). In figures 2, 7 and 8, the individual data points are represented by vertical lines; the length of the line indicates the variance of the relative data point intensity.

3. Theoretical methodology

We performed geometry optimizations for the neutral and radical cation states of oligothiophenes of size varying from one to eight monomers, referred to hereafter as \( T_n \) (1 ≤ \( n \) ≤ 8), followed by calculation of the harmonic vibrational frequencies and NMs. The calculations were performed at the density functional theory (DFT) level using the B3LYP functional (involving the exchange functional by Becke (1988, 1993b) and the correlation functional by Lee et al. 1988) and the BHandHLYP functional (Becke’s (1993a) ‘half-and-half functional’), as implemented in GAUSSIAN98 (Frisch et al. 1998). A split-valence plus polarization 6-31G** basis set (Ditchfield et al. 1971; Hehre et al. 1972; Hariharan & Pople 1973, 1974; Gordon 1980) was used in all the calculations reported here.

The B3LYP functional has a good track record for describing the vibronic properties of the charged states of oligoacenes (Coropceanu et al. 2002b; Gruhn et al. 2002; da Silva et al. 2004; Malagoli et al. 2004; Sánchez-Carrera et al. 2006) and anthradithiophene (Kwon et al. 2004). However, recent investigations (Geskin & Bredas 2003) of the geometric and electronic structure and charge
localization in radical cations of oligothiophene chains favour the BHandHLYP functional (which includes a higher percentage of Hartree–Fock exchange) as the better choice for these systems. We have used the results of the UPS measurements to identify which functional is more appropriate to reproduce the relaxation energies in oligothiophenes.

4. Results and discussion

(a) Ultraviolet photoelectron spectroscopy data

The valence photoelectron spectra of the oligomers $T_3$, $T_4$, $T_6$ and $T_8$ are shown in figure 1, which illustrates the general similarities that exist among the spectra. Close-up spectra of the ionizations from 6 to 10.5 eV are shown in figure 2; the
ionizations in this region are deconvoluted with the minimum number of Gaussians needed to give a good representation of the data. The positions of the Gaussians are listed in Table 1. Spectra recorded for \( T_3, T_4, T_6 \) and \( T_8 \) are similar to previously reported photoelectron spectra (Telesca et al. 2001). Exact peak positions in terms of ionization energies were not reported in that earlier work; however, visual comparison of relative peak positions, intensities and widths are in good agreement.

Thiophene itself has two ionizations located at energies lower than 11 eV, which arise from the removal of an electron from each of the two highest occupied \( \pi \) orbitals; these belong to \( a_2 \) and \( b_1 \) symmetry under the \( C_{2v} \) point group. The \( b_1 \) orbital has a node passing approximately through the \( \alpha \)-carbons that participate in the inter-ring bonds (Figure 3); therefore, there is little

Figure 2. Close-up gas-phase photoelectron spectra of (a) terthiophene \( (T_3) \), (b) quaterthiophene \( (T_4) \), (c) hexathiophene \( (T_6) \) and (d) octathiophene \( (T_8) \). The Gaussian functions used for the deconvolution are also shown.
coupling and splitting between $b_1$ orbitals in the oligomers; the $b_1$-based ionizations of each of the oligomers fall around approximately 9 eV under a band that is deconvoluted with two Gaussians. In contrast, the $a_2$ orbitals (figure 3) have good overlap across inter-ring bonds, which results in the spread of ionizations that surround the intense $b_1$-based ionizations. The three $a_2$-based ionizations of $T_3$ are clearly observed at 7.38, 8.65 and 9.88 eV. Only three of the four $a_2$-based ionizations of $T_4$ are clearly observed; if the ionizations are more or

Figure 3. Symmetry elements of the $C_{2v}$ point group.

Table 1. Characteristics of the asymmetric Gaussians used to fit the UPS bands from figure 2.

<table>
<thead>
<tr>
<th>position (eV)</th>
<th>high</th>
<th>low</th>
<th>average</th>
<th>relative peak area</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_3$  7.38</td>
<td>0.69</td>
<td>0.35</td>
<td>0.52</td>
<td>1</td>
</tr>
<tr>
<td>8.65</td>
<td>0.44</td>
<td>0.16</td>
<td>0.30</td>
<td>1.05</td>
</tr>
<tr>
<td>9.00</td>
<td>0.28</td>
<td>0.23</td>
<td>0.26</td>
<td>1.33</td>
</tr>
<tr>
<td>9.23</td>
<td>0.35</td>
<td>0.24</td>
<td>0.30</td>
<td>2.12</td>
</tr>
<tr>
<td>9.88</td>
<td>0.53</td>
<td>0.53</td>
<td>0.53</td>
<td>1.04</td>
</tr>
<tr>
<td>$T_4$  7.17</td>
<td>0.75</td>
<td>0.42</td>
<td>0.59</td>
<td>1</td>
</tr>
<tr>
<td>8.14</td>
<td>0.89</td>
<td>0.29</td>
<td>0.59</td>
<td>1.15</td>
</tr>
<tr>
<td>8.92</td>
<td>0.32</td>
<td>0.24</td>
<td>0.28</td>
<td>2.07</td>
</tr>
<tr>
<td>9.20</td>
<td>0.45</td>
<td>0.34</td>
<td>0.40</td>
<td>3.68</td>
</tr>
<tr>
<td>9.91</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
<td>1.13</td>
</tr>
<tr>
<td>$T_6$  6.98</td>
<td>0.53</td>
<td>0.49</td>
<td>0.51</td>
<td>1</td>
</tr>
<tr>
<td>7.63</td>
<td>0.51</td>
<td>0.51</td>
<td>0.51</td>
<td>1.32</td>
</tr>
<tr>
<td>8.34</td>
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<td>0.49</td>
<td>0.49</td>
<td>1.59</td>
</tr>
<tr>
<td>8.83</td>
<td>0.34</td>
<td>0.34</td>
<td>0.34</td>
<td>3.98</td>
</tr>
<tr>
<td>9.14</td>
<td>0.46</td>
<td>0.41</td>
<td>0.44</td>
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</tr>
<tr>
<td>9.72</td>
<td>0.77</td>
<td>0.61</td>
<td>0.69</td>
<td>2.44</td>
</tr>
<tr>
<td>$T_8$  6.85</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>1</td>
</tr>
<tr>
<td>7.24</td>
<td>0.54</td>
<td>0.41</td>
<td>0.48</td>
<td>1.43</td>
</tr>
<tr>
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<td>0.54</td>
<td>0.42</td>
<td>0.48</td>
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<td>0.38</td>
<td>0.38</td>
<td>1.62</td>
</tr>
<tr>
<td>8.81</td>
<td>0.40</td>
<td>0.34</td>
<td>0.37</td>
<td>7.49</td>
</tr>
<tr>
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<td>0.50</td>
<td>0.37</td>
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<td>9.82</td>
</tr>
<tr>
<td>9.79</td>
<td>0.71</td>
<td>0.58</td>
<td>0.65</td>
<td>2.83</td>
</tr>
</tbody>
</table>

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less spaced equally, the fourth is probably obscured by the $b_1$-based ionizations. Only four $a_2$-based ionizations are clearly observed for $T_6$; one is again most probably obscured by the $b_1$-based ionizations; it is possible that one is more stable than 11 eV and is obscured by the $\sigma$-bond ionizations present in that energy range. Increasing the number of thiophene rings in the oligomer has the effect of destabilizing the first ionization band from 7.38 eV for $T_3$ to 7.17 eV for $T_4$, 6.96 eV for $T_6$ and 6.85 eV for $T_8$.

The lineshape of the lowest UPS band is directly related to the geometry relaxation energy, $\lambda^1$, calculated when going from the neutral ground state geometry to the cation optimal geometry; $\lambda^1$ closely corresponds to one-half of the vibrational reorganization energy for intramolecular hole transfer (Bredas et al. 2004). In the present case, in contrast to the situation found in oligoacenes, the first ionization does not show any vibrational fine structure. Although in the absence of vibrational structure the analysis of the UPS spectrum is less straightforward and less informative, the UPS data do provide significant insight on the relaxation processes. As seen from table 1, the bandwidth of the first ionization initially increases when going from $T_3$ to $T_4$ and then decreases with the size of the system. This trend suggests that the strength of the overall vibronic interactions also initially increases with the size of the system and then decreases in longer systems. This behaviour is in marked contrast with that found for oligoacenes and their derivatives (Coropceanu et al. 2002a, 2006; Malagoli et al. 2004; Sánchez-Carrera et al. 2006) where the total relaxation energy is inversely proportional to the size of the system. In addition, as seen from table 1, the profile of the first ionization in small systems is highly asymmetric; this asymmetry, however, gradually decreases with system size, so that in $T_8$ the band can be modelled with a perfectly symmetric Gaussian shape. Since the source of asymmetry is probably related to interactions with high-frequency vibrations, this result, taken together with the trends for the total bandwidth, indicates that the strength of interactions with high-energy vibrations decreases monotonically with system length and more sharply than the strength of other mechanisms contributing to broadening (interactions with low-frequency vibrations, quadratic vibronic couplings, etc.).

\[ \text{(b) Geometry} \]

A number of theoretical studies at the Hartree–Fock, DFT, CASPT2 and MP2 levels of theory with various basis sets have been reported in the literature on the geometrical parameters of the ground and excited states of charged and neutral oligothiophenes (Viruela et al. 1998; Geskin & Bredas 2003; Geskin et al. 2003; Rubio et al. 2003). The comparison of the calculated structures with experimental X-ray data as well as gas-phase and solution conformational studies has also been carried out (see Diaz-Quijada et al. (2002) for review). Most of these studies have concentrated on the rotational barrier and its impact on the spectroscopic and photophysical properties of oligothiophenes.

Here, we are interested in the effect of this barrier in the context of total relaxation energy. For the largest oligomer analysed, $T_8$, the dihedral angles at the centre and the ends are calculated, at the B3LYP (BHandHLYP) level, to be 171.5 and 162.5° (160.9 and 156.4°), respectively; as expected, the central dihedral angle is larger than the dihedral angle at the ends. The B3LYP

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functional results in more planar structures than the BHandHLYP functional. The Hartree–Fock component of the functional seems to be the main reason behind this difference; the B3LYP/BHandHLYP comparison is consistent with the fact that Hartree–Fock methods lead to less planar structures; for instance, the dihedral angles are around 150° with AM1 (Cornil et al. 1995). Our findings are in agreement with a recent investigation by Viruela et al. (1998) of the internal rotation of 2,2′-bithiophene using DFT and MP2. The MP2/6-31G* s-trans–gauche minimum appears at 142.2° while this minimum disappears when the local (non-hybrid) functional S-VWN is used.

Although direct structural data for charged species of π-conjugated chains are rather scarce (Baitoul et al. 2000), quantum chemical calculations concur in pointing out that charged oligothiophenes tend to relax to a quinoid geometry with an inverse bond length alternation pattern (Bredas & Street 1985). The change in dihedral angle in going from the neutral to the charged state plays an important role in the analysis of the gas-phase UPS spectra, as highlighted in §4c.

(c) Ionization potentials

The obtained total energies of neutral and cation states have been used to compute the vertical and adiabatic ionization potentials. The comparison between the theoretical values and the experimental data extracted from the gas-phase UPS spectra is shown in table 2. We found that the best fit of the data as a function of chain length, n, is obtained when assuming an exponential dependence

\[ IP(n) = A \cdot \exp\left(\frac{-n}{t}\right) + IP_\infty, \]  

with \( IP_\infty \), A and t being fitting parameters; \( IP_\infty \) can be recognized as the polymer (infinite chain) ionization potential. A similar equation has been used before to describe the optical spectra (Meier et al. 1997; Gierschner et al. 2006).
The HOMO energy was also used to estimate the ionization potential in the framework of Koopmans’ (1933) theorem. While it remains unclear whether this theorem can be applied to DFT energies (Chong et al. 2002), our results indicate that the evolution of the HOMO (Kohn–Sham) energy provides the best agreement with the experimental evolution of the ionization potential as a function of oligomer length (A and t parameters), although a larger uniform shift is needed to better match the experimental and calculated evolutions ($IP_\infty$ parameter). An extrapolated polymer ionization potential ($IP_\infty$) of 6.90 eV obtained from the experimental values matches previous estimates by Jones et al. (1990).

The energetic splitting between the first and second ionizations provides another useful parameter to compare the performance of the two functionals. Using Koopmans’ (1933) theorem, the energies of the first and second ionizations can be estimated from the HOMO and HOMO-1 energies. In the case of short oligomers ($T_3$ and $T_4$), the B3LYP estimates are closer to the values that are extracted from the experimental spectra (table 1). For long oligomers ($T_6$ and $T_8$), the fitting used to extract this parameter from the UPS spectra becomes less accurate and does no longer allow one to determine which functional performs best.

(d) Reorganization energy

The importance of the relaxation energy in the description of the transport properties of organic semiconductors has been described in detail elsewhere (Bredas et al. 2004). We recall that the intramolecular reorganization energy for self-exchange consists of two terms related to the geometry relaxation energies upon going from the neutral-state geometry to the charged-state geometry ($\lambda^1$) and vice versa ($\lambda^0$)

$$\lambda = \lambda^1 + \lambda^0,$$

$$\lambda^1 = E^{1/0} - E^{1/1},$$

$$\lambda^0 = E^{0/1} - E^{0/0}.$$  \hspace{1cm} (4.2)

Here, $E^{0/0}$ and $E^{1/1}$ are the ground state energies of the neutral and cation states, respectively; $E^{0/1}$ is the energy of the neutral molecule at the optimal cation geometry and $E^{1/0}$ is the energy of the cation state at the optimal geometry of the neutral molecule.

Another important aspect to be investigated here is how the total relaxation energy is distributed among the vibrational modes. By expanding the potential energies of the neutral and cation states into a power series of the normal coordinates, the total relaxation energy can be written as follows:

$$\lambda = \lambda^0 + \lambda^1 = \sum (\lambda^0_j + \lambda^1_j) = \sum \left( \frac{k^0_j}{2} + \frac{k^1_j}{2} \right) \Delta Q^2_j,$$  \hspace{1cm} (4.3)

where $k^0_j$ and $k^1_j$ are the force constants and $\Delta Q_j$ represents the displacement along NM $j$ between the equilibrium positions of the two electronic states (cation and neutral). $\Delta Q_j$ and the corresponding relaxation energies were obtained by means of the DUSHIN program developed by Reimers (2001).

The B3LYP and BHandHLYP values for the relaxation energy in the $T_1$–$T_8$ oligomers calculated from the adiabatic potential surfaces (APS) and from a NM analysis are reported in table 3. When comparing the B3LYP results for
oligothiophenes with similar results for oligoacenes, we note two significant
differences. Firstly, in oligoacenes, $\lambda^1$ and $\lambda^0$ are very similar; in contrast,
in oligothiophenes, especially in the smaller systems, these two quantities differ
significantly, which means that the overall curvatures of the corresponding PESs
are also different. Secondly, while in oligoacenes, the relaxation energy obtained
from either the APS or NM approach is nearly the same, this is not the case in
oligothiophenes. For instance, the relaxation energy $\lambda^0$ obtained from a PES
analysis is approximately 10 meV smaller than that computed using the NM
approach. Since the NM calculations assume anharmonic PES, this difference is an
indication of anharmonicity effects. The values obtained at the BHandHLYP level
are significantly larger than those calculated at the B3LYP level and show a
different trend with oligomer length. For instance, when going from $T_2$ to $T_8$, the
NM/B3LYP calculations result in a decrease of $\lambda^1$ by 104 meV, which is in marked
contrast with the NM/BHandHLYP evolution of only 3 meV.

It is also important to note that the relative contributions of each vibration to
the relaxation energy do not scale in the same way at the B3LYP and
BHandHLYP levels but are mode dependent. This fact is clearly seen in figure 4,
which shows the decomposition of the cation relaxation energy ($\lambda^1$) into NMs for
$T_3$. The largest difference is observed for the lowest torsional mode.

It is also interesting to note that the ratio between the contributions of high-
and low-energy vibrations to relaxation energy depends on the oligomer size.
This is shown in figure 5, where we collect separately the contributions to the
reorganization energy coming from modes with frequency smaller than 200 cm$^{-1}$
($\lambda^\text{low}_0$ and $\lambda^\text{low}_1$) and larger than 200 cm$^{-1}$ ($\lambda^\text{high}_0$ and $\lambda^\text{high}_1$). With both functionals,
the low-frequency contribution to the total reorganization energy reaches
saturation for the octamer. However, for the high-frequency components, the
B3LYP relaxation energies decrease significantly with chain length, while the
BHandHLYP values remain almost constant within approximately 40 meV.

In the solid-state, the oligothiophenes tend towards a more coplanar
conformation (Fichou 2000); this makes the impact of the dihedral angle on the
relaxation energy less important. In order to evaluate this effect, we investigated

Table 3. Relaxation energies for the thiophene oligomers obtained from normal mode (NM) and
adiabatic potential surface (APS) calculations.

<table>
<thead>
<tr>
<th>system</th>
<th>B3LYP</th>
<th>BHandHLYP</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>NM</td>
<td>PES</td>
</tr>
<tr>
<td></td>
<td>$\lambda^0$ (meV)</td>
<td>$\lambda^1$ (meV)</td>
</tr>
<tr>
<td>$T_1$</td>
<td>212</td>
<td>200</td>
</tr>
<tr>
<td>$T_2$</td>
<td>198</td>
<td>187</td>
</tr>
<tr>
<td>$T_3$</td>
<td>168</td>
<td>162</td>
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<td>$T_4$</td>
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<td>$T_5$</td>
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<td>$T_6$</td>
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</tr>
<tr>
<td>$T_7$</td>
<td>138</td>
<td>126</td>
</tr>
<tr>
<td>$T_8$</td>
<td>132</td>
<td>119</td>
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the situation where the neutral geometry was forced to remain coplanar during the optimization. We note that the cation state is coplanar according to the calculations with both functionals. The relaxation energies computed with and without planarity constraints using both B3LYP and BHandHLYP functionals are shown in figure 6.

Figure 4. Contribution of each NM to the cation relaxation energy using the BHandHLYP and B3LYP functionals for terthiophene (T₃).

Figure 5. Evolution, as a function of oligomer length, of the low- and high-frequency components of the neutral and cation relaxation energies at the (a) B3LYP and (b) BHandHLYP levels.

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As seen from figure 6, in the coplanar case, the B3LYP estimates of $\lambda_0$ and $\lambda_1$ nearly coincide. When going from a coplanar to a non-coplanar situation, the cation relaxation energy ($\lambda_1$) increases significantly (54–31 meV for $T_2$–$T_8$); in contrast, the relaxation energy ($\lambda_0$) of the neutral state is not affected by the torsion. These results can be easily understood from the shape of the PESs. The PES of the cation with respect to the torsional degree of freedom is harmonic and reaches its absolute minimum at the coplanar geometry. On the other hand, at the B3LYP level, the PES of the neutral state along these coordinates displays two equivalent minima separated by a very shallow transition state located at the coplanar conformation (which means that the PES is flat). It is clear that, when the geometry of the neutral molecule is kept coplanar, there cannot be large contributions from torsional motions to both $\lambda_1$ and $\lambda_0$. In contrast, for a non-coplanar neutral geometry, there is a significant contribution to $\lambda_1$ coming from the geometry relaxation along the torsional degree of freedom; however, due to the flatness of the neutral-state PES, $\lambda_0$ is not affected by torsional motions. At the BHHandHLYP level of calculation, the corresponding activation barrier of the neutral state is calculated to be much larger. Therefore, the BHHandHLYP estimates of $\lambda_0$ obtained with and without planarity constraints are different.

(e) Frank–Condon analysis of the ultraviolet photoelectron spectra

The NM analysis has been further exploited to simulate the shape of the first ionization peak in the UPS spectra. As in the case of oligoacenes, we first use a procedure based on a linear vibronic model described in detail in Malagoli et al. (2004). The results of the simulation for $T_3$ are shown in figure 7.

We have recently shown (Sánchez-Carrera et al. 2006) that in oligoacenes BHHandHLYP overestimates the relaxation energies related to ionization processes in oligoacenes, while the non-hybrid BLYP functional underestimates the relaxation (by up to 30%); overall, the best agreement between simulated and experimental UPS spectra in oligoacenes was obtained at the B3LYP level. In the case of oligothiophenes, neither BHHandHLYP nor B3LYP is actually able
to reproduce very well the shape of the first ionization band. It appears that at least for the high-energy vibrations of oligothiophenes, BHandHLYP overestimates the vibrational coupling and B3LYP underestimates it; however, a definitive conclusion is difficult to draw at this stage. As is clear from figure 7, despite a significant contribution to the relaxation energy from the torsional degrees of freedom, the linear vibronic model cannot explain the lack of

Figure 7. Experimental and simulated B3LYP and BHandHLYP first ionization peak for terthiophene (T₃).

Figure 8. Experimental and simulated first ionization of T₄: (1) linear vibronic model; (2) linear and quadratic vibronic model. The linear coupling constants were obtained at the B3LYP level and multiplied by a factor of 1.3. ω₀ was chosen to be 10 cm⁻¹ for the neutral state and 100 cm⁻¹ for the cation state.
vibrational structure in the UPS spectra of oligothiophenes. Thus, other mechanisms, such as strong mode mixing, quadratic vibronic coupling (Gierschner et al. 2002) and/or anharmonicity of the PES (Heimel et al. 2005), are contributing to the broadening of the UPS bands. As an illustration, in figure 8 we show how the results obtained for $T_4$ from a linear vibronic model (displaced oscillators) evolve when a quadratic vibronic coupling (distorted oscillator) to a vibrational mode $\omega_0$ that changes from 10 to 100 cm$^{-1}$ upon ionization is added to the linear vibronic model. As seen from figure 8, the inclusion of quadratic coupling reproduces reasonably well the experimental shape. Since these are only model calculations, a more detailed study of this issue is needed and will be reported elsewhere. However, it can be stated that, while the flexibility of the oligothiophene backbone is responsible for the large broadening of the UPS spectra, this broadening is not simply due to the additional relaxation coming from large torsional motions.

5. Conclusion

DFT was used to compute the electronic structure of a series of thiophene oligomers in the neutral and cation states using two functionals, B3LYP and BHandHLYP. The calculated ionization potentials obtained from potential energy differences and using Koopmans’ (1933) theorem were compared with the experimental data; the best agreement was obtained with the B3LYP functional. The relaxation energy calculated with the BHandHLYP functional is larger than with the B3LYP functional; the difference mainly comes from the high-frequency mode contributions. The evolution, as a function of oligomer length, of the low-frequency component of the reorganization energy is qualitatively the same for both functionals; this evolution differs from that of the high-frequency term, where the B3LYP values decrease with chain length, whereas the BHandHLYP values remain constant within 40 meV. Our result reveals that in oligothiophenes, as in the case of oligoacenes, BHandHLYP overestimates the vibrational coupling and B3LYP underestimates it. Overall, however, the B3LYP estimates seem to better reproduce the experimental trends.

The lineshape of the first ionization bands in $T_3$ and $T_4$ were compared with the simulated spectra computed using the B3LYP and BHandHLYP Frank–Condon factors. We have shown that despite a significant contribution to the relaxation energy from the torsional degrees of freedom, the linear vibronic model cannot explain the lack of vibrational structure in the UPS spectra of oligothiophenes, and that other mechanisms, such as quadratic vibronic coupling, also contribute to the broadening of the UPS bands.

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