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Triplet states in oligomeric materials: Electron energy loss spectroscopy of thiophene and bithiophene and extrapolation to the polymer

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High-resolution electron-energy-loss spectra of thiophene and bithiophene have been measured in the range of the low-lying singlet–triplet excitations. In combination with *ab-initio* calculations the observed vibrational structure within the $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ bands of thiophene is assigned and adiabatic transition energies are determined. The study of bithiophene aimed at the search for the $S_0 \rightarrow T_2$ band. This transition has not been unambiguously located. The adiabatic $S_0 \rightarrow T_1$ energy of thiophene, together with previous results from literature, yields a consistent set of solid phase data that can be used to model the chain length dependence of $S_0 \rightarrow T_1$ excitation energies in oligothiophenes. Based on this data set and others, currently used extrapolation procedures aiming at a prediction of polymer excitation energies are evaluated. In addition, it is shown that recent semiempirical calculations do not correctly describe the convergence of the $S_0 \rightarrow T_1$ energies towards infinite chain length. It is therefore advisable to apply suitable modern *ab-initio* methods to this problem.

1. Introduction

Triplet excitations are relevant to the function of molecular materials in optoelectronic applications because they are formed with high quantum yield when intersystem crossing is effective. Their long lifetime enhances energy migration and consequently trapping and charge carrier formation.[1] Therefore a comprehensive characterization of triplet energy levels in molecular materials is important.

Oligomers attract particular attention among the optoelectronic molecular materials because their electronic properties can be tuned by variation of the molecular chain length. Furthermore, an extrapolation of the excitation energies towards infinite chain length can provide an estimate of polymer properties. Recently, such an extrapolation by means of a simple particle-in-a-box model (free electron molecular orbital, FEMO model[2,3]) has been attempted for the lowest triplet states of oligothiophenes.[4,5] One of these studies[4] included an excitation energy for the monomer thiophene that was deduced from a weak phosphorescence band and assigned to the adiabatic $S_0 \rightarrow T_1$ transition.[6] Unless Franck–Condon overlap is poor due to strong geometry changes the use of adiabatic in contrast to vertical transition energies is preferable for studying the chain length dependence of oligomer properties, because their experimental determination is less ambiguous. Difficulties in using vertical transition energies stem from the fact that the center of gravity of the total band intensity, which defines the vertical transition, can often not be determined because only part of the band is investigated or

observable. Also, the maximum of the band which is frequently used as alternative means to locate the vertical transition may shift depending on the energy resolution of the spectroscopic method. In contrast to that, adiabatic transition energies are unambiguously defined as the lowest vibronic transition of an electronic band. Therefore, the use of adiabatic transition energies also facilitates the comparison of results from excitation spectroscopy of the neutral species and recent photodetachment photoelectron spectroscopy (PD-PES)[1] which involves anion states.

Previous measurements of the triplet excitation energies in thiophene using gas phase electron energy loss spectroscopy (EELS) did not reveal any vibrational fine structure.[7] Information on the solid phase, *i.e.* an environment relevant to applied materials, does not exist at all. As most important problem, the adiabatic $S_0 \rightarrow T_1$ transition of both gaseous and solid thiophene remains to be located. Similarly, the position of the second triplet state of bithiophene has not been unambiguously determined.[1] Therefore we have decided to reinvestigate the monomer and the dimer by use of high-resolution EELS. In addition, as intermolecular interactions can have an influence on the exact position of an electronic transition, we also investigated the magnitude of this effect by comparing transition energies for gaseous and solid thiophene. Only the gas phase spectrum allows us to determine the difference between the adiabatic and the vertical transition energy which is necessary for a comparison with recent theoretical results.[8] In contrast, solid phase EEL spectra are subject to multiple scattering effects that produce an asymmetric broadening of the electronic bands. Finally, the validity of the previous extrapolation procedures is discussed on the basis of the set of $S_0 \rightarrow T_1$ transition data augmented by our new results.

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2. Experiments and calculations

The experiments on solid samples were performed using a high-resolution electron energy loss spectrometer (HREEL) consisting of a double pass monochromator and a single pass analyser with cylindrical deflectors as energy dispersing elements contained in an ion pumped UHV system. The setup was described in detail previously.[9] All spectra were acquired under a specular scattering geometry with both monochromator and analyser set at an angle of 60° with respect to the surface normal. The energy resolution was adjusted around 10 meV. The incident energy (E_0) was calibrated to within ±0.2 eV using the onset of the current transmitted through the deposited films (transmission curve) and corrected for cut-off effects of the lenses. The energy-loss scale was calibrated within ±1 meV with respect to the maximum of the elastic peak.

Thiophene and 2,2′-bithiophene were purchased from Acros and Merck at stated purities of > 99% and 97%. Thiophene was further purified following the directions given in ref. 10, while bithiophene was purified by sublimation. Both substances were subjected to repeated pump–thaw cycles before film deposition. Thin films were prepared by condensing the gas on top of a polycrystalline platinum substrate at temperatures between 30 and 35 K. The film thickness of thiophene was estimated from the amount of gas needed to deposit a monolayer. The monolayer was calibrated by comparison with previous experiments on benzene[11] assuming the number density within one layer was similar for the two compounds. The amount of gas needed to deposit a monolayer of bithiophene was estimated from this by taking into account the difference in molecular size. A UV spectrum of bithiophene was recorded using a Shimadzu UV-2401PC spectrometer.

The trochoidal electron spectrometer used in the present gas phase experiments has been described in detail previously.[12–14] It uses magnetic collimation of the electron beams, trochoidal monochromators as electron energy filters, and a collision chamber with small apertures for the incident and scattered electron beams. The experiment involves intercepting the sample vapor at low pressure ($\sim 10^{-3}$ mbar) with a beam of electrons of varying incident energy E_0 and detecting electrons scattered at a fixed residual energy E_r. The present spectrum was recorded with a low residual energy, that is under conditions where singlet–triplet excitations are favored. The cross-sections for excitation of the triplet states are not forward peaked, but more isotropic with respect to the scattering angle. The capacity of the present instrument to detect the backward and forward scattered electrons with nearly equal efficiency thus significantly enhances the detection of triplet states.

The calculations were performed with the program Gaussian98[15] using the CIS method and 6-311+G(d,p) basis set. The CIS method has recently successfully been applied to predict the vibronic structure of the lowest excited states of cyclopentadiene[16] and is therefore assumed to be suited for the present problem. Other basis sets were applied as well and give similar results. Optimized geometries of S_0, T_1, and T_2 were calculated without symmetry restrictions and using different starting geometries. Cartesian force constants were obtained from analytical second derivatives. The frequencies were scaled using a constant factor chosen to yield the best possible agreement between calculated and experimental ground state frequencies. The same scaling factor was then applied in the excited state calculations. The spectral intensities within the electronic band were calculated from Franck–Condon factors between the S_0 zero vibrational level and the T_n fundamentals i resulting from displacement parameters B_i defined by[17]

$$B_i = \left(\frac{\omega_i}{\hbar}\right)^{1/2} Q_{i0}^1 \qquad (1)$$

with

$$Q_{i0}^1 = (\boldsymbol{x}_0 - \boldsymbol{x}_j)^{\mathrm{T}} \boldsymbol{M}^{1/2} \boldsymbol{L}_i^1, \qquad (2)$$

where $\boldsymbol{x}_j$ is the $3N$-dimensional vector of the equilibrium Cartesian coordinates in the jth state, $\boldsymbol{M}$ is the $3N \times 3N$ diagonal matrix of the atomic masses, and $\boldsymbol{L}_i^1$ the $3N$ vector of the normal coordinate i in terms of mass-weighted coordinates. The intensity of a vibronic band with vibrational quantum number $v = \{v_1, v_2, \ldots, v_n\}$ is then given by

$$I_v^{S_0 - T_j} \propto \prod_{k=1}^{n} \frac{(B_k^{2v_k})}{2^{v_k} v_k!} \qquad (3)$$

The calculated spectra are finally generated by representing the single vibronic bands by Gaussian functions with a width that reproduces the experimental resolution.

3. Results

Survey EEL spectra of thiophene recorded at an incident energy of 10.5 eV in the solid phase and at a residual energy of 3.3 eV in the gas phase are shown in Fig. 1. The two lowest triplet bands, 1^3B_2 and 1^3A_1, are clearly discernible. They have been observed in an earlier gas phase study but their fine structure could not be resolved.[7] The 1^3B_2 band has an onset at 3.2 eV and a broad maximum around 3.9 eV in the solid phase and 3.74 eV in the gas phase. It is diffuse with only weak fine structure visible (shown more clearly further below) close to the onset in the solid phase spectrum. A more comprehensive gas phase study has shown that the position of the maximum does not depend on the impact energy.[14] The high energy shift of the maximum in the solid is rather due to multiple electron scattering which tends to broaden bands towards high energy losses. The 1^3A_1 band has a distinct vibrational fine structure with peaks at 4.47, 4.58, and 4.69 eV in the solid phase and at 4.50 and 4.62 eV in the gas phase, indicating a gas-to-solid phase shift of about 30 meV. This is of the same order of magnitude as shifts observed previously for triplet bands in other molecules.[11,18] The gas phase spectrum reveals an additional weak shoulder at 4.38 eV that has no correspondence in the solid phase. Its origin will be discussed below.

In order to locate the energy of the $S_0 \rightarrow T_1$ transition more exactly, the solid phase spectrum was refined between 3.0 and
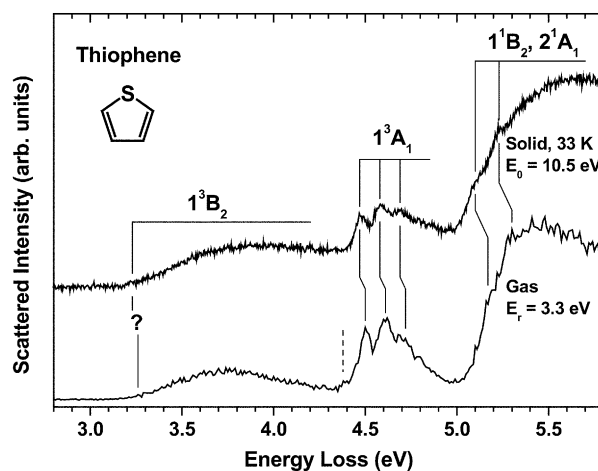

Fig. 1 EEL spectrum of a solid 10-layer film of thiophene deposited at 33 K recorded under specular geometry at a constant incident energy of 10.5 eV and gas phase EEL spectrum of thiophene recorded with the trochoidal spectrometer at a residual energy of 3.3 eV. ? indicates that gas to solid phase shift is uncertain due to weakness of the fine structure in the gas phase.
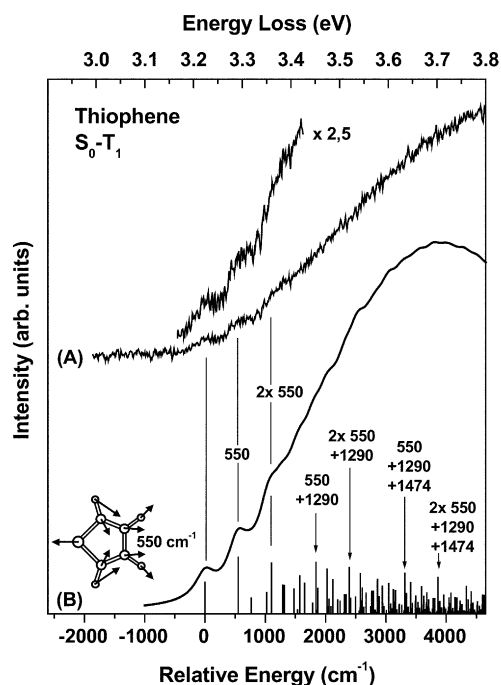
Fig. 2 (A) Refined solid phase EEL spectrum of the $S_0 \rightarrow T_1$ band of thiophene recorded under the same conditions as the survey spectrum in Fig. 1 and (B) Franck–Condon fine structure and strongest active vibration predicted from a CIS/6-311+G(d,p) calculation. The energy scale refers to the vibronic 0–0 band as deduced from the calculated spectrum.

3.8 eV (Fig. 2). This spectrum shows more clearly two bands at 3.23 and 3.30 eV. At higher energy losses the band is diffuse. The value of 3.23 eV is considerably lower than the presumed 0–0 band at 3.42 eV reported from the phosphorescence study of thiophene in solid solution[6] and would imply an environmental shift of 190 meV between the solution and the pure solid phase. A shift of this magnitude is much larger than values reported for other compounds of similar size. For example, the $S_0 \rightarrow T_1$ (0–0) transition for benzene has been reported to vary from 3.655 eV in dioxane (90 K)[19] and 3.658 eV in cyclohexane (4.2 K)[20] to 3.665 eV and 3.676 eV in an amorphous and crystalline solid film (33 K).[11] Other examples documenting similarly small $S_0 \rightarrow T_1$ shifts are collected in ref. 17. In the light of these results and given that the solid phase and gas phase $S_0 \rightarrow T_1$ excitation energies of thiophene nearly coincide, a shift 190 meV between different environments appears unlikely. Therefore our results raise doubts about the origin of the weak phosphorescence signal reported earlier.[6]

The question remains if the band at 3.23 eV is the 0–0 transition to the 1^3B_2 state or whether the origin lies at an even lower energy. We attempt to answer this question by simulating the band profile using CIS force field calculations for the ground and excited state. Table 1 shows the calculated frequencies and B values for the totally symmetric vibrations. The simulated spectrum, included in Fig. 2, is very similar to the experimental result. It is characterised by two distinct maxima at the onset of the band followed by a shoulder and diffuse structure at higher energy. The good agreement between the experimental and calculated profiles confirms that the first maximum of the experimental 1^3B_2 band is the 0–0 transition. The apparent lack of vibrational structure at higher energies is explained by a high Franck–Condon activity of a low frequency ring deformation mode calculated at 550 cm^{-1} (68 meV), which is best described as an elongation of the ring along the axis cutting through the S atom, $i.e.$ a movement involving CCC and CSC bending (Fig. 2). In the line spectrum at the bottom of Fig. 2 this vibration appears alone and in

Table 1 Frequencies of totally symmetric vibrations of thiophene and B values for the $S_0 \rightarrow T_n$ excitations predicted by CIS/6-31+G(d,p)

S_0		T_1		T_2	
ν_{exp}/cm^{-1} [a]	ν_{calc}/cm^{-1} [b]	ν_{calc}/cm^{-1} [b]	B	ν_{calc}/cm^{-1} [b]	B
609	655 (605)	595 (550)	1.90	588 (543)	0.66
840	884 (817)	830 (767)	1.00	833 (770)	1.10
1036	1097 (1014)	1105 (1021)	1.16	953 (881)	1.31
1082	1196 (1105)	1189 (1099)	0.68	1190 (1100)	0.33
1364	1515 (1400)	1396 (1290)	1.35	1442 (1332)	0.30
1410	1569 (1450)	1595 (1474)	1.26	1668 (1541)	0.51
3097	3364 (3108)	3373 (3117)	0.00	3387 (3130)	0.00
3126	3398 (3140)	3405 (3146)	0.14	3415 (3155)	0.14

[a] From ref. 21. [b] Values in parenthesis are scaled by a factor of 0.924.

combination with several other modes. Only a few representative combinations are marked by arrows there.

The diffuse nature of the $S_0 \rightarrow T_1$ transition is in accord with previous experimental findings for the same band in cyclopentadiene[14,22] and furan.[23] In the latter case it was argued that the diffuseness may stem from a fast photochemical reaction.[23] Theoretical evidence for cyclopentadiene,[16] on the other hand, is in line with our interpretation that the apparent lack of structure results from the activity of low-frequency vibrations that can not be resolved at a resolution typical of EELS. In particular, the diffuse nature of the cyclopentadiene $S_0 \rightarrow T_1$ band has been ascribed to the Franck–Condon activity of a low frequency CCC bending vibration.[16] The good agreement between the $S_0 \rightarrow T_1$ band shapes of thiophene and cyclopentadiene is not surprising given that the calculated geometry changes upon excitation are similar.[24] The bonds S–C$_1$ in thiophene and C–C$_1$ in cyclopentadiene expand slightly whereas C$_1$–C$_2$ is in both cases enlarged by roughly 8% upon excitation to T$_1$. C$_2$–C$_{2'}$, on the other hand, shrinks by 6% in thiophene and 7% in cyclopentadiene.

It is also instructive to compare calculated and experimental Stokes shifts, $i.e.$ the difference between adiabatic and vertical transition energies. Although the adiabatic transition in cyclopentadiene has been resolved both in gas phase spectra at 2.55 eV[14] and solid phase spectra at 2.555 eV[22] a Stokes shift can only be extracted from the experimental gas phase results because of the effect of multiple scattering on the solid phase band maximum. From the gas phase band maximum at 3.15 eV[14] we obtain an experimental Stokes shift of 0.60 eV. This is in good agreement with the calculated value of 0.66 eV.[16] In the case of thiophene the Stokes shift is estimated at 0.51 eV from the gas phase band maximum and the presumed solid phase 0–0 transition assuming only a minor gas to solid shift for the $S_0 \rightarrow T_1$ band. This is again close to the calculated difference between the adiabatic and vertical transition energies as seen in Fig. 2. This provides additional evidence that the assignment of the 3.23 eV band to the adiabatic $S_0 \rightarrow T_1$ transition of thiophene is indeed correct.

The main features of the $S_0 \rightarrow T_2$ band shape are equally well reproduced by the calculations (Table 1 and Fig. 3). Again, only the assignments of the most intense vibronic bands are marked in the plot. The good agreement between experiment and calculation implies that the first vibronic band in the solid state spectrum is the 0–0 transition. The calculation does not account for the weak band at the onset of the transition in the gas phase spectrum. The observation that this structure is missing in the solid phase spectrum recorded at much lower temperature suggests an assignment as hot band. This is supported by the fact that its observed relative intensity is comparable to that of a hot band with similar frequency in the gas phase spectrum of benzene.[25]

The difference between the band shapes of the $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ transitions of thiophene is explained by the different
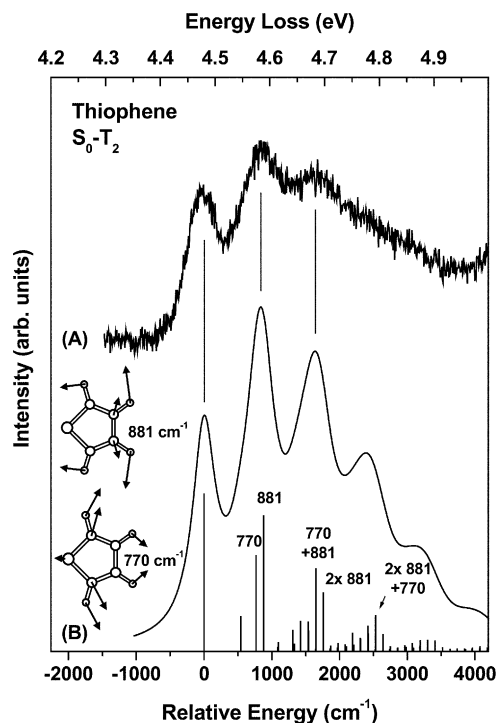
Phys. Chem. Chem. Phys., 2003, **5**, 827–833 **829**

Energy Loss (eV)

4.2 4.3 4.4 4.5 4.6 4.7 4.8 4.9

Thiophene
S_0-T_2

Intensity (arb. units)

(A)

881 cm^{-1}

770 cm^{-1}

(B)

881

770

770
+881

2x 881

2x 881
+770

Relative Energy (cm^{-1})

-2000 -1000 0 1000 2000 3000 4000

Fig. 3 (A) Refined solid phase EEL spectrum of the $S_0 \rightarrow T_2$ band of thiophene recorded under the same conditions as the survey spectrum in Fig. 1 and (B) Franck–Condon fine structure and strongest active vibrations predicted from a CIS/6-311+G(d,p) calculation. The energy scale refers to the vibronic 0–0 band as deduced from the calculated spectrum.

structural properties of the two excited states.[24] The T_1 structure shows an inversion of the relative C–C bond lengths with respect to the ground state. Thiophene must therefore exhibit a more biradicaloid character in this state. In contrast, the T_2 geometry is similar to the ground state but the bonds are generally longer. Therefore the $S_0 \rightarrow T_1$ transition is dominated by the low frequency ring elongation mode while the ring enlargement during the $S_0 \rightarrow T_2$ transition is better reproduced by the 770 cm^{-1} (95 meV) and 881 cm^{-1} (109 meV) modes of which the former can be described as ring breathing and the latter is largely represented by the stretching of the long C–C single bond (Fig. 3).

The solid phase EEL spectrum of bithiophene (Fig. 4) shows the expected lowering of the excitation energies with respect to the monomer. The $S_0 \rightarrow T_1$ transition appears as a diffuse band with an onset at ~2.3 eV. This value is close to the position of the adiabatic transition observed in both the photodetachment photoelectron spectrum (PD-PES) of gaseous bithiophene anion [2.28 eV (ref. 1)] and the phosphorescence excitation spectrum of crystalline bithiophene [2.26 eV (ref. 5)]. The band shift with respect to the monomer is smaller for the lowest triplet band than for the lowest singlet band where it amounts to roughly 1.5 eV.

While PD-PES of tertthiophene and quaterthiophene clearly showed T_2 this state is most probably overlapping with S_1 in the PD-PES spectrum of bithiophene.[1] Therefore we carefully searched the EEL spectrum of bithiophene for contributions from the $S_0 \rightarrow T_2$ transition. A comparison with the UV spectrum obtained in cyclohexane solution hints towards broadening of the EEL spectrum at the low-energy side of the lowest singlet band. This additional intensity could tentatively be assigned to contributions of the $S_0 \rightarrow T_2$ transition, indicating that T_2 lies adiabatically slightly below S_1. The shift between the two transitions is estimated from the onsets in the UV and EEL spectrum (Fig. 4) not to exceed 40 meV. On the other hand, exact solvent shifts for the singlet band of bithiophene
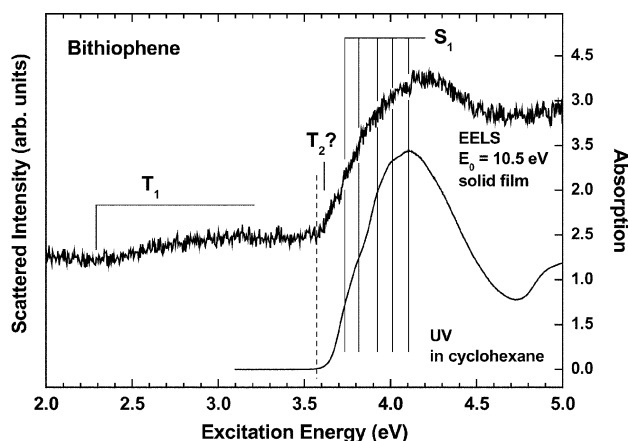
Bithiophene

T_1

T_2?

S_1

Scattered Intensity (arb. units)

EELS
E_0 = 10.5 eV
solid film

UV
in cyclohexane

Absorption

Excitation Energy (eV)

2.0 2.5 3.0 3.5 4.0 4.5 5.0

Fig. 4 EEL spectrum of solid bithiophene deposited at 33 K and recorded under specular geometry at a constant incident energy of 10.5 eV and UV spectrum of a solution of bithiophene in cyclohexane. The dashed line serves as a guide to the eye for the comparison of the onset.

with respect to the solid phase are not known so far. In addition, a similar broadening with respect to solution spectra was previously observed in an optical spectrum of a solid quaterthiophene film [26] and must consequently be ascribed to an effect of intermolecular interactions on the singlet excitons. A similar mechanism may be effective in the present bithiophene sample. Therefore the evidence for the location of the $S_0 \rightarrow T_2$ transition is not entirely firm.

4. Discussion

With the new value for the $S_0 \rightarrow T_1$ excitation energy of thiophene a consistent set of experimental data for the investigation of chain length dependent properties of oligothiophenes can be established. All values represent adiabatic excitation energies from solid phase measurements, that is from an environment relevant to molecular materials. The data, together with alternative data sets from gas-phase photodetachment photoelectron spectroscopy (PD-PES) and photoacoustic calorimetry (PAC) in dioxane solution, are collected and compared to theoretical excitation energies in Table 2.

In order to predict the excitation energy of longer oligomers or the polymer, an extrapolation of excited state energies for shorter oligomers to the value for infinite chain length is required. This has repeatedly been attempted for the lowest excited states of oligothiophenes.[1,4,27,28] The simplest extrapolation procedure relies on the assumption of a $1/N$ dependence of the excitation energies on the chain length with N representing the number of π-electrons in the conjugated chain.[1,4,5] Depending on the data set used the $1/N$ plot only yields a roughly linear fit. Visual inspection of the figures in refs. 1 and 4 suggests that the previously obtained phosphorescence signal is somewhat too high when compared to the other values from both the PAC[4] and PD-PES[1] data sets. Fig. 5(a) shows the T_1 energies from the solid phase experiments, from PAC and PD-PES. A $1/N$ fit was obtained for each set excluding the monomer value. It is obvious that a very good fit can be obtained for the oligomer values of each data set while the monomer energies deviate from this linear behavior. This deviation might be explained by the fact that the monomer values stem from different experiments but it is especially strong for the PAC data set although the presumed monomer phosphorescence has also been obtained in solution.[6] Unfortunately, the solvent was not reported so we can only speculate on the reason for this deviation. On the other hand, this simple extrapolation procedure does not take into account geometry

Table 2   Electronic transition energies (in eV) and FEMO fits from different experiments and from semiempirical calculations

Molecule	$S_0 \rightarrow S_1{}^a$ max, in dioxane	$S_1 \rightarrow S_0{}^b$ first max, in dioxane	$S_0 \rightarrow S_1{}^c$ (0–0), in dioxane	$S_0 \rightarrow T_1{}^d$ (0–0), gas	$S_0 \rightarrow T_1{}^e$ (0–0), in dioxane	$S_0 \rightarrow T_1{}^f$ (0–0), solid	$S_0 \rightarrow T_1{}^g$ vert. INDO/MRDCI
1T			4.93	3.44^i	3.50^i	3.23	
2T	4.05	3.67^h	3.71	2.28	2.23	2.28	1.84
3T	3.49	3.04	3.17	1.92	1.92	1.88	1.68
4T	3.16	2.75	2.86	1.76	1.81	1.67	1.61
5T	2.99	2.57	2.69		1.72	1.58	1.61
6T	2.85	2.45	2.55				1.65
7T			2.50		1.60		
FEMO:							
d/Å	1.39	1.40			2.45	1.75	1.8
l	1 (const.)	1 (const.)	1.347		−0.418	1 (const.)	0.88
V_0/eV	2.167	1.74	1.87		1.43	1.02	1.07

^{a} Refs. 27 and 28. ^{b} Ref. 27. ^{c} Ref. 4, value estimated from the intersection of normalised absorption and fluorescence. The d value has not been reported. ^{d} Ref. 1, photodetachment photoelectron spectroscopy (PD-PES). ^{e} Ref. 4, photoacoustic calorimetry (PAC). The d value has not been reported and was obtained by reproducing the plot in ref. 4. ^{f} Value for 1T from present EELS, otherwise from ref. 5, phosphorescence excitation spectroscopy. ^{g} Ref. 8. ^{h} Ref. 29. ^{i} Ref. 6, phosphorescence, in variance with present EEL data.

changes upon excitation. These changes, on the other hand, are likely to be stronger in smaller π-electron systems as for example obvious from the increasing relative intensity of the 0–0 band within solution fluorescence spectra of larger oligothiophenes.[6] Therefore the deviation from a simple fit function should be strongest for the monomer. Interestingly, the slope of the linear fit is much smaller for the PAC data from solution than for the solid phase and gas phase results. We will come back to this observation below.

Another frequently used extrapolation procedure makes use of the FEMO (free electron molecular orbital) model[2,3] which employs a particle-in-a-box treatment assuming independent electrons. From this the excitation energies as function of N result as

$$\Delta E = \frac{h^2}{8 m_e d^2} \frac{(N+1)}{(N+l)^2} + V_0 \left(\frac{1}{N}\right) \qquad (4)$$

where d is identified with the average bond length along the chain, V_0 is a parameter expressing the tendency towards bond localisation, and l allows to adjust the effective length of the model box. The large number of parameters facilitates finding a good fit to the excitation energies including the monomer.

Table 2 also summarises the FEMO fits to data sets from different experiments. Singlet excitation energies are included for comparison. Absorption and fluorescence energies of the lowest singlet state generally appear to be well described.[1,4,27,28] The absorption bands are generally broad so that vertical transitions are often used while the fluorescence bands are structured and therefore yield adiabatic energies. Two of the fits[27,28] keep l constant and find a d parameter of about 1.4 Å (Table 2) which is a reasonable average value for conjugated double bonds. V_0, which represents the energy for infinite chain length, is larger for a fit to the absorption maximum than for a fit to the highest energy fluorescence maximum, as expected. An intermediate value results from a 3-parameter fit to the intersection of absorption and fluorescence curves which has been used to estimate the position of the adiabatic transition.[4] This consistent result supports the use of the FEMO model in the case of oligothiophenes.

The situation is different for the $S_0 \rightarrow T_1$ energies. Two previous studies have tried to obtain a FEMO fit to these data,[1,4] but both did not report the resulting d values. From the figures in ref. 1 and similar to the $1/N$ fit it is obvious that the gas phase $S_0 \rightarrow T_1$ energies augmented by the phosphorescence value[6] are less well described by the FEMO fit than the singlet excitations. In contrast, the results from photoacoustic calorimetry[4] together with the phosphorescence value[6] lead to a better fit. We have reproduced this fit and included it in Fig. 5b together with the FEMO fit to the solid phase $S_0 \rightarrow T_1$ energies. Most strikingly, a good fit to the $S_0 \rightarrow T_1$ energies can only be obtained with d values that are considerably larger than reasonable values of CC bond lengths (Table 2). A search for a fit with different parameters by using different starting
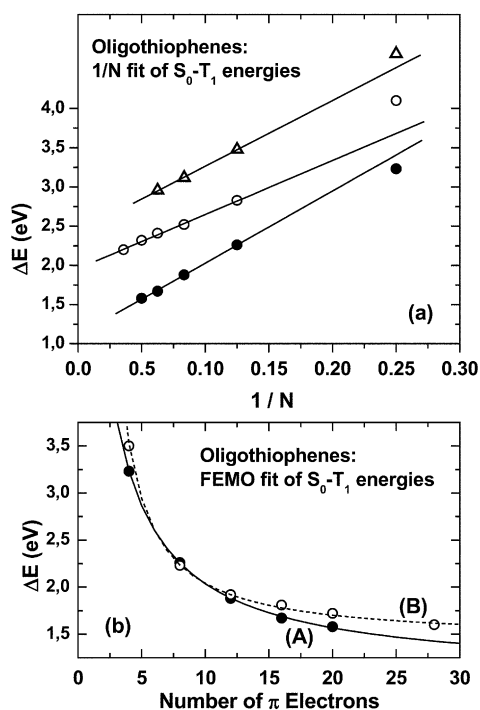

Fig. 5 (a) $1/N$ fit to the adiabatic $S_0 \rightarrow T_1$ transition energies from PD-PES in gas phase (△) offset by 1.2 eV,[1] from PAC in dioxane solution (○) offset by 0.6 eV,[4] and from solid phase measurements (●) of ref. 5 and the present work. Values for thiophene are included as used in the original work (△, ○) and obtained from the present EEL spectra (●) but not used in the fit. (b) FEMO fit to the solid phase (●, A) and PAC (○, B) data sets for the adiabatic $S_0 \rightarrow T_1$ transitions of oligothiophenes including all values. The resulting parameters are (A) $d = 1.80$ Å, $l = 0.88$, $V_0 = 1.07$ eV; (B) $d = 2.45$ Å, $l = -0.418$, $V_0 = 1.429$ eV (l and V_0 fixed according to ref. 4). Fits were obtained by using the Levenberg-Marquart algorithm implemented in Origin 6.0.[30]

values during the fit procedure was not successful. This is in line with the findings of a previous study on the low-lying excited states of different thiophene polymers that also did not produce a satisfactory FEMO fit for the triplet data.[31] Our result shows that the $S_0 \rightarrow T_1$ excitation energies can only be described within the FEMO model when clearly unphysical parameters d are used. An interpretation of the d values in terms of bond length must therefore be considered with caution regarding the $S_0 \rightarrow T_1$ transition of oligothiophenes and possibly also for other oligomers. This result is not surprising given that FEMO neglects electron interaction and is therefore not capable of describing energetic differences between different spin states. The FEMO model should therefore be regarded as a mere sophisticated fitting formula and previous attempts to ascribe some physical meaning to the effective box length described by the parameter l[4,28] should be treated with caution.

Similar care must be applied concerning the results of the semiempirical INDO/MRD-CI calculations[8] included in Table 2. In this study a rapid convergence of the excitation energies was ascribed to a more localised character of the triplet excitation along the chain as compared to singlet excitations. On the other hand, a comparison with the experimental data set in Table 2 shows that INDO/MRD-CI also does not correctly describe the convergence of the $S_0 \rightarrow T_1$ excitation energies with chain length. The vertical INDO/MRD-CI energies vary to a much smaller extent than the adiabatic experimental values. An increase of the excitation energy is even predicted between 5T and 6T. The gas phase EEL spectrum of thiophene (Fig. 1) shows that the vertical $S_0 \rightarrow T_1$ transition is located more than 0.5 eV above the adiabatic transition. The solid phase spectra of Figs. 1 and 4 demonstrate that the vertical transition also does not considerably move towards the 0–0 band in bithiophene. In contrast, the vertical INDO/MRD-CI transition energy for bithiophene is much lower than the experimental 0–0 band. Similar to the vertical and adiabatic excitation energies of singlet states[6] the two values probably approach each other in the triplet bands of larger oligomers. If this is true the vertical excitation energies should vary even stronger with chain length than the adiabatic values. In this light the INDO/MRD-CI results appear even worse. Conclusions about the localisation of the triplet excitation from this study therefore have to be questioned. The seemingly rapid convergence of the excitation energy is most probably produced by the spatial cut-off conditions for interaction terms inherent in semiempirical methods. Therefore, *ab-initio* calculations are highly desirable in order to obtain a better description of the electronic excitations.

Interestingly, the $S_0 \rightarrow T_1$ energies obtained from PAC in solution vary less with increasing chain length than the solid phase values (Fig. 5b). Such a difference can be explained by differences in the molecular geometries between the solid phase and the solution. While π–π interactions in the solid phase tend to stabilise a planar structure, twisting around the single bond linking the monomer units may occur in solution. This weakens conjugative interactions and therefore leads to a weaker variation of the excitation energies with chain length. The comparison of the $S_0 \rightarrow T_1$ energies in the two different environments underlines that a successful determination of polymer excitation energies by an extrapolation procedure also requires some insight into the actual conformation along the chain.

5. Conclusions

The vibrational structure within the two lowest triplet transitions of thiophene is observed for the first time. The general shapes of these bands are described well by Franck–Condon factors computed from the CIS method. This helps to locate the 0–0 band of the $S_0 \rightarrow T_1$ transition with certainty.

A previously reported phosphorescence signal[6] is in variance with the new result. A weak band at the onset of the $S_0 \rightarrow T_2$ transition that is observed in the gas phase is not explained by the calculations and is reassigned to a hot band. In contrast, convincing evidence about the location of the second triplet band of bithiophene is not obtained. This proves that T_2 in bithiophene is not located significantly, *i.e.* not more than 0.1 eV below S_1.

The new value for the $S_0 \rightarrow T_1$ excitation energy of thiophene allows us to establish an enlarged set of experimental data on the chain length dependent triplet excitation energy of oligothiophenes in the solid phase. This data set contains exact adiabatic excitation energies from the present and previous[5] measurements. Attempts to fit these data using the FEMO model show that the physical significance of the resulting parameters must be questioned at least in the case of spin-forbidden excitations. This is obvious from the fact that the fit produces an average C–C bond length that is much too large. Similarly, previous semiempirical calculations[8] clearly do not correctly describe the convergence of the excitation energies with chain length.

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