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Optical spectra of oligothiophenes: vibronic states, torsional motions, and solvent shifts

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Abstract

Low temperature fluorescence and absorption spectra of α,α' -quinguethiophene (5T) are almost mirror symmetrical due to small differences in the nuclear displacements of the vibronic modes in the electronic S_0 and S_1 states. The spectra are in good accordance with Franck–Condon calculations based on ab initio Hartree–Fock (HF/6-311G^{*}) and restricted configuration singles (RCIS/6-311G^{*}) quantum chemical calculations. With increasing temperature the spectra are broadened and blue-shifted, and the mirror symmetry between fluorescence and absorption is lost. The spectral shifts can be quantitatively correlated to the changes in the polarizability of the environment. Inhomogeneous broadening is simulated by convolution of the spectra with appropriate distribution functions. The loss of mirror symmetry, which occurs exactly at the melting point of the solvent, is well described by the excitation of torsional modes. Measurements of the oligothiophenes in different solvents allow the determination of the adiabatic transition energies in vacuo, which are compared to the quantum chemical calculations.

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Keywords: Oligothiophenes; Fluorescence spectra; Franck–Condon calculation; Temperature effects; Solvent shift; Quantum chemical calculations

1. Introduction

Oligothiophenes (nT , see Fig. 1) have been a prominent subject of research activities in the last 20 years for their potential in optoelectronic applications [1]. However, the complexity of the excited state deactivation processes in condensed materials, which is due to intermolecular interactions, requires a quantitative understanding of the optical and photophysical properties of the molecules in weakly interacting media such as solutions. Optical spectra of nT s were recorded in various solvents at different temperatures [2–12], but a systematic study on solvent shifts and inhomogeneous line broadening processes has not yet been presented.

In this work, the characteristics of the fluorescence and fluorescence excitation spectra of α,α' -quinguethiophene (5T), i.e. band positions, intensity distributions, and inhomogeneous line broadenings at different temperatures, are reproduced by a theoretical approach, which combines: (i) ab initio quantum chemical calculations of the involved electronic and vibronic states; (ii) calculation of low temperature

spectra from the obtained vibronic states by a Franck–Condon calculation; (iii) simulation of room temperature spectra by considering torsional motions; and (iv) consideration of solvent induced shifts.

2. Experimental

Fluorescence measurements of the oligothiophenes nT in different hydrocarbons (*iso*-pentane, 3-methyl-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, cyclohexane, decalin, polystyrene), were carried out on a Spex Fluorolog 222 spectrofluorimeter. For low temperature measurements, 5T was dissolved in tetradecane and the sample was placed in a closed cycle He cryostat.

The refractive indexes of the solvents at the wavelength of 5T fluorescence $n_{\text{solv}}(\lambda_e)$ were interpolated from literature values [13a] using Cauchy's dispersion equation. In order to obtain $n_{\text{solv}}(\lambda_e)$ of tetradecane at different temperatures, $n_{\text{solv}}(589 \text{ nm})$ was calculated by the molar refraction formula, inserting the atomic molar refractions [14a] and the density of tetradecane at the respective temperature, $\rho(T)$. The density $\rho(T)$ was calculated by $\rho = \rho_0/(1 + \alpha\Delta T)$ from the coefficient of volume expansion α and the densities $\rho_0(T = 20^\circ\text{C}) = 0.7628 \text{ g/ml}$ [14b] and $\rho_0(T \rightarrow 0 \text{ K}) \approx 1.08 \text{ g/ml}$ [15]. The refractive indexes $n_{\text{solv}}(\lambda_e)$ were then

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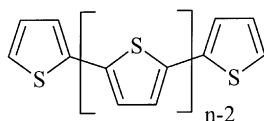


Fig. 1. Oligothiophenes nT ($n = 2–6$).

obtained from n_{solv} (589 nm) by correlating the calculated values of n_{solv} for various hydrocarbons with the experimental ones and extrapolating the straight line to the corresponding value for tetradecane.

The quantum chemical calculations, including: (i) the adiabatic transition energies; (ii) the equilibrium geometries; and (iii) the nuclear displacements of the vibrational modes were obtained at the ab initio Hartree–Fock (HF/6-311G*) and restricted configuration singles (RCIS/6-311G*) level of theory. The vibrational frequencies were calculated by the B3LYP/6-311G* method, rather than scaling the HF and RCIS frequencies, which are known to overestimate the experimental frequencies by about 10%. All quantum chemical calculations were carried out with the Gaussian98 program, assuming a planar geometry (C_{2h} for $n = \text{even}$, C_{2v} for $n = \text{odd}$). The Franck–Condon calculation of vibronic coupling as well as the numerical convolution of the spectra were performed with in-house programs.

3. Results and discussion

3.1. Fluorescence and absorption spectra

At low temperatures in appropriate solvents (e.g. 5T in tetradecane, see Fig. 2), the fluorescence emission and excitation spectra of oligothiophenes nT are almost mirror symmetrical. Thus, the frequencies and nuclear displacements of the vibrational modes, which couple to the $S_0 \leftrightarrow S_1$

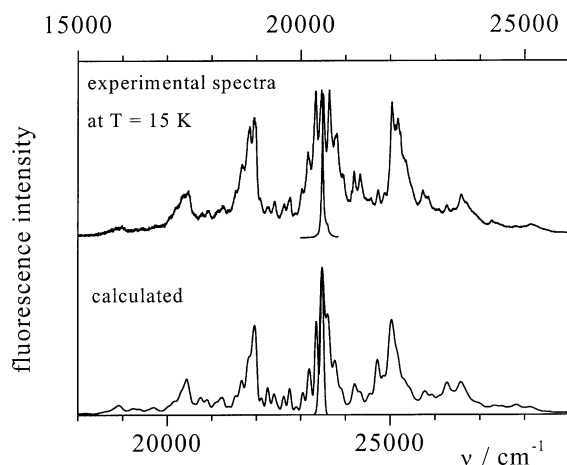


Fig. 2. Low temperature fluorescence emission (left) and excitation spectra (right) of 5T. Top: experimental spectra in tetradecane at $T = 15$ K. Bottom: calculated at the HF/6-311G* and RCIS/6-311G* level. Inserted Gaussian half-widths: 130 cm^{-1} .

electronic transition, are very similar in the S_0 and S_1 states, respectively. The low temperature fluorescence and absorption spectra are calculated by a Franck–Condon calculation, using the adiabatic transition energies, as well as the equilibrium geometries and the nuclear displacements and frequencies of the complete sets of the total symmetrical vibrational modes in the S_0 and S_1 states, as obtained from the quantum chemical calculations (details of the calculation are given elsewhere [15]). The calculated fluorescence and absorption spectra are in good accordance with the experimental ones. Larger deviations in the intensity distribution are only found for the longitudinal in-plane deformation modes, which are predicted at the B3LYP/6-311G* level to be 120 and 136 cm^{-1} , and which underestimate the experimental Huang–Rhys S_k factors by about 30%. However, the overall intensity distribution is very similar in the experimental and calculated spectra, which becomes apparent from the comparison of the experimental and theoretical equilibration energies Δv . Experimentally, Δv is given by the difference between the center of gravity of the fluorescence spectrum and the electronic origin [15], yielding $\Delta v_{\text{exp}} = 1670 \text{ cm}^{-1}$. Using the results of the quantum chemical calculations, the equilibration energy is calculated [16] to be $\Delta v_{\text{calc}} = \sum S_k v_k = 1710 \text{ cm}^{-1}$ for the absorption spectrum, and 1770 cm^{-1} for the fluorescence spectrum, respectively.

With increasing temperature, the fluorescence and absorption spectra are broadened due to thermal excitations of vibronic modes but also due to the increase in the inhomogeneity of the solvent (Fig. 3). However, the fluorescence spectrum still reveals some vibronic structure, whereas the absorption spectrum is unstructured and asymmetrically shifted to the blue. Thus the mirror symmetry, which is

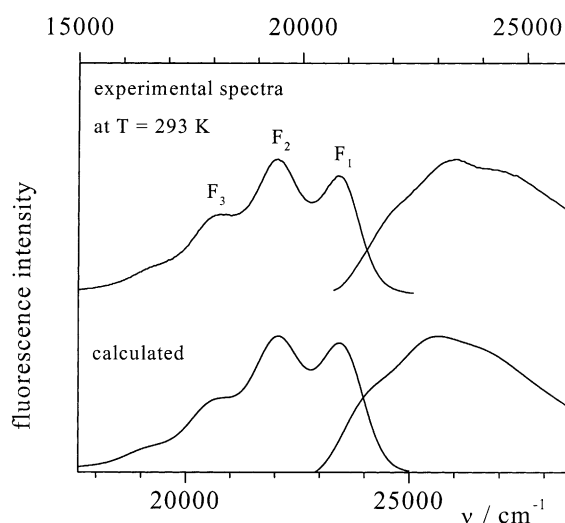


Fig. 3. Room temperature fluorescence emission (left) and excitation spectra (right) of 5T. Top: experimental spectra in tetradecane at $T = 293$ K. Bottom: calculated at the HF/6-311G* and RCIS/6-311G* level. The spectra were convoluted with a Gaussian distribution (half-width: 1100 cm^{-1}), and with an exponential distribution ($D = 9.0$, $T = 293$ K).

present at low temperatures, is lost. These effects are ascribed to the higher torsional mobility of the *n*Ts (or comparable molecules like oligophenylenevinyls) in the electronic ground state S_0 compared to the S_1 state [4–7,15], so that the average geometrical structure in the S_0 state is non-planar at room temperature [17]. The broadening of both the fluorescence and absorption spectra can be approximated by a convolution of the low temperature spectra with a combination of a Gaussian and an exponential distribution. The Gaussian distribution $G_1(v') = \exp(-4 \ln 2 (v'/\gamma)^2)$ is mainly due to the increase of fluctuations in the polarizability of the environment. The exponential term $G_2(v')$ reflects the steeper potential of the out-of-plane torsional modes in the S_1 state as compared to the S_0 state due to the shortening of the $C_\alpha C_{\alpha'}$ bonds in the S_1 state. For fluorescence emission spectra $G_2(v')$ is given by [15]

$$G_2(v') = \exp(-hcv'D/(D-1)kT) \quad (1)$$

and for absorption

$$G_2(v') = \exp(-hcv'/(D-1)kT) \quad (2)$$

Fig. 3 compares the experimental fluorescence and absorption spectra of 5T at room temperature to the simulated spectra, which are obtained by convolution of the calculated low temperature spectra in Fig. 2 with G_1 and G_2 , inserting $D = 9.0$ and a Gaussian half-width of $\gamma = 1100 \text{ cm}^{-1}$. The calculated intensities and energy spacings between the F_i sub-bands in the fluorescence spectrum agree well with the experimental spectrum. Moreover, the simulated absorption spectrum is in good accordance with the experimental results, reproducing the additional broadening and asymmetrical blue-shift of the spectrum.

Both, the additional broadening and asymmetrical blue-shift of the absorption spectrum occur exactly above the melting point of tetradecane at $T_m = 6^\circ \text{C}$, see Fig. 4. In contrast to the spectrum at $T > T_m$, where the calculated spectrum requires $D = 9.0$ in Eq. (2), the absorption spectrum below the melting point has to be simulated by $D = 3.5$ (Fig. 5). This clearly indicates that the thermal excitation of torsional modes is hindered in rigid media, where the differences between the potential curves in S_0 and S_1 are much less pronounced.

3.2. Spectral shifts and transition energies

Fluorescence and absorption spectra of the *n*Ts in solution are significantly red-shifted with increasing refractive index n_{solv} of the solvent and with increasing oscillator strength of the oligomers. A quantitative representation is given in Fig. 6, where the spectral positions of the high energy fluorescence sub-band F_1 (for notation see Fig. 3) of the *n*Ts are plotted against the refractive indexes n_{solv} of various alkanes according to the Onsager relation $(n_{\text{solv}}^2 - 1)/(2n_{\text{solv}}^2 + 1)$. The extent of the red-shift is up to 2000 cm^{-1} for 5T in

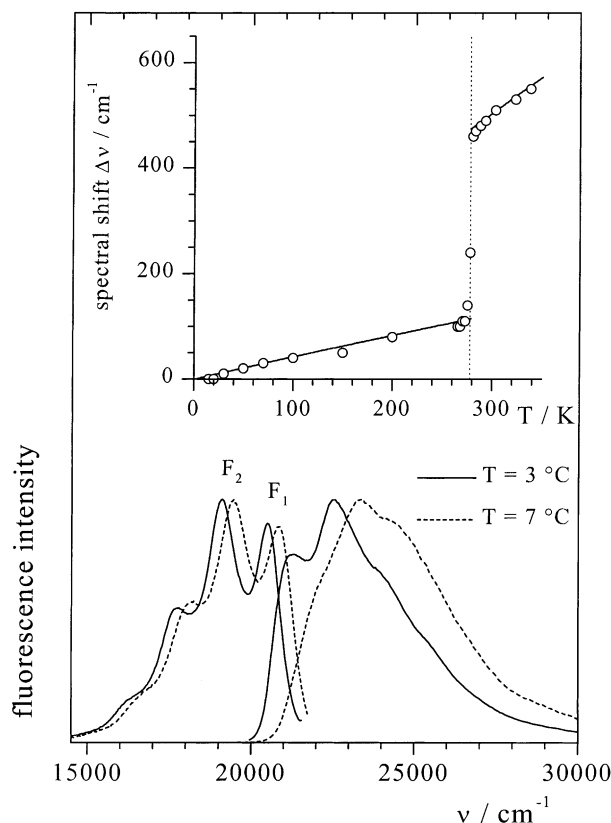


Fig. 4. Fluorescence emission and excitation spectra of 5T in tetradecane at $T = 3^\circ \text{C}$ (solid lines) and $T = 7^\circ \text{C}$ (dashed lines). Inset: spectral shifts with respect to the spectrum at $T = 15 \text{ K}$ for the fluorescence emission spectra as a function of the temperature. Solid lines are linear fits to the experimental values (see text).

tetradecane (Fig. 3) as compared to the position in vacuo. Also, the observed additional red-shift of 520 cm^{-1} in tetradecane upon decreasing the temperature to $T = 15 \text{ K}$, see Fig. 2, is mainly caused by the increase of the refractive index to $n_{\text{solv}}(\lambda = 486 \text{ nm}) \approx 1.64$, due to the increase in the

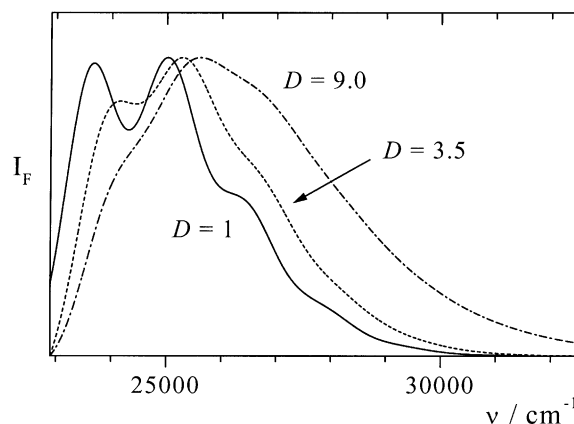


Fig. 5. Calculated absorption spectra of 5T (HF/6-311G*, RCIS/6-311G*), convoluted with a Gaussian distribution (solid line, half-width: 1100 cm^{-1}) and with an additional exponential distribution ($T = 279 \text{ K}$), with $D = 3.5$, (dashed line), $D = 9.0$ (dashed-dotted line).

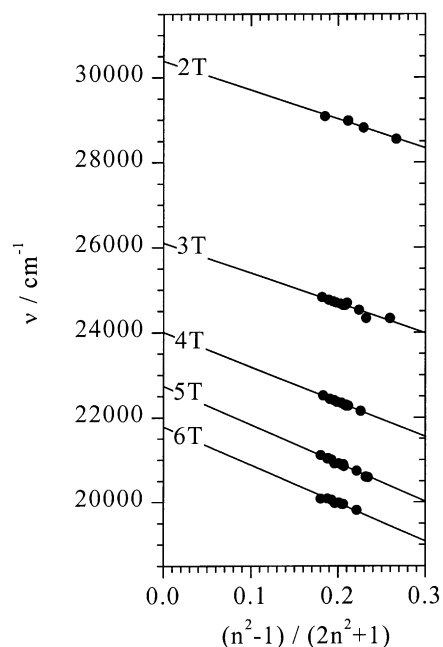


Fig. 6. Spectral positions of the high energy fluorescence sub-band F_1 (see Fig. 4) of the n Ts in a series of saturated alkanes (C_5 – C_{14}) as a function of the refractive index n_{solv} according to the Onsager relation.

density of the medium. The main red-shift of 340 cm^{-1} is observed exactly at the melting point of tetradecane. Above the melting point the spectral positions of F_1 can be fitted by inserting the coefficient of volume expansion $\alpha_{\text{liquid}} = 1.0 \times 10^{-3} \text{ K}^{-1}$ (see Fig. 4), which is in good agreement with the literature value of $0.89 \times 10^{-3} \text{ K}^{-1}$ [13b]. For solid tetradecane $\alpha_{\text{solid}} = 2.5 \times 10^{-4} \text{ K}^{-1}$ is obtained.

The solvent dependence of the F_1 spectral positions is used to determine the adiabatic transition energies ν_{00} in vacuo by extrapolating the linear fits of Fig. 6 to $n_{\text{solv}} = 1$. The extrapolated values are in good agreement with the results of ab initio quantum chemical RCIS/6-311G* calculations (Fig. 7). The theoretical results are improved by taking diffuse functions (RCIS/6-311+G*) into account. This results in deviations of less than 3% from the experimental data, see Table 1. QCFF/PI calculations [16] yield

Table 1
Experimental and calculated adiabatic transition energies of n Ts ($\times 1000 \text{ cm}^{-1}$)

Adiabatic transition energies ν_{00}			
	Calculated		Experimental ^a in vacuo
	RCIS/6-311G*	RCIS/6-311+G*	
2T	31.5	30.5	30.4
3T	27.0	26.3	26.1
4T	24.7	24.1	24.0
5T	23.5	23.0	22.7
6T	22.8	22.4	21.8

^a Position of the F_1 band extrapolated to $n_{\text{solv}} = 1$, see Fig. 6 (precision of the method $\pm 100 \text{ cm}^{-1}$).

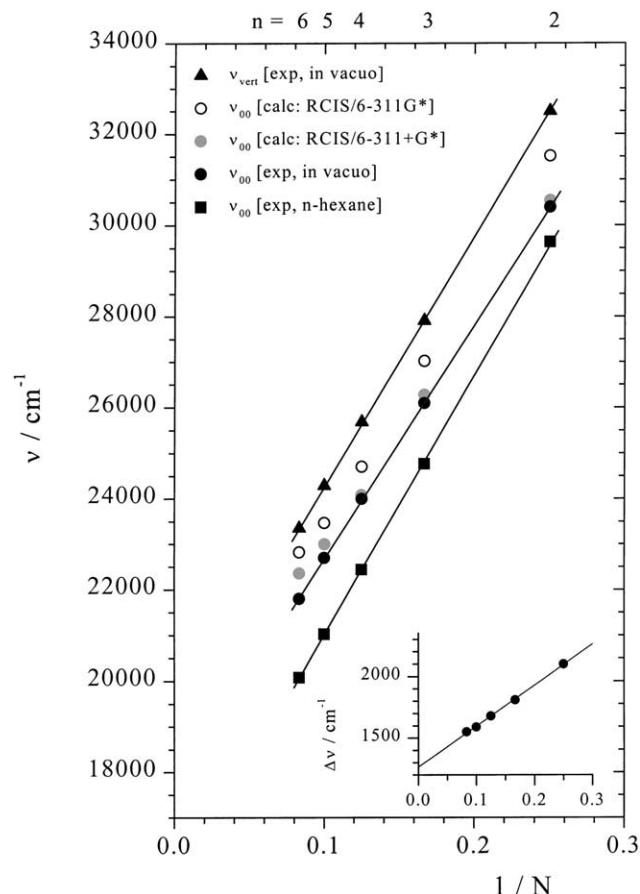


Fig. 7. Electronic transition energies of the n Ts as a function of the inverse chain length: experimental adiabatic transition energies in n -hexane (■) and in vacuo (●), vertical transition energies (▲), calculated adiabatic transition energies (RCIS/6-311G*: (○) RCIS/6-311+G*: (●)). Inset: experimental equilibration energies $\Delta\nu_{\text{exp}}$.

significantly higher values for ν_{00} . Experimental values of the vertical transition energies are obtained by addition of the equilibration energies $\Delta\nu$ to ν_{00} (the common way of identifying the vertical transition energy with the maximum of absorption is problematic because of the additional blue-shift of the absorption spectrum, see Section 3.1). The plot of $\Delta\nu$ against the inverse chain-length $1/N$ of the n Ts (Fig. 7), allows the extrapolation to the value for the ideally conjugated polymer to $\Delta\nu_{\text{extra}} = 1260 \text{ cm}^{-1}$.

4. Conclusions

Fluorescence and absorption spectra of 5T at different temperatures were investigated in a combined experimental and theoretical approach. At low temperatures the spectra are almost mirror symmetrical in accordance with ab initio quantum chemical calculations, whereas at room temperature the absorption spectrum undergoes an additional broadening and blue-shift. These effects are ascribed to the thermal excitation of low frequency out-of-plane torsional vibronic modes, which are only effective in non-rigid

environments. The adiabatic transition energies in vacuo for a homologous series of oligothiophenes were determined from the solvent dependence of the spectral positions of the fluorescence spectra. The results are in excellent agreement with ab initio quantum chemical RCIS/6-311+G* calculations.

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