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Stray-light induced artefacts in absorption spectra of crystalline oligothiophenes

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Abstract. The absorption spectra of oligothiophene single crystals and thin films are discussed in terms of stray light induced experimental artefacts. After typical experimental problems have been overcome, absorption spectra can be collected over a wide spectral range in the UV-Vis region that has often not been included in the literature data. A clear similarity is found between the absorption spectra of single crystals and highly ordered thin films.

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Recently, molecular materials have received a lot of attention due to their possible use in optoelectronic devices, such as light emitting diodes and transistors [1–5], and in this field crystalline oligothiophenes are considered very promising materials. In addition, oligothiophenes can also serve as interesting prototype materials for fundamental studies on molecular crystals, *i.e.* solid state systems displaying collective properties. A lot of experimental data on the optical properties of oligothiophenes have been published, but some controversy has arisen due to interpretations based on absorption spectra from a restricted energy range in the case of single crystals compared to those obtained for thin films. In particular, only in the low energy region has a direct correspondence been found [6]. By contrast, features in the spectra of both thick films and crystals above few μm thickness are less obvious [7–14]. Common to this case is the effect of saturation, which we wish to address in the following discussion and which also plays a role in determining the overall lineshape of thin film spectra, therefore affecting the interpretation of disorder-induced broadening [5,15]. On this point we will not elaborate any further, only to make aware that in extreme experimental conditions the spectra can be artificially transformed to resemble rather featureless broad spectra. Most of the literature absorption data on oligothiophene single crystals show saturation [7–14] due to their relatively large thickness, which is typically a few microns, whereas the effect is less common in thin films, whose thickness can be controlled down to few nanometers. Notwithstanding saturation due to a normal thickness effect, it can be noted that in many published spectra the saturation limit is achieved at very low absorbance values, lower than the typical saturation limit of commercial instruments. This effect can be due to stray light, *i.e.* to light that does not pass through the sample either because the beam cross-section is larger than the sample size or, more critically, if it passes through microscopic holes and cracks, thus masking the intrinsic absorption structures of the sample.

In this paper, we compare the typical spectra of high quality thin films and single crystals of quaterthiophene (4T), demonstrating their equivalence over a wider spectral range than reported in the literature. This result has been achieved after stray light induced experimental problems have been overcome, as discussed here in detail.

4T was synthesized according to one of the standard procedures [16] and was purified by sublimation. Single crystals were grown from the vapour phase as thin flakes, about 1 mm^2 in size and about 1 μm in thickness, which present microscopic inhomogeneities, such as pinholes and cracks. Prior to measurements, the crystals homogeneously extinguishing the light intensity under crossed polarisers were selected for the optical measurements. 4T films from 2 to 80 nm thick were grown by organic molecular beam deposition (OMBD [17]), under about 5×10^{-10} torr base pressure using a Knudsen cell as a source, with double heater and temperature control; the deposition temperatures were 165 °C and 175 °C at the cell bottom and at the effusion orifice, respectively, deposition rate was about 3 Å/min, and the substrates were kept at room temperature. Single crystalline substrates of potassium acid phthalate (KAP) were used to

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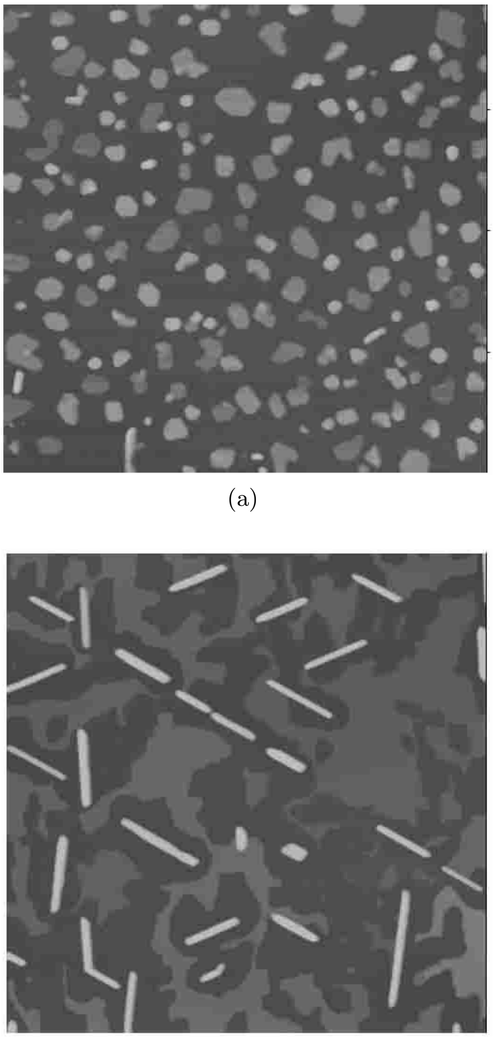
make the films grow polycrystalline and macroscopically oriented [18,19], with the known crystal structure of the low temperature 4T polymorph, with four molecules per unit cell [20], and with the *ab* lattice plane as contact plane with the KAP substrate [21]. Silica substrates were also used, thus making the films polycrystalline, with the same crystal structure as the films grown on KAP, but with a random orientation of the crystalline grains [21]. The surface morphology of the films was investigated by collecting 10 μm$\times$10 μm images using a Digital Nanoscope IIIa atomic force microscope in tapping mode. Optical transmission measurements were performed in the spectral range from 1.5 to 6 eV, with resolution down to 2 meV, with polarised light using a Perkin-Elmer Lambda 900 spectrometer equipped with Glan-Taylor calcite polarisers. Low temperature measurements down to 7 K were performed using an Oxford bath cryostat. The transmission measurements on the single crystals were carried out at room temperature by coupling the spectrometer to a microscope equipped with sheet polarisers and with an objective (0.5 numerical aperture) to reduce the light spot on the sample down to 4 μm $\times$ 4 μm.

The morphology of 4T thin films deposited on silica and on KAP can be observed in Figure 1, as obtained by atomic force microscopy (AFM). In both images, the dark regions correspond to the bare substrate, while different brightnesses indicate different heights of the 4T islands. Slightly different morphologies can be observed, in both cases leaving some regions of the substrate uncovered. On the basis of these images, it is clear that when performing absorption measurements some stray light can be collected, as also happens with single crystals through holes and cracks. In addition, commercial instruments for optical spectroscopy have a typical beam size of several mm^2, which is much bigger than the crystals, so that some stray light can also originate from this experimental condition. The light intensity reaching the detector without probing the sample can be responsible for a spectrum saturation at low absorbance values, sometimes preventing the collection of the intrinsic spectrum. When the light beam with intensity I_0 and spot area S_0 impinges on a sample much smaller than S_0 or with microscopic holes and cracks, the transmitted light intensity is the sum of the two contributions I_S and I_{stray}, the first one having probed the actual sample area S, and the second one passed through holes and cracks, therefore representing the stray light. The measured transmittance $T_m = (I_S + I_{stray})/I_0$ differs from the real sample transmittance $T = (I_S S_0)/(I_0 S)$, being related by

$$T_m = 1 - \frac{S}{S_0}(1-T) = 1 - \frac{S}{S_0}\{1-\exp(-\alpha d)\}, \qquad (1)$$

where the last term includes the commonly used Lambert-Beer law (which neglects reflectance), α is the sample absorption coefficient and d its thickness (αd is also called optical density). Equation (1) can also be rewritten in terms of measured absorbance $A_m = -\log T_m$. A trivial case described by equation (1) is that of a completely absorbing sample ($T = 0$), for which $S < S_0$ causes the measured transmittance $T_m \neq 0$ to be entirely due to stray light, *i.e.* T_m does not carry any information on the sample optical properties.


(a)

(b)

Fig. 1. Atomic force microscopy images (10 μm $\times$ 10 μm) of 10 nm thick 4T films deposited on silica (a) and on a (010)-oriented KAP crystal (b).

In general, equation (1) can be used to predict the measured transmittance as a function of the amount of stray light reaching the detector and consequently the difference between T and T_m. In Figure 2, such an evaluation is performed by calculating the experimental absorbance A_m (black triangles) for a series of αd values, when S/S_0 is 0.900, 0.990, or 0.999, due to inhomogeneities and pinholes. While for low αd the absorbance A_m gives a good approximation of the real absorbance, Figure 2 clearly shows that for higher αd, A_m reaches a false absorbance saturation limit. Moreover, as S/S_0 decreases, the value of such a saturation absorbance decreases and is attained for lower and lower αd. Even for a small stray light

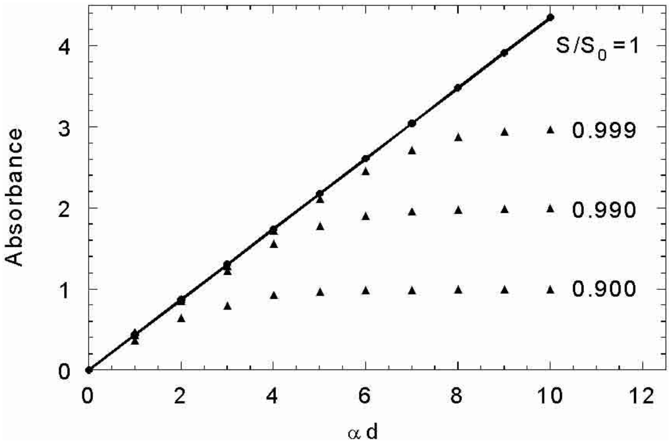


Fig. 2. Measured absorbance values of a sample as a function of the optical density, calculated using equation (1) for different S/S_0 values (indicated close to each set of data); triangles and dots refer to $S < S_0$ and $S = S_0$ (no stray light reaches the detector), respectively.

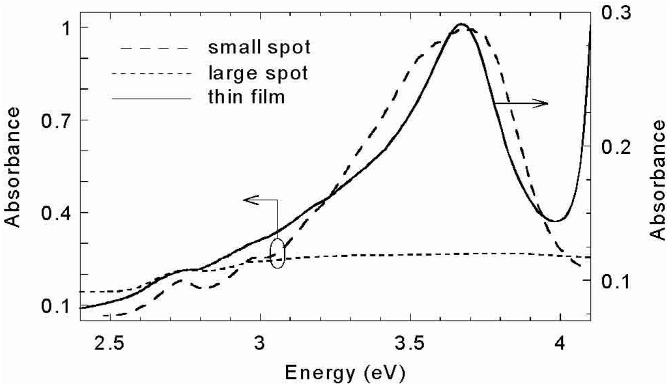


Fig. 3. Experimental absorption spectra collected at room temperature on a 4T single crystal using different spot size (dotted and dashed lines) and on a 10 nm thick polycrystalline 4T film (continuous line) deposited on KAP. All the spectra are collected under normal incidence on the *ab* 4T lattice plane, with the electrical field of the incident light along the *a* axis. The absorption edge of KAP above 4 eV is detected in the film spectrum.

contribution, *i.e.* $S/S_0 = 0.999$, the A_m saturates at 3, which is much lower than the usual maximum obtained by good spectrometers (up to 5 or 6 absorbance units). In addition, it should be noted that αd values for which A_m saturates are common for molecular crystals; for oligothiophene single crystals, αd ranges from 10 to 100 (α usually is about 10^4–10^5 cm^{-1} and the thickness up to 10 μm). When considering most of the literature data on oligothiophene single crystals, spectral saturation is found at very low values [7–14], suggesting that measurements have not taken into consideration the experimental caveats expressed above. Only in some cases, do the detected spectra resolve the high energy region, in spite of such a saturation [12].

The experimental assessment of the above discussion is reached by performing two absorption measurements on a crystal: one with a very small light spot on an homogeneous sample region to be sure to probe the sample without recording stray light, and another one with a large spot, intentionally larger than the sample to stress the effect of stray light. The results are shown in Figure 3, which reports the absorbance spectra collected on the same 4T single crystal under the two different experimental configurations (16 μm^2 spot, dashed curve, and 1 mm^2 spot, dotted curve) at normal incidence to the *ab* lattice plane with light polarised along the *a* crystal axis. A striking difference can be observed: the measurements performed on the small spot reveal an absorption peak at about 3.7 eV, which is otherwise obscured in the saturation region of the spectrum using the large spot. In the same figure, a spectrum of a 10 nm thick polycrystalline 4T film grown on KAP by OMBD is also reported (continuous curve), taken at normal incidence to the *ab* lattice plane with light polarised along the *a* axis of the 4T crystal. A similar absorption spectrum, with a main peak at about 3.7 eV, has also been found in the case of 4T films deposited on silica. In the measurements on the thin films, the incident beam has not been masked; nonetheless, the spectra do not show saturation. Indeed, the experimental artefacts due to stray light are unusual for molecular thin films, even for the case of samples displaying an island morphology, due to their low αd values (see Fig. 2). Indeed, for low αd, the measured A_m substantially differs from the real absorbance only when S/S_0 assumes very low values, *i.e.* when a very large amount of the incident intensity passes through holes and cracks. Furthermore, even for a low S/S_0 ratio, in the region of low αd the measured and real absorbance values are directly proportional, so that the shape of the spectrum is not modified. This can be made explicit by expanding equation (1) for $\alpha d \ll 1$, thus obtaining

$$A_m = \frac{S}{S_0}\frac{\alpha d}{2.3}, \tag{2}$$

which illustrates that for samples with a low optical density, the measured absorbance approximates to the actual value by the scaling factor S/S_0. For example, if $\alpha d = 0.05$ and $S/S_0 = 0.900$, the measured A_m is about 90% of the real absorbance, as deduced from equation (1) and in agreement with equation (2); moreover, $S/S_0 = 0.900$ gives a saturation limit of 1, much higher than A_m, therefore permitting a reliable absorption spectrum to be measured.

Between $\alpha d \ll 1$ and high αd values leading to saturation, lies the region which has the effect of altering the shape of a given spectrum, *i.e.* where a false saturation limit is not attained, but neither is the real absorbance measured. In this region, the spectrum gets compressed irregularly, such that the transitions with higher αd reduce in the measured absorbance more than transitions of lower αd. Hence, the overall effect is to flatten the spectrum, giving erroneous values for the peak widths. For oligothiophene spectra, this has important consequences, since

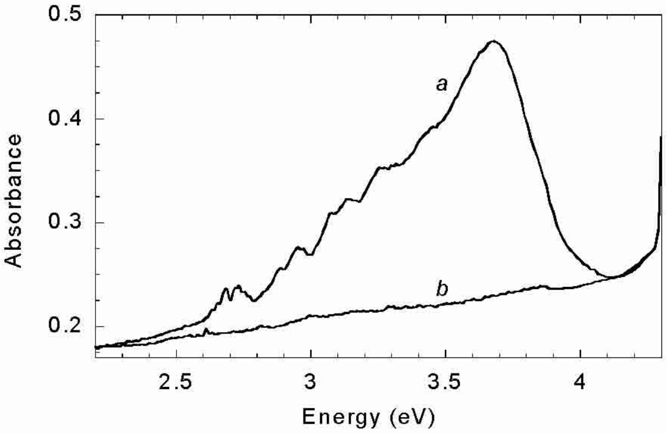


Fig. 4. Experimental absorption spectra collected at 7 K on a 45 nm thick polycrystalline 4T film deposited on KAP. The spectra are collected under normal incidence on the *ab* lattice plane of 4T, with the electrical field of the incident light along the *a* and *b* axes. The absorption edge of KAP above 4.5 eV is detected in the film spectrum, at higher energy than in Figure 3 due to the low temperature.

apparently disordered thick films exhibiting broad spectra could be actually affected by the above experimental problems. For example, oligothiophene films with thickness of hundreds of nanometers have usually an optical density corresponding to this intermediate region, so that rather low S/S_0 ratios affect the shape of the absorption spectrum, without reaching saturation. Also in the case of the single crystal spectrum in Figure 3, this intermediate region can be responsible for the larger width of the main peak with respect to the film spectrum, even if the use of the microscope objective to focus on the sample could also play a role.

The above discussion indicates that the differences in the literature absorption spectra of 4T thin films and single crystals may include effects from stray light, particularly in the case of single crystals. Once these experimental problems have been overcome, the spectra of both single crystals and highly organised thin films are found to be almost equivalent, as in Figure 3. Furthermore, the correspondence between the crystal and film spectra can be even more marked when 4T films grown on KAP are considered, which are macroscopically oriented (in contrast to those deposited on silica that are isotropic around the azimuth direction). Figure 4 shows the spectra of a 4T film deposited on KAP, taken at 7 K, with the electric field of the incident light polarised along the *a* and *b* axis of the 4T unit cell. An extremely large anisotropy is found both for the peak at about 3.7 eV and for a peak at about 2.6 eV, detectable in the *b*-polarised spectrum only, as for 4T single crystals [10]. These findings are particularly relevant for the interpretation of the optical properties of crystalline oligothiophenes, which must be fully consistent for single crystals and thin films.

In conclusion, the typical artefacts often affecting the absorption spectra of samples presenting microscopic inhomogeneities are discussed and demonstrated to originate from stray light collected during the measurements. In the case of crystalline 4T, considered as a prototype molecular material, these experimental problems have been overcome and the results definitely show that the absorption spectra of single crystals and thin films display the same features over a wider spectral range than discussed in the literature.

References

1. A. Dodabalapur, L. Torsi, H.E. Katz, Science **268**, 270 (1995)
2. Z. Bao, A.J. Lovinger, A. Dodabalapur, Appl. Phys. Lett. **69**, 4108 (1996)
3. F. Garnier, Acc. Chem. Res. **32**, 209 (1999)
4. J.H. Schön, A. Dodabalapur, C. Kloc, B. Batlogg, Science **290**, 963 (2000)
5. C. Ziegler, in *Handbook of Organic Conductive Molecules and Polymers*, edited by H.S. Nalwa, Vol. 3 (John Wiley and Sons, Chichester, 1997)
6. R.N. Marks, M. Muccini, E. Lunedei, R.H. Michel, M. Murgia, R. Zamboni, C. Taliani, G. Horowitz, F. Garnier, M. Hopmeier, M. Oestreich, R.F. Mahrt, Chem. Phys. **227**, 49 (1998)
7. G. Horowitz, S. Romdhane, H. Bouchriha, P. Delannoy, J.L. Monge, F. Kouki, P. Valat, Synth. Metals **90**, 187 (1997)
8. D. Fichou, F. Demanze, G. Horowitz, R. Hajlaoui, M. Constant, F. Garnier, Synth. Metals **85**, 1309 (1997)
9. M. Muccini, E. Luneidei, C. Taliani, D. Beljonne, J. Cornil, J.L. Brédas, J. Chem. Phys. **109**, 10513 (1998)
10. M. Muccini, M. Schneider, C. Taliani, M. Sokolowski, E. Umbach, D. Beljonne, J. Cornil, J.L. Brédas, Phys. Rev. B **62**, 6296 (2000)
11. S. Möller, G. Weiser, F. Garnier, Phys. Rev. B **61**, 15749 (2000)
12. F. Kouki, P. Spearman, P. Valat, G. Horowitz, F. Garnir, J. Chem. Phys. **113**, 385 (2000)
13. S.V. Frolov, C. Kloc, S. Berg, G.A. Thomas, B. Batlogg, Chem. Phys. Lett. **326**, 558 (2000)
14. S.V. Frolov, C. Kloc, B. Batlogg, M. Wohlgenannt, X. Jiang, Z.V. Vardeny, Phys. Rev. B **63**, 205203 (2001)
15. Y. Kanemitsu, N. Shimizu, K. Suzuki, Y. Shiraishil, M. Kuroda, Phys. Rev. B **54**, 2198 (1996)
16. C. Van Pham, A. Burkhardt, A. Nkansah, R. Shabana, D.D. Cunnigham, H.B. Mark, H. Zimmer, Phosphorus, Sulfur, Silicon Relat. Elem. **46**, 153 (1989)
17. R. Tubino, A. Borghesi, L. Dalla Bella, S. Destri, W. Porzio, A. Sassella, Opt. Mater. **9**, 437 (1998)
18. A. Sassella, D. Besana, A. Borghesi, F. Meinardi, S. Tavazzi, R. Tubino, Synth. Metals **121**, 1421 (2001)
19. A. Borghesi, D. Besana, A. Sassella, Vacuum **61**, 193 (2001)
20. T. Siegrist, C. Kloc, R.A. Laudise, H.E. Katz, R.C. Haddon, Adv. Mater. **10**, 379 (1998)
21. A. Sassella, B. Besana, A. Borghesi, M. Campione, S. Tavazzi, B. Lotz, A. Thierry, Synth. Metals (in press, 2002)