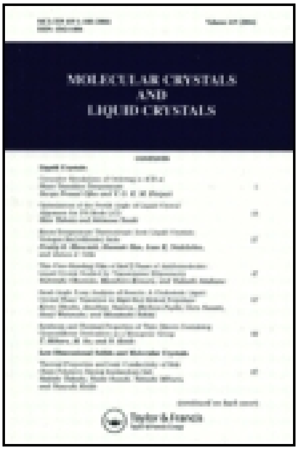

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Study of the Lowest Electronic States in a Polythiophene Oligomer, α-Sexithienyl, by One and Two-Photon Spectroscopy

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STUDY OF THE LOWEST ELECTRONIC STATES IN A POLYTHIOPHENE OLIGOMER, α-SEXITHIENYL, BY ONE AND TWO-PHOTON SPECTROSCOPY

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Abstract. α-sexithienyl (T_6) is a large rigid rod molecule with twelve conjugated double bonds. The electronic structure of T_6 has been investigates by one-photon and two-photon spectroscopy as well as by photoconductivity. From the single crystal polarized spectra at 4.2K we observe that the lowest allowed π-π transition (λ_{max} = 478 nm) is polarized parallel to the long molecular axis and a second intense transition at 370 nm is polarized parallel to the short in plane axis. The two-photon excitation spectra in polycristalline thin films have been investigated at 4.2 K in the spectral range between 910 and 1180 nm of the fundamental laser radiation. The intense two-photon absorption band at 544.9 nm is assigned to the 2^1A_g exciton band origin. The lowest "gerade" exciton level lies therefore at 898 cm^{-1} above the lowest one-photon allowed 1^1B_u exciton level. The photophysics of T_6 is studied by photoconductivity and one-photon excitation spectroscopy. An efficient pathway for carrier generation open up at energies in the proximity of the 2^1A_g exciton. We suggest that T_6 is a good model compound for polythiophene (PT) and therefore the energetics of PT should be very similar to T_6.

Introduction

Interest in the electronic structure of conjugated polymers stems from fundamental theoretical aspects as well as from the possible implications that the electronic level ordering has in the remarkable charge transport and nonlinear optical properties of these materials. Polythiophene is a prototype of conjugated polymers having a non degenerate ground state structure; its electronic structure may be envisaged as a polyene in which the conjugated C=C double bonds are "locked" in place and only slightly perturbed by the sulphur atoms.

In this work we address the problem of the location of the lowest excited electronic states in polythiophene by studying a long oligomer containing 12 double bonds by means of linear and nonlinear spectroscopy in the condensed phase. It has been shown in fact that the hexamer of polythiophene is a good prototype for modelling the geometrical structure of the polymer and is long enough to accommodate the lattice relaxation associated to a bipolaron[1]. The molecular structure of T_6 is shown in the inset of Fig. 1.

One-photon absorption

The polarized electronic spectra along two principal optical directions of a single crystalline face of T_6 at 4.2K are shown in Fig. 1. Details of the work are given in Ref. 2. The first intense electronic absorption is strongly polarized parallel to the || direction with a maximum at 478 nm. The polarized IR spectra indicate that the long axis of T_6 projects strongly in the || direction. Hence the symmetry of the lowest allowed electronic exciton is B_u ||L. A second electronic absorption at about 370 nm is polarized orthogonally to the first.

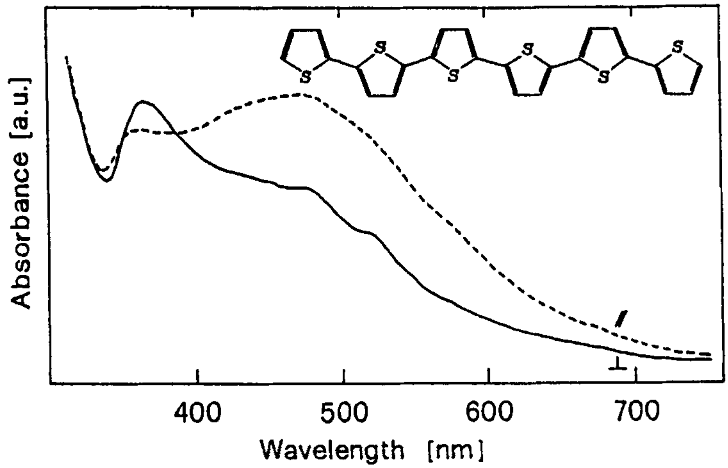

Fig. 1. Polarized electronic spectra of the α-sexithienyl single crystal at 4.2K. Polarization refers to the cleavage direction.

Since the states which are polarized perpendicular to the molecular plane are, in aromatic molecules, at higher energies we assign this second allowed electronic absorption to a B_u exciton ||M. This observation is in agreement with the ordering of the allowed electronic levels in thiophene[3].

Two-photon absorption

The two-photon excitation spectrum of the T_6 film at 4.2 K is shown in Figure 2. Preliminary results on this investigation have been reported in Ref. 4. The spectrum is plotted against the one-photon wavelength scale for a ready comparison with the one-photon excitation spectrum (Figure 2b). Prominent two-photon excitation peaks are observed at 572.7, 544.9, 519.2, 510.0, and 502.0 nm. The T_6 molecule belongs to the C_{2h} point group and the electronic states are classified according to the B_u and A_g representations. Crystal packing calculations[5] predict that the center of symmetry is preserved in the crystal. The mutual exclusion of "g" and "u" states in linear and nonlinear absorption should therefore hold in the crystal also. The presence of a center of symmetry in the molecule makes the g←g transition formally forbidden. Therefore, while the $1^1B_u \leftarrow 1^1A_g$ transition is one-photon allowed, the $2^1A_g \leftarrow 1^1A_g$ transition is one-photon forbidden and two-photon allowed.

The one-photon excitation peak at 573.0 nm (17452cm^{-1}) is assigned to the origin of the 1^1B_u exciton band. This is in agreement with the rather fast PL decay (<600 ps) indicating a spin allowed transition. The lowest energy weak band at 572.7 nm in the two-photon absorption spectrum coincides with the one-photon excitation peak and is hence assigned to the 1^1B_u origin made partially allowed by disorder. This may be due to relaxation of the selection rules caused by the reduction of the molecular symmetry.

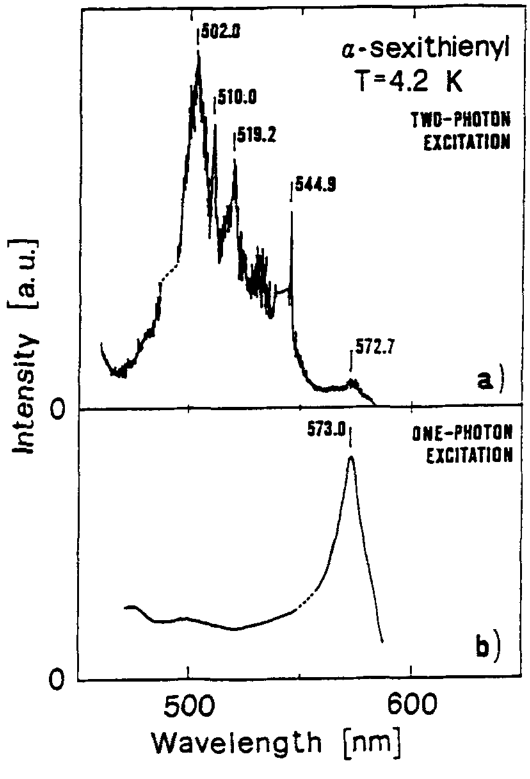

Fig. 2. (a) Two-photon and (b) one-photon excitation spectra for the thin film of T_6 at 4.2 K. For the two-photon spectrum the excitation is at twice the wavelength shown in the figure. The dashed lines indicate regions in which the data were discarded because of sharp variations of the dye laser energy.

The lowest energy two-photon peak at 544.9 nm is assigned to the zero phonon electronic transition to the bottom of the 2 ^1A_g exciton band (i.e. 898

cm^{-1} above the 1^1B_u state). The other bands at 910, 1257 and 1570 cm^{-1} above the origin are assigned to totally symmetric vibronic levels of the 2^1A_g electronic manifold. The possible candidates are the ring stretching (863 cm^{-1}), C-H deformation or ring breathing (1219 cm^{-1}) and the C=C stretching (1459 cm^{-1}). The numbers in brackets refer to the ground state FT-Raman frequencies that we measured[2] in T_6. The rather broad excitation peak at 502.0 nm may be caused by vibronic congestion (i.e envelope of combinations and/or progressions). The energy level diagram for T_6 that we derive by comparing the two-photon and one-photon spectra is shown in Figure 3. Two-photon excitation generates excitons into the 2^1A_g exciton band, then the electronic energy relaxes into the 1^1B_u electronic manifold and finally emits radiatively from the bottom of the 1^1B_u exciton band leading to the ground state.

Since the PL of PT[6] is very similar to that of T_6 we infer that the lowest excited electronic state in PT has also a ^1B_u character. The 2^1A_g electronic level in PT would therefore be at higher energies. In view of the empirical observation that the emission from molecular crystals at low temperature occurs almost universally from the lowest singlet excited state[7] (known also as Kasha's rule) and considering the similarities of the PL spectra we suggest that the electronic energetics of PT follows the same excited states ordering in T_6.In PT however we should expect an additional inhomogeneous broadening due to conjugated chain length distribution and morphological disorder as in the case of PPV[8]. The direct identification of the location of the lowest "g" state in T_6 has important implications in the nonlinear optical properties of this polythiophene oligomer. It has in fact been shown that the cubic nonlinear optical coefficients of T_6 are rather high[9-10], approaching the values of the polymer.

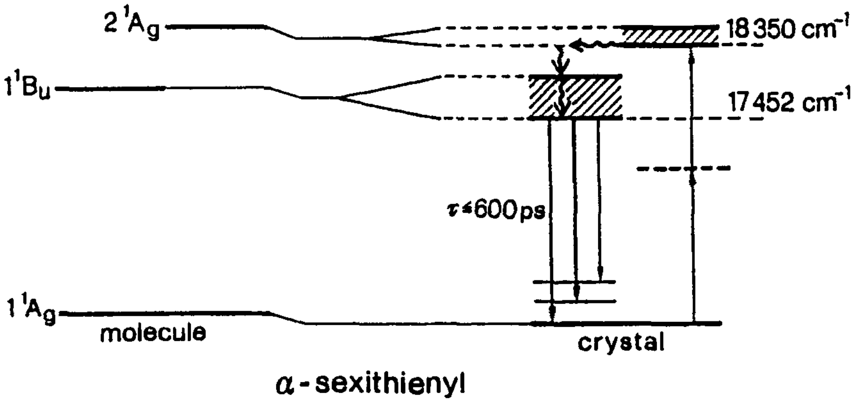

Fig. 3. Energy level diagram for molecular and crystalline T_6. The excited state vibronic levels are not indicated for simplicity. Congestion of vibronic levels provides an efficient pathway for electronic relaxation from the 2^1A_g to the $1\,^1B_u$ exciton manifold.

The knowledge of the location of the 2^1A_g electronic level allows us to predict that the electronic $\chi^{(3)}(-3\omega,\omega,\omega,\omega)$ response should show a two-photon resonance in the proximity of 1.09 μm of the fundamental laser wavelength. In view of this we suggest that the maximum in the $\chi^{(3)}(-3\omega,\omega,\omega,\omega)$ spectrum of T_6, observed at the fundamental wavelength of 1.06 μm and attributed to a three-photon resonance[11] is due rather to a two-photon resonance. Fine tuning of the fundamental laser wavelength may allow us to get a higher resonance enhancement at 1.09 μm because the two-photon resonance is narrow (fwhm = 25 cm^{-1} at 4.2 K).

The photoconductivity action spectrum was measured in thin evaporated film on a test pattern in which the gap between the electrodes was 10 μm. The threshold for e-h generation is at higher energy than the bottom of the 1 ^1B_u exciton band. This new pathway offers an efficient relaxation mechanism which is associated with the quenching of PL at higher energies as it is shown in Fig. 2.

In conclusion we have studied the location of the lowest electronic excited states of T_6 showing that the lowest level is ^1B_u while the 2^1A_g is slightly higher in energy (0.1 eV). Direct photogeneration of charge carriers occurs at energies close to the 2^1A_g level and opens a new efficient relaxation pathway. It should be noticed also that T_6 supports photogenerated polarons as it is shown in the photoinduced absorption study[12]. We suggest that T_6 is a good model compound of PT and therefore this excited states ordering is maintained in PT.

Acknowledgements

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