

Location of the Low-Energy 1A_g State in a Polythiophene Oligomer by Two-Photon Absorption Spectroscopy: α -Sexithienyl

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The two-photon excitation spectrum in polycrystalline α -sexithienyl (T_6) thin film has 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 $18\,350\text{ cm}^{-1}$ is assigned to the $2{}^1A_g$ exciton band origin. The comparison of the one-photon and two-photon excitation spectra shows that the lowest "gerade" exciton level lies at 898 cm^{-1} above the lowest one-photon-allowed $1{}^1B_u$ exciton level.

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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 non-linear optical properties of these materials. For these reasons a large number of theoretical and experimental investigations have been carried out in recent years on this subject. The majority of these investigations deal with the simplest conjugated polymer, polyacetylene $(\text{CH})_x$, but the considerations may be extended to other conjugated polymers with a nondegenerate ground-state structure.

Polythiophene is a prototype of this class of conjugated polymers; its electronic structure may be envisaged as a polyene in which the conjugated $\text{C}=\text{C}$ double bonds are "locked" in place and weakly perturbed by the sulfur atoms.

The original one-electron treatment [1] has been able to account for many physical aspects of these materials but there is still an open question on the nature of the lowest excited electronic state in polyenes. Extensive experimental spectroscopic investigations [2] on matrix-isolated short polyenes have revealed that the lowest excited state is the covalent $2{}^1A_g$ and more recently polyene data extending to eight double bonds [3] extrapolate smoothly to $(\text{CH})_x$ and place the $2{}^1A_g$ at about 0.9 eV. Infrared photoluminescence [4] of *trans*- $(\text{CH})_x$ at 1.2 eV suggests also that the $2{}^1A_g$ state is the lowest electronic excitation in "infinite" polyenes. On the other hand, indirect evidence of the location of a two-photon state in $(\text{CH})_x$ by third-harmonic generation [5,6] indicates that the one-photon and two-photon optical gaps have the same energy. The location of the optically forbidden $2{}^1A_g$ state below the optical gap is well understood within models which involve explicitly electron-electron interactions at various levels of sophistication like the full configuration-interaction (CI) treatment to five double bonds [7] and other CI methods [8,9]. The calculated two-photon absorption spectrum of interacting π electrons in conjugated polymers shows that *e-e* correlations are essential to describe the electronic spectrum [10]. The excited state ordering for the infinitely long conjugated

chain is, however, still debated. Moreover it is well known that in molecular crystals the energy shift of the electronic levels from the free molecule to the crystal depends on the nature of the states and on the extent of the intermolecular interactions [11-13]. Therefore the ordering in the isolated molecule may in principle be different from that of the condensed phase. An application of this concept to the case of two interacting polyene chains has recently been discussed [14].

The most direct approach to the problem of the location of even and odd parity states consists in the experimental investigation of the two-photon spectrum as has been performed for short polyenes [3], polydiacetylenes [15], and polysilanes [16].

In this Letter we address the problem of the location of the lowest excited electronic states in polythiophene by studying a long oligomer containing twelve alternating double bonds by means of two-photon excitation spectroscopy (TPE) in the condensed phase. It has been shown, in fact, that the hexamer of polythiophene is a good prototype for modeling the geometrical structure of the polymer, and it is long enough to accommodate the lattice relaxation associated with a bipolaron [17].

The setup for the TPE experiment is shown in Fig. 1. Tunable, nanosecond infrared (IR) laser pulses were generated by Raman shifting the output of an Nd-doped yttrium aluminum garnet (Nd-YAG) pumped dye laser. The two-photon excited photoluminescence was detected by a photomultiplier tube (PMT) in combination with an IR blocking filter and fed to a boxcar averager for processing. Pulse-to-pulse intensity fluctuations were corrected in a standard way by monitoring the reference signal provided by the second-harmonic-generation (SHG) output from a cuvette filled with potassium dihydrogen phosphate (KDP) powder. For each laser shot, the data of TPE and SHG were manipulated by an on-line computer that controlled the entire experiment. The TPE spectrum was corrected for the wavelength-dependent efficiency of SHG generation in KDP particles [18], and the transmittance of the filter in the reference arm. A one-photon excitation spectrum was obtained by using a tunable nanosecond laser as the excitation source of

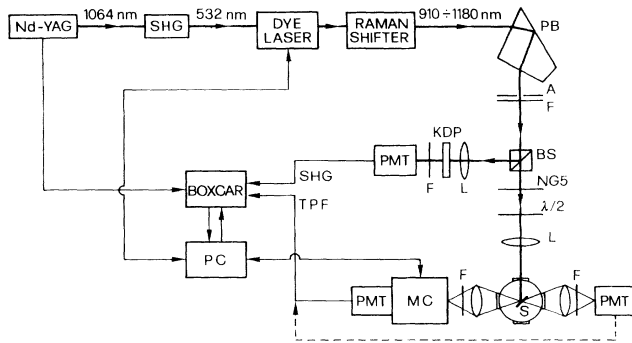


FIG. 1. Schematic of the experimental setup for the two-photon excitation experiment. A, aperture; BS, beam splitter; F, filters; L, lens; MC, monochromator; NG5, neutral density filters; PB, Pellin-Broca prism; PC, personal computer.

about $1 \mu\text{J}$ of pulse energy.

Thin films of T_6 with thicknesses in the range of $1.0 \pm 0.1 \mu\text{m}$ were prepared on quartz plates by vacuum evaporation. X-ray scattering, IR spectra, and polarizing microscope observations show that the film is polycrystalline and the individual crystalline domains have a common orientation.

The TPE spectrum of the T_6 film at 4.2 K is shown in Fig. 2(a). The spectrum is plotted against the one-photon wavelength scale for a ready comparison with the one-photon excitation spectrum [Fig. 2(b)]. Prominent excitation peaks are observed at 572.7, 544.9, 519.2, 510.0, and 502.0 nm. The one-photon excitation peak at 573.0 nm (17452 cm^{-1}) indicates the origin of the 1^1B_u exciton band. This is in agreement with the rather fast photoluminescence (PL) decay ($\tau < 600 \text{ ps}$) which indicates a spin allowed transition. Both the origin of the excitation and the fluorescence spectra are intrinsically rather broad ($\text{FWHM} = 660 \text{ cm}^{-1}$). The Stokes shift of 445 cm^{-1} from the PL origin band at 588.0 nm suggests a substantial geometrical relaxation in the excited 1^1B_u state. Relaxation in the B_u excited state was observed in short polyenes [2] and it was derived theoretically in $(\text{CH})_x$ oligomers of increasing length [19].

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. The ground state is 1^1A_g . In the crystal the electronic states are classified according to the space group [12]. Unfortunately the crystal structure of T_6 is not yet available. Crystal packing calculations [20], however, predict that the center of symmetry is preserved in the crystal. The mutual exclusion of "g" and "u" states in linear and nonlinear absorption, which is valid in the free molecule, should therefore hold in the crystal also. The relative location of these states is of crucial importance for the understanding of the energetics of T_6 . The presence of a center of symmetry in the molecule makes the $g \leftarrow g$ 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 forbid-

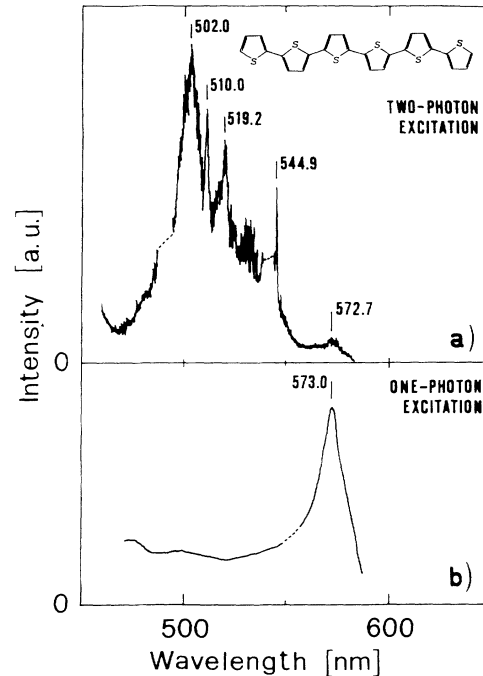


FIG. 2. The (a) two-photon and (b) one-photon excitation spectra for the thin-film sample of T_6 at 4.2 K. For the two-photon spectrum the exciting radiation is at twice the wavelength shown in the figure. The dashed lines indicate regions in which the data were discarded because of sharp variations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

den and two-photon allowed.

The lowest-energy weak band at 572.7 nm in the TPE spectrum coincides with the one-photon excitation peak and is hence assigned to 1^1B_u origin made partially allowed by disorder. This may be due to (a) a relaxation of the selection rules due to the reduction of the molecular symmetry, i.e., a rotation around the inter-ring single bond; or (b) a local crystal distortion which would decrease the factor group symmetry causing a mixing of the crystal states. In any case the two-photon absorptivity of this band is much weaker than appears in the excitation spectrum if one takes into account the excitation-wavelength-dependent fluorescence quantum yield from the 1^1B_u state [21]. The other prominent bands at 544.9 , 519.2 , 510.0 , and 502.0 nm mark intrinsic two-photon transitions. 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 at 18350 cm^{-1} (i.e., 898 cm^{-1} above the 1^1B_u level). 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 parentheses refer to the ground-state Fourier-transform Raman frequencies that we measured

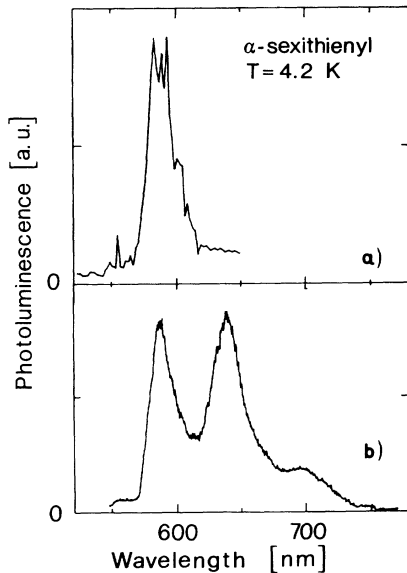


FIG. 3. Photoluminescence (PL) spectra from a polycrystalline thin film of T_6 at 4.2 K upon (a) two-photon excitation at $1.045 \mu\text{m}$ and (b) one-photon excitation at 532 nm . The two-photon excited PL does not show the higher vibronic bands because of the cutoff filters used to block the scattered infrared light.

[22] in T_6 . The agreement is rather satisfactory. The former two vibrational modes show a moderate shift in the excited state compared to the ground state. On the other hand, the remarkable frequency increase of the C=C stretching mode indicates that there is a strong variation of the equilibrium geometry in the excited state along this normal coordinate. A similar large frequency increase in the C=C stretching has also been observed in the A_g excited state in polyenes oligomers [2]. The rather broad excitation peak at 502.0 nm may be caused by vibronic congestion (i.e., envelope of combinations and/or progressions).

The PL spectrum obtained by exciting via two-photon absorption at $1.045 \mu\text{m}$ is shown in Fig. 3(a). The PL band at 588 nm is identical to that obtained by one-photon excitation monitoring the PL at 588 nm [see Fig. 3(b)] indicating that PL occurs indeed from T_6 molecules; higher vibronic bands are cut off by the optical filter used to block the scattered infrared exciting laser radiation. The PL intensity is proportional to the square of the infrared laser intensity proving the two-photon absorption process. The energy-level diagram for T_6 that we derive by comparing the two-photon and one-photon spectra is shown in Fig. 4. In molecular crystals the electronic levels are amalgamated into tight-binding exciton bands also called Frenkel excitons [12,13]. Crystal field effects shift the $k=0$ transitions to lower energy compared to the free molecule [12,13]. TPE generates excitons in the 2^1A_g exciton band; then the electronic energy relaxes into the 1^1B_u electronic manifold and finally em-

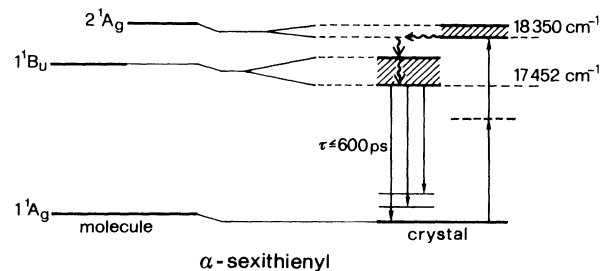


FIG. 4. Energy-level diagram for molecular and crystalline T_6 . The excited state vibronic levels are not indicated for simplicity. Congestion of vibronic levels provides an efficient pathway for electronic relaxation from the 2^1A_g to the 1^1B_u exciton manifold.

its radiatively from the bottom of the 1^1B_u exciton band leading to the ground state. PL possesses the typical totally symmetric vibronic replicas due to the strong electron-molecular vibration interaction that is a typical characteristic of Frenkel excitons [12,13].

Since the PL of polythiophene (PT) is very similar [23] to that of T_6 we infer that the lowest excited electronic state in PT also has a 1^1B_u character. The 2^1A_g electronic level in PT would therefore be at higher energies. This refers to "real" PT which has a finite average conjugation length opposed to the "ideal" infinitely conjugated chain. In view of the empirical observation that the emission from molecular crystals at low temperature occurs almost universally from the lowest singlet excited state [13] (known also as Kasha's rule [13]) and considering the similarities of the PL spectra we suggest that the electronic energetics of "real" PT follows the same excited states ordering as 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 poly(paraphenylene vinylene) (PPV) [24].

The direct identification of the location of the lowest g state in T_6 suggests that $e-e$ correlations are weaker in the nondegenerate ground-state conjugated polymers than in the degenerate ones. It also has relevant implications in the photophysics of this class of conjugated systems compared to polyenes. In fact in polyenes the excited state energy ordering is $2^1A_g < 1^1B_u$, while in polythiophene oligomers it is the opposite. We notice that the energy difference between the two lowest electronic levels is rather small and therefore the relative location of levels may be perturbed for instance by modification of the intermolecular interaction. The location of the 2^1A_g state also has relevance for the interesting nonlinear optical properties of α -sexithienyl which have been shown [25,26] to approach those of the polymer. We predict that the electronic $\chi^{(3)}(-3\omega, \omega, \omega, \omega)$ response should show a two-photon resonance in the proximity of $1.09 \mu\text{m}$ 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 [27] at the fundamental wavelength of $1.06 \mu\text{m}$ and attributed to a three-photon resonance [27,28], is rather due to a two-photon resonance.

In conclusion, we have shown that the low-lying A_g singlet exciton in crystalline α -sexithienyl is at slightly higher energy than the B_u . This excited state ordering is likely to be maintained in "real" polythiophene if not in the ideal infinitely conjugated chain.

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