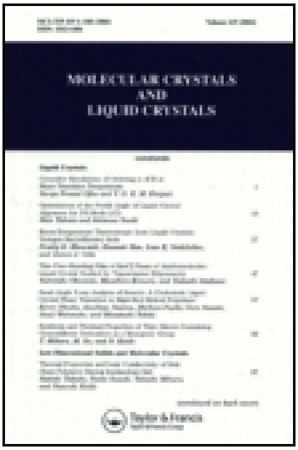

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Study of Photogenerated Nonlinear Excitations in a Polythiophene Model Compound: α-Sexithienyl

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STUDY OF PHOTOGENERATED NONLINEAR EXCITATIONS IN A POLYTHIOPHENE MODEL COMPOUND: α-SEXITHIENYL

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Abstract. Photogeneration of nonlinear excitations in the six thiophene unit oligomer of polythiophene has been studied. The formation of polarons is inferred from the observation of IRAV modes associated with midgap electronic transitions confirming the theoretical expectations that these electronic excitations are stable in short oligomers.

Introduction

Electrical as well as nonlinear optical properties of polyconjugated systems gave rise to a tremendous interest in the field of conjugated polymers[1].

All chemically or electrochemically synthesized conjugated polymers possess a low degree of order and structural dishomogeneity (difference in chain lengths, side chains, conjugation interruption, etc.) which affect their electronic properties. Most of the polyconjugated systems synthesized up to now have a nondegenerate ground state and among them polythiophene (PT) is the most widely studied. It has been calculated that pairs of bond alternation defects are stabilized if the overall defect is charged and extends for at least four thiophene units[2-4].

The aim of this work is to investigate on the stability of nonlinear excitations in a well defined conjugated system consisting of six thiophene units (α-sexithienyl) by means of photoinduced absorption spectroscopy (PA). We will show that T6 is a good model compound for PT.

Experimental

α-sexithienyl (T6) was synthesized by means of a catalytic coupling of Grignard salts obtained from 2,2'dithienyl with 5,5'dibromo 2,2'dithienyl, by using [1,2-bis(diphenilphosphino)ethane] nickel chloride as a catalyst. This procedure allows us to use a two order of magnitude smaller amount of catalyst with respect to that reported in ref. 5.

The photoinduced absorption spectra have been measured by means of a modified FT-Interferometer (Bruker IFS-88) in which an Ar^+ laser beam was allowed to illuminate a very good quality pellet of T6 in KBr (0.06 % in wt.). The visible transparency of the pellet allowed us to make PA up to 18000 cm^{-1}.

A MCT detector with KBr and Quartz/SB beamsplitters were used to cover the region 600 - 10000 cm^{-1} (0.074 - 1.24 eV) whereas a Si-Diode detector with appropriate filters and a Quartz/UV beamsplitter covered the 10000 - 18000 cm^{-1} (1.24 - 2.23 eV) region. The details of the data handing are described elsewhere[6]. Care was taken in order to avoid any sample heating by the laser. Consecutive sets of interferograms with laser on and off, with a period of one minute were stored in order to avoid continuous shining of the sample.

Results and Discussion

The spectroscopic observables of nonlinear excitations in conjugated systems are infrared activated vibrations (IRAV) reflecting the local lattice distortion, two confined mid-gap states reflecting the interaction between the two confined mid-gap non-bonding P_z, and the bleaching of the first allowed π-π^* electronic transition. The IRAV of T6 at 4.2 K excited by 2.41 eV Ar^+ laser line (power = 8 mW/cm^2) are shown in figure 1. These are the signatures of the presence of charge carriers which are formed due to direct injection of e-h pairs by photons. The overall IRAV features are strikingly similar to that of PT where they are considerably more intense. In T6 the IRAV bands are relatively sharper in agreement with its molecular crystal character.

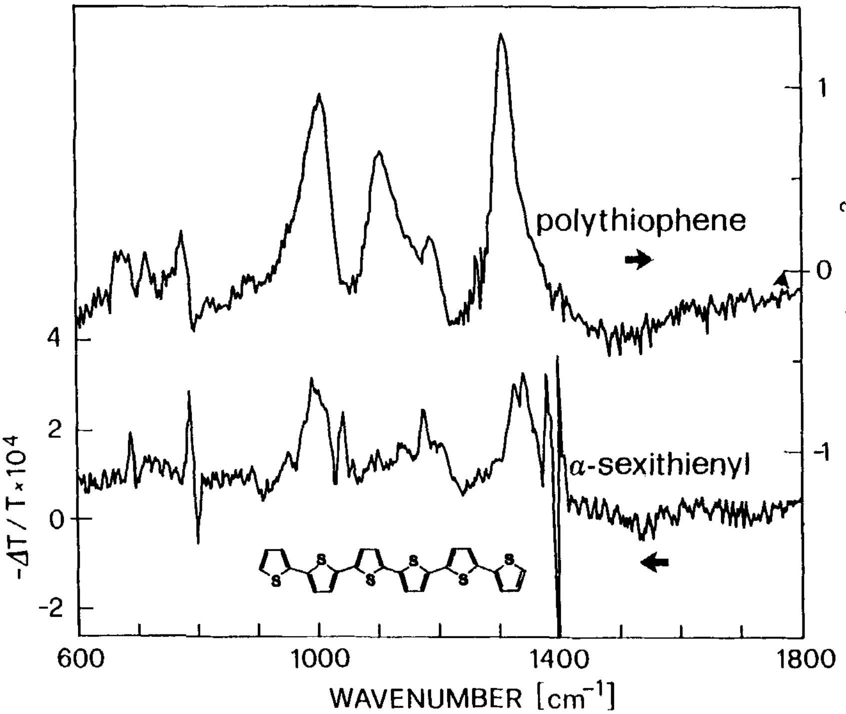

Fig.1 Photoinduced Absorption spectra of PT (upper) and T6 (lower).

The PA spectrum at higher energies shows two electronic PA bands at 6000 and 11900 cm^{-1}. These bands are relatively narrower than the PA bands of PT. The laser intensity dependence of the two PA bands has been studied between 0.8 to 100 mW/cm^2. The intensities of both bands change as the square root of the laser intensity and then at higher power show saturation. Both bands start to deviate from power half dependence at the same laser power suggesting a similar origin. This type of power half dependence and then saturation at higher laser power can be explained in terms of bimolecular recombination kinetics and can be expressed as a rate equation of the following form:

$$(dn/dt) = \alpha I - \beta n^2 - \gamma I$$

where n is the number of excitations, I is the laser power and α, β, γ are constants. The first term of the right hand side of the equation represents the generation process, the second represents the standard bimolecular recombination, and the last term refers to the decay of photogenerated carriers. At low laser power, one can neglect the last term and this will give rise to the $I^{1/2}$ dependence of the PA bands and at higher laser power I, one expects saturation. This type of dependence is also observed in polymers[7]. We infer that the two electronic photoinduced states are due to the formation of stable polarons.

In conclusion we demonstrate the photogeneration of stable nonlinear excitations in a well defined conjugated system. The photogeneration of polaron as well as the IRAV features in T6 allows us to confirm previous theoretical calculation about the extension of stabilized charged defects and to assume T6 as a model compound for PT. The electronic structure of T6, that we have studied by linear and nonlinear spectroscopy[8], indicates indeed that T6 is a good model for PT. Moreover, the PA of T6 suggests that NLO properties of T6[9,10] are related to the nonlinear photoinduced excitations.

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References

1. T.Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed., 12, 11 (1974); "Nonlinear Optical Effects in Organic Polymers", Ed. by J. Messier, F. Kajzar, P. Prasad and D. Ulrich (NATO ASI Series E Vol. 162, Kluwer Acad. Publ., 1989).

2. K. Fesser, A.R.Bishop and D.K. Campbell, Phys. Rev. B., 27, 4804 (1983)

3. J.L. Bredas, R.R. Chance and R. Silbey, Phys. Rev. B, 26 5843 (1982)

4. J.L. Bredas, F. Wudl and A.J. Heeger, Solid State Commun., 63, 577 (1987)

5. J. Kagan and S.K. Arora, Heterocycles, 20, 1937 (1983)

6. C. Taliani, G. Ruani, R. Zamboni, A. Bolognesi, M. Catellani, S. Destri, W. Porzio and P. Ostoja, Synth. Met., 28, C507 (1989)

7. H.E. Shaffer and H.J. Heeger, Solid State Commun. 59, 415 (1986)

8. C. Taliani, R. Danieli, N. Periasamy, G. Ruani and R. Zamboni, this conference proceedings.

9. M.T. Zhao, B.P. Singh and P.N. Prasad, J. Chem. Phys., 89, 5535 (1988)

10. D. Fichou, F. Garnier, F. Charra, F. Kajzar and J. Messier, Spec. Publ. Royal Soc. Chem., 69, 176 (1989)