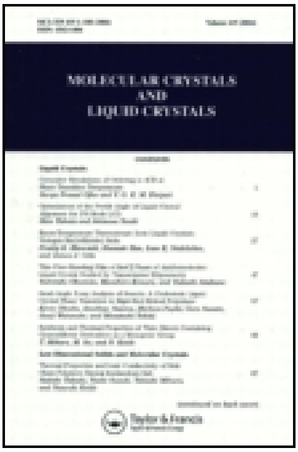

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Photomodulation Spectroscopy in α-Sexithyenil

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CW PHOTOMODULATION SPECTROSCOPY IN α-SEXITHYENIL

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Abstract The CW photoinduced absorption technique has been applied to α-sexithyenil (T_6) vacuum evaporated films. We observed new electronic transitions which appear deep in the gap. We assigned these structures to charged species separated on different molecular layers and trapped to defects. The narrow line shape of the photoinduced features is indicative of the molecular solid character of T_6 thin films and it provides an upper limit for the charge symmetry breaking of 0.04 eV.

INTRODUCTION

α-sexithyenil (T_6) is a rod shaped molecule containing twelve π-conjugated double bonds which displays interesting electronic, optical and structural properties. As a matter of fact the possibility of growing this organic semiconductor in highly homogeneous polycrystalline thin films by vacuum deposition is suitable for several applications [1–2–3–4]. The absorption spectra of cations $T_6^{\cdot+}$ and di-cations T_6^{++} radical species have been measured in chemically doped T_6 solution showing the formation of charged species [5]. Alternatively photoexcitation can produce charge carriers in molecular solids provided that the photon energy is above a minimum threshold generally at energy higher than the first excited singlet state. In T_6 this threshold has been located at 2.16 eV by a comparison of the one photon excitation curve for radiative recombination and the action spectrum [6]. For this reason we have applied the quasi-steady state photomodulation technique in the NIR region to a T_6 vacuum evaporated film.

EXPERIMENT

T_6 was synthesized according to the procedure reported in Ref. 7. A thin film of T_6 with thickness of about 2000 Å was deposited onto a sapphire substrate by evaporation at about 295 K of the powdered oligomer under vacuum. A standard phase sensitive detection technique with mechanical modulation of the pump beam was used to measure the photoinduced change in the trasmission of a probe light provided by a tungsten lamp in the range from 0.4 to 2.2 eV. The excitation was the 514.5 nm line of a CW ion-argon laser.

RESULTS AND DISCUSSION

Fig.1 shows the PA spectrum at 77 K using a 20 Hz modulation of the pump light and an average laser intensity of 60 mW/cm^2. There are two intense photoinduced bands at 0.74 and 1.43 eV and two minor features at 0.92 eV and 1.085 eV. These structures are much sharper than those observed previously in polythiophene [8].

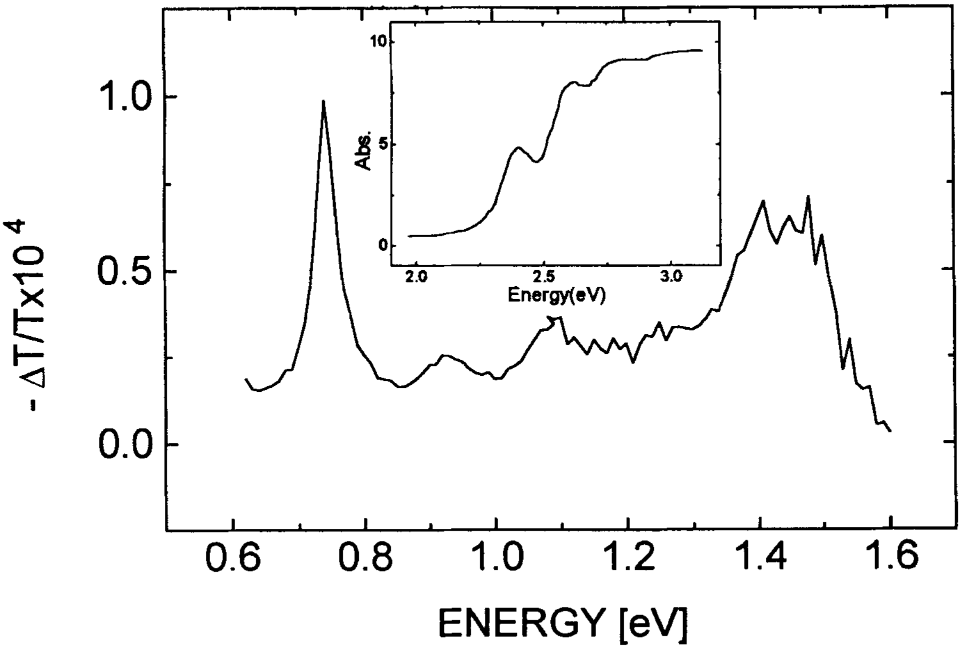

FIGURE 1 Photoinduced absorption spectrum for a T_6 film at 80 K. The inset shows the linear absorption and the energy of the photons.

At energy higher than 1.6 eV a strong photoluminescence prevents the detection of the

PA signal. The inset shows the characteristic linear absorption of the T_6 film which displays vibronic replica. Bi-molecular recombination can be conjectured for the 1.43, 0.92 and 0.74 eV bands since they show a square root dependence on excitation intensity ($I^{0.51}$) (Fig.2). On the contrary we cannot derive any conclusion about the recombination mechanism of the 1.085 eV band because the intensity dependence is $\sim I^{0.67}$(Fig.2). The modulation frequency dependence of the PA signal was measured by changing the chopping frequency between 3 to 3000 Hz at 77 K at 1.085 eV, 0.92 eV and 0.74 eV. A plot in log-log scale is shown in Fig. 2. From these measurements we deduce a characteristic decay time of about 3 ms for the 0.92 and 0.74 eV bands, and about 500 μs for the weak structure at 1.085 eV.

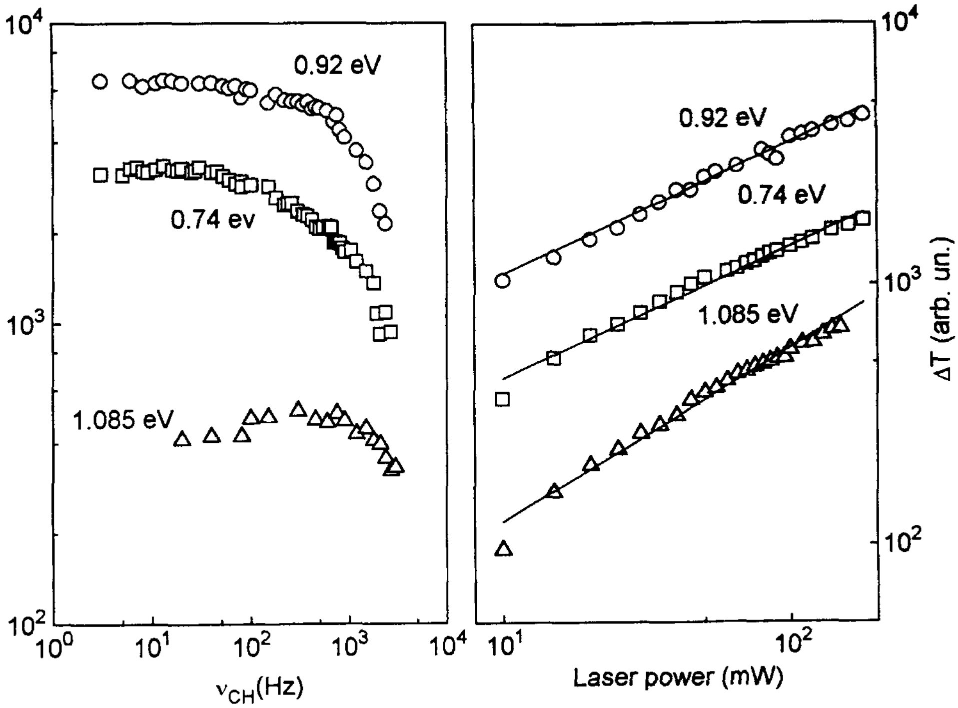

FIGURE 2 Left: Modulation frequency dependence of the PA bands at 80 K; Right: Excitation intensity dependence of the PA bands. Fitting by a power law I^{α} yields $\alpha = 0.51$ for the 0.92 and 0.74 eV bands and $\alpha = 0.67$ for the 1.085 eV band.

A comparison of the spectra at 80 K and 295 K in the energy range between 0.6 and 1.25 eV is reported in Fig. 3. The 0.92 eV and the 0.74 eV bands persist at room temperature, their energy being slightly blue-shifted, whereas the 1.085 eV structure is almost completely disappeared. These data point again to a different origin for the latter band. Based on our experimental results we then propose a common origin for the two bands at 0.74 and 1.4 eV and the weak stucture at 0.92 eV. In order to propose an assignment the following points should be taken into consideration:

1) The PA spectrum measured in T_6 pellet between $600 cm^{-1}$ and $1800 cm^{-1}$ and using the same excitation of the present experiment shows characteristic IR active vibrations [7];

2) The observed PA bands at 0.74, 0.92 and 1.4 eV have a one-to-one correspondence to the chemically doping induced (DI) features in T_6 solution and assigned to $T_6^{;+}$ radical cations[5];

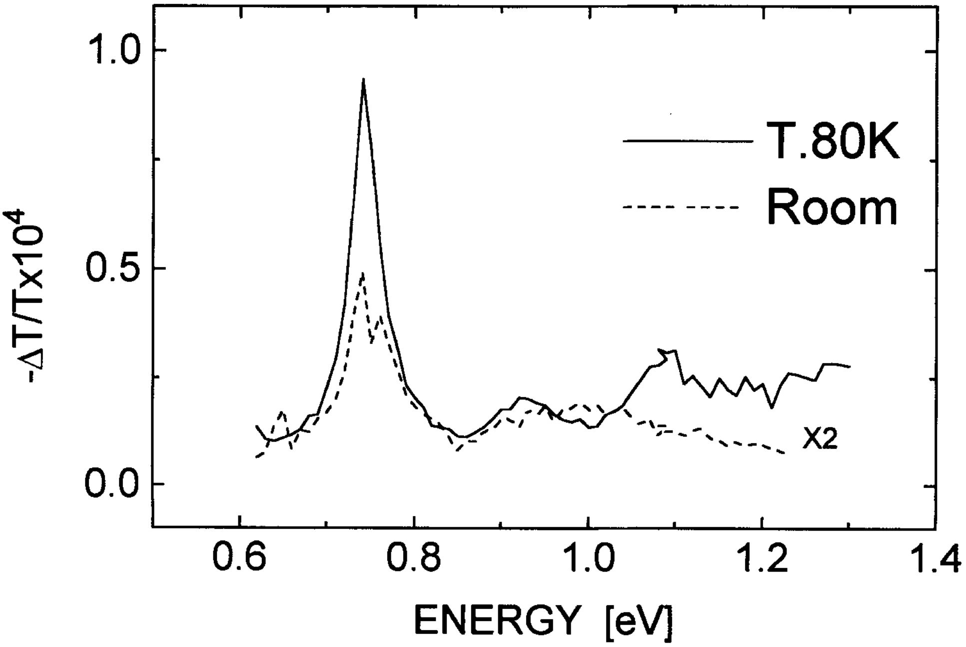

FIGURE 3 Comparison of PA spectra at room temperature and 80 K.

3) The same spectrum is measured for spectra of chemically doped Didodecyl-T_6 (DT6) solution and assigned again to $T_6^{;+}$ cations [9];

4) DI features are observed at energy higher than PA ones. This is possibly caused by the

counter-ion coulomb binding energy term, which is absent in the photogeneration case, but can alternatively be accounted for by the solvent effect on the radical species in solution. From 1), 2), 3) and 4) we proposed that the three PA structures at 0.74, 0.92 and 1.43 eV could be accounted for by spatially confined polarons, i.e. mono-valent ions, which appear to be the stable charged state in T_6 at the experimental concentration N_{ex}. In a CW illumination experiment this can be evaluated using the simple formula which holds for thin samples (i.e. $\alpha D < 1/\alpha_{Pu}$ where α_{Pu} is the absorption coefficient at the pump wavelength)

$$-\Delta T/T = N_{ex}\sigma D \tag{1}$$

where D is the film thickness and σ is the absorption cross-section of the species. From the observed signal at 77 K for the 0.74 ev PA band ($\sim 10^{-4}$), a film thickness $D = 2.2 \times 10^{-5}$ cm and a cross-section [10] $\sigma = 4 \times 10^{-17}$ cm^2 we obtain $N_{ex} = 1 \times 10^{17}$ cm^{-3}.

Within this assignment the 0.74 eV and the 1.43 eV bands are electronic transitions of the ionic species. Since photoexcitation generates both kinds of charges we conclude that the energy separation of the electronic transitions of the positive and negative ions is smaller than 0.04 eV. The 0.92 eV structure, based on our experimental results, is associated with the same charged state and it is assigned to a vibronic replica, consistently with the energy separation of 0.18 eV.

The band at 1.085 eV has a different origin from the other three, and it could possibly be associated to a small concentration of di-valent ions, since the position fits with what has been observed in DI experiments for di-cations. About this possibility we note however that in highly diluted conditions the probability of di-valent ions generation appears negligible. A triplet-triplet transition can alternatively be proposed, the small strength of the signal being consistent with the short lifetime (300 ns) proposed for the triplet exciton in T_6 [11]. In fact a sizeable spin-orbit coupling due to the heavy atom effect from sulfur, allows intersystem crossing from singlet to triplet. This can account for the different I-dependence of the 1.085 eV band because confined polarons undergo bimolecular recombination ($\sim \sqrt{I}$) whereas triplets have more than one route of recombination (for instance triplets quenching by $^3O_2$). We propose the following scenario for the energy relaxation. The optically excited neutral Frenkel exciton thermalizes into a charge transfer exciton[12] which eventually undergoes a disorder induced separation into free charges.

If these charges stay in different molecular layers their recombination probability results strongly decreased because of the anisotropy of T_6 crystal yielding lifetimes of the order of ms [6].

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