

# Davydov splitting in triplet excitons of tetracene single crystals

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**Abstract:** This work reports room temperature Davydov splitting in triplet transitions  $T_n \leftarrow T_1$  of tetracene single crystals. This was observed through femtosecond transient absorption spectroscopy with polarized  $\parallel b$  and  $\perp b$  probing on the (ab) face of the 300 nm thick crystal. A Davydov splitting of 0.04 eV ( $286 \text{ cm}^{-1}$ ) was obtained on an excited state absorption signal ascribed to triplet excitons in Birech *et al*, jcp, Vol. 140, 114501, 2014.

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## 1. Introduction

Tetracene (Tc) is an organic solid gaining a lot of academic and industrial interest lately due to its potential for fabricating novel opto-electronic devices such as high efficiency solar cells [2,3] and ambipolar organic light emitting diodes (OLETs) [4]. Frenkel excitons (bound electron-hole pairs) transport excitation energy within the crystal lattice. They are classified as either singlet,  $S$  (total spin of system  $\mathbf{S}=0$ ) or triplet,  $T$  (total spin  $\mathbf{S}=1$ ). The latter has the longest decay lifetime and largest diffusion lengths and are formed on an ultrafast timescales via singlet exciton fission after absorption of a photon [1, 10]. The interactions of two translationally inequivalent molecules in Tc's unit cell upon optical excitation results in Davydov splitting (DS) of 0.08 eV in the 0-0 vibrational band of the  $S_1 \leftarrow S_0$  transitions as obtained from steady state absorption spectroscopy [1,7] and calculations [5,6]. Reports on experimental determination of DS in triplet excitons are rare in literature most likely due to use of polycrystalline Tc films or thick crystal samples. In the former and latter, the presence of randomly oriented crystallites on the substrate and the high absorptivity (of the order of  $10^5 \text{ cm}^{-1}$  at the maximum of their  $S_1 \leftarrow S_0$  absorption) respectively frustrates the observation of this splitting. There has been, however, a report on a calculation of DS in Tc triplet excitons done by Tiberghien and Delacote [8]. In anthracene, a close relative of tetracene in the linear polyacene group of molecular crystals, DS in the  $S_0 \leftarrow T_1$  transitions as measured from delayed fluorescence spectra has been reported to be  $21 \text{ cm}^{-1}$  [9,11].

Researchers are keen on finding ways of utilizing triplet excitons (extract the holes and electrons) in improving efficiency of solar cells. In this work, we report DS at room temperature in triplet excitons ( $T_n \leftarrow T_1$  transitions) in the 300 nm thick Tc using femtosecond transient absorption spectroscopy. The sublimation grown thick (100-500  $\mu\text{m}$ ) crystal platelates with extended (ab)-facets were microtomed to an appropriate thickness for the experiment. The experimental setup used and excitation conditions have been described in detail in reference [1].

## 2. Results and discussion

Figure 1 shows both the steady state absorption (SSA) (Figure 1 (a)) and transient absorption (TA) spectral traces (Figure 1 (b,c)) obtained from the 300 nm thick tetracene single crystals. A DS of 0.08 eV in 0-0 vibrational band of the  $S_1 \leftarrow S_0$  transitions was reported in reference [1]. The two SSA spectra (Perp b and Para b) in Figure 1 (a) were obtained with the incident optical field polarized  $\parallel b$  and  $\perp b$  on the (ab) crystal face. Also noted was very low splitting in higher vibrational bands (e.g 0.01 eV for the 0-2 vibrational band) implying minimum resonance interaction in higher excitonic states. The positions of the vibrational peaks in the SSA spectra appeared as negative peaks in the TA signals indicating positions of ground state bleach (GSB) signals. The displayed TA spectral traces were obtained with probe beam polarized  $\parallel b$  (Figure 1 (b)) and  $\perp b$  (Figure 1 (c)) thus interrogating changes in absorption at the lower and upper Davydov components respectively in either  $S$  or  $T$  states of the excited (pumped) crystal.

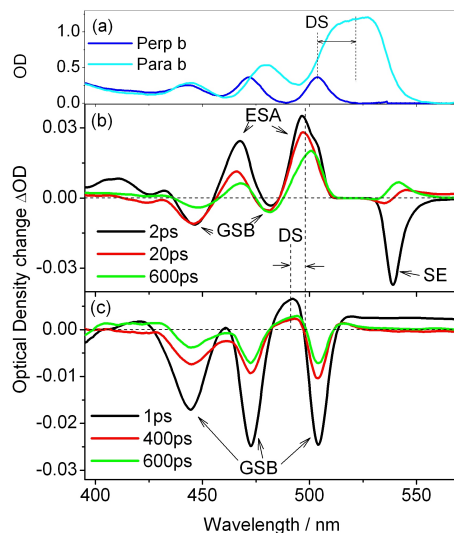


Fig. 1. The figure showing (a) the steady state absorption (SSA) spectra (b) and (c) transient absorption spectral traces at selected times obtained with probe beam polarized  $\parallel b$  and  $\perp b$  respectively of the 300 nm thick tetracene single crystals.

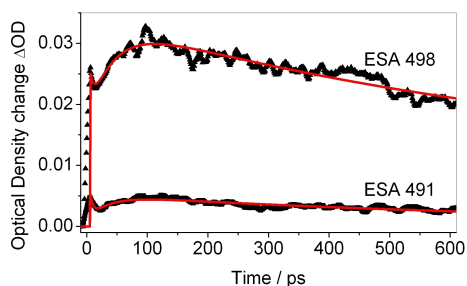


Fig. 2. The temporal decay kinetics of the ESA signals at 498 nm and 491 nm with probe polarized  $\parallel b$  and  $\perp b$  respectively. Similar values of decay constants were obtained in both signals after fitting a multiexponential function (red line) on the data (black)

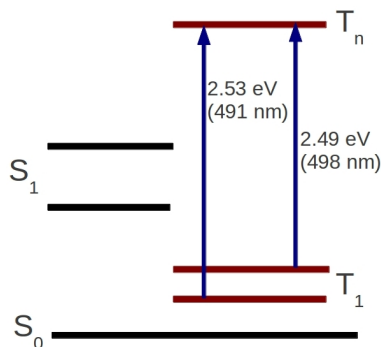


Fig. 3. A schematic showing the origin of the observed DS in the ESA signal attributed to  $T_n \leftarrow T_1$  transitions. Both upper and lower Davydov components are shown in the  $S_1$  and  $T_1$  states. Splitting in  $T_n$  states were considered negligible.

The signal at around 498 nm (2.49 eV) in Figure 1 (b) ascribed to  $T_n \leftarrow T_1$  transitions in references [1] and [10] was blue shifted to 498 nm (2.49 eV) when the crystal was probed with beam polarized  $\perp b$  as shown in Figure 1 (c). This gives a DS of 0.04 eV (286  $\text{cm}^{-1}$ ). The two signals also displayed identical temporal decay dynamics thus indicating that they originate from the same excitonic species (see Figure 2). Since TA spectroscopy probes absorption from transient states, the origin of these two signals can then be ascribed to  $T_n \leftarrow T_1$  transitions as schematically represented in Figure 3. Triplet excitons are known to be formed on an ultrafast timescale (direct fission on  $\approx 300\text{fs}$  and thermally on  $\approx 40\text{ps}$  [1]) through singlet exciton process. In singlets, DS results from dipole-dipole interactions between the two molecules per unit cell but this interaction is forbidden in triplets due to Pauli principle [9]. Term splitting in triplets occur only via the allowed exchange interactions. Splitting in  $T_n$  states was considered negligible considering that in singlet excitons lower and lower splittings were observed in higher vibrational bands. In  $T_1$  states, a DS of 30  $\text{cm}^{-1}$  (or 0.000372 eV) was calculated by Tiberghien and Delacote [8].

### 3. Conclusion

Ultrafast transient absorption spectroscopy on tetracene single crystals employing polarized probing can provide information on Davydov splitting in triplet excitons. A DS value of 0.04 eV (286  $\text{cm}^{-1}$ ) in the  $T_n \leftarrow T_1$  transitions is exhibited by tetracene single crystals at room temperature.

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