

Vibrational Coherence Reveals the Role of Dark Multiexciton States in Ultrafast Singlet Exciton Fission

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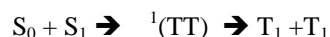
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Abstract: We use 2D electronic photon-echo spectroscopy to study ultrafast singlet exciton fission in pentacene. Our observations and analysis of vibronic coherences provide insight to the role played by dark multiexcitonic states in mediating fission.

OCIS codes: (320.7130) Ultrafast processes in condensed matter, semiconductors, (350.6050) Solar energy

Singlet exciton fission has been attracting increasing attention recently due to its potential for use in excitonic solar cells, enabling the generation of two electron-hole pairs per photon absorbed. This allows better use of high-energy photons in the solar spectrum and could enable solar cells to overcome the Shockley-Queisser limit on the power conversion efficiency of a single junction cell [1]. The first steps in the process have been taken with all organic cells based on pentacene that show external quantum efficiencies above 126%, the highest for any solar technology till date [2]. The basic equation describing fission can be written as:



Here S_0 is a chromophore in the ground state, S_1 a chromophore in the excited singlet state, T_1 the molecular triplet state. ${}^1(TT)$ is a doubly excited state that can be described as a pair of triplets coherently coupled to form an overall spin singlet. The ${}^1(TT)$ is the theoretically required multiexcitonic intermediate state in the fission process, however it is optically dark and has a very short lifetime. For these

reasons no experimental data about the electronic structure of this state have yet been presented. This combined with a lack of information about the role of vibrational coupling mean that a comprehensive mechanistic picture of the efficient singlet fission is currently lacking. Here we study pentacene, a model system for ultrafast fission [3], using ultrafast 2D electronic photon echo (2DPE) spectroscopy. We demonstrate that this technique allows us to study not only previously ‘dark’ multiexcitonic $^1(TT)$ state but also the underlying vibrational and electronic dynamics that mediates transfer between S_0S_1 and $^1(TT)$.

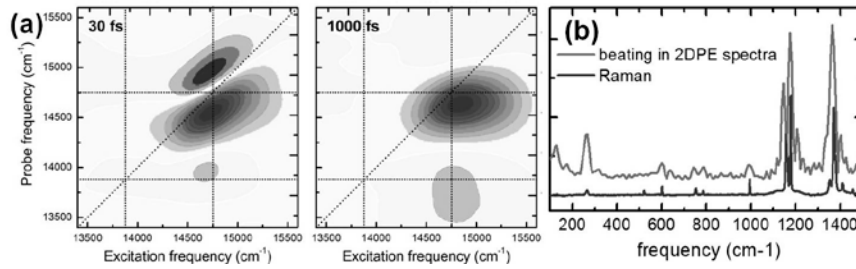


Figure 1. (a) 2DPE real-part spectra of pentacene molecular crystal at different evolution times. (b) Spectrum of evolution-time oscillations observed in 2DPE data compared to the Raman spectrum of pentacene.

Figure 1a presents three time slices showing the evolution of the real-part of the 2D spectra of a polycrystalline pentacene film. On the right the pump-probe spectra at the same time delay are shown for comparison. The 2D spectra are dominated by a large positive peak on the diagonal at 1.83eV, which corresponds to ground-state bleach (SGB) of the main excited singlet transition and at short times (<90fs) also includes a contribution from stimulated emission (SE) from the singlet exciton. At 30fs a PIA feature, seen as negative peak at 1.87eV probe energy, is present. We assign this feature to the PIA of singlet excitons in agreement with previous pump-probe measurements. At longer waiting times, this PIA is lost as singlets undergo fission and a new PIA feature at 1.65eV probe energy appears, which corresponds to the transition from the lowest triplet state T_1 to the T_2 state. Importantly, no feature is observed at pump energy of 1.72eV where the $^1(TT)$ state is predicted to be. This indicates that the state can not excited directly from the ground state.

The quality of the 2D spectra obtained allows us to reveal not just the kinetics of the triplet state formation but also to map and investigate the role of intermediate states. For this we analysed the coherent beatings observed in the 2DPE data along the evolution-time axis. The spectrum of these beatings is shown in the figure 1b. Figure 2 shows 2D FT ‘beating-maps’ for frequencies ranging from 170 cm^{-1} to 1500 cm^{-1} . For all the 2D beating-maps presented the most intense oscillatory component is found at $\omega_{excitation} = \omega_{probe} = 1.83eV$, i.e. the position of the singlet exciton, $\omega_{singlet}$. It can also be seen that peaks occur that are separated from this main peak by the energy of the vibrational mode, as indicated by the arrows in the figure. For example, peaks can be seen at probe frequency $\omega_{singlet} - 605cm^{-1}$ in

Figure 4b and at probe frequency $\omega_{\text{singlet}} - 1170\text{cm}^{-1}$. These and additional peaks that occur below and to the right of the diagonal are caused by the coupling of vibrational modes to an electronic transition, in this case the singlet, ω_{singlet} .

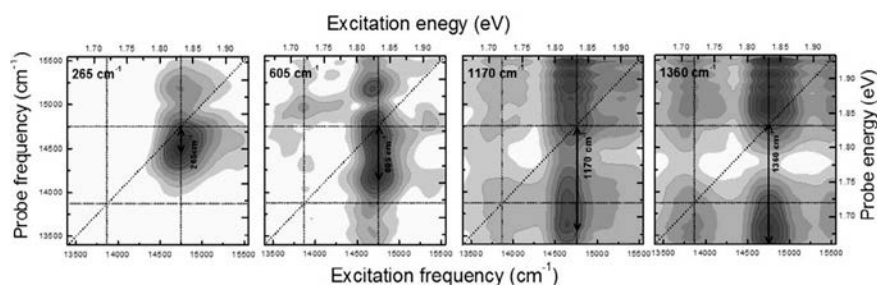


Figure 2. The 2D maps of beating in 2DPE spectra corresponding to the strongest oscillatory features observed in figure 1b.

Quite surprisingly, the higher energy beating-maps at 1170cm^{-1} and 1360cm^{-1} an additional peaks at the excitation frequency of 13900cm^{-1} are observed. This peak is absent from the lower energy beating-maps and is not predicted within the displaced-oscillator theoretical framework, within which peaks should not appear at lower energies on the diagonal.[5] The position of the new peak is at $\omega_{\text{excitation}} = 1.72\text{eV}$, i.e. at the expected position for the $^1(\text{TT})$ state. We note that no state was observed here in the absorptive 2D maps shown in Figure 1a. This suggests that the previously ‘dark’ $^1(\text{TT})$ state is being revealed via vibrational coherence because there are transitions with strong dipoles contributing to the 4-wave mixing signals observed. The presented work thus demonstrates a novel method of revealing and studying such ‘dark’ states, not accessible via conventional optical methods.

Interestingly, the dark $^1(\text{TT})$ state only contributes to the vibrational coherence when the vibrational mode can bridge the energy gap between S_1 and $^1(\text{TT})$. This suggests that it is vibronic rather than direct electronic coupling that strongly mixes $^1(\text{TT})$ and S_1 , allowing for ultrafast fission.

References

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