Probing atomic motions accompanying singlet exciton fission in pentacene

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Abstract: We investigate the structural dynamics accompanying singlet fission in pentacene single crystals with femtosecond electron diffraction. The data reveal incoherent and coherent contributions to the structural dynamics. We discuss the implications for singlet fission properties.

1. Introduction

Singlet exciton fission (SF) is a process occuring in molecular semiconductors by which a singlet exciton splits into two independent triplet excitons. Due to the possibility to generate two electron hole pairs per absorbed photon, the SF process has generated tremendous attention in photovoltaics research. Since its discovery in the late sixties by static measurements of the magnetic dependence of fluorescence [1], much progress has been realized in understanding and exploiting the SF mechanism, as reviewed by Smith et al. and lately by Miyata et al. [2–4]. It is now well-established that the SF properties, such as efficiency and rate, strongly depend on subtle details of the molecular packing. While the lattice dynamics is thought to play an essential role in the destruction of the electronically correlated triplet pair and the subsequent spatial separation of the independent triplets, a direct probe of the molecular motions involved in a singlet fission process has been lacking.
Here we directly observe the structural dynamics accompanying the singlet fission process in single crystal pentacene using femtosecond electron diffraction (FED). Our data reveal the presence of incoherent motions, as well as coherent atomic motions below 1 THz. Molecular dynamics (MD) simulations enable us to attribute these coherent motions to collective inter-molecular motions involving several molecules and featuring high dynamic heterogeneity. By moving entire molecules against each other, these motions transiently modify the transfer integral between orbitals of different molecules, and may modulate the singlet fission rate.

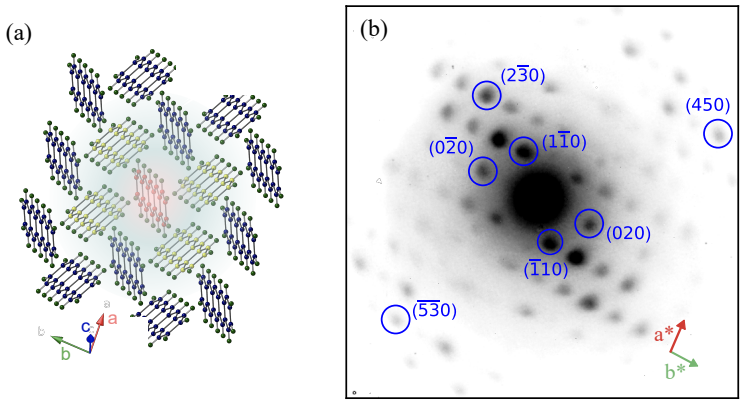

Fig. 1. (a) Illustration of the crystal structure as viewed along the [001] surface normal (long axis). Theoretical works indicate that the lowest excited singlet state is delocalized over several molecules [5], represented by the blue halo. (b) Examplary transmission electron diffraction pattern from a 40 nm thin [001] pentacene single crystal slab.

2. Methods

To investigate the structural dynamics of the pentacene crystals directly, we employ the FED method [6–8]. Technical details of the method can be found elsewhere [9]. Here, we use a 50 fs optical pump centered at 680 nm and polarized along the *a* axis (see Figure 1(a)) to excite the crystal, resonant with the lower Davidov component of the lowest singlet exciton transition. Bandedge excitation minimizes heating effects, and enables us to isolate the structural dynamics arising from SF. The probe is a femtosecond bunch of electrons which diffracts off the photo-excited crystal some time after the pump. By tuning the pump-probe delay, a series of time-resolved diffraction patterns is recorded, providing information about atomic motions in reciprocal space with a temporal resolution of 250 fs. An examplary diffraction pattern is shown in Figure 1(b). We apply an incident fluence of 1.5 mJ/cm^2, yielding an estimated excitation density of 1 per 30 molecules. The photo-excited crystal subsequently undergoes exothermic singlet fission with a yield close to 100% . The accompanying structural dynamics is directly probed by analysing changes in the time-resolved diffraction patterns.

3. Results

An overview of the time-resolved data is shown in Figure 2, revealing rich structural dynamics. The time-dependence of a few selected Bragg reflections is shown in Figure 2(a). The observed behaviour, with some Bragg reflections increasing and some decreasing, departs from simple heating effects. By performing a global fit on the ensemble of time-resolved traces (20 peaks), we show that the structural dynamics can be captured by a fast picosecond component of 1.6 $\pm$ 0.2 ps and a slower component with a time constant of 28 $\pm$ 1 ps. These time constants unambiguously reveal the timescales of the incoherent vibrational dynamics accompanying the singlet exciton fission process in pentacene. We discuss these results in light of complementary literature, and tentatively assign the fast time constant to the destruction of the electronically correlated triplets (TT) via vibrations, while the slow time constant is assigned to the triplet separation and diffusion. At late times (t $>$ 50 ps), we observe a structural distortion which lasts longer than our largest delay of 1 ns, see the difference diffraction pattern in Figure 2(b).

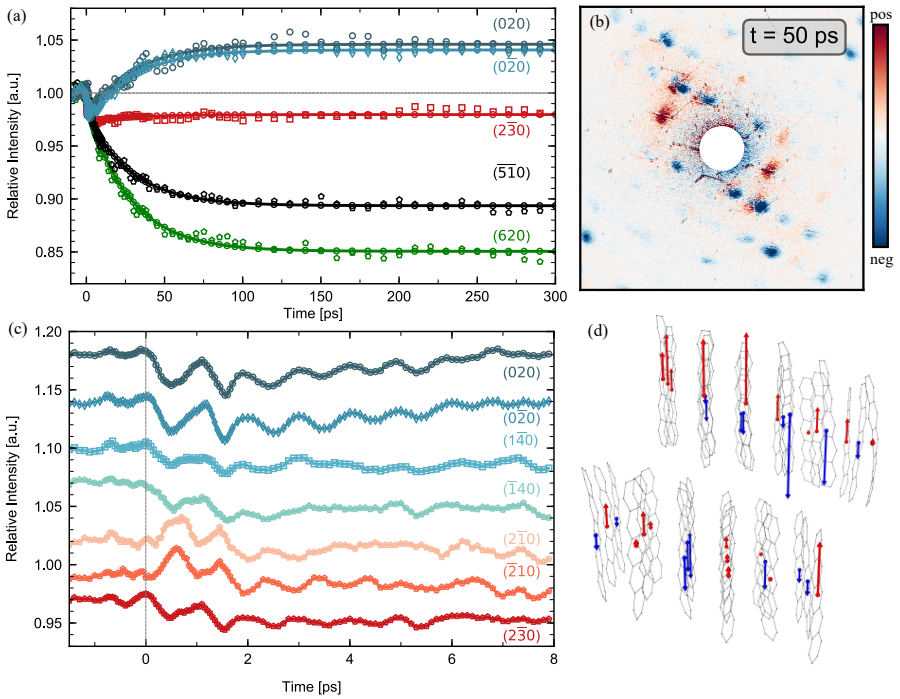

Fig. 2. (a) Time-dependence of the relative intensities of few selected Bragg reflections. Fits are obtained from the global fitting procedure. (b) Difference between the diffraction pattern 50 ps after photoexcitation and the pattern prior to photoexcitation. (c) Several Bragg reflections show pronounced coherent dynamics at 1 THz. The time-resolved traces are treated with a 4-point running average window here. (d) Molecular dynamics simulations reveal the real space motion at the origin of the oscillations around 1 THz. The arrows represent the displacement vectors for a given snapshot of the MD run.

A closer look into the first ten picoseconds of the structural dynamics shows that the intensity of several Bragg reflections is modulated at 1 THz. Periodic modulation of Bragg reflections intensities arise from periodic modulation of the structure factor, which directly reveals the presence of periodic intra- or intermolecular (or superimposed) oscillations [10]. The photo-excited singlet state of pentacene is delocalized over several molecules in the (ab)-plane of the crystal (see Figure 1(a)), and expresses a pronounced charge transfer character. The consequence of the instantaneously generated electron hole separation (during the laser pulse) is a Coulomb force, in this case between the absorbing molecule and its nearest neighbors. It acts on the atoms and can explain the generation of coherent lattice oscillations in the pentacene crystal, similar to the displacive excitation of coherent phonon process (DECP) [11].

To provide a real space picture of the 1 THz motions, we perform classical MD simulations. The MD results reveal the atomic motions in all their complexity, and demonstrate the importance of long range correlations and phonon-phonon coupling to provide a realistic picture in soft organic crystals. Simulated diffraction patterns from MD snapshots (not shown) enable us to link the MD and experimental results. By projecting the overall motion onto the three Cartesian coordinates and following the center-of-mass of the molecules/benzene rings, the motion can be distilled into a few dominant contributions, the largest of which are shown in Figure 2(d). These results show that the 1 THz motion is mostly inter-molecular in nature, involves several molecules and features high dynamical heterogeneity. Such dynamically disordered motion yields large changes in the transfer integral between adjacent molecules, which facilitates the generation of independent triplets by destroying electronic correlation. This finding indicates that singlet fission properties may be strongly impacted by such low-frequency collective modes.

4. Conclusions

Our experiments provide direct access to the rich lattice dynamics accompanying a singlet fission process. This study provides a new look on the SF mechanism, complementing the wealth of existing ultrafast studies. These results demonstrate the role of incoherent and coherent motions in electronically separating the triplets.

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