

Coherent phonon dynamics in singlet fission of rubrene single crystal

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Abstract: We observed wavepacket motions in singlet fission of rubrene single crystal at 35 K. A coherent phonon shows a transient frequency shift, indicating that a transition from S_1 to an intermediate state of the fission occurs within 2 ps.

1. Introduction

Singlet fission (SF) in organic materials, which is the fission of a singlet exciton (S_1) into two triplet excitons ($2T_1$) within picoseconds time scale, gathers growing interests recently because of their potential to boost the light conversion efficiency of organic photovoltaic devices [1]. A better understanding of the microscopic mechanisms of SF is necessary to achieve improved SF yields. Intensive discussion has been focused on a role of a charge transfer (CT) state under SF process: whether the SF proceeds via formation of a transient CT state or direct fission from the S_1 to multiexciton ($2T_1$) state occurs [2-4].

In a rubrene single-crystal, SF is supposed to be thermally-activated with substantial temperature dependence on its rate [4], indicating that low-frequency phonons are involved. Thus, in order to gain deeper insight of SF in a rubrene single-crystal, it is vital to understand a role of phonons. However, no previous study has addressed the role of electron-phonon coupling on SF dynamics in rubrene single-crystal. In this report, we focus on coherent phonon oscillation under SF process in rubrene single-crystal at 35 K with ultrafast pump-probe measurements, and discuss oscillatory feature observed at the absorption edge of triplet-triplet absorption band.

2. Experimental Methods

The pump-probe measurement was done by using a home-built noncollinear optical parametric amplifier (NOPA) pumped by a second harmonics of a outputs of a Ti:Sapphire regenerative amplifier (1 kHz) [5]. The NOPA outputs at 500-550 nm (40 fs) were split into two and one was used for pumping at the 510 nm edge of the rubrene crystal and the other was used for probe detected by photodiodes equipped with narrowband filters at 512 nm. A Glan polarizer was inserted in front of the photodiode to eliminate scattered pump light. The rubrene single crystal grown by physical vapor transport was cooled down to 35 K using a He cryostat mounted on a high vacuum cell. The polarization direction of pump and probe pulse were set to be parallel to b - and a -axis of the crystal, respectively. Pump power has been kept low enough to avoid multiple phonon absorption effect or light absorption induced heating.

3. Results and Discussion

Fig. 1. (a) shows transient absorption (TA) trace at 512 ± 5 nm from rubrene single-crystal under 35 K. The signal is mainly contributed from T_1 - T_n transient absorption [6]. In addition to a rise of background that corresponds to the formation of T_1 state, a clear oscillatory feature was observed. The Fourier spectrum of the oscillatory signal is shown in Fig. 1 (b); the spectrum shows strong peak at 83 cm^{-1} and small peaks at 108 cm^{-1} and 124 cm^{-1} . These frequencies agree with previous Raman study and indicate that the oscillatory signal is due to coherent phonons [7].

Fig. 1(c) and (d) show a spectrogram of the oscillatory signal obtained with 1 ps time window and transient intensity of the strongest peaks at each time window, respectively. Notable things are a transient frequency shift from 76 to 83 cm^{-1} and the increase of the oscillation amplitude both occur within 2 ps after excitation. Because these features are not expected for nuclear wavepackets in the ground state, the oscillatory signal is due to coherent phonons in the excited states. The rising time of the oscillatory signal in Fig. 1(d) coincides with the decay time of phonon oscillation observed in the previous work at S_1 - S_n absorption edge [8]. Thus, the transient frequency shift indicates an electronic transition from S_1 to another state: possibly to the intermediate state for the SF process [2].

Our results suggest that coherent phonon observed by conventional TA measurements can be a sensitive probe of such a dark intermediate state. Additionally, the dephasing time of 6 ps suggests that the coherence of nuclear motion is preserved through the electronic transition from S_1 to the intermediate states.

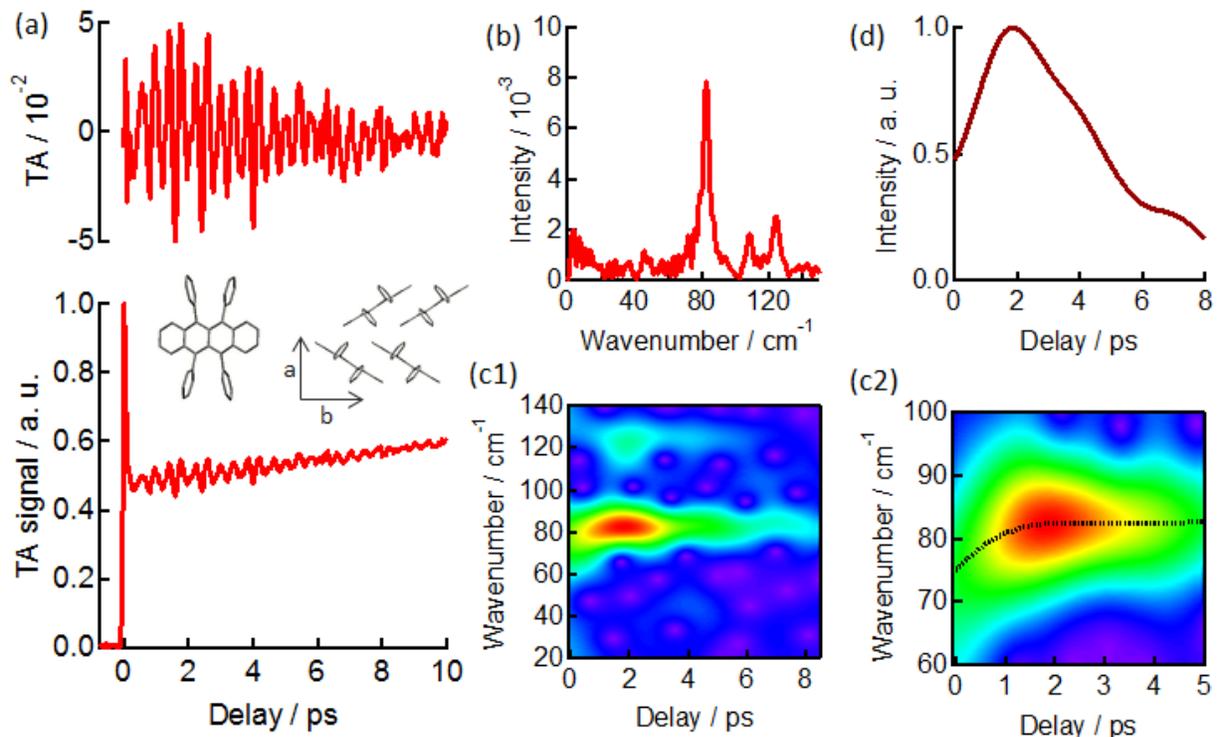


Fig. 1. (a) Transient signal (bottom) and oscillatory signal (top) observed from a rubrene single-crystal at 35 K. Inset is the molecular structure and crystalline structure of rubrene single-crystal. (b) Fourier spectrum of the oscillatory signal (c1,c2) spectrogram of the oscillatory signal and its enlarged scale plot, respectively. Black dot line is a trace of the peak wavenumber at each delay. (d) Peak intensity plot of Fourier spectra in spectrogram

Acknowledgements.

This work was supported by the Grant-in-Aid for Scientific Research (A) from the Japanese Society for the Promotion of Sciences (Grant No. 22245001), Grant-in-Aid for Challenging Exploratory Research from Japan Society for the Promotion of Science (Grant No. 24655011), Kyoto University Global COE program, Grants for Excellent Graduate Schools, MEXT, Japan, and the program of Network of Joint Research Center for Advanced Materials and Devices.

References

- [1] M. B. Smith and J. Michl, *Chem. Rev* 110, 6891 (2010)
- [2] T. C. Berkelbach, M. S. Hybertsen, and D. R. Reichman, *J. Chem. Phys.* 138, 114103 (2013).
- [3] P. M. Zimmerman, Z. Zhang, and C. B. Masgrave, *Nat. Chem.* 2, 648 (2010).
- [3] W. -L. Chan, M. Ligges, A. Jailaubekov, L. Kaake, L. Miaja-Avila, and X. -Y. Zhu, *Science*, 334, 1541 (2011).
- [4] L. Ma, K. Zhang, C. Kloc, H. Sun, C. Soci, M. E. Michel-Beyerle, and Gagik G. Gurzadyan, *Phys. Rev. B*, 87, 201203(R) (2013).
- [5] K. Watanabe, K. Inoue, I. F. Nakai, M. Fuyuki, and Y. Matsumoto, *Phys. Rev. B*, 80, 075404 (2009).
- [6] L. Ma, K. Zhang, C. Kloc, H. Sun, M. E. Michel-Beyerle, and Gagik G. Gurzadyan, *Phys. Chem. Chem. Phys.*, 14, 8307 (2012).
- [7] J. R. Weinberg-Wolf, L. E. McNail, S. Liu, and C. Kloc, *J. Phys.: Condens. Matter*, 19, 276204 (2007).
- [8] S. Tao, N. Ohtani, R. Uchida, T. Miyamoto, Y. Matsui, H. Yada, H. Uemura, H. Matsuzaki, T. Uemura, J. Takeya, and H. Okamoto, *Phys. Rev. Lett.*, 109, 097403 (2012).