

Vibration-mediated coherent mixing of exciton and polaron pair in a conjugated polymer

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Coherent electronic and vibronic features in the two-dimensional (2D) electronic spectra of a conjugated polymer where polaron pairs are formed on a sub-100 fs timescale are investigated theoretically. We identify signatures of coherent couplings and demonstrate that incoherent models cannot account for 2D spectra that have recently been obtained experimentally.

Organic solar cells have attracted considerable interest in recent years due to their potential as efficient and low-cost solar energy converters. For various conjugated polymers in solar cell applications, experimental studies have reported ultrafast charge dissociation of excitons at the interfaces between polymers and fullerenes on a sub-100 fs timescale [1]. It was suggested that vibronic coupling plays a central role in the excitonic dynamics of light harvesting [2], while time-dependent density functional theory suggested that strong electronic and vibronic couplings of organic photovoltaics may support ultrafast charge separation dynamics [3]. However, the functional relevance of the coherent electronic and vibronic couplings under noise and disorder and their experimental verification remain open questions. Here we theoretically investigate the polaron pair formation in a reference conjugated polymer for solar cell applications by means of 2D electronic spectroscopy. We show that experimentally observed polaron pair formation on a sub-100 fs timescale is governed by coherent electronic and vibronic couplings even in the presence of a high noise level at room temperature and a large energetic disorder of the conjugated polymer. We show that in contrast to an incoherent model, a coherent, vibronic model can reproduce the main features of experimental findings. Based on model parameters estimated from experimental data, we show that non-equilibrium vibrational motions of the C=C stretch mode of the conjugated polymer underpin ultrafast polaron pair formation and that this mechanism is robust against noise and disorder due to the strong electronic coupling and large Huang-Rhys factors of the present system.

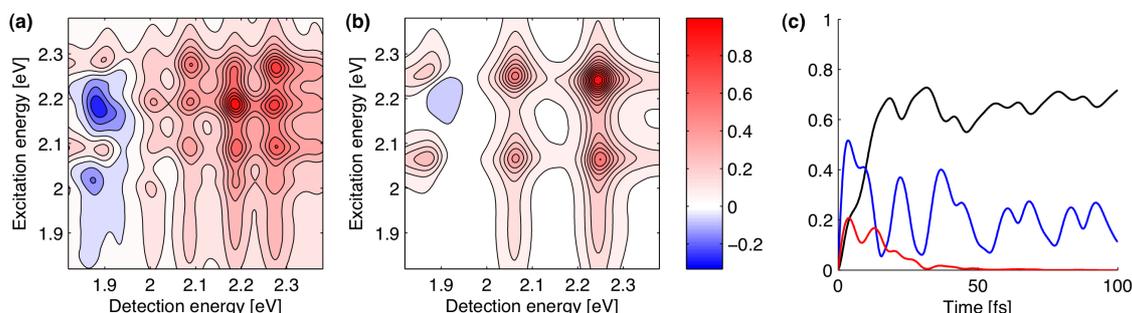


Fig.1 Absorptive 2D spectra simulated based on (a) a coherent, vibronic model and (b) an incoherent model. (c) The time evolution of the polaron pair population (black), coherence between exciton and polaron pair (blue), and entanglement between electronic and vibrational motion (red) in the coherent model with noise and disorder.

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[2] J. Prior et al., Phys. Rev. Lett. **105**, 050404 (2010); A.W. Chin et al., Nature Phys. **9**, 113 (2013).

[3] S. M. Falke et al., Science **344**, 1001 (2014).