Two-dimensional coherent photocurrent excitation spectroscopy of a hybrid lead-halide perovskite solar cell

Pascal Grégoire,[1] Eleonora Vella,[1] Ajay Ram Srimath Kandada,[2] Chen Tao,[2] Richard Leonelli,[1] Guglielmo Lanzani,[2] Annamaria Petrozza[2] and Carlos Silva[1]*

[1] Département de physique & Regroupement québécois sur les matériaux de pointe, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal H3C 3J7, Canada, *carlos.silva@umontreal.ca
[2] Center for Nano Science and Technology @Polimi, Istituto Italiano di Tecnologia, via Giovanni Pascoli 70/3, Milan 20133, Italy

We report two-dimensional coherent photocurrent excitation spectroscopy in efficient hybrid lead-halide perovskite solar cells. We identify weakly bound exciton and continuum excitation features in the total correlation spectrum. Via the absolute zero-time rephasing spectrum, we also measure the temperature-dependent homogeneous linewidth and thus address the proposed polaronic nature of photocarriers.

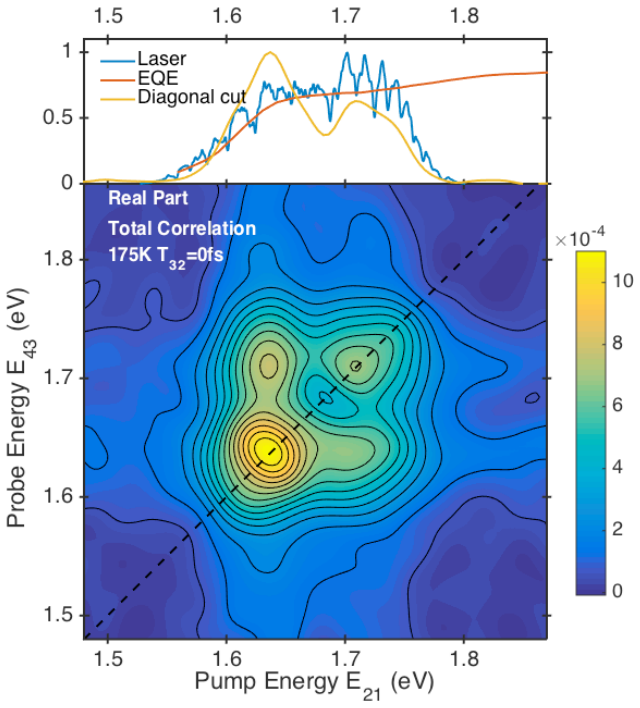

Figure 1. Real part of the total correlation spectrum at population waiting time of 0 fs, measured at 175 K. The laser spectrum and the external quantum efficiency (EQE) spectrum of the device (the linear photocurrent excitation spectrum) are shown in the top panel.

Hybrid halide perovskite (for example, $CH_3NH_3PbI_3$) solar cells now display solar power conversion efficiencies exceeding 20% [1]. In these materials, excitonic and free-carrier regimes of primary photoexcitations are possible depending on crystalline microstructure of the active layer and excitation density [2]. Recent literature suggests that photocarriers in these materials may be large polarons [3], with this notion motivated by observation that charge transport is limited by acoustic phonon scattering, and not by impurities and crystalline defects present ubiquitously in these polycrystalline microstructures. In order to explore the nature of photocarriers in these materials, we implement two-dimensional coherent photocurrent excitation (2D-PCE) spectroscopy as described elsewhere [4] on an optimized solar cell based on $CH_3NH_3PbI_3$ [5]. Fig. 1 displays the total correlation spectrum measured at a population waiting time of 0 fs, displaying both excitonic and continuum resonances. Via the temperature dependence of the rephasing zero-time spectrum, we explore the possible polaronic character of the exciton and continuum resonances and address directly whether this measurement reflects such phonon coupling.

[1] NREL Solar Cell Efficiency Chart.
[2] Grancini et al, *Nat. Photonics* 9, 695−701 (2015).
[3] X.-Y. Zhu & V. Podzorov, *J.Chem. Phys. Lett.* **6**, 4758−4761 (2015).
[4] arXiv:1602.04205 [cond-mat.mtrl-sci]
[5] Tao et al, *Energy Environ. Sci.* 8, 2365 (2015).