Room-Temperature studies of Electronic Coherences in Two-Dimensional Nanostructures

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Abstract: We use two-dimensional electronic spectroscopy to study the lineshapes and linewidths of excitons in colloidal nanoplatelets at room temperature and the coherences induced by the superposition of the two first excitonic states.

Since their first observation at low temperature, electronic coherence (EC) has aroused more and more attention for its possible role in energy transfer in various systems and for quantum information applications. Despite an increasing number of reports, direct observation of EC at room temperature (RT) remains challenging and controversial due to the presence of additional vibrational states and the large contribution of static and dynamic effects on the spectral linewidths. Here we use two-dimensional electronic spectroscopy (2DES) to study at RT a model system with narrow spectral lineshapes: colloidal nanoplatelets (NPLs). Unlike epitaxial quantum dots or quantum wells that have been widely studied at cryogenic temperature, it is recently that colloidal nanocrystals started to be measured in 2DES and at room temperature [1,2]. By tuning the laser spectrum to cover the two first transitions and compressing the pulse to about 10 fs, we were able to measure quantum beats in the amplitude of diagonal and cross peaks. In the first part of this summary, we discuss the different origins of the spectral linewidths. In the second part we study the time evolution of the amplitude of the different peaks of the 2D spectra and conclude by showing direct evidence of the superposition of excitonic states.

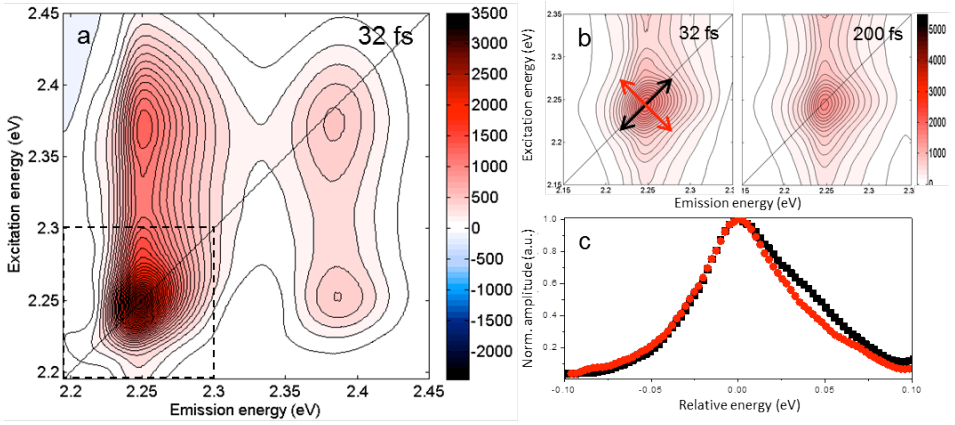

Fig.1. a: Absorptive 2D spectrum (total, real part) of CdSe NPLs for a waiting time of T_2=32 fs. b: Zoom of the photon-echo 2D spectra (rephasing, magnitude) in the lower diagonal peak, for T_2=32 and 200 fs. c: diagonal (black squares) and cross-diagonal (red dots) lineshapes extracted from the lower diagonal peak of the rephasing spectrum at T_2=32 fs (location schematized by the two arrows in b).

NPLs have received considerable attention in the colloidal community due to their one-dimensional confinement and the ability to control their thickness with atomic precision [3]. The room temperature absorption spectrum of CdSe NPLs show several well-defined transitions characteristic of strongly bound excitons. The growth of a CdZnS shell around these NPLs has for consequences to shift drastically the transitions to lower energy, to increase the linewidths and to enlarge the energy between the two first transitions.

The absorptive 2D spectrum of CdSe NPLs for a wainting time of 32 fs is shown in Fig.1a. We can clearly resolve two diagonal peaks from the heavy hole and light hole excitons (X_{hh} and X_{lh}) and two cross peaks resulting from the strong coupling between them (same electron state). Analyzing of the lower diagonal peak of the rephasing (photon-echo) 2D spectrum shows the sample presents a pure homogeneous broadening ("star"-shaped peak, Fig.1b, Lorentzian lineshapes with similar width in the diagonal and cross-diagonal directions, Fig.1c).

In Fig.2, left panel, is shown the absorptive 2D spectrum of the corresponding heterostructure for T_2=52 fs. Analysis of the lower diagonal peak reveals that CdSe/CdZnS NPLs exhibit larger homogeneous broadening (similar diagonal and cross-diagonal linewidths larger than in the core sample and Gaussian lineshapes) which was

attributed to *inhomogeneous broadening at single particle level*. Indeed, due to its delocalization along the platelet plan, the exciton suffers the effects of the shell inhomogeneities.

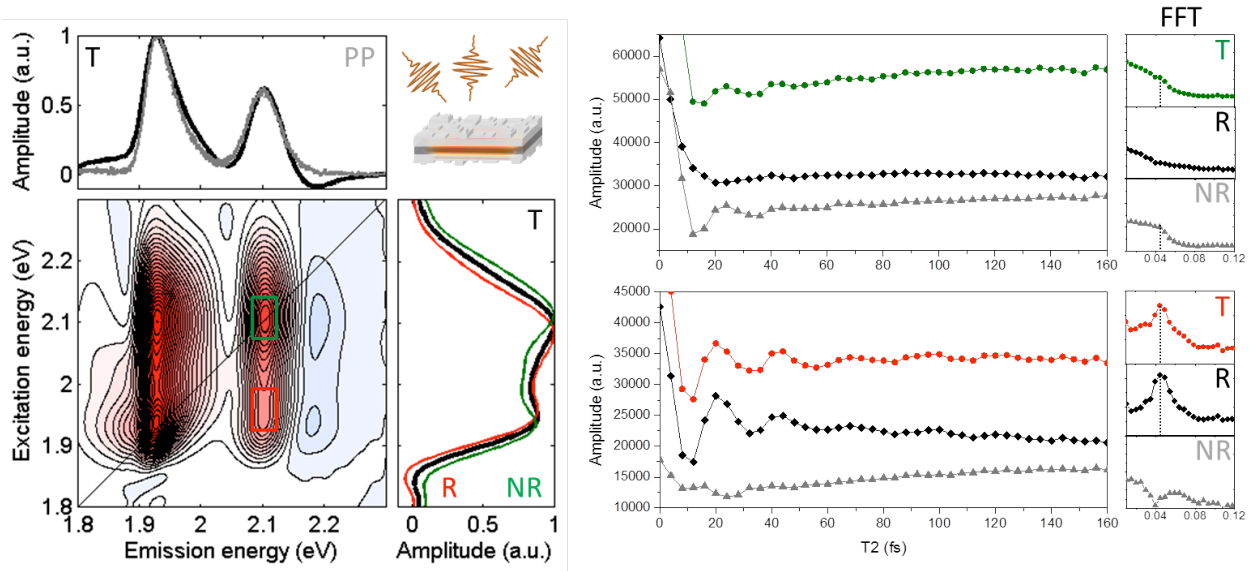

Fig. 2. Left panel: absorptive 2D spectrum of CdSe/CdZnS NPLs with a core thickness of 1.5 nm (see schematic). Its projection over the emission axis is shown on top in black with the pump-probe spectrum for comparison (PP, grey line). Its projection over the excitation axis is shown on the right side, in black, together with the rephrasing (R, red line) and non-rephasing (NR, green line) ones. Right panel: evolution of the amplitude of the high energy diagonal peak (green dots) and low cross peak (red dots) along the waiting time T_2. The origin of the oscillations is shown by plotting the rephasing and non-rephasing signals (black diamonds and grey triangles, respectively). The FFT of the respective signals is shown on the right side.

The time evolutions of the amplitude of all the different peaks in the 2D spectrum of CdSe NPLs and its corresponding heterostructure were studied within the first hundreds of femtoseconds. In Fig. 2, right panel, we show the amplitude evolution of the higher energy diagonal peak (green dots) and lower cross peak (red dots) of the absorptive 2D spectrum (total, real part) of CdSe/CdZnS NPLs. Oscillations are clearly visible in both signals and result from the non-rephasing pulse sequence in the case of the diagonal peak and from the rephasing pulse sequence for the cross peak, as expected for electronic coherences [4]. Moreover, analyzing three samples having different splitting energy between X_{hh} and X_{lh} reveals the match with the oscillation frequency measured along T_2 and expected from the superposition (see Fig. 2).

In conclusion, colloidal nanoplatelets are ideal systems that unambiguously reveal electronic coherences at room temperature. CdSe NPLs with pure homogeneous broadening allow to discuss the decoherence pathways. In addition, study of the corresponding heterostructure presenting shell inhomogeneities reveals that inhomogeneous broadening limits the observation of the coherences as previously reported [5].

[1] D.B. Turner, Y. Hassan and G.D. Scholes, "Exciton superposition states in CdSe nanocrystals measured using broadband two-dimensional electronic spectroscopy" Nano Lett. **12,** 880-886 (2012).

[2] G.B. Griffin, S. Ithurria, D.S. Dolzhnikov, A. Linkin, D.V. Talapin and G.S. Engel, "Two-dimensional electronic spectroscopy of CdSe nanoparticles at very low pulse power" Chem. Phys. **138**, 014705 (2013).

[3] S. Ithurria, M.D. Tessier, B. Mahler, R.P.S.M. Lobo, B. Dubertret and Al. L. Efros, "Colloidal nanoplatelets with two-dimensional electronic structure" Nat. Mat. **10**, 936-941 (2011).

[4] Y-C Cheng, G.R. Fleming, "Coherence quantum beats in two-dimensional electronic spectroscopy" J. Phys. Chem. A 112, 4254-4260 (2008).

[5] A. Ishizaki and G.D. Fleming, "On the interpretation of quantum coherent beats observed in two-dimensional electronic spectra of photosynthetic light harvesting complexes" J. Phys. Chem. B **115**, 6227-6233 (2011).