2D-Photon Echo on chlorophyll a: relaxation dynamics of the Q_y band.

Cristina Leonardo*, Elena Meneghin and Elisabetta Collini

Dept. of Chemical Sciences, University of Padova, via Marzolo 1, 35131 PD Italy

2D-PhotonEcho is particularly suitable in the analysis of coherent relaxation dynamics in complex systems. The use of different laser bandwidths, carefully tuned to sweep specific energy ranges, enables the characterization of dynamics in Chl a involving different vibrational coherences and their description beyond the simplified model of the displaced oscillator.

Chlorophyll *a* is one of the main pigments involved in light-harvesting processes in nature. The aim of this work is to fully characterize this pigment as isolated chromophore as preliminary step in the analysis of more complex antenna systems. In particular, the relaxation dynamics within the Q_y band during the first 800 fs after photoexcitation has been characterized.

Two sets of measures have been performed using different exciting bandwidths acting as spectral filter for specific states. In a first set of measurements we tune the laser to clearly identify the vibrational levels of the ground and the first excited state, in agreement with the displaced oscillators (DO) model. In a second set, slightly shifting the laser band, the presence of a new feature in the evolution of the 2D-maps has been highlighted. Evidences for coherent ultrafast energy relaxation among vibronic states of the Q_y band have been found and the associated dynamics have been fully characterized. This peculiar relaxation, driven by oscillating superposition between these states, cannot be described only on the base of the DO model (Fig.1). [1]

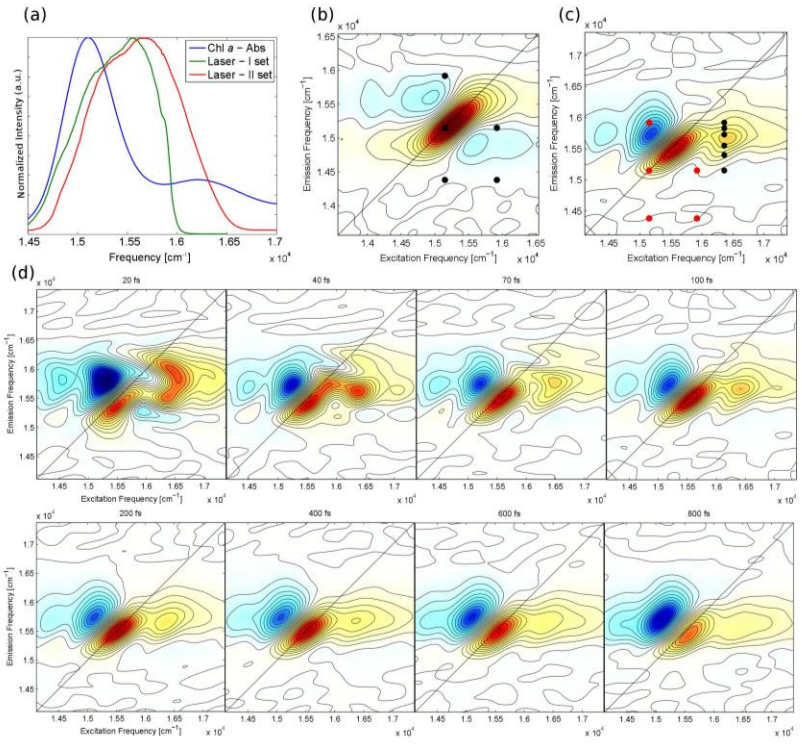

Fig.1 (a) Absorption spectra of chlorophyll *a* in methanol solution and laser bands in the two sets. (b) 2D-map at t_2 = 100 fs for the first set. The black spots pinpoint the positions where vibrational coherences are expected to contribute ('chair symmetry'), here shown for the 770 cm^{-1} mode. (c) 2D-map at t_2 = 100 fs for the second set. In this case the full 'chair symmetry' (red spots) cannot be fully characterized, but the more interesting dynamics of the highlighted levels (black spots) is enhanced. (d) 2D-maps of the second set at different values of population time (t_2).

[1] C. Leonardo *et al.*, manuscript in preparation (2016).