Fluorescence Detected Two-Dimensional Spectroscopy (FD2DS) of Coupled Chromophores

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Two-dimensional action spectroscopies provide information on the dynamics of quantum systems which is complementary to that of well-established coherent photon echo type setups. FD2DS in particular has been shown to give direct access, e.g, to the early time evolution of weakly coupled chromophores thus unraveling the role of quantum delocalization. Here, it benefits from an intricate cancelation of ground state bleach and excited state absorption contributions to the cross-peak signals. Details depend on the interplay between time scales for exciton-exciton annihilation, exciton relaxation, and radiative decay [1,2]. FD2DS enabled, for instance, the observation of the initial exciton delocalization between the B800 and B850 pigment pools in the LH2 complex of purple bacteria [3]. Viewed from the traditional concept of Förster excitation energy transfer, FD2DS provides a glimpse at the transient regime directly following excitation.
In this contribution I will discuss the theory of FD2DS, which is rooted in fourth-order perturbation theory and associated multi-time response functions. The role of different time scales will be highlighted using a Redfield-type relaxation model for two coupled chromophores.

[1] M. Schröter, T. Pullerits, O. Kühn, *Using Fluorescence Detected Two-Dimensional Spectroscopy to Investigate Transient Exciton Delocalization Between Coupled Chromophores*, J. Chem. Phys. 149, 114107 (2018)
[2] O. Kühn, T. Mancal, T. Pullerits, *Viewpoint: Interpreting Fluorescence Detected 2D Electronic Spectroscopy*, J. Phys. Chem. Lett. 11, 838 (2020)
[3] K. J. Karki, J. Chen, A. Sakurai, Q. Shi, A. T. Gardiner, O. Kühn, R. J. Cogdell, T. Pullerits, *Before Förster. Initial Excitation in Photosynthetic Light Harvesting,* Chemical Science 10, 7923 (2019)