Two-dimensional electronic spectroscopy (2DES) of biomolecules

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In condensed-phase molecular photophysics, two-dimensional electronic spectroscopy (2DES) was initially developped to investigate energy transfer processes in natural lightharvesting chromophore-protein complexes.[1] 2DES is superior to conventionnal femtosecond “pump-probe” spectroscopy since it provides simultaneously high temporal and spectral resolution of the excitation wavelength by implementing the principle of Fourier Transform spectroscopy.[2] Nowadays, 2DES has become a method of choice for the investigation of: i) structural or chemical heterogeneities; ii) excitation energy transfer, iii) ultrafast photo-reactivity of complex molecular system to disentangle electronic from vibrational couplings; and iv) competing ultrafast photochemical processes.[3] However, 2DES implementation faces two main technical challenges: i) the generation of ultra-short and ultra-broadband pulses, and ii) the control of interferometric relative stability between pulse pairs (precision of few nanometers).

The general aim of this PhD project is to unravel the photodynamics of molecular heterogeneous systems with co-existing ground state structures or chemical species by 2DES (Figure 1).[4] More specifically, the PhD student will adapt a challenging non-collinear 2DES setup that our team developed within the ANR project Femto-2DNA, for the near-UV region, a first in France. The second objective is to unravel the photophysical mechanisms and photo-chemical reactions in multichromophoric biomolecular systems, such as fluorescently labeled oligonucleotides or DNA hairpins, which we already investigated partly with fluorescence spectroscopy.[5] The long-term objective is to demonstrate the use of 2DES as a relevant spectroscopic tool to monitor protein structure and dynamics.

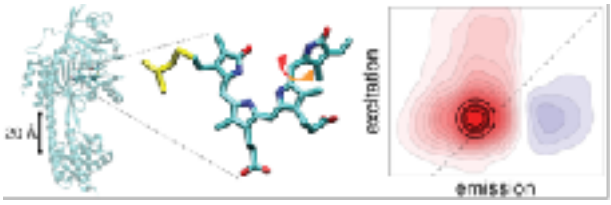

Figure 1: As an illustrated example, the photoisomerization of the phytochrome Cph1 consists of a complex photocycle. Its interpretation has been controversial: i) coexistence of ground state conformational subpopulations (heterogeneous model), or ii) a single ground state conformation which undergoes through multiple sequential intermediates in the excited state (homogeneous model). 2DES results strongly support the homogeneous model.[4]

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[5] K. Voltz, J. Léonard, P. Tourón-Touceda, J. Conyard, Z. Chaker, A. Dejaegere, J. Godet, Y. Mély, S. Haacke and R. H. Stote, Nucleic Acids Res. **44**, 3408 (2016).