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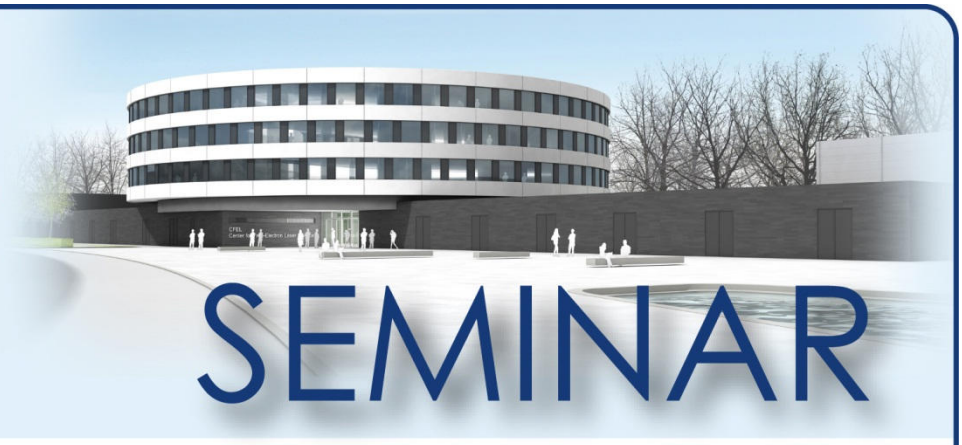

SEMINAR

Wednesday, 11 May 2011, 14:15
Building 28c (Flash Hall) Seminar Room

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Electronic and Vibrational Quantum-Packets in Bio-Inspired Porphyrine – Aggregates – The Power of 2D-Optical Correlation Spectroscopy

By employing 2D - Electronic Correlation Spectroscopy (2D-ECS) with cutting-edge, ultra-broadband ($\Delta\omega$ ~ 0.6 eV) sub-10 fs VIS pulses, first experiments on bio-mimetic *single* (monomer) and *double* (dimeric) Porphyrine - type compounds have enabled to look into the evolution of Franck-Condon (FC) *vibronic* couplings which are considered as the fundamental underpinnings of intra-molecular motion in the fore-field of photo-chemical dynamics. While the monomeric porphyrine-derivative (Zn-phthalocyanine) shows strongly coupled quantum-packets, 2D- measurements on the dimer Lu(phthalocyanine)$_2$, primarily, expected to sense both electronic *and* vibronic quantum-packets, give rise to strong deviation from the "usual". The electronic cross-term in the lower right quadrant ($\omega_1 > \omega_3$) is missing at waiting time $t_2 = 0$, but emerges as t_2 evolves as a result of population-transfer indicating the instantaneous degeneracy of the entire quantum-mechanical correlation matrix, upon excitation, probably, caused by a Jahn-Teller distortion, typically, expectable for this symmetry. The pathological short-time behavior, complicated by charge-transfer mixing and wave-function configuration interaction, seems to monitor the net-result of a break – down of the electronic Condon-approximation caused by a vibronic wave-packet traversing a *Mexican-hat* conical intersection (CI). 2D-snapshots of vibronic couplings in the FC-progression of linear 1D –absorption spectra may have considerable impact on the complementary understanding of quantum-coating effects in long-lived oscillatory electronic quantum transport at physiological temperatures for the FMO-complex and related light-harvesters. Preliminary 2D-results on the coherent ET- dynamics in a Carotene-Purpurin dyad and in natural chlorosomal tubes are discussed.

Host: Valentyn Prokhorenko, CFEL