"Excitation energy transfer in gas-phase biomolecules: Towards accurate modelling of nuclear - electronic coupling"

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A recent transposition of excitation energy transfer (EET) dependent spectroscopic techniques to the gas-phase[1–3] gives hope to apply the "spectroscopic ruler[4]" also in a regime where the selection of single species by their mass and charge is possible - but which requires in-depth knowledge about the involved photophysics. In the gas-phase, single- and multiphoton photoexcitation as well as fluorescence and fragmentation as deactivation channels compete. J. Megow (researcher in the group of P. Saalfrank) has developed a semiclassical description of nuclear-electronic coupling in the frame of excitation energy transfer[5–7], while A. Kulesza focused on (electronic) structure-modelling of large biomolecules[8] interfaced with experiments[9,10] and ab-initio description of excited states[11]. We have recently shown for Xanthene-analogues (as attractive EET dyes), that vibronic progression can be of importance for the bandwidth addressable in the experiment and that excited to excited transitions[12] play a major role.
In the proposed short-term scientific mission (STSM), we will combine our forces to tackle the accurate description of excitation energy transfer in benchmark dye-tagged biomolecules the gas-phase where accurate and puzzling ongoing measurements are yet to be explained. The visit of P. Saalfranks group effectively allows training A.K in the use of semiclassical methods for electron-nuclear dynamics. With our common set of tools we will initiate theoretical work to uncover the mechanisms for enhanced fragmentation at small dye separations and the connection to (homo-dye) self-quenching experiments in the gas-phase. Preparatory work for the cooperative endeavor will be the parametrization of dyes performed in Lyon and setup of topologies for MD simulations with an atomistic force field to simulate structural ensembles. Secondly, electronic structure calculations will be dispatched, for common analysis (Task 2).
Task 1: We will set up and perform simulations obtaining structural ensembles for the small test system (dye-tagged three and 5-aminoacid peptides). We will exchange expertise how to perform structural sampling using generalized ensemble methods (T-REMD) applicable for large biomolecules (Ubiquitin protein). While the small system can finish on time, we will only start simulations for the big system for later remote analysis.
Task 2: For the calculation of EET characteristica, we will use molecular dynamics simulations to describe the thermal fluctuations and will utilize Megows mixed quantum–classical formulation of the transition rates. These will be compared to Förster theory rates. The needed calculation of transition charges will be exercised for one of the used dyes upon our ab-initio data. Förster theory analysis will comprise extraction of dye configuration distribution from the REMD data.
Task 3: With the preliminary results for the small test system (analysis of EET rates), we will be able to hypothesize the impact of the presence of higher excited states. We will set up a qualitative photophysical model and to draft the outline for a common paper and computer time (for the next GENCI call) to treat bigger chromophores and more complex biomolecules (e.g heat-shock protein complexes) in an HPC project.

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