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

STSM Number	ECOST-STSM-CM1405-080117-082227
STSM Applicant	Dr. Alexander Kulesza
HOME Institution	Institut Lumière Matière, Lyon, France
HOST Institution	Universität Potsdam, Potsdam, Germany
STSM start and end dates	08-01-2017 to 15-01-2017
STSM duration	5 working days

The objective of the STSM was to combine different theoretical methods to tackle the accurate description of excitation energy transfer in dye-tagged biomolecules the gas-phase. Within our envisaged approach, Replica-Exchange MD samples structures of biomolecules in the gas-phase, while we use the ground-state classical path approximation to determine time-dependent energy gaps and coulomb-coupling in the description of excitation energy transfer. The theoretical work aims at addressing mechanisms for enhanced fragmentation in ongoing experiments on mass-selected biomolecules. During the STSM we have finished important steps towards the accurate description of excitation energy transfer. Work was done for 1.) sampling structures of gas-phase biomolecules by MD, 2.) describing the electronic coupling and spectral overlap of the involved optical units. Preparatory work has been carried out by calculating ground- and excited state geometries of the involved dyes Atto 520, Rhodamine 575 and QSY7. Cartesian force constants were obtained from ground/excited state Hessian calculation, all using the Gaussian09 suite of software. Atom-centered representations of the transition density were obtained by the CHELPG charge fitting approach of TDDFT transition densities (own grid-based implementation) at the CAM-B3LYP/def2-SVP level of theory (NWChem 6.3). We set up and ran parallel tempering (REMD) sampling with classical Amber99/GAFF force fields for CAC and CAAKAAC peptides tagged with Atto520 dyes (Figure 1, bottom and top, respectively). For this task, we used GROMACS 5.3 with PLUMED 2.3 plugged in. After sampling 10 ns of trajectory, 500 frames were extracted and distributions of Coulomb couplings as well as transition-dipole moment orientations and separations calculated. The sampled dye separations in CAC (around 1 nm) are significantly smaller than the one for CAAKAAC (around 2-4 nm). Especially in the former case, deviations from Förster theory are to be expected, which we evidenced in a marked difference between the numerical values of the squared couplings for CAC using both approaches (up to a factor of 2). Excitation energy transfer in the weak coupling limit was quantified by Förster Theory and using a rate expression with the more complete transition charge Coulomb coupling. We used a Gaussian-shaped density of states for the spectral overlap integral as a simple working example. With the available force constants and excited state charges, we are able to calculate the vibrational and electrostatic energy gaps along the MD trajectories to calculate more accurate spectral overlap integrals. As as first step towards the full quantum-classical treatment, we calculated time dependent electrostatics upon Atto 520 excitation along the sampling trajectory of CAC. We also checked the validity of the weak coupling limit by setting up and solving a simple excitonic two-state Hamiltonian with our couplings. Indeed, excitonic splitting (present in CAC, bottom of figure 1) and a predicted drop in transition strength of the lowest calculated exciton state, could explain the increase of fluorescence quenching (smaller radiative deactivation rate, see Einstein A coefficients in Figure 1). With the established knowledge, and theoretical workflow, we are able to address the photophysics of Atto520 versus Rh575/QSY7 labeled peptides and proteins. As a first application, we will study the excitation energy transfer versus self-quenching behavior of CAC, CAAKAAC and Ubiquitin for which this STSM provides the data for the separated dyes as well all electrostatic components for a rate description of EET and an excitonic model based on the transition dipole moment and transition charge coulombic couplings. The results will be included together with the ones for Ubiquitin protein (which will be finished next month) into our experimental-theoretical paper and the basis for further cooperation of the groups.

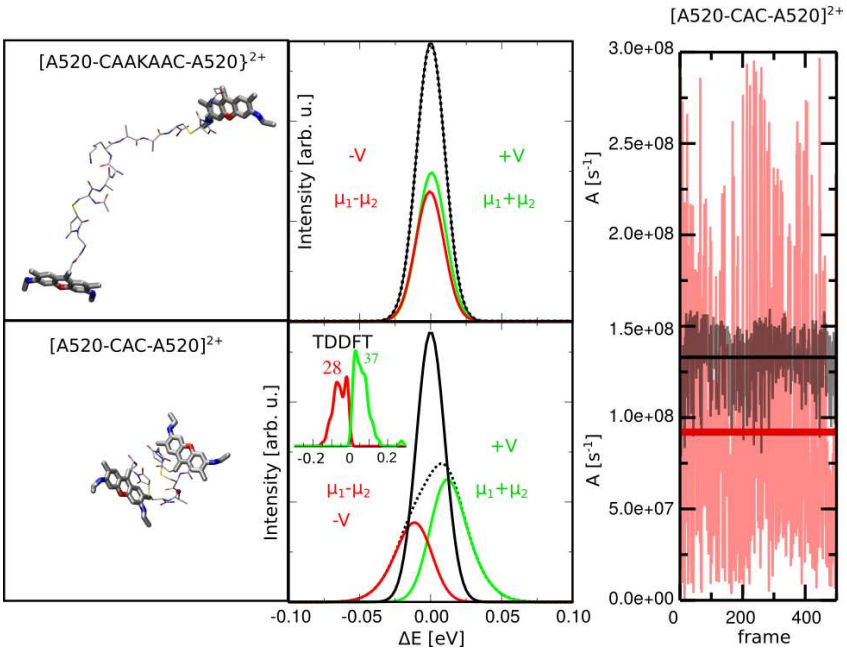
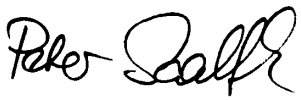


Figure 1: Representative structures of Atto520 labeled CAAKAAC (top) and CAC (bottom) peptides. In the middle, transition-charge coupling-based excitonic splittings of the REMD sampled dye configurations are shown. The drop in average emission rate for CAC explains the experimentally measured enhanced fragmentation efficiency (fluorescence self-quenching)

Confirmation of the host of the successful execution of the STSM

I, Prof. Peter Saalfrank, hereby confirm that Alexander Kulesza (Institut Lumière Matière, France) worked in our group at the University of Potsdam in the period from 08-01-2017 to 15-01-2017. The visit has been successful and the results obtained are described above.



(Prof. Peter Saalfrank)