Contribution ID : **174** Type : **Poster Presentation**

EuCompChem2025 – Gabriele Iuzzolino – Oral Contribution

The Ultrafast Fluorescence of a DNA-Protein Photo-Crosslinking Model, interpreted by Non-Adiabatic Molecular Dynamics

Isolation of transient nucleoprotein complexes in their biological conformation is a challenging task: a promising technique is to induce in vivo crosslinking between the nucleic acid and the protein, by UV light. The photo-cyclization of 5-benzyluracil (5BU) to 1,2-indaneuracil has been proposed as a model reaction to study the mechanism of photo-crosslinking.[1] In competition with the reactive path, 5BU also exhibits an ultrafast radiative decay - probed by Fluorescence Up-Conversion (FlUC) – whose fastest component is debated to be due either to a decay from the upper excited states to S1, or to a vibrational relaxation of the first excited state.[2]

In this context, we present a theoretical study of the ultrafast photo-activated dynamics of 5BU in methanol, exploiting the framework of the DFT and TD-DFT[3]. At the same time, we propose a new protocol to simulate FlUC spectra, making easier the comparison between simulation and experiment.

We first characterized the ground-state thermal equilibrium and the photophysics, via an ab-initio molecular dynamics, exploiting the ADMP[4] extended Lagrangian formalism, the ONIOM[5] QM/MM partition scheme and non-periodic boundary conditions[6]: we discovered the presence of two conformers in equilibrium at room temperature and multiple excited states responsible for the absorption propaedeutic to the photocyclization, whose brightness depends by the conformation and microsolvation of 5BU.[7]

Thereafter, to give a molecular interpretation of the fluorescence signal, we conducted a non-adiabatic mixed quantum/classical molecular dynamics of 5BU in implicit (C-PCM) methanol, by adopting the Fewest-Switches Surface Hopping approach.[8] The initial conditions were generated by sampling a quantum Wigner distribution for each of the two conformers and for each involved transition.

The simulated time-resolved spectrum and the FlUC experiment have different time scales, since the first starts from the absorption regime and the latter, having an IRF of 300 fs,[2] starts from an already advanced point of the excited-state evolution of the system: our new protocol, based on the fit of the simulated spectral peaks, gave us a clear and direct comparison with the experimental data.

We were thus able to simulate the transient emission spectrum; we then performed a vibrational analysis through an innovative protocol, based on the wavelet transform of time resolved generalized modes extracted from the trajectories. We thus detailed the molecular mechanisms underlying the formation of the high-energy emission band, the red shift of the low-energy band and the ultrafast component of the decay of both bands.

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