Photo-induced non-adiabatic dynamics in biosystems: intrinsic dual photoresponse of anionic chromophores and selective tuning by proteins

A. V. Bochenkova¹,²

¹ Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark
² Department of Chemistry, M.V. Lomonosov Moscow State University, 119991 Moscow, Russia

E-mail: bochenkova@phys.au.dk

In contrast to the well-established paradigms in science that take for granted a decoupling of nuclear and electronic motions, our work aims at highlighting the importance and ubiquity of the non-adiabatic processes in nature, in which the electronic and nuclear dynamics are coupled with a remarkable efficiency. Such an electron-to-nuclei pairing is shown to be a key in understanding mechanisms by which the photoactive proteins tune the response of their light-absorbing molecular units and guide photochemical reactions that lie behind their functioning. By using state-of-the-art electronic structure theory combined with the experimental results obtained through a time-domain approach to action spectroscopy, we reveal a striking fundamental interplay between electronic and nuclear dynamics in competing excited-state decay channels of the deprotonated chromophore of the Green Fluorescent Protein (GFP). A non-adiabatic nature of the excited-state dynamics bridges the gap between their inherent timescales and unexpectedly results in co-existing mutual energy-borrowing mechanisms in the frame of a single molecular anion. We show that specific vibrational modes can facilitate fast energy exchange between nuclei and electrons on the (sub)picosecond timescale. The mode-specific non-adiabatic couplings result in either photoinduced vibrationally-mediated electron emission or electronic de-excitation through conical intersections. Remarkably, the relative efficiencies of these channels are wavelength dependent, since an emission-active vibrational mode is directly excited upon photoabsorption. We show that photodetachment proceeds via vibrational autodetachment out of the bound excited state at low energy, whereas electron ejection is facilitated by vibrational Feshbach resonances at higher energy. We underscore similarities anticipated in the excited-state behaviour of anionic tyrosine-based chromophores of various photoactive proteins, as well as compare the properties of the bare chromophore to those inside the protein. We show remarkable similarity of the early-time photo-induced nuclear dynamics in the gas phase and in the protein and emphasize the close interrelation between the excited-state dynamics and the corresponding spectral shapes. Finally, we discuss the ways, by which the GFP-like proteins may use the intrinsic dual electron-to-nuclei coupling to promote a selective photoresponse.

This work was granted access to the HPC resources of the Leibniz and RZG Supercomputing Centers (Garching, Germany) made available within the Distributed European Computing Initiative by the PRACE-2IP, receiving funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement RI-283493. A Marie Curie European Career Integration Grant within the 7th European Community Framework Programme and the Russian Foundation for Basic Research (Grant No. 11-03-01214) are acknowledged.