

Dual photoresponse of isolated biological chromophores

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The vast mass difference between electrons and nuclei simplifies the description of molecular systems and normally makes the electronic and nuclear motions separable. Here 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, as a case in point. 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. By using an original time-domain approach to action photoabsorption spectroscopy and state-of-the-art electronic structure theory, 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 (PD) or electronic de-excitation through conical intersections (IC, Fig.1). 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 biological chromophores of various photoactive proteins, in particular, of the photoactive yellow protein, as well as compare the properties of the bare chromophores to those inside the proteins. Our results pave the way for direct ultrafast control of the functioning of light-sensitive proteins via selective vibrational pre-excitation and highlight the importance and ubiquity of non-adiabatic processes in nature.

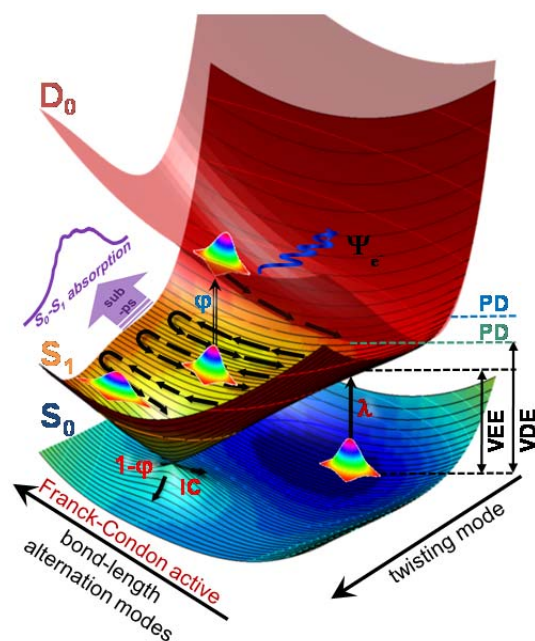


Figure 1. Semi-classical nuclear dynamics on conceptual potential energy surfaces. The initial excitation prepares a vibrational wave packet in the S_1 state. The early-time dynamics determines the absorption profile observed experimentally. After that, at a given excitation wavelength there is a certain PD/IC branching ratio.

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