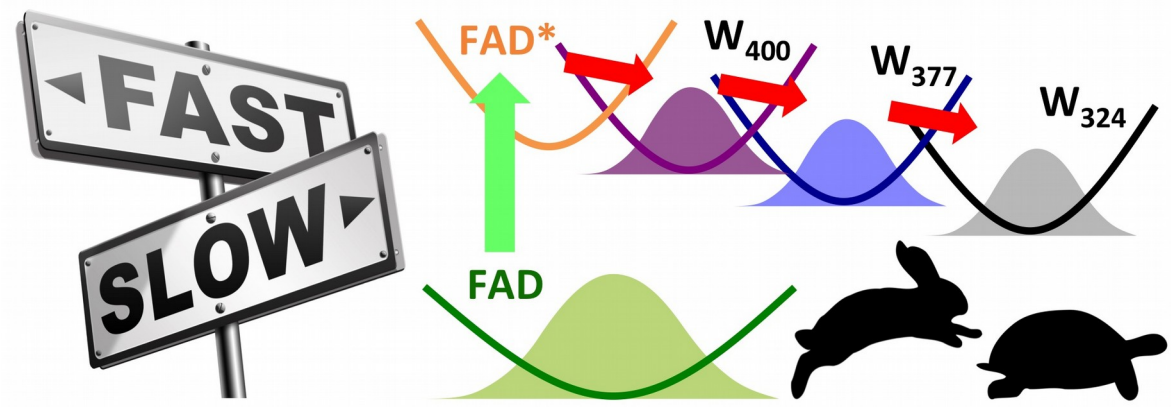
Multidimensional quantum mechanical modeling of electron transfer and electronic coherence in plant cryptochromes: the role of initial bath conditions

MENDIVE-TAPIA David[A]; MANGAUD Etienne[B]; FIRMINO Thiago[C]; DE LA LANDE Aurélien[C]; DESOUTER-LECOMTE Michèle[C]; MEYER Hans-Dieter[A]; GATTI Fabien[D]

A) Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, INF 229, D-69120 Heidelberg, Germany B) *Laboratoire Collisions Agrégats Réactivité, UMR 5589, IRSAMC, Université Toulouse III Paul Sabatier, F-31062, Toulouse, France* C) Laboratoire de Chimie Physique, CNRS, Université Paris-Sud, Université Paris Saclay, Orsay F-91405, France D) Institut des Sciences Moléculaires d'Orsay, UMR-CNRS 8214, Université Paris-Sud, Université Paris Saclay, Orsay F-91405, France.

Contact: david.mendive-tapia@pci.uni-heidelberg.de

A multi-dimensional quantum mechanical protocol is used to describe the photo- induced electron transfer and electronic coherence in plant cryptochromes without any semi-empirical, e.g. experimentally obtained, parameters. Starting from a two-level spin-boson Hamiltonian we look at the effect that the initial photo- induced nuclear bath distribution has on an intermediate step of this biological electron transfer cascade for two idealized cases. The first assumes a slow equilibration of the nuclear bath with respect to the previous electron transfer step that leads to an ultrafast decay with little temperature dependence; whilst the second assumes a prior fast bath equilibration on the donor potential energy surface leading to a much slower decay, which contrarily displays a high temperature dependence and a better agreement with previous theoretical and experimental results. Beyond Marcus and semi-classical pictures these results unravel the strong impact that the presence or not of equilibrium initial conditions has on the electronic population and coherence dynamics at the quantum dynamics level in this and conceivably in other biological electron transfer cascades.



KEYWORDS: CRYPTOCHROME; ELECTRON TRANSFER; SOLVATION; SPIN-BOSON; QUANTUM MOLECULAR-DYNAMICS; MCTDH METHOD; MULTI-LAYER.