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Modelling nonadiabatic dynamics of excitonic and plasmonic photoswitchable systems

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Nonadiabatic dynamics determine the fate of photoexcitation in complex excitonic and plasmonic systems. While the former feature the presence of multiple chromophores in close proximity to each other, the latter exhibit coupling of molecules and metal nanoparticles. Understanding photoinduced dynamics of these systems requires nonadiabatic treatment involving multiple excited states and numerous nuclear degrees of freedom, thus posing a challenge for modelling. In this contribution, we report on surface hopping simulations using semiempirical quantum chemical methods for excitonic and plasmonic systems featuring azobenzene—a prototypical molecular photoswitch.

First, we consider multichromophoric azobenzene systems. We model their photoinduced, nonadiabatic dynamics using an on-the-fly surface hopping approach combined with the semiempirical rAM1/FOMO-CI method [reparameterized Austin Model 1 / floating occupation molecular orbital – configuration interaction]. A transition density matrix analysis is used to characterize exciton (de)localization and evolution. In particular, we focus on exciton localization timescales, excited state lifetimes, and isomerization quantum yields in the aggregated state [1,2]. We also study how the inclusion of double excitations in addition to singles into the semiempirical CI surface hopping simulations affect exciton dynamics of multiazobenzenes [3].

Second, we report on nonadiabatic surface hopping TD-DFTB [time-dependent density functional tight binding] dynamics of a plasmonic gold nanocluster–azobenzene system exhibiting hundreds of electronically excited states [4]. Specifically, we study excited-state relaxation after molecular and plasmonic excitations, providing direct insight into elementary steps relevant to plasmonic chemistry.

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3. Titov, E. J. Phys. Chem. Lett. 2024, 15, 7482.
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