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Assessing density functional excited-state descriptions by full-dimensional TSH dynamics simulations [1]

Ultrafast excited-state dynamics are at the heart of photofunctional molecules, determining their applicability and efficiency. Time-resolved (pump-probe) experiments utilizing ultrashort (ps-fs) pulses are powerful tools to resolve excited-state mechanisms, however, analysis of the obtained data can be problematic, often leading to contradictory interpretations. Theory — in particular time-dependent approaches — can deliver valuable excited-state data that might be difficult to access by experimental techniques, due to, e.g., limited time resolution and/or overlapping signals. The interplay of experiments and theory thus has a crucial importance in deciphering all details of the ultrafast dynamics.

One of the most important factors governing the accuracy of excited-dynamics simulations is the level of quantum chemistry. For the transition metal complexes studied by the group, the state of the art of electronic structure theory is still heavily dominated by (time-dependent) density functional theory (DFT/TD-DFT) methods. While being computationally rather efficient, the PESs obtained by these methods may highly depend on the chosen exchange-correlation functional, in particular, when electronic states with different spin multiplicities are considered. Herein, using full-dimensional trajectory surface hopping (TSH) dynamics simulations carried out on linear vibronic coupling (LVC) potentials, we assess the performance of various DFT/TD-DFT descriptions (RPBE, OPBE, BLYP, B3LYP, B3LYP*, PBE0, TPSSh, CAM-B3LYP, and LC-BLYP). We exploit the existence of time-resolved X-ray emission spectroscopy (XES) data for the $[Fe(bmip)_2]^{2+}$ and $[Fe(terpy)_2]^{2+}$ prototypes for dynamics between metal-to-ligand charge transfer (MLCT) and metal-centered (MC) states (see Figure 1), which serve as a reference to benchmark the calculations (bmip = 2,6-bis(3-methyl-imidazole-1-ylidine)-pyridine, terpy = 2,2’:6’,2''-terpyridine). We base our assessment on identifying qualitative features and timescales in the simulated and experimentally extracted population dynamics. We consider our approach as an interesting alternative to contrasting full-dimensional DFT/TD-DFT dynamics against those carried out at higher level of quantum chemistry, such as CASPT2, which are currently not feasible for complexes such as $[Fe(bmip)_2]^{2+}$ and $[Fe(terpy)_2]^{2+}$. The results show that the simulated ultrafast population dynamics between MLCT and MC states with various spin multiplicities (singlet, triplet, quintet, see Figure 1) highly depend on the utilized DFT/TD-DFT method with the percentage of exact (Hartree-Fock) exchange being the governing factor. Importantly, B3LYP* and TPSSh are the only DFT/TD-DFT methods with a satisfactory performance, best reproducing the experimentally resolved dynamics for both complexes, signalling an optimal balance in the description of MLCT-MC energetics. This work demonstrates the power of combining TSH/LVC dynamics simulations with time-resolved experimental reference data to benchmark full-dimensional potential energy surfaces.

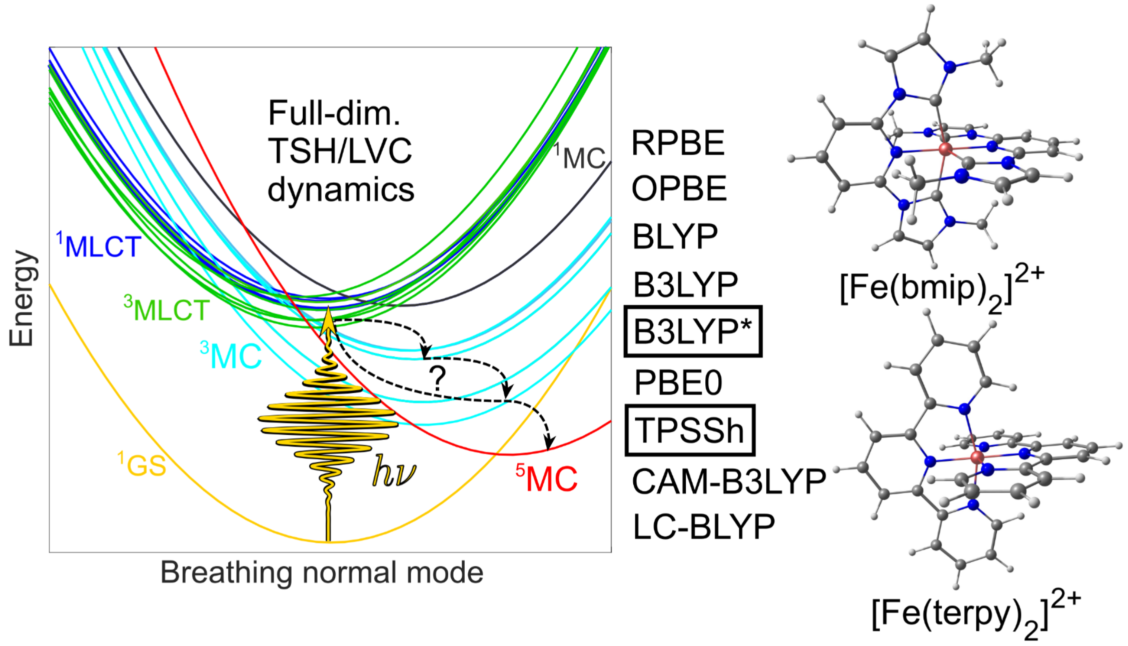

Figure 1. Graphical summary of the presented work: one-dimensional potential energy surfaces of Fe(II) complexes (left), the set of tested exchange-correlation functionals (middle), and molecular structure of

References:

[1] M. Pápai, *Simulation of Ultrafast Excited-State Dynamics of Fe(II) Complexes: Assessment of Electronic Structure Descriptions*, Journal of Chemical Theory and Computation, DOI: 10.1021/acs.jctc.4c01331 (2025) https://doi.org/10.1021/acs.jctc.4c01331