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Simulating and Screening Photophysics of Transition-Metal Complexes

The study of excited-state dynamics of transition-metal complexes is challenging due to their large number of vibrational degrees of freedom and many close-lying electronic states.[1] When quantum dynamics is used to simulate transition-metal complexes, this imposes the use of truncated models with typically only few degrees of freedom and electronic states, where the electronic potentials are often described in parameterized vibronic-coupling models. An alternative to quantum dynamics that can include all degrees of freedom and large number of electronic states is given by on-the-fly surface hopping (SH) methods. However, the repeating cost of the underlying electronic structure calculations restricts the range of possible simulation times for molecules the size of transitionmetal complexes severely.

By using SH on vibronic-coupling potentials, we can now lift the simulation-time restriction in SH and enable full-dimensional nonadiabatic dynamics simulations of transition-metal complexes on picosecond time scales.[2,3] This is first demonstrated for a near-infrared emitting vanadium(III) complex with an open-shell triplet ground state. Using multi-reference CASSCF-derived linear vibronic-coupling (LVC) potentials, we can unravel the relaxation mechanism populating the phosphorescent singlet state.[4] Based on the mechanistic insights, several derivatives of the complex are proposed to improve luminescence and their excited-state dynamics are simulated as well, an effort only possible due to the efficiency of the SH/LVC approach.

[1] Zobel and González, *JACS Au*, 1, 1116-1140 (2021)

[2] Plasser et al., *Phys. Chem. Chem. Phys.* 21, 57-69 (2019)

[3] Zobel et al., *Acc. Chem. Res.*, 54, 3760-3771 (2021)

[4] Zobel et al., *Chem. Sci.*, 12, 10791-10801 (2021)