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Investigating Anti-Kasha dynamics with quantum-mechanically derived force-fields and non-adiabatic molecular dynamics.

It was recently reported that Pt quinoxdt dithiolene complexes show a photochemical response, which markedly depends on the excitation wavelength revealing an anti-Kasha (AK) behavior. AK response originates from a competition between the functional process in upper photo-excited states and internal conversion towards the lowest excited state of a given multiplicity. Experimental evidence shows that internal conversion, which is typically a few femtoseconds, is in these systems astonishingly slowed down to 1-2 ps.[1-2] In addition, the excitation to higher excited states allows the molecular system to access long-lived conformational configurations not accessible from the lowest excited state. Such systems have raised considerable interest because of the possibility to conceive multi-response molecular devices or to explore novel photochemical routes. This rich body of experimental evidence motivated us to start a computational study based on time-dependent density functional theory aimed at clarifying several unanswered questions: the cause of such low efficient internal conversion, illustrating the complete photocycle including possible intermediated states, revealing is the structure of the long-lived configuration. In this contribution, we will explore the excited state dynamics using two complementary approaches: Surface Hopping including Arbitrary Couplings (SHARC)[3-4] and quantum-derived force field Joyce[5-7]. The former allows for tracking down non-adiabatic molecular dynamics of the earliest moments after excitation (for instance Figure 1 shows the total singlet and triplet state population from different excited states). The latter will allow us to explore longer time scales and adopt a statistical approach.

Figure 1: Non adiabatic molecular dynamics from states S4 and S10, grouped by total Singlet and Triplet populations, calculated by SHARC. According to experimental and computational evidence, the excitation of S4 and S10 induce Kasha and anti-Kasha responses from the system, respectively. The latter is evident from the remarkable extension of the single states population.

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