Ultrafast photo-induced processes in organic materials are crucial to several applications, including organic solar cells and LEDs. Such processes include exciton transport and singlet fission. Understanding the microscopic mechanism of these processes from a theoretical perspective is crucial in order to formulate molecular design rules and efficiently guide the experimental search for those structures that optimise them. However, the simulation of the real-time dynamics of ultrafast processes poses a significant challenge, due to the hundreds of molecular vibrations that interact very strongly with the excited charge carriers, often constituting traditional perturbative methods insufficient, and causing commonly employed approximations such as the Markov and Born-Oppenheimer approximations to break down.

In this talk, I will present a novel theoretical framework based on tensor network methods, for the simulation of the full quantum mechanical non-perturbative dynamics of ultrafast processes, which does not rely on any of the aforementioned approximations. This methodology is applied to very large molecules with up to 108 atoms. The large size of the studied molecules has allowed us to study them experimentally, subjecting our theoretical approach to a rigorous comparison with experimental results, and revealing its accuracy. We uncover the full microscopic mechanism of singlet fission in a covalent pentacene dimer and find that two different groups of vibrational modes coordinate in a precise manner in order to enable efficient fission through an avoided crossing [1].

For a dimer of tetracene, we reveal the impact of the specific pathway of vibrational relaxation on charge transfer, and show that selective excitation of vibrations can increase its efficiency by up to 26% [2].

Finally, we combine the insights from the above studies to build a simple model for singlet fission, which combines the effects of excess energy photoexcitation, molecular vibrations and the polarity of the molecular environment. We show that utilising the subtle interplay between these factors allows for switching into the coherent regime of singlet fission in a controlled manner, accelerating the process by an order of magnitude, as also confirmed experimentally [3].

Hosted by David Reichman