How far can we go to compute excited-state rate constants? A computational perspective.

Mariana do Casal

Department of Chemistry, Physical Chemistry and Quantum Chemistry Division, KU Leuven, 3001 Leuven, Belgium

Light is at the heart of many critical processes, from OLED design to photosynthesis. Common among all those fields is that an excited molecule must release energy to return to the ground state. However, deciphering how molecules release this energy is not trivial. It involves identifying all the possible competing deactivation pathways, the electronic structure character of the relevant states and how the excited-state decay rates dictate the system's fate. To advance light-related applications, we must map these possibilities.

To understand these processes, two main computational approaches are used: the static and dynamic approaches. In the static approach, one can estimate the excited-state decay rate (e.g., radiative, internal conversion, intersystem crossing, etc.) from only a few important points of the potential energy surface [1]. This approach is ideal for well-behaved, large systems where the computational cost of exploring a larger region of the excited-state potential surfaces is prohibitive. In the dynamic approach, no restrictions are imposed, and the molecule can evolve freely in time and space, and the decay rates are extracted from this evolution [2].

In this talk, I will discuss how to disentangle different photochemical processes from the computational perspective and the limitations and advantages of both approaches. I will discuss how to integrate both of these approaches using as a test case the anti-Kasha proton transfer of 3-HTCA (5-(3-hydroxy-4-oxo-4H-chromen-2-yl)thiophene-2-carbaldehyde). By combining them, we can uncover a more comprehensive understanding of how molecules behave in excited states.

References:

[1] M. T. do Casal *et al*. JPCA, 127, 48, 10033-10053 (2023).

[2] J. M. Toldo *et al.*, PCCP, 25, 8293-8316 (2023).

[3] H.-W. Tseng *et al*., Chem. Sci., 2016, 7, 655–665.