SIMULATING FLUORESCENCE: AN INVESTIGATION OF TRIAZAPENTALENES DECAY PATHWAYS

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Fluorescent compounds have diverse applications in many technological fields such as bio-imaging, chemical sensors, and light-emitting devices (OLEDs).[1] In any fluorescence applications, achieving precise control of the emission wavelength as well as of its intensity is key to success. Fluorescence occurs usually on the nanosecond timescale and thus obtaining an experimental overview of the exact mechanisms involved remains challenging.
In this presentation, I will present an in-depth theoretical study of the emissive properties of a series of 1,3,6-triazapentalene (TAP) molecules. While the bare TAP core is experimentally reported to be non-fluorescent ($\Phi_f = 0$), many TAP derivatives are good emitters. Indeed, TAPs present a broad range of fluorescence quantum yields (Φ_f ranging from 0.1 up to 0.8).[2] To investigate the phenomena at work behind this behavior, various theoretical approaches are combined. First, we simulated high-resolution UV-Vis spectra using vibronic calculations.[3] Then, the fluorescent quantum yields are simulated, and to this end the kinetics rates of both radiative processes (k_r) and internal conversion (k_{IC}) are estimated.[4] While this scheme is sufficient to accurately simulate most of the experimental trends, some compounds still stand out and present unexpectedly low quantum yields. Interestingly, in the bare TAP core, a conical intersection between the ground state (GS) and first excited state (ES) is easily reached during ES relaxation, hence explaining the quenching of the fluorescence. To assess the relative importance of such non-radiative pathways in other compounds, the presence of Minimal Energy Crossing Points (MECP) between the GS and ES is investigated. Finally, the kinetics of such processes (k_{MECP}) are evaluated and included in our quantum yield simulations, providing an accurate depiction of the fluorescence intensity in this molecular series, on par with experimental observations.

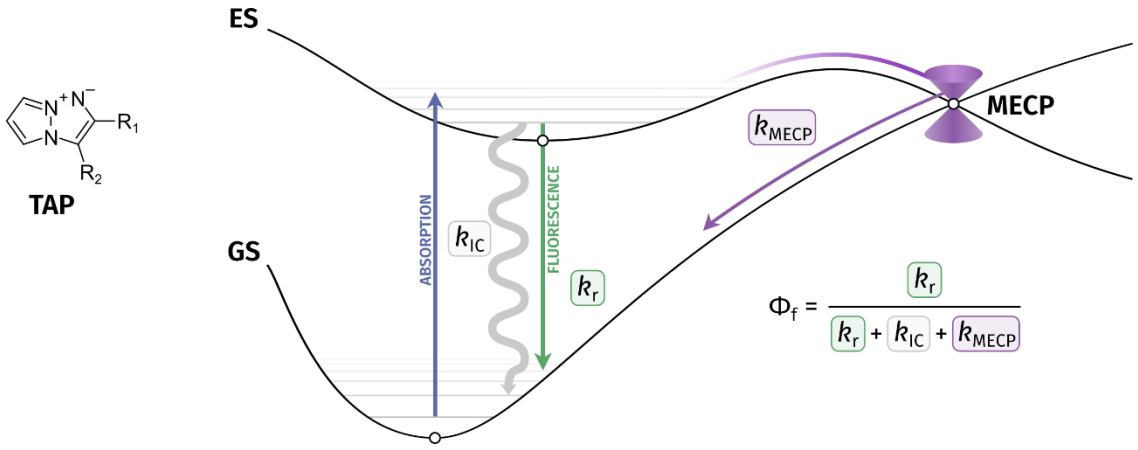

Figure 1. Jablonsky diagram featuring the different radiative (k_r) and non-radiative (k_{IC}, k_{MECP}) processes included in our fluorescence quantum yield (Φ_f) simulations.

Keywords: Fluorescence, TD-DFT, Quantum yield, Vibronic, Conical intersection

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