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EuCompChem2025 – Raoul Carfora – Oral - Transient vibrational dynamics unveil the intricate mechanism of ultrafast photorelaxation in a molecular rotor

Light-driven molecular rotary motors represent an elegant way to convert photon energy into controlled unidirectional motion and are thus directly linked to the development of nanoscale devices [1]. Among these, overcrowded alkene-based rotary motors have garnered significant interest as prototypical systems for investigating photoinduced structural dynamics [2]. Extensive experimental and computational studies were performed on these systems, in order to understand the interplay between nuclear and electronic degrees of freedom, which governs non-radiative relaxation pathways. Despite these studies, their ultrafast vibrational dynamics following photoexcitation is not fully resolved. In this work, we carried out a theoretical and computational study of the photoisomerization pathway of a second-generation molecular rotor (CPNY-F) [3]. Our approach, grounded in density functional theory (DFT) and its time-dependent version (TD-DFT) [4,5], combined with ab-initio molecular dynamics (AIMD) simulations [6-10] in both the ground and excited electronic states, along with the wavelet transform analysis [11,12], allowed us to map the evolution of key vibrational modes and identify those responsible for tuning electronic relaxation. Our simulations uncover the key role of transient vibrational dynamics in shaping the photorelaxation of CPNY-F in solution. Specific low-frequency modes, including torsions and pyramidalizations, modulate the emission properties and control access to non-radiative decay pathways. This work establishes a direct link between time-resolved vibrational activity and molecular function, offering a mechanistic basis for the design of efficient light-responsive systems.

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Primary author(s) : Mr. CARFORA, Raoul (Scuola Superiore Meridionale); Dr. COPPOLA, Federico (Scuola Superiore Meridionale); Prof. CIMINO, Paola (Università degli Studi di Napoli Federico II); Prof. PETRONE, Alessio (Università degli Studi di Napoli Federico II); Prof. REGA, Nadia (Università degli Studi di Napoli Federico II)

Presenter(s) : Mr. CARFORA, Raoul (Scuola Superiore Meridionale)