SimDOME

User Story: Automatized simulation of Transient Absorption UV/Vis spectroscopy

Aims

- Simulate Transient Absorption spectra for medium-to-big size chromophores embedded in complex environments

Methodology

- Upscaling of COBRAMM sofwtare capabilities
- Developing interface and auxiliary scripts to automatize the simulation

Results

- Developed a protocol and interface to simulate end-to-end transient absorption of chromophore in complex environment
- Reproduced the experimental and simulated spectrum of DMABN in acetonitrile

Summary

A series of new implementations were introduced in the academic software developed at UNIBO-CHIMIND to simulate photochemistry in complex environments. This development offers an automatized workflow to simulate time-resolved transient absorption (TA) spectra of medium-to-big chromophore embedded in a complex environment. The spectroscopic signals are simulated along nonadiabatic dynamics performed with trajectory surface hopping, while the possibility of treating systems from medium to big size is given using time-dependent density functional theory (TD-DFT). Finally, the presence of the environment is considered employing a hybrid quantum mechanics/molecular mechanics (QM/MM) scheme. The protocol was applied to simulate the TA spectrum of a test-case molecule.

Case Description

DMABN is a molecule known for its interesting dual fluorescence, which has intrigued scientists and led to the characterization of its time-resolved TA spectrum in different solvents to better understand this phenomenon. For this reason, DMAB TA spectrum is well-known and represented a perfect test-case to proof the implementations in COBRAMM and evaluate their reliability.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement number 814492.

Developed Methodology Description

The workflow implemented in COBRAMM consists in several steps, each of them handled by a part of the code (Figure 1). An interface to AMBER software allows the solvation of the chromophore and the setup of the system as well as the molecular mechanics (MM) calculation. The interface to Gaussian software handles the quantum mechanical (QM) ones, at TD-DFT level. COBRAMM internal routines combine the results and give QM/MM energies and gradient for single point calculations, geometry optimizations and frequency calculations. Additionally, brand new routines allow to simulate excited states dynamics with trajectory surface hopping (TSH) and setup and analyse the TA spectrum.

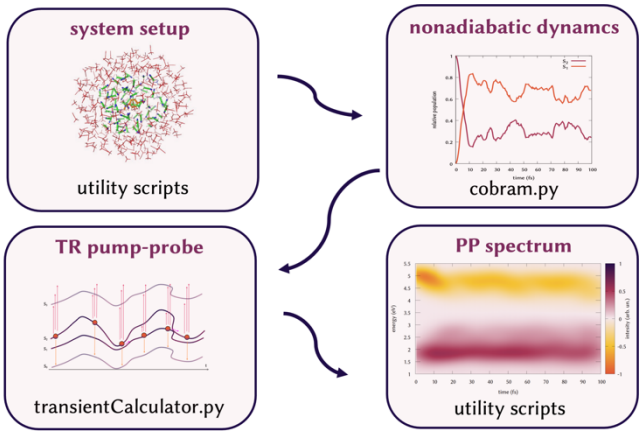

Figure 1 Schematic representation of the workflow implemented [1]

Results

TSH simulations are possible thanks to the development of an algorithm to approximate nonadiabatic couplings by wavefunction overlap between two TD-DFT calculation at two consecutive steps, which allows to speed up of 100 times this calculation with respect to the rigorous exact calculation. We developed a set of auxiliary scripts that automatize the whole workflow, from the system setup to the convolution of the TA spectrum, and allow to extend the possibility to run complex state-of-the-art calculations to a wider users base thus providing a unicum in the specialized software for excited state simulations. Finally, the TA spectrum of DMABN in acetonitrile was successfully simulated, reproducing properly the stimulated emission at 5 eV and the excited states absorption at 2 eV and their relative intensities (Figure 2).

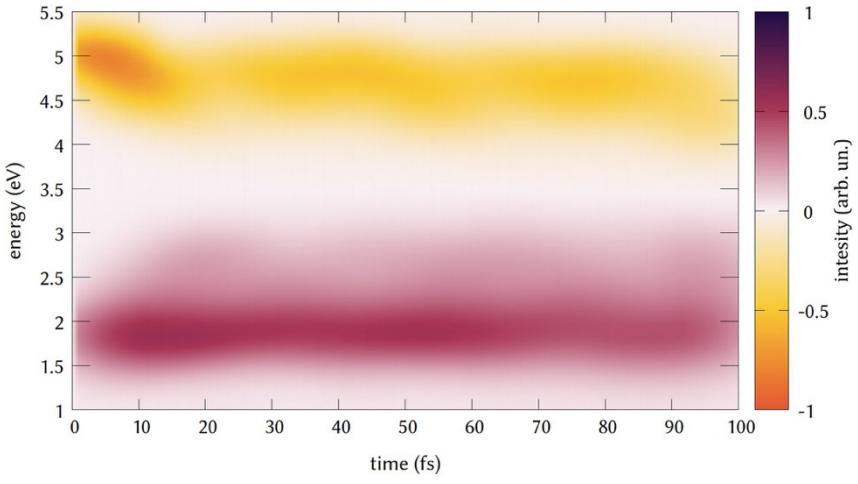

Figure 2 Transient absorption spectrum of DMABN in acetronitrile [1]

References

[1] Avagliano, D., Bonfanti, M., Nenov, A., Garavelli, M., *J. Comput. Chem.* 2022, 43(24), 1641. https://doi.org/10.1002/jcc.26966

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