

## Strong light-molecule coupling can enhance the photoisomerization quantum yield.

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The control of photochemical reactions calls for the selective enhancement and quenching of individual processes among those occurring when light, molecules and environment interact. To this aim, the strong coupling between molecules and cavities offers a toolbox of new effects to control the photochemical reactions[1]. In this regime, the molecular degrees of freedom mix with the resonant cavity photons[2], yielding hybrid light-matter states: polaritons.

In this work, we resort to a FOMO-CI[3] based approach to investigate the influence of the strong coupling on the azobenzene excited state taking into account all the molecular complexity. Traditionally, the study of photochemical processes relies on a compromise between efficiency and accuracy. In this regards, non-adiabatic dynamics techniques in the semiclassical framework have been developed (Surface hopping algorithms)[4]. By reworking one of such techniques, we take into account the hybrid light-matter nature of polaritonic states and investigate the photochemistry on polaritonic states of azobenzene in vacuum[5]. Basing our QM/MM simulations on a recent experimental realisation[6], we present the results of the photochemistry for a realistic system under the strong coupling regime. We describe how such coupling deeply affects the quantum yields of a photoisomerization process and its mechanism, discussing how suitable conditions can be found to selectively suppress or enhance reaction quantum yields. Finally, we comment on the impact of such modified photochemistry on the control of the concentration of product at the photostationary state.

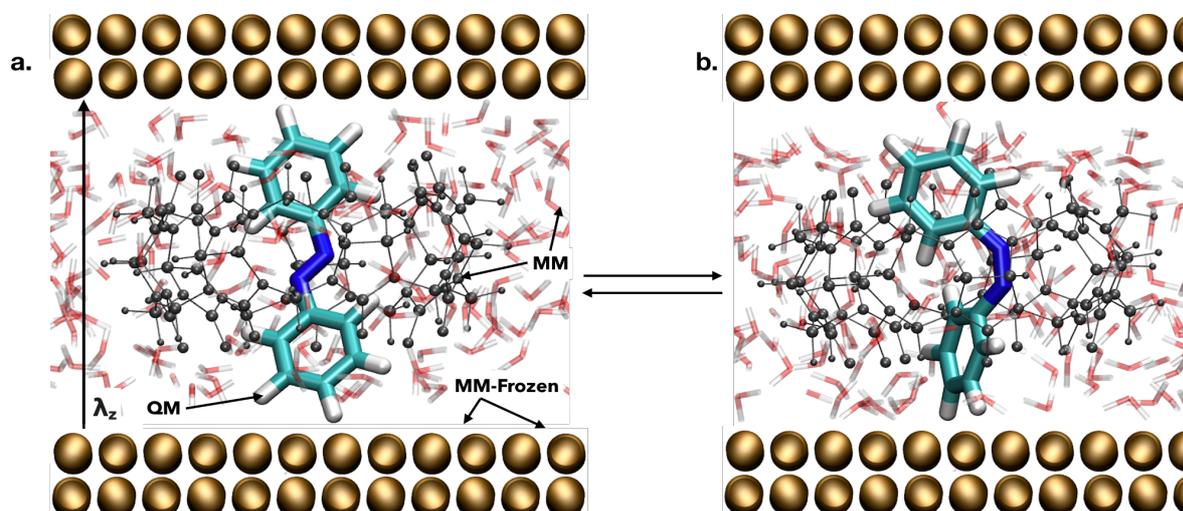


Figure 1: Simulated azobenzene photoreversible switch between trans(a) and cis(b) under strong coupling regime. The system mimics the experimental realization of ref.[6] by treating azobenzene at QM level. The environment is modeled by electrostatic embedding plus Lennard-Jones potentials.

### References

- [1] T. Schwartz, J. A. Hutchinson, C. Genet, T. Ebbesen, *Angew. Chem. Int. Ed.* **51**, 272 (2012).
- [2] J. Galego, F. J. Garcia-Vidal, J. Feist, *Phys. Rev. X*, **5**, 041022 (2015).
- [3] T. Cusati, G. Granucci, E. Martinez-Nunez, F. Martini, M. Persico, S. Vazquez, *J. Chem. Phys.*, **55**, 562 (1971).
- [4] J. C. Tully, R. K. Preston, *Angew. Chem. Int. Ed.* **51**, 272 (2012).
- [5] J. Fregoni, G. Granucci, E. Coccia, M. Persico, S. Corni, *Nat. Commun.* **9**, 4688 (2018).
- [6] R. Chikkaraddy *et al.*, *Nature*, **535**, 127 (2016).