

## A TD-DFT Approach for Polariton Chemistry: Polaritonic and Charge Transfer Excitations in Azobenzene Photoisomerization

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**Abstract:** The desire to control the interaction between surface plasmons and quantum systems as cells, molecules, polymeric macromolecules has boosted the progress in theoretical and experimental techniques for the effective manipulation of such objects. The work here presented is somehow at the frontier between quantum chemistry and nanophotonics, providing, within the TD-DFT framework, a deeply understanding of the coupling mechanisms between the azobenzene photoswitch and a prototype plasmonic nanocluster, showing the effects of the localized plasmon on strong-coupling and charge-transfer phenomena.

Fabrication and characterization techniques are nowadays able to finely control light-matter interaction at sub-nanometer scales where classical electrodynamics fails. New theoretical frameworks able to overcome the limits of the classical vision and to fully take into account quantum mechanical effects (i.e. nonlocality, electron spill-out, charge transfer) are, thus, required. By means of a fully atomistic TDDFT approach, in this work we show how the potential energy surfaces for a photochemical system of practical interest as azobenzene, can be importantly modified by both classical electromagnetic and charge transfer effects in the presence of a metal nanostructure. Inspired by the pioneering work in 2012 by Ebbesen's group [1], polaritonic chemistry, i.e., the field caring of manipulating chemical structure and reactions through the formation of polaritons, hybrid half-light half-matter states, has become the attraction of several experimental and theoretical researches in the last few years. From a theoretical point of view, the problem of the perturbations induced on the potential energy surfaces of a molecule by photonic modes has been largely faced in the framework of Quantum Electrodynamics (QED) [2]. In this work a fully-QM scheme, based on an atomistic description in the linear response framework of the TD-DFT of both the matter and light components, is proposed to analyze a chosen isomerization pathway for an azobenzene molecule interacting with a plasmonic nanocluster put in its proximities (Fig. 1). Azobenzene represents one of the simplest photochromes able to interconvert between trans- and cis- forms. Despite its isomerization process has not yet been fully understood, numerous applications have been developed: in biomedicine, in bioimaging, in photopharmacology, etc. The metallic counterpart is a tetrahedral cluster of Ag<sub>20</sub>. This choice is due to the fact that this cluster has a simple spectrum dominated by only one narrow excitation in the same spectra range of Azobenzene which can be associated to a localized plasmon [3]. Recent works have shown that the strong coupling between surface plasmon-polariton mode and excitons could lead to the formation of hybrid states, namely polaritons or plexcitons [4]. Here we show the onset of these new states for particular conditions and how these can modify the potential energy landscape of the molecule. Moreover we introduce a

new figure of merit defined *Polaritonic Index* (PI) which allow us to identify all the hybrid excitations and among them to distinguish polaritonic (Fig. 1) from charge-transfer states (Fig. 2).

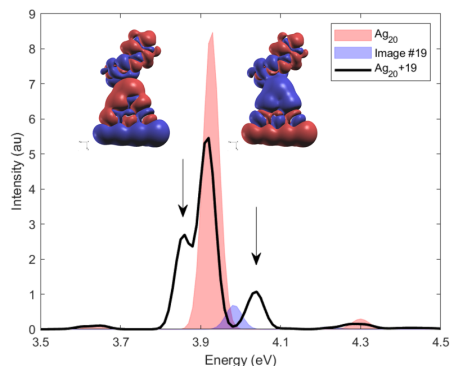


Fig. 1 Comparison between the TD-DFT absorption spectra of the isolated Ag, isomer #19 and the hybrid systems composed of  $Ag_{20}$  + isomer #19 (Gaussian broadening of 0.02 eV). Inset: transition densities of the lower and upper polaritonic states.

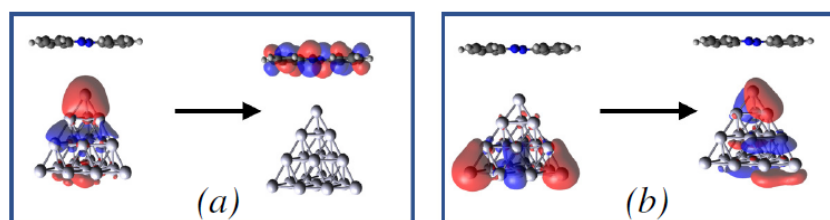


Fig. 2 First two Natural Transition Orbitals pairs for the lowest energy CT state appearing under  $S_2$ .

While polaritonic states appear only in the barrier region, charge transfer excitations seem to be present along the selected isomerization pathway from trans- to cis- conformation in between  $S_1$  and  $S_2$ , this possibly providing additional channels whose relevance is likely dependent on the relative molecule-metal distance and orientation [4]. The work has a double mission. From one side it shows how a theoretical scheme beyond classical EM descriptions is required to properly explain the physics underlying the interaction between metallic and molecular excitations. From the other one, it presents a possible scenario of plasmon-induced perturbations in the photoisomerization of a switch of practical interest, as azobenzene, opening the way to polariton chemistry applications.

## References

1. Henzl, J., M. Mehlhorn, H. Gawronski, K.H. Rieder, and K. Morgenstern, "Reversible cis–trans isomerization of a single azobenzene molecule", *Angew. Chem. Int.*, Vol. 45, No. 4, 603–606, 2006.
2. Feist, J., J. Galego, and F.J. Garcia-Vidal, "Polaritonic chemistry with organic molecules", *ACS Photonics*, Vol. 5, No. 1, 205-216, 2018.
3. D'Agostino, S., R. Rinaldi, G. Cuniberti and F. Della Sala, "Density functional tight binding for quantum plasmonics", *J. Phys. Chem. C*, Vol. 122, No. 34, 19756– 19766, 2018.
4. Giannone, G., F. Della Sala and S. D'Agostino, "Atomistic investigation of hybrid plasmonic systems", *Nanomater. Nanotechnol.*, Vol. 9, 1847980419856534, 2019.