Nantes Université

Proposition de Stage Master CMT

Stage de M1 ☒ et/ou Stage de M2 ☒

Titre du stage : Theoretical study of the trans-to-cis photoisomerization dynamics of bisazobenzene

Equipe d'accueil : ModES team (CEISAM lab)

Responsable du stage :

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Description du stage proposé :

Azobenzene is a widely studied photoswitch used in various fields.[1–3] It is known to violate Kasha's rule, meaning that different initial electronically excited states result in different photoisomerization outcomes (because of different pathways).[4,5] Numerous studies have investigated its *trans*-to-*cis* photoisomerisation, showing that the doubly excited state plays an important role in this process upon excitation of the second excited state.[6]

Bisazobenzene, which consists of two azobenzene units linked by a central phenyl ring, is also a well-known compound. However, to the best of our knowledge, only one theoretical study has simulated its dynamics and studied the photoisomerisation mechanism.[7] This project aims to simulate the *trans*-to-*cis* photoisomerization dynamics of bisazobenzene and investigate the role of the doubly excited state in that system. Two isomers will be studied during the internship: meta-bisazobenzene and para-bisazobenzene. These two isomers appear to exhibit different photoisomerisation outcomes, which will be a key aspect of the investigation.

The student will carry out DFT and TDA-DFT calculations to describe the electronic structure of both bisazobenzene isomers. In the second part of the internship, the student will perform mixed quantum-classical non-adiabatic surface hopping dynamics. The goal is to assess the impact of excluding the doubly excited state in simulations of *trans*-to-*cis* photoisomerization.

1. Sun CL, Wang C, Boulatov R. Applications of Photoswitches in the Storage of Solar Energy. ChemPhotoChem. 2019;3(6):268-283. doi:10.1002/cptc.201900030

2. Klajn R. Immobilized azobenzenes for the construction of photoresponsive materials. Pure and Applied Chemistry. 2010;82(12):2247-2279. doi:10.1351/PAC-CON-10-09-04

3. Schatz D, Wegner HA. Electrochemistry of Azobenzenes and Its Potential for Energy Storage. J Org Chem. Published online April 14, 2025:acs.joc.5c00315. doi:10.1021/acs.joc.5c00315

4. Nenov A, Borrego-Varillas R, Oriana A, et al. UV-Light-Induced Vibrational Coherences: The Key to Understand Kasha Rule Violation in trans-Azobenzene. J Phys Chem Lett. 2018;9(7):1534-1541. doi:10.1021/acs.jpclett.8b00152

5. Cisnetti F, Ballardini R, Credi A, et al. Photochemical and Electronic Properties of Conjugated Bis(azo) Compounds: An Experimental and Computational Study. Chemistry – A European Journal. 2004;10(8):2011-2021. doi:10.1002/chem.200305590

6. Casellas J, Bearpark MJ, Reguero M. Excited-State Decay in the Photoisomerisation of Azobenzene: A New Balance between Mechanisms. ChemPhysChem. 2016;17(19):3068-3079. doi:10.1002/cphc.201600502

7. Floß G, Saalfrank P. The Photoinduced E → Z Isomerization of Bisazobenzenes: A Surface Hopping Molecular Dynamics Study. J Phys Chem A. 2015;119(20):5026-5037. doi:10.1021/acs.jpca.5b02933

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