

Multidimensional Photochemistry Models: Application to Aminobenzonitrile and Benzopyran

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Abstract: To understand the photoreactivity of aminobenzonitrile and benzopyran, their electronic structures and the potential energy landscapes were analyzed at the CASSCF level and models were developed to perform quantum dynamics calculations.

Over the last decades, progresses in experimental techniques combined with theoretical simulations have given access to studying and controlling the photochemical reactivity of large molecular systems with numerous technological applications. For example, it has been shown that the shape of the laser pulse that initiates the photoisomerization of spiropyrans into merocyanines was determining for using them as optically-controlled molecular switches [1,2]. Aminobenzonitrile-like molecules are another example where different fluorescence patterns are observed, depending of the solvent or its substituents. Such properties are crucial in the field of organic materials to understand and design fluorescent markers or photoswitches [3,4].

One major challenge in theoretical chemistry concerns the study of photochemical processes of large molecules (several tens of modes), where conical intersections (CI) play a major role by transferring population between electronic states [5]. This requires the calculation of more than one electronic states and the non-adiabatic coupling between them, the development of quantum chemistry models, and the use of modern quantum dynamics simulation methods. Our strategy is summarized as follows.

- (i) Exploring the potential energy surfaces and optimizing specific points (e.g., CI, minima, and TS) with quantum chemistry calculations. In a first stage, these are run at the CASSCF level of theory with a polarized extended basis sets, and the solvent effect is described implicitly with the PCM model.
- (ii) Generating the full-dimensional potential energy surfaces as analytical functions of the nuclear coordinates. More precisely, the diabatic surfaces and the electronic couplings are expressed as quadratic and linear expansions around reference geometries, respectively. The energy and geometry parameters of the model are extracted from the ab initio calculations. The linear parameters of the electronic couplings are determined with the ab initio branching-space vectors at the conical intersection (CI). The curvatures of the diabatic potentials are obtained through a self-consistent procedure using the second-order Jahn Teller effect that includes the electronic couplings between the adiabatic potentials.
- (iii) Solving the time-dependent Schrödinger equation for the nuclei for all the degrees of freedom. This is achieved with the multilayer multiconfiguration time-dependent Hartree method (ML-MCTDH) [6].

This work is focussed on two photoreactive processes:

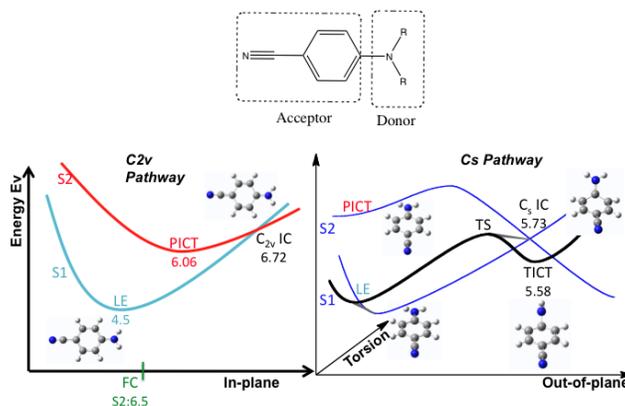
Aminobenzonitrile (ABN, R=H) vs. dimethylaminobenzonitrile (DMABN, R=CH₃) charge transfer

The second excited state (S_2) absorbs a UV photon, and CIs between S_2 and S_1 deactivate the system to S_1 . Experimentally, one fluorescence band from a locally-excited (LE) electronic state (S_1) is observed for both molecules in the gas phase. In polar solvents, DMABN presents a second fluorescence band from an intramolecular charge transfer (ICT) electronic state (S_1) [3,4].

A C_s pathway is already known [4,7]. Nevertheless, we have found a new C_{2v} pathway. Both are complementary and in competition during the photoinduced process.

The C_s pathway is along the out-of-plane benzene deformation. The C_s CI $_{S_2/S_1}$ is linked to the formation of LE. The twisted (C-NH₂ torsion) ICT (TICT) minimum is reached when the wave packet is developed along the torsion mode once on the seam (see figure).

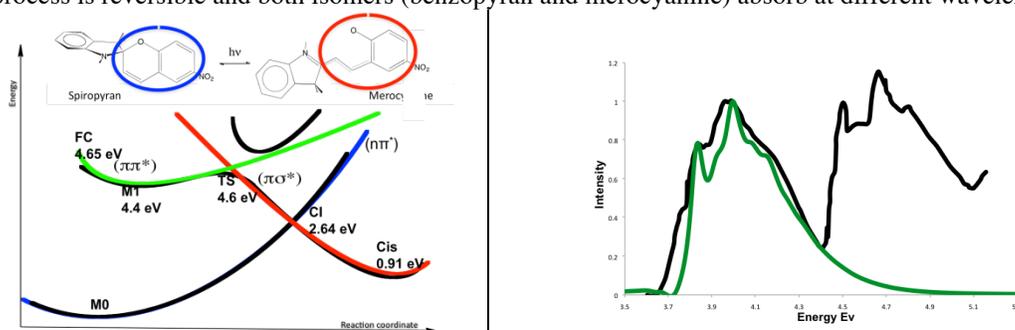
The C_{2v} pathway is along the in-plane quinoidic deformation. This motion drives the system to a sloped C_{2v} CI $_{S_2/S_1}$ leading to the formation of LE (see figure). One should expect the C_{2v} pathway to be more efficient than the C_s one in the gas phase, thus explaining the absence of dual fluorescence for both molecules.



In a polar solvent, the ICT state will be strongly stabilized. Our preliminary results show that the planar-ICT (PICT) conformation is the ICT minimum on S_1 , which differs from the gas phase minimum (e.g., TICT). The quantum chemistry studies of ABN and DMABN in the gas phase and in a solvent are still ongoing. Quantum dynamics simulations will follow.

Photoisomerisation of benzopyran (the spirocyan chromophore).

Absorption of a UV photon excites the system to the S_1 state. Through vibrational relaxation, the system reaches a $CI_{S1/S0}$ where it deactivates to the ground state without fluorescence (see figure). Part of the wave packet goes back to the closed form (benzopyran), the other part goes to the opened form (merocyanine). It is a photochromic system [8]: the process is reversible and both isomers (benzopyran and merocyanine) absorb at different wavelengths.



The quantum chemistry of benzopyran was the center of numerous studies and it is nowadays well known [1,2,8]. Therefore, we applied our multidimensional model, and a UV spectrum was obtained after a 100 fs dynamics. The theoretical spectrum is in good agreement with the experimental results (see figure). Intrinsic anharmonicity are important to describe the photoreactivity and will be include in our future models.

- [1] S.-R. Keum, M.-S. Hur, P. M. Kazmaier, and E. Buncel. Thermo- and photochromic dyes: indolino-benzospirocyranes. part 1. UV-VIS spectroscopic studies of 1,3,3-spiro(2h-1-benzopyran-2,2'-indolines) and the openchain merocyanine forms; solvatochromism and medium effects on spiro ring formation. *Canadian Journal of Chemistry* 69, 12 (1991), 1940–1947.
- [2] M. Saab, L. Joubert-Doriol, B. Lasorne, S. Guerin, and Fabien Gatti, “A quantum dynamics study of the benzopyran ring opening guided by laser pulses”, *Chem. Phys.* (2014) in press.
- [3] C. Bosshard, K. Sutter, P. Pretre, J. Hulliger, M. Florsheimer, P. Kaatz, and P. Gunter. *Organic Nonlinear Optical Materials*, Advances in Nonlinear Optics. Gordon and Breach Publishers, New York, (1995).
- [4] Z. R. Grabowski and K. Rotkiewicz, “Structural changes accompanying intramolecular electron transfer: Focus on twisted intramolecular charge-transfer states and structures”, *Chem. Rev* **103**, 3899-4031 (2003).
- [5] G.A. Worth, L.S. Cederbaum. “Mediation of ultrafast electron transfer in biological system by conical intersections”, *Chemical Physics Letters* **338**,219-223 (2001)
- [6] O. Vendrell and H-D Meyer, “Multilayer multiconfiguration time-dependent Hartree method: Implementation and application to a Henon-Heiles Hamiltonian and to pyrazine”, *J. Chem. Phys.* **134**, 044135 (2011)
- [7] J. Gómez, M. Reguero, M. Boggio-Pasqua, and M. A. Robb, “Intramolecular charge transfer in 4-Aminobenzonitriles does not necessarily need the twist”, *J. Am. Chem. Soc* **127**,19 (2005)
- [8] L. Joubert-Doriol, B. Lasorne, D. Lauvergnat, H-D Meyer, F. Gatti, “A generalised vibronic-coupling Hamiltonian model for benzopyran”, *The Journal of Chemical Physics* **140**, 044301 (2014)