XIX SBQT
Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Photophysics and photochemistry of nitrobenzene and 1-nitronaphthalene performing CASPT2//CASSCF static computations and DD-vMCG dynamics.

Angelo Giussani, Graham A. Worth

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

Abstract: Nitrobenzene (NB) and 1-nitronaphthalene (1NN) can be regarded as the most simple nitroaromatic compounds, and yet they are characterized by a complex photophysics and photochemistry. Both molecules are common pollutants of urban atmosphere due to their production as a consequence of incomplete combustions [1], while NB is also an important model of energetic materials [2] and it has applications in the drug delivery sector [3]. NB' photophysics is characterized by three lifetimes (100 fs, 6 ps, and 480 ps)[4] and by a particularly high value of the triplet quantum yield, equal to 0.67 [5]. Under UV radiation the system can photoreact leading to the formation of different photoproducts, as NO_2, NO and O [6]. 1NN is also characterized by a first lifetime equal to 100 fs, attributed to the decay into the triplet manifold and consequently making 1NN the organic compound with the fastest multiplicity change ever measured, [7] and by a high value of the triplet quantum yield (0.63) [5], while only the formation of NO has been reported as a consequence of its UV-induced photodegradation [8]. The photophysics and photochemistry of these two similar but yet different compounds have been studies by means of static CASPT2//CASSCF computations in the framework of the so-called "photochemical reaction path approach" [9,10], and performing dynamics simulations with the direct dynamics variational multi-configurational Gaussian (DD-vMCG) method, which is a full quantum dynamics methodology, allowing the resolution of the time-dependent nuclear Schrödinger equation variationally [11]. A comparison of the photophysical and photochemical reaction paths characterized for the systems highlighting the differences and similarities in relation to the know experimental data on the molecules will be presented, together with the dynamics results obtained up to date.

Key-words: nitrobenzene, nitronaphthalene, CASPT2//CASSCF, DD-vMCG
Support: This work has been supported by the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie Grant Agreement No. 658173. A.G. also acknowledges the support of Project No. CTQ2014-58624-P of the Spanish MINECO and Project. No. GV2015-057 of the Generalitat Valenciana.

References:

[1] L. Möller, I. Lax, L.C. Eriksson, Environ. Health Perspect. 101, 309, (1993).
[2] T.B. Brill, K.J. James, Chem. Rev. 93, 2667, (1993).

[3] H. Nakagawa, K. Hishikawa, K. Eto, N. Ieda, T. Namikawa, K. Kamada, T. Suzuki, N. Miyata, J. Nabekura, ACS Chem. Biol. 8, 2493, (2013).
[4] M. Takezaki, N. Hirota, M. Terazima, J. Chem. Phys. 108, 4685, (1998).
[5] R, Hurley, A.C. Testa, J. Am. Chem. Soc. 90, 1949, (1968).
[6] D.B. Galloway, J.A. Bartz, L.G. Huey, F.F. Crim, J. Chem. Phys. 98, 2107, (1993).
[7] R. Morales-Cueto, M. Esquivelzeta-Rabell, J. Saucedo-Zugazagoitia, J.J. Peon, Phys. Chem. A 111, 552, (2007).
[8] C.E. Crespo-Hernandez, R.A. Vogt, B. Sealey, Mod. Chem. Appl. 1, 106, (2013).
[9] A. Giussani, G.A. Worth, J. Chem. Theory Comput. 13, 2777, (2017).
[10] A. Giussani, J. Chem. Theory Comput. 10, 3987, (2014).
[11] G.W. Richings, I. Polyak, K.E. Spinlove, G.A. Worth, I. Burghardt, B. Lasorne, Int. Rev. Phys. Chem. 34, 269 (2015).