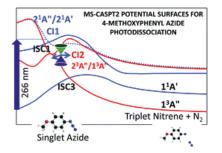
An MS-CASPT2 Study of the Photodecomposition of 4-Methoxyphenyl Azide. Role of Internal Conversion and Intersystem Crossing

Daniel Aranda, Francisco J. Avila, Isabel López-Tocón, Juan F. Arenas, Juan C. Otero, Juan Soto

Department of Physical Chemistry, Faculty of Science, University of Málaga E-mail: aranda@uma.es

Aryl azides photochemistry is strongly dependent on the substituent relative position, as has been studied by time resolved resonant Raman (TR³) spectroscopy for 4-methoxyphenyl azide and its isomer 3-methoxyphenyl azide. irradiated 266 former 4.4'-[1,2] When at nm, the results in dimethoxyazobenzene whereas the latter forms 1,2-didehydroazepine. It is proposed that the key step of the reactions is the formation of a nitrene derivative. Recently, it has been proposed by us that nitrenes might have a relevant role in the Surface-Enhanced Raman Scattering (SERS) of paminothiophenol, [3] however, the molecular mechanism is not well known in neither of these cases. Therefore, we studied the photodecomposition of 4methoxyphenyl azide [4] using multiconfigurational self-consistent field methods (MC-SCF) with the CAS-SCF and MS-CASPT2 approximations and calculated the resonant Raman spectra of the relevant species using a multi-state version of Albrecht's vibronic theory. The results propose that the reaction follows a two steps sequence after irradiation at 266 nm: an intersystem crossing 2¹A'/2³A" which decays through a 2¹A'/2¹A" conical intersection producing molecular nitrogen and triplet 4-methoxyphenyl nitrene in its ground state.



References

[1] S. Y. ONG, P. Y. CHANG, P. ZHU, K. H. LEUNG AND D. L. PHILIPPS, J. PHYS. CHEM. A, 2003, 107, 3858–3865.

[2] W. M. KWOK, P. Y. CHAN AND D. L. PHILLIPS, J. PHYS. CHEM. A, 2005, 109, 2394–2400.

[3] M. R. LOPEZ-RAMIREZ, D. ARANDA RUIZ, F. J. AVILA FERRER, S. P. CENTENO, J. F. ARENAS, J. C. OTERO AND J. SOTO, J. PHYS. CHEM. C, 2016, 120, 19322–19328.

[4] D. ARANDA, F. J. AVILA, I. LÓPEZ-TOCÓN, J. F. ARENAS, J. C. OTERO AND J. SOTO, PHYS. CHEM. CHEM. PHYS., 2018, 20, 7764—7771.