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

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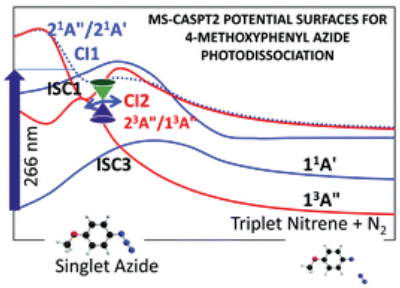
Aryl azides photochemistry is strongly dependent on the substituent relative position, as has been studied by time resolved resonant Raman (TR^3) spectroscopy for 4-methoxyphenyl azide and its isomer 3-methoxyphenyl azide. [1,2] When irradiated at 266 nm, the former results in 4,4'-dimethoxyazobenzene 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 *p*-aminothiophenol, [3] however, the molecular mechanism is not well known in neither of these cases. Therefore, we studied the photodecomposition of 4-methoxyphenyl 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 $2^1A'/2^3A''$ which decays through a $2^1A'/2^1A''$ 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.