Micro-Raman and Computational Study of the Azoxybenzene Photorearrangement to 2-Hydroxybenzene

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When azoxybenzene **(1)** is irradiated by light with wavelength less than 400 nm, the molecule undergoes an intramolecular rearrangement to yield 2-hydroxyazobenzene **(2)** as photoproduct with a quantum yield of formation of ~ 0.020, independent of temperature, concentration and wavelength in the range 250 – 400 nm [1]. As shown in Fig. 1, left, the lowest absorption region of **(2)** is red-shifted with respect to that of the reactant azoxybenzene, in particular in alkaline ethanolic solution.

The micro-Raman spectroscopy [2] can afford to characterize the vibrational properties of the photoproduct due to the possibility of focusing the exciting radiation on the tiny microcrystals of **(2)** obtained by slow evaporation of the solvent. This application of the technique is appealing when only minute amounts of the reaction product are available. In our case, the Raman spectrum of **(2)** of Fig. 1, right lower, has been measured on fibrous microcrystals ~ 150 μm long by examination with the focusing microscope.

The combination of the experimental results with *ab initio* DFT calculations of vibrational frequencies and Raman intensities further helps to identify the crystalline photoproduct. Calculated data for **(2)** and for the tautomeric imino molecule confirm that **(2)** has been obtained during the irradiation.

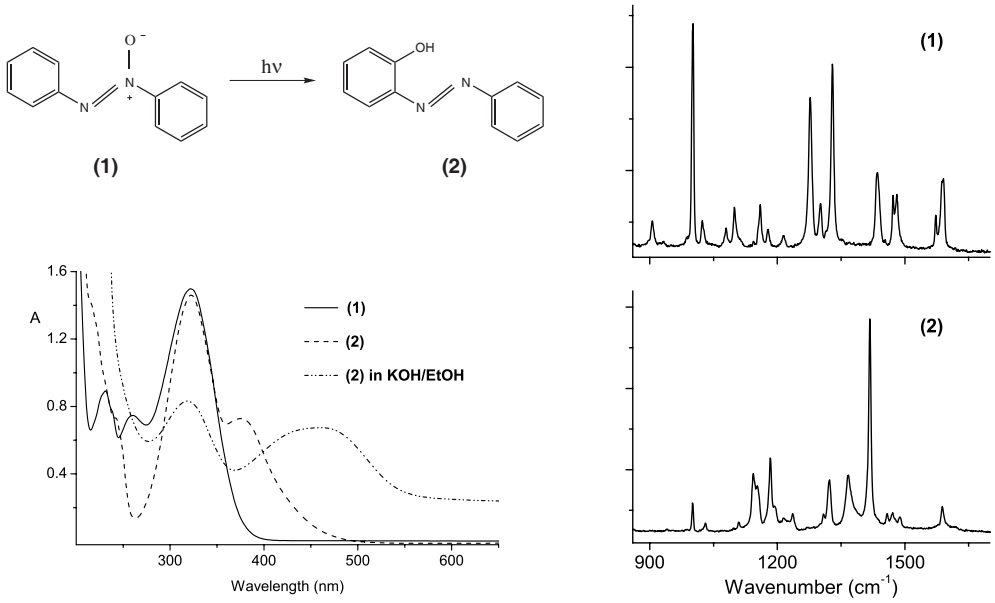

Fig. 1: Left, upper: the photochemical rearrangement of **(1)** to **(2)**; lower: absorption spectra of ~ 10^{-4} M solution of **(1)** in ethanol before and after **(2)** irradiation. Right: micro-Raman spectra of **(1)** and **(2)** microcrystals at room temperature exciting at 785 nm.

[1] N.J. Bunce, J. LaMarre, S.P. Vaish, Photochem. Photobiol. 39 (1984) 531-533.
[2] *Modern Tecniques in Raman Spectroscopy*, J.J. Laserna ed., Wiley, Chichester (England), 1996.