Keynote lecture

Probing radical and nitrene intermediates in narrowband UV-induced photoreactions in cryogenic inert matrices

Rui Fausto

1 CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
e-mail: rfausto@ci.uc.pt

Radical and nitrene intermediates play a fundamental role in chemical reactivity. However, their capture and characterization, as well as the precise description of their reactivity, pose always enormous challenges to investigation.

Matrix isolation is a powerful tool to study short-living species, and is nowadays a mature technique suitable to address complex problems of chemical reactivity involving reaction intermediates. In fact, when used together with contemporary computational methods of quantum chemistry and up-to-date narrowband tunable light sources, matrix isolation may be used very successfully for investigation of elusive reaction intermediates, in a very elegant and direct way.

In this talk, I will describe a series of possible strategies for research on the structures and reactivity of radical and nitrene intermediates participating in photochemical processes, based on the conjugated use of theoretical methods and matrix isolation coupled with spectroscopic probing. Recent results on the photochemistry of phenols and thiophenols, in which radicals play a prominent role, and of several types of nitrene precursors, like isoxazoles, azides and tetrazoles, will be presented. In these studies, narrowband tunable light sources were used to selectively excite the different species formed along the targeted reactions, allowing the unequivocal identification of the transient radicals and nitrenes formed along these processes, their structural characterization and the evaluation of their specific reactivity. On the way, the first direct observation of a tunneling reaction involving a nitrene, and the production of several rare high-energy species resulting from photochemical processes where radical and nitrene intermediates play central mechanistic roles will be reported.

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