

The role of conical intersections in the photoinduced bond cleavage of benzhydryl derivatives

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Photoinduced bond cleavage is often employed for the generation of carbocations, which are central to S_N1 reactions. Benzhydryl derivatives are prominent precursors in organic chemistry. Depending on the leaving group the photoinduced bond cleavage occurs on a femtosecond to picosecond time scale and typically leads to two distinguishable products, the desired benzhydryl cations and as competing by-product the benzhydryl radicals. Conical intersections are the chief suspects for such ultrafast branching processes. We show for two typical examples, the neutral benzhydrylchloride and the charged diphenylmethyltriphenylphosphonium ions that the role of the conical intersections is not straightforward as expected in early literature but more complex and furthermore differs significantly for both precursors.

Quantum chemical, quantum dynamical and on-the-fly calculations are performed to unravel the photochemical process from the initial excitation to the formation of the optical signal for both channels. The experimental optical signal we use for comparison is recorded by the Riedle group (LMU, Physik) with extreme temporal resolution. Including the dynamic effect of the solvent, we could clarify the role of the conical intersections and the influence of the immediate environment. In case of benzhydrylchloride we can directly connect the observed signals to two early conical intersections close to the Franck Condon region, in case of the diphenylmethyltriphenylphosphonium ion dynamic solvent effects are needed to activate a conical intersection at larger distances along the reaction coordinate.