



Mittwoch, 11.05.2016, um 16:00 Uhr

Ort: Reichenhainer Str. 90;

Zentrales Hörsaal- und Seminargebäude, Raum 2/N013

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Molecular features in complex environment: cooperative team players during excited state bond cleavage

Photoinduced bond cleavage is often employed for the generation of highly reactive carbocations in solution and to study their reactivity. Benzhydryl derivatives are prominent precursors in polar and moderately polar solvents like acetonitrile or dichloromethane. 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 diphenylmethyltriphenyl-phosphonium ions that the role of the conical intersections depends on the interplay of molecular features with the environment. It turns out to differ significantly for both precursors.

Our analysis is based on quantum chemical, quantum dynamical and on-the-fly calculations. The experimental optical signal we use for comparison is recorded by the Riedle group (LMU, Physik) with high temporal resolution. 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.

We developed two methods with increasing complexity to describe the dynamic impact of the solvent environment within a quantum dynamical description. The first method includes the solvent effects in a continuum-like fashion [1], the second treats the solvent environment explicitly [2]. Both methods show that the solvent cage hinders the free dissociation and thus opens the pathway to the conical intersection that allows the formation of the experimentally observed diphenylmethyl cations.

[1] S. Thallmair, M. Kowalewski, J.P.P. Zauleck, M.K. Roos, and R. de Vivie-Riedle, *J. Chem. Phys. Lett.* **5**, 3480 (2014).

[2] S. Thallmair, J.P.P. Zauleck, and R. de Vivie-Riedle, *J. Chem. Theory Comput.* **11**, 1987 (2015).



Alle Zuhörer sind ab 15:45 zu Kaffee und Tee vor dem Hörsaal eingeladen.