Deceleration of dissociating molecular wave packets by solvent cage: the dynamic continuum ansatz

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Carbocations are intensely studied reactive species in organic chemistry and biochemistry. A well-established approach to generate them in solution is photolytic bond cleavage (BC). Electrostatic solvent effects are known to influence the reactivity of the solute significantly. In photochemical reactions where dissociative processes are included not only the electrostatic but also the dynamic impact of the solvent becomes important. For bulky leaving groups, like in phosphonium salts [1], the solvent cage substantially decelerates the photogenerated fragments depending on the viscosity of the solvent. We present theoretical insight into the BC process after photo excitation of diphenylmethylphosphonium ions. After a local π-π* excitation a charge transfer state initiates the BC [2]. It is homolytic in the first excited state leading to carbon radical formation missing the conical intersection (CoIn) with the ground state (Fig. 1). On the contrary ultrafast broadband transient absorption measurements almost exclusively show the formation of diphenylmethyl cations implying a heterolytic BC [1].

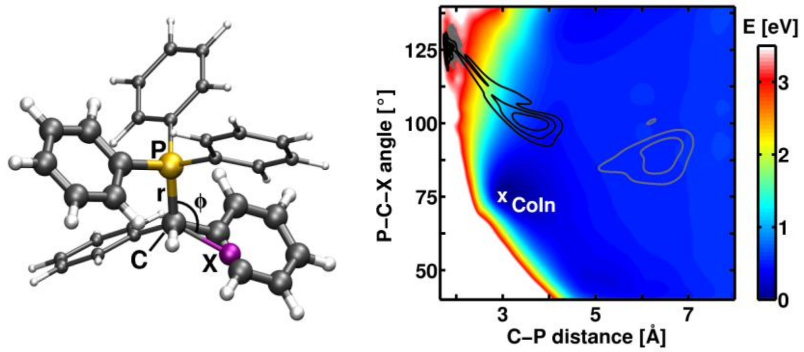

Fig. 1: Reactive coordinates for the photochemical BC of diphenylmethyltriphenylphosphonium ions (left) and dissociating wave packets on the first excited state (right). The snapshots are taken for 100 fs (black) and 220 fs (grey).

Both homolytic and heterolytic channel lead to the formation of one neutral and one positively charged fragment. Therefore the electrostatic solvent effect does not change the reaction dynamics. Only the dynamic effect of the solvent cage comes into play [3]. During the BC both fragments are accelerated. This leads to a deformation of the first solvation shell which in response slows down the dissociation process. Its frictional deceleration is treated by our dynamic continuum ansatz in a quantum mechanical formalism including Stokes law and the dynamic viscosity. About 200 fs after the dissociation has started, the wave packet has lost almost all its kinetic energy. It now can evolve along an angular coordinate with smaller gradient, which directly points towards the CoIn that enables the fast and efficient formation of the carbocations. The photolytic BC of diphenylmethylphosphonium ions particularly illustrates the importance of the dynamic solvent effect treated with our dynamic continuum ansatz. It affects the bond cleavage on a 200 fs timescale and explains the reaction outcome.

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