

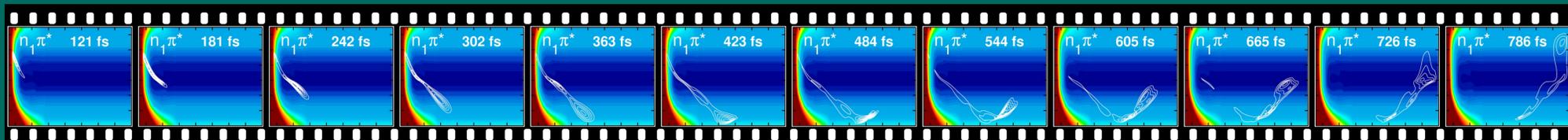
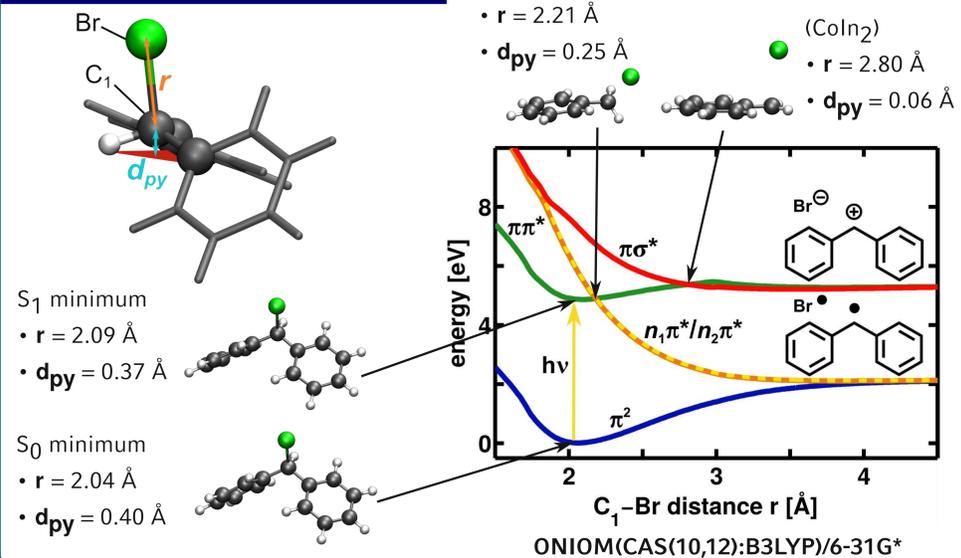
Abstract

Carboradicals and -cations are key intermediates for many chemical reactions. They may be generated by UV-laser excitation of carbonyl compounds such as diphenylmethyl bromide. Here, a local $\pi\pi^*$ excitation occurs, followed by the C-Br bond cleavage leading to radical or ion pairs within a femtosecond timescale. We use both, quantum dynamical and semiclassical on-the-fly dynamical methods to simulate the reaction. In both approaches we employ an ONIOM two-layer method with CASSCF as high level method. We verify for both simulations the decisive role of two consecutive conical intersections for the product splitting, like we recently showed [1] for chlorine as leaving group. Nonetheless, we report remarkable differences compared to the chlorine case and we especially discuss the role of the pyramidalization of the central carbon atom. We evaluate the motion of the wave packet of the quantum dynamical simulation where we see an oscillation comparable to experimental results [2]. Furthermore we calculate time-resolved spectra using the velocity autocorrelation function obtained by the on-the-fly dynamics. Here we see the importance of different normal modes for both reaction channels.

[1] S. Thallmair, M. K. Roos, R. de Vivie-Riedle, *Struct. Dyn.* **3** 043205 (2016).

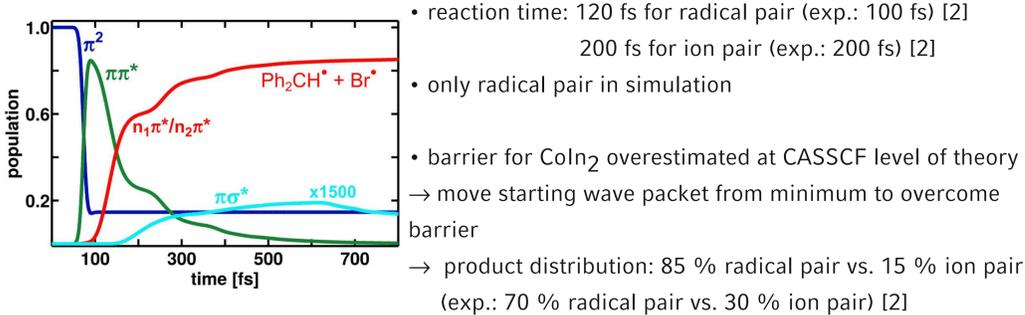
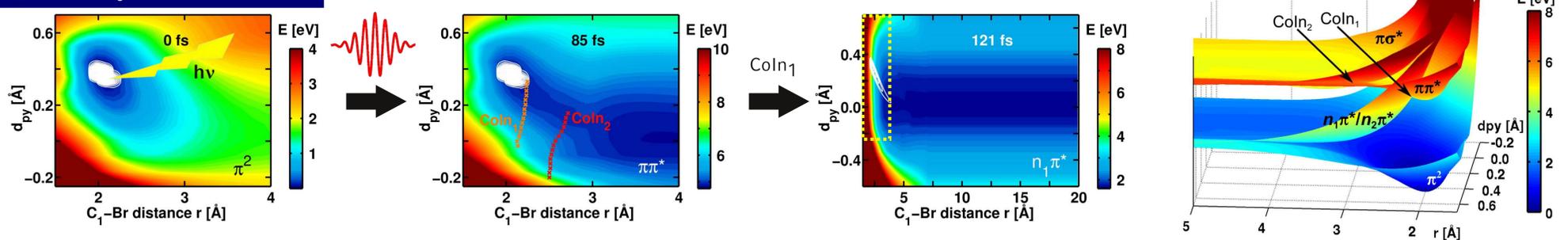
[2] C. F. Sailer, E. Riedle, *Pure Appl. Chem.* **7** 1487-1498 (2013).

Diabatic potential energy surfaces

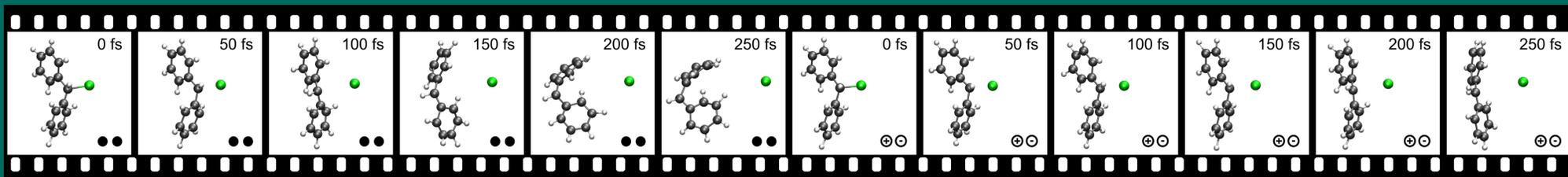
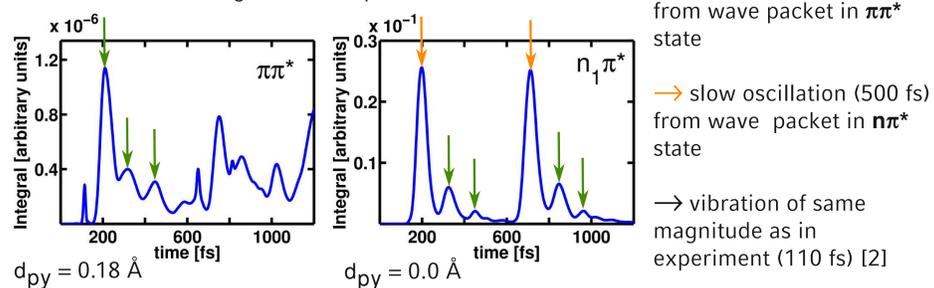


Quantum dynamical simulation

ONIOM(CAS(10,12):B3LYP)/6-31G*

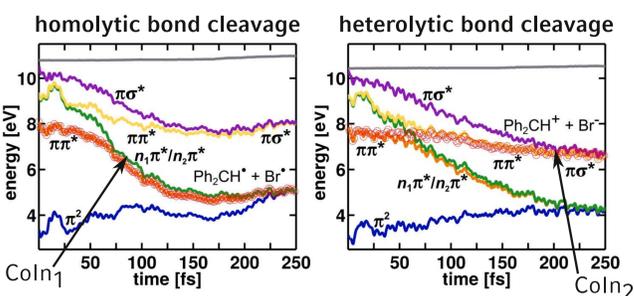


Oscillation of wave packet in coordinate dpy

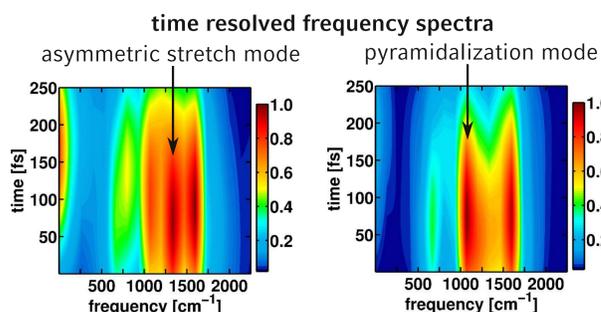


Semi classical trajectory simulation

ONIOM(CAS(12,10):HF)/6-31G*

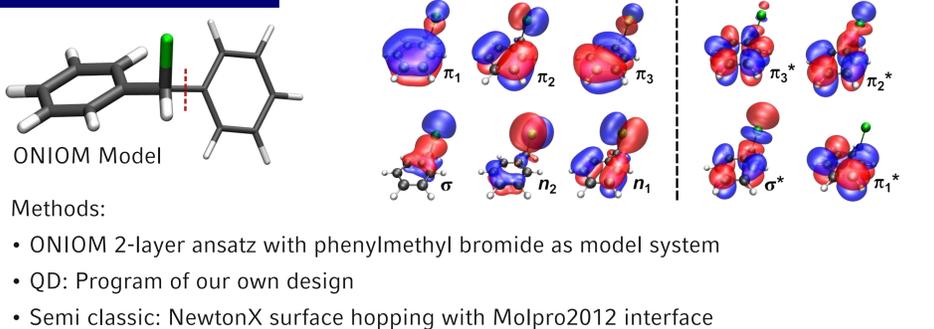


• reaction time: 80-100 fs for radical pair, 180-220 fs for ion pair
 • 60 % homolytic vs. 40 % heterolytic bond cleavage



• propagation time too short to see experimental frequency of 300 cm⁻¹ for the radical and 350 cm⁻¹ for the cation [2]
 • pyramidalization mode especially important for heterolytic bond cleavage

Computational details



Conclusion

• two consecutive Con determine product splitting: the more important Con1 leads to a homolytic bond cleavage, whereas Con2 leads to a heterolytic bond cleavage
 • pyramidalization mode important for dissociation reaction, especially for heterolytic bond cleavage
 • oscillation detected in experiment can be explained by the oscillation of the undissociated molecule in the excited $\pi\pi^*$ state (S_1)