Wavepacket Splitting in the First 100 fs Determines the Products from the Bond Cleavage of Diphenylmethylchloride

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Abstract. An elementary chemical reaction proceeds through two distinct conical intersections. Benzhydryl radicals are formed with a delay of 80 fs, cations after 125 fs. The optical signal increases more slowly due to planarization and solvation.

1 Ultrafast chemical dynamics induced by conical intersections

It is now well established that the fastest processes in molecules after optical population of excited states proceed via conical intersections (CoIn's). In the simplest case of an internal conversion, the system relaxes with unity yield back to the electronic ground state. In the case of a ring opening or an isomerization the initially prepared wavepacket splits at the conical intersection toward the ground state of the reactant or the photochemical product. Calculations have shown that in larger molecules a multitude of conical intersections can exist in the vicinity of the lower excited electronic states due to their high density. The existence and relative importance of these multiple CoIn's is not observable in photophysical processes as there are no distinct and secure signatures of the various pathways. In diphenylmethylchloride two chemically and spectroscopically different products result from the optically-induced bond cleavage. We demonstrate that these products appear at different times and can directly connect this observation to the two early CoIn's close to the Franck Condon region predicted by the calculations. The optical signal for both channels continues to increase after the product formation due to planarization and solvation.

2 Detection and interpretation of the ultrafast photofragment generation

For the observation of the bond cleavage of diphenylmethylchloride an extreme temporal resolution is needed according to the predictions of quantum chemical calculations [1]. We use 25 fs pump pulses centered at 270 nm and probe pulses at either 327 nm or 436 nm [2]. The transmission changes of the probe pulses can monitor the appearance and evolution of the radical and cation product, respectively, since they have their strongest absorption bands at these wavelengths. This has been identified by broadband transient absorption measurements [3,4,5]. To avoid any pulse broadening and coherent artifacts due to cell windows, we perform the pump-probe experiment in a 50 µm free-flowing jet.

Figure 1 shows the results of the transient absorption measurements. In the lower panel of (b) the experimental signal for the radical (black dots) is shown together with the simulation (red line).

Simultaneous with the UV excitation the absorption increases and then starts to weakly decrease. This is due to excited state absorption of the reactant and the beginning wavepacket motion out of the Franck-Condon region. At a delay $\Delta t = 76$ fs the signal starts to strongly increase. This is the direct signature of the bond cleavage toward the benzhydryl radical and chlorine radical.
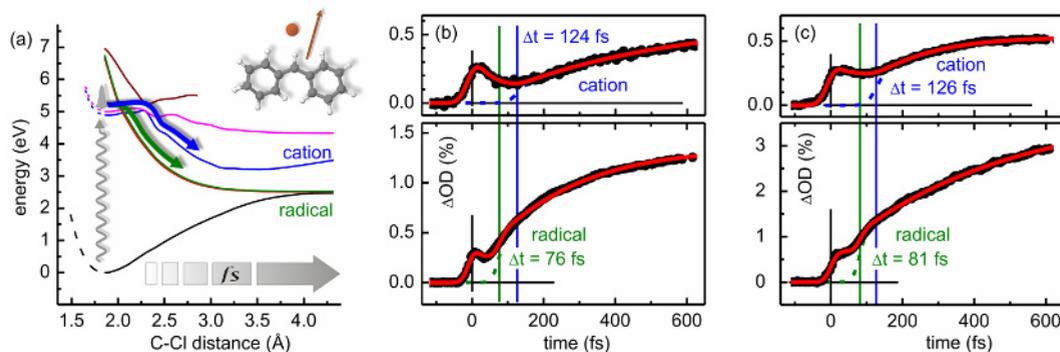

Fig. 1. (a) Potential energy surface of diphenylmethylchloride. After ballistic motion out of the Franck-Condon region, the excited wave-packet splits, leading to the ultrafast generation of radical and ion pairs. (b) Transient absorption of the photoproducts. Due to the nearer interaction region, the radical appears ~50 fs earlier than the cation. (c) A similar dynamics is observed in the 3-fluoro derivative.

For the cation channel at 436 nm a very similar behavior is found. The main difference is that the stepwise increase due to the bond cleavage is now found at 124 fs. The inequality of the delay time for the appearance of the two products is a direct proof that they are generated via two distinct paths. The stepwise appearance in each case instead of the normally observed exponential increase can only be interpreted as the motion of a compact wavepacket and nearly instantaneous reaction once the proper location on the excited potential hypersurface is reached.

The excited state potential energy curves were calculated at the CASPT2-CASSCF(14,12) level of theory with an aug-pVDZ basis set. The active space explicitly includes the lone pairs of the chlorine. We find a strong interaction between the optically accessible $\pi\pi^*$ state (S_1) and the repulsive states leading to either homolytic bond cleavage (radical pair) or heterolytic cleavage (ion pair). The repulsive states and their interaction with the weakly bound excited state lead to two distinct CoIn's separated by about 0.3 Å along the carbon-chlorine stretching coordinate (see Fig. 1a)). This is the decisive coordinate for the bond cleavage.

The two CoIn's are approached by the excited state wavepacket consecutively. At the first one a major fraction splits into the radical channel, while a much smaller fraction leads to the ion channel at a later time when the second CoIn is reached. The small energy barrier encountered by the wavepacket right outside the Franck-Condon region and the multidimensionality of the evolution is the cause for a propagation that is slower than would be expected for a direct und unhindered dissociation. These results can be linked one-to-one to the experimental observations. We have thereby directly determined the time when the wavepacket passes through the two distinct CoIn's. The different times for the radical and the ion can only be explained by the existence of two distinct CoIn's. The topology of the potential hypersurfaces determines the evolution at very early times and the implication for the chemical outcome is persistent for long times. This is distinctly different from previously reported cases where multiple pathways for nonradiative relaxation all lead to the same final result.

In diphenylmethylchloride dissolved in acetonitrile a further increase of the cation and radical signal is seen with about a 300 fs time constant. Through micro-solvation calculations performed with on-the-fly molecular dynamics we can identify this signal increase with the planarization of the products from the sp^3 to the sp^2 configuration [4]. This leads to a strong increase of the optical absorption strength in many combinations of substituted diphenylmethylchlorides and solvents

investigated (see Fig. 2 a) and b)). In addition, the solvation by the polar solvent contributes. Overall, the 300 fs signal increase is not due to a further increase of population but solely to the change in optical transition strength. This is seen in the comparison of the experimental and the theoretical signal with the population readily known in the calculation (see Fig. 2c)).
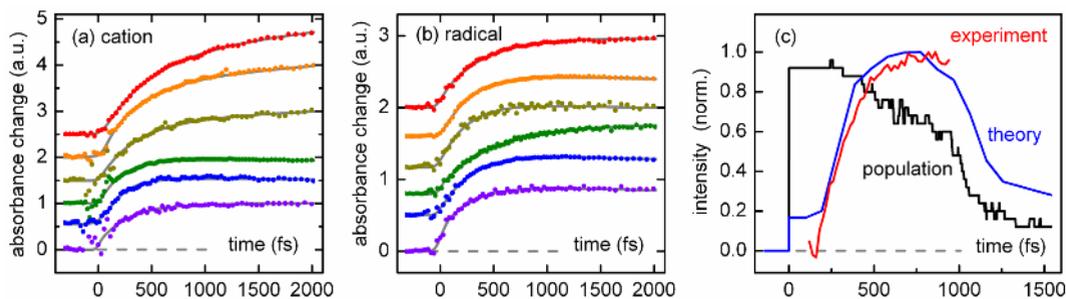

Fig. 2. After UV excitation, many combinations of diphenylmethylchloride derivatives and solvents, a generic ~300 fs rise time constant for the transient absorption of (a) the benzhydryl cation and (b) the benzhydryl radical is found. (c) On-the-fly MD simulations on a benzhydryl cation directly after bond cleavage and surrounded by a solvent shell can reproduce the signal rise independent from the actual cation population. The signal rise can be attributed to a relaxation / planarization of the nascent cation.

For diphenylmethylchloride in acetonitrile a further increase of the cation signal and a decrease of the radical signal is observed. These two changes can be modeled with the identical stretched exponential function with $\tau_{SE} = 11.1$ ps. The changeover is due to electron transfer within the radical pair that leads to the ion pair [5,6]. The electron transfer is fastest for the pairs with the closest distance and eventually stops because the near neighbors are used up and the other pairs diffuse apart. In a solution of 3-fluoro-diphenylmethylchloride in methanol the electron transfer is not observed. We can therefore observe the very early events without interference.

In summary, the combined experimental and theoretical study allows the first direct observation and analysis of wavepacket motion through multiple conical intersections. It shows that such complicated situations are indeed the microscopic basis for a seemingly simple chemical situation like the parallel homolysis and heterolysis. For a proper interpretation of the yields this complexity has to be unraveled.

The electron transfer within the radical pair that leads to ion pairs is already seen at the very early times discussed above. In the next tens of picoseconds it further changes the relative product yields. The electron transfer is terminated by diffusional separation of the remaining radical pairs. On an even longer time scale the ions can recombine, a process that is again stopped by diffusion. At some hundreds of picoseconds the final product distribution is reached. This is the distribution that is of central interest for the chemical application of the photogeneration of benzhydryl cations.

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