Journal of Physics: Conference Series **635** (2015) 112033 doi:10.1088/1742-6596/635/11/112033

Laser pulse duration can control the breakage of multiple chemical bonds

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Synopsis We show that the interplay of electron removal and nuclear dynamics on the few femtosecond range, controlled by the duration of few-cycle laser pulses, determines the ratio of $C_2H_4^{3+}$ fragmentation into two respectively three moieties.

Using ethylene (C_2H_4) as an example, we experimentally demonstrate control of complex fragmentation reactions that involve the breakage of more than one chemical bond using ultrashort intense laser pulses with pulse durations from 4.5 fs to 25 fs. We show that the dynamics of removing three electrons by strong-field ionization determines the ratio of fragmentation of the molecular trication into two respectively three moieties.

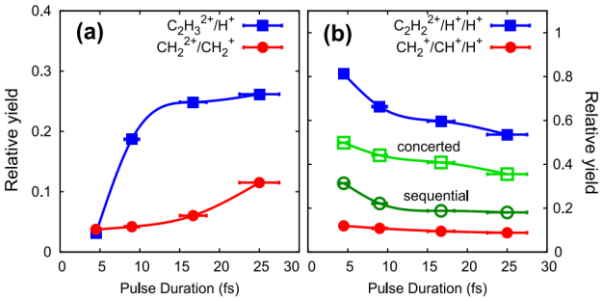

Figure 1. Normalized yield of (a) two-body and (b) three-body fragmentation channels (as indicated) as a function of laser pulse duration. Normalization is such that the sum of the yields of all four channels is 1 at each pulse duration. In (b) the yield of the three-body channel resulting in two protons (blue squares) is divided into the yields due to concerted and sequential fragmentation dynamics, respectively.

In our experiments we measured ionic fragments from $C_2H_4^{3+}$ in coincidence using the COLTRIMS technique [1] as a function of pulse duration from 4.5 fs to 25 fs (FWHM) with a constant peak intensity of 8×10^{14} W/cm^2. From all detected fragments we extracted the relative yield of in total four two- and three-body fragmentation channels, see Fig. 1. It can be seen that the probability of two-body fragmentation via breaking of a C-H bond dramatically increases as the pulse duration is increased from 4.5 fs to about 12 fs, and levels off for longer pulse durations. Fig. 1(a) furthermore shows that also the relative yield of two-body fragmentation via breaking of the center C-C bond monotonically increases with pulse duration. However, the slope is much smaller than in the case of the C-H bond, and the yield is still increasing at the longest measured pulse duration. In contrast to the two-body channels, the relative yields of the three-body fragmentation channels, for both the concerted and sequential fragmentation reactions, decrease with pulse duration [Fig. 1(b)].

Based on the dependence of the kinetic energy release and proton spectra as well as the angular momentum distributions on the pulse duration, and by performing intricate quantum dynamical simulations we explain the findings of Fig. 1 as follows. During the triple-ionization process the intermediate doubly charged ion is reached on an electronically excited PES as a result of removing (at least) one of the two electrons from an inner-valence shell. For sufficiently long laser pulse durations the C-H and C-C bonds do have enough time to significantly stretch on this excited PES. In contrast, for short pulse durations (4.5 fs) the nuclei stay essentially frozen. Thus, for short pulses the third ionization step prepares the triply charged molecular ion in a configuration close to the neutral's equilibrium configuration. For longer pulses (25 fs), however, the triply charged molecular ion is reached with significantly stretched C-H and also slightly stretched C-C bonds. Thus, with longer pulses the triply charged ion is prepared energetically further down the dissociative PES, i.e., on a position with lower potential energy as compared to short pulses. As a consequence, for longer pulses the potential energy is too small to overcome the energy barrier towards triple fragmentation and only two-body fragmentation is possible. In effect, the two-body fragmentation probability becomes strongly enhanced with increasing pulse duration, as observed in the experiment [Fig. 1]

References

[1] X. Xie *et al* 2012 *Phys. Rev. Lett.* **109** 243001