

# Controlling the fragmentation of aligned polyatomic molecules by selective inner-valence ionization

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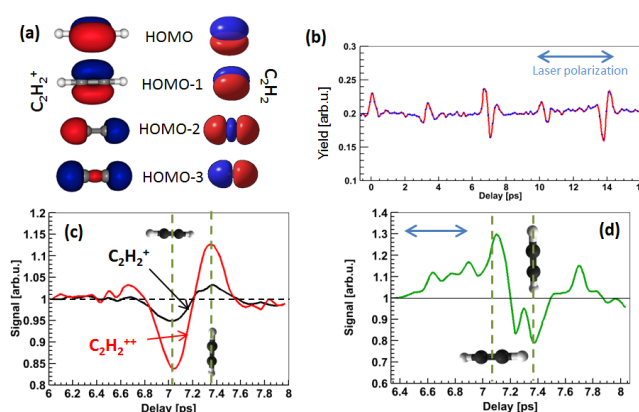
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We show experimentally and theoretically that the strong preponderance of ionization from specific molecular orbitals to the alignment of the molecular axis [Fig. 1(a)] with respect to the laser polarization direction [1] allows for control of the fragmentation pathway of polyatomic molecules. Using the acetylene molecule,  $C_2H_2$ , as an example we demonstrate control over the three fragmentation pathways (1)  $C_2H_2^{++} \rightarrow CH_2^+ + C^+$ , (2)  $C_2H_2^{++} \rightarrow C_2H^+ + H^+$ , (3)  $C_2H_2^{++} \rightarrow CH^+ + CH^+$  using the field-free alignment of the molecule as a control knob.

In our experiments we impulsively align initially randomly aligned  $C_2H_2$  molecules. Time-delayed  $\sim 4.5$ fs pulses are used to ionize and fragment the molecules and the momentum vectors of the resulting ions and ionic fragments were measured by the COLTRIMS method.

The basic principle of the here introduced control method relies on the fact that in many cases a molecular fragmentation reaction can be associated with nuclear dynamics taking place on one (or few) excited (dissociative) electronic surfaces. Population of a specific excited electronic surface in the dication can be achieved by the controlled selective removal of two electrons from certain inner-valence electronic orbitals.

Fig. 1(c) demonstrates the control scheme for the example of putting  $C_2H_2^+$  and  $C_2H_2^{++}$  into a non-dissociative electronic state, accomplished by removing electrons from the HOMO and HOMO-1 orbitals. Fig. 1(d) shows the yield of the fragmentation pathway (1) as a function of delay after the alignment pulse. The yield is enhanced for parallel alignment and suppressed for perpendicular alignment, in agreement with population of the  ${}^3\Pi_u$  level accomplished by removing a HOMO-2 electron during the dominant second ionization step, which is maximized for parallel alignment. Similar dependence on the transient molecular alignment is measured also for the pathways (2) and (3), demonstrating the selectivity of fragmentation control by inner-valence shell ionization. At the conference we will also present the results of supporting simulations employing density functional theory (DFT) and will discuss the dependence of the fragmentation on the laser intensity and pulse duration



**Fig. 1** (a) Shape of electronic orbitals of  $C_2H_2$  and  $C_2H_2^+$ . (b) Alignment dependent molecular fragmentation signal (yield of ejected protons). (c) Yield of  $C_2H_2$  and  $C_2H_2^+$  over delay after the alignment pulse. (d) Yield of the  $C_2H_2^{++} \rightarrow CH_2^+ + C^+$  fragmentation channel over delay after the alignment pulse

References:

[1] X. Tong et al., Phys. Rev. A 66, 033402 (2002)