

# Sub-Femtosecond Steering of Carbonhydrogen Bonds

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**Abstract:** During sub-femtosecond double ionization of acetylene vibrational wavepackets are formed which contain the directional information on the targeted hydrocarbon bond. The mechanism for preferential deprotonation of individual bonds is demonstrated by quantum dynamical simulations.

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## 1. Introduction

Carbonhydrogen bond cleavage is one of the most important dynamic reactions in chemistry, motivating considerable efforts to monitor and ultimately control the process. Various examples of efficient strong-field-induced proton ejection and hydrogen migration were reported [1-5]. They all reveal an extremely rapid hydrogen motion, making its real-time observation and control a challenge. Waveform-controlled few-cycle laser pulses have been successfully employed to manipulate the yields of ionization, fragmentation and hydrogen migration in hydrocarbons [5]. The full control of the reaction, however, would require also a directional control and has not been demonstrated yet. In our example of acetylene this means the control on which C-H bond is broken. We demonstrate the steering of proton ejection on sub-femtosecond (fs) timescales prior to the breakup of the molecular dication. On the basis of quantum dynamical calculations, the experimental results are interpreted in terms of a novel sub-fs control mechanism involving non-resonant excitation and phase-controlled superposition of vibrational states. The universal mechanism permits control over the directionality of chemical reactions in highly symmetric molecules.

## 2. Carrier envelope dependent asymmetry of the deprotonation in acetylene dication

The electric field of few-cycle light pulses can be described as  $E(t) = E_0(t) \cos(\omega t + \phi)$ , where  $E_0(t)$  is the amplitude envelope,  $\omega$  the carrier frequency, and  $\phi$  the carrier-envelope phase (CEP). In the experiments CEP-tagged reaction microscopy (REMI) was employed. The interaction of acetylene molecules with the intense light pulses results in the dissociative ionization and isomerization. We focus on the deprotonation after two consecutive ionization steps (Fig. 2, left). After population of the first excited state of the dication, the molecule breaks up into  $H^+$  and  $C_2H^+$ , which are detected with the REMI in coincidence. The directional control of the deprotonation is then recorded by analyzing the  $H^+$  fragments. The asymmetry parameter  $A(\phi)$  with  $N_{pos}(\phi)$  ( $N_{neg}(\phi)$ ) the yield for positive (negative)

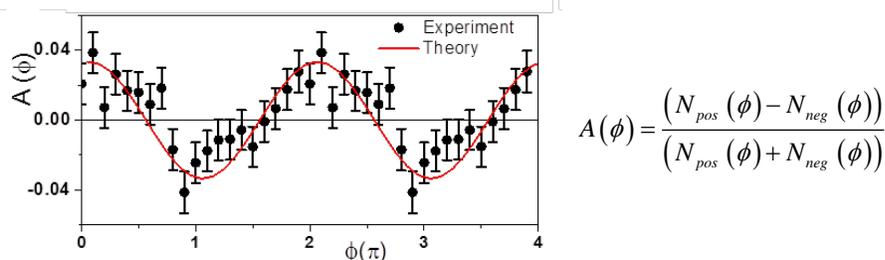


Fig.1: The asymmetry parameter,  $A(\phi)$ , integrated over all momenta for  $H^+$  ions. The clear oscillation in the asymmetry for the directional emission of  $H^+$  as a function of CEP demonstrates the CEP-control of the hydrogen emission direction.

momentum of  $H^+$  ( Fig. 1) is taken as a measure. The observed preferential CEP-dependent ejection of protons to the left and right of the laser polarization axis illustrates the sub-fs steering of the hydrogen ejection.

## 3. Mechanism of the directional control via the carrier envelope phase

The deprotonation of the dication is steered by a phase sensitive preparation of vibrational wavepackets. The precise preparation of vibrational superposition states has been established as the fundamental concept of molecular

quantum computing [6]. In the present study it is the underlying mechanism for the observed asymmetry. The relevant coordinates for the deprotonation are the symmetric  $|0m\rangle$  and the anti-symmetric  $|n0\rangle$  C-H stretching mode with  $m, n$  the vibrational quantum numbers. The notation  $|0m\rangle$  includes the time evolution factor  $\exp(-iE_m/\hbar)$ . The superposition state  $1/\sqrt{2}(|0m\rangle \pm |n0\rangle)$  will induce a wavepacket motion along either one of the C-H bonds. When such a wavepacket is transferred onto a repulsive potential along the C-H bond, dissociation of either the left or the right H-atom will occur. To extract how the control mechanism is realized in the experiment, two-dimensional (2D) surfaces along these two coordinates ( $R_{\text{sym}}, R_{\text{anti}}$ ) are calculated for all states involved. Exemplarily, the first excited state of the dication is shown in Fig. 2. The constraints for the acetylene are that the symmetric mode  $|0m\rangle$  cannot be

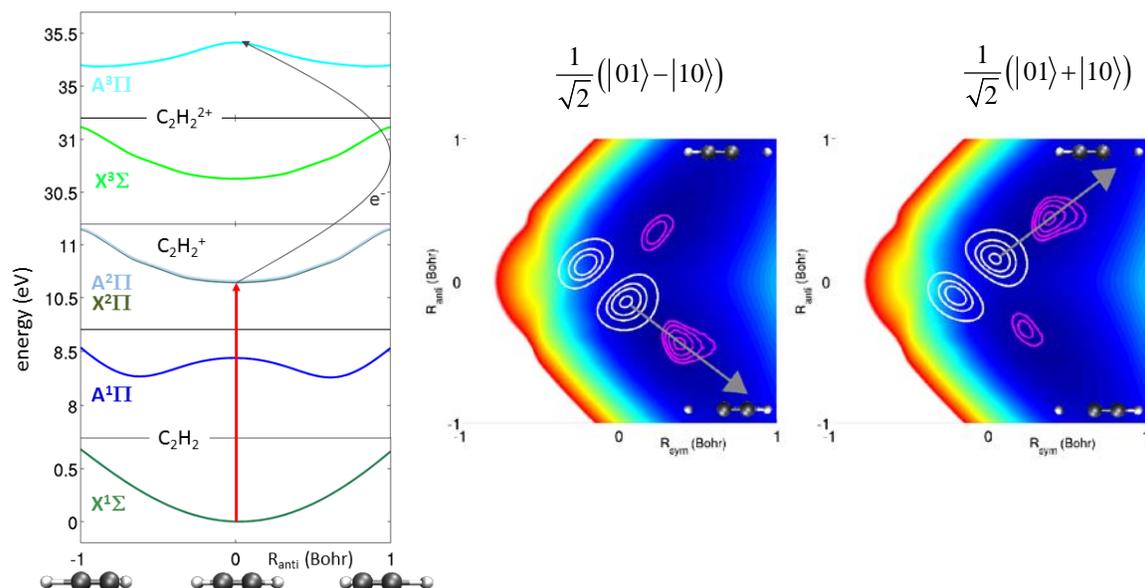


Fig. 2. Left: 1-D cut of the states involved in the ionization and deprotonation of acetylene. Shown are ground (green) and first excited state (blue) of the neutral, the cation ground (light blue) and degenerate first excited state (grey), and the dication ground (green) and first excited state (cyan) along the anti-symmetric stretching coordinate  $R_{\text{anti}}$  at  $R_{\text{sym}}=0$ . The red vertical line indicates the tunneling ionization, the grey curved line the second ionization step by electron recollision. Right: 2D-surface of the first excited state of the dication along  $R_{\text{sym}}$  and  $R_{\text{anti}}$ . The arrows indicate the two directions for deprotonation. The control process is illustrated by wavepackets generated as ideal superposition of  $|01\rangle$  and  $|10\rangle$ . The initial wavepacket is shown in white, a snapshot after 2.4 fs in magenta.

optically addressed by the applied IR-field, only the anti-symmetric mode  $|n0\rangle$  is IR-active. Our quantum dynamical analysis shows that the superposition is prepared in the neutral and cationic molecule and mainly from  $m, n=1$  states. The  $|01\rangle$  component is populated due to the field induced ionization, while the  $|10\rangle$  component is directly populated via the interaction with the non-resonant light field. Also a phase ( $|10\rangle \exp(i\phi_{\text{CEP}})$ ) is imprinted and can be controlled relative to the  $|01\rangle$  mode via the CEP ( $\phi_{\text{CEP}}$ ) of the light field. Variation of the CEP changes the phase and thus the sign in the superposition  $1/\sqrt{2}(|01\rangle \pm |10\rangle)$ . The superposition exhibits a modulation with a periodicity of  $2\pi$ , which shows up in the asymmetry  $A(\phi)$  for the directional emission of the  $H^+$  ions and agrees well with the experimental results (Fig. 1).

In summary, the presented data support a new and very general coherent-control scheme, where the direction of proton ejection in a symmetric hydrocarbon is steered through manipulating of the phases of the individual components of a vibrational wavepacket. The scheme can be transferred to control the direction of the proton migration and by tuning the IR pulse in resonance with the active mode the control can be enhanced significantly.

#### 4. References

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