

Controlling Fragmentation Reactions of Polyatomic Molecules with Impulsive Alignment

Xinhua Xie¹, Katharina Doblhoff-Dier², Huailiang Xu^{1,3}, Stefan Roither¹, Markus Schöffler¹, Daniil Kartashov¹, Sonia Erattuphuza¹, Tim Rathje⁴, Gerhard G. Paulus^{4,5}, Kaoru Yamanouchi⁶, Andrius Baltuška¹, Stefanie Gräfe², Markus Kitzler¹

¹Photonics Institute, Vienna University of Technology, Gusshausstrasse 27, A-1040 Vienna, Austria,

²Institute for Physical Chemistry, Friedrich-Schiller University Jena, D-07743 Jena, Germany,

³State Key Laboratory on Integrated Optoelectronics, Jilin University, Changchun 130012, China

⁴Institute of Optics and Quantum Electronics, Friedrich-Schiller University Jena, D-07743 Jena, Germany

⁵Helmholtz Institute Jena, D-07743 Jena, Germany

⁶Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

xinhua.xie@tuwien.ac.at

Abstract: We experimentally and theoretically demonstrated effective control of molecular ionization and fragmentation in strong laser fields with impulsive alignment of a molecule. Channel selective control over molecular fragmentation reactions can be realized.

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1. Introduction

Control over the photodissociation dynamics of molecules has become a vivid research topic in the past decades (for reviews see e.g. [1]). By applying temporally shaped femtosecond laser pulses, the vibrational dynamics of a molecule can be accessed and steered directly. However, only since a few years, it has become possible to observe and control the ultrafast electronic dynamics in molecules. Control over the electronic dynamics of a molecule is typically achieved via control over the carrier-envelope phase (CEP) of few-cycle laser pulses [2]. In this submission, we demonstrate that molecular alignment serves as an effective control tool to steer the electron dynamics and govern the relative probability of reaction pathways of polyatomic molecules in intense laser fields.

2. Results and discussion

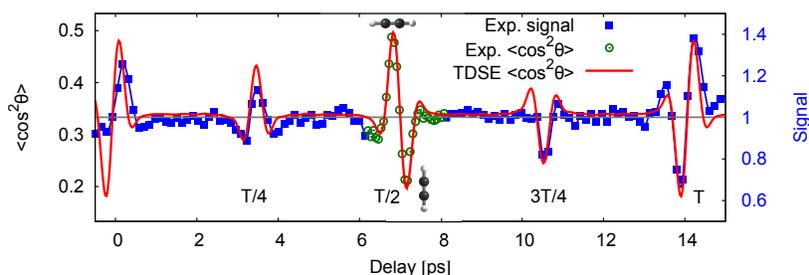


Fig. 1. The blue filled green squares with lines present high energy proton signal for the measurements. Calculated $\langle \cos^2(\theta) \rangle$ value as a function of evolution time for acetylene. Measured $\langle \cos^2(\theta) \rangle$ values for acetylene are illustrated as green opened circles near half revival.

In our experiments, we impulsively align [3] C_2H_2 molecules in an ultra-high vacuum chamber (1.3×10^{-10} mbar) applying a weak 795 nm 50 fs, linearly polarized laser pulse from a 5 kHz Titanium-Sapphire laser amplifier system. As probe (ionization) pulse, the remaining portion of the laser output is spectrally broadened and recompressed to a duration of 4.5 fs full width at half maximum (FWHM). A time delay between alignment pulse and probe pulse can be precisely controlled via a piezo stage. The resulting momenta of the ions and ionic fragments are measured in

coincidence by a reaction microscope [4] on a single shot basis, allowing channel-resolved examination of individual fragmentation.

The signature of the time evolution of C_2H_2 rotational wavepacket was presented in Fig. 1 as a function time delay between alignment and probe laser pulses. Measured $\langle \cos^2(\theta) \rangle$ values are derived from a complete fragmentation channel of acetylene, which indicates that the maximum value of $\langle \cos^2(\theta) \rangle$ reaches 0.5 in our experiments.

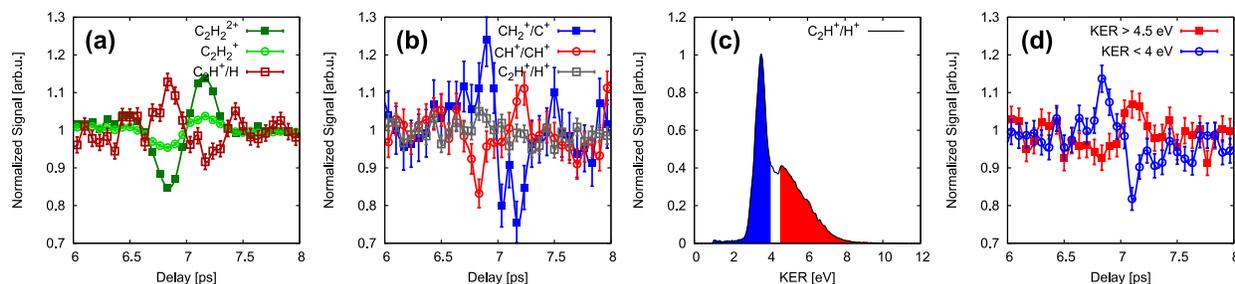


Fig. 2. (a) Normalized yield of channels $C_2H_2^+$ (light green), C_2H^+/H (dark red), $C_2H_2^{2+}$ (dark green) as a function of time delay. (b) Normalized yield of channels CH_2^+/C^+ (blue), CH^+/CH^+ (red), and C_2H^+/H^+ (gray). (c) KER spectra of channel C_2H^+/H^+ as a function of time delay. (d) KER-resolved yield of channel C_2H^+/H^+ .

The delay dependence of several fragmentation and ionization yields is shown in Fig. 2(a,b) for probe pulses with intensity of $I = 4 \times 10^{14}$ W/cm² and pulse duration 4.5 fs (FWHM). The yields of most channels feature a pronounced dependence on the time delay and hence on the relative orientation of the molecular axis to the laser polarization direction. The figure evidently demonstrates that the channels show an individual alignment dependence. This allows to efficiently tune not purely the overall fragmentation yield [2], but also access the relative yields between different fragment channels by adjusting the time delay.

We found that the featured control is based on different angular-dependent ionization rates of inner and outer valence electrons. For single and double ionization channels, the molecules are ended at stable ground ionic states of acetylene cation and dication by removing one HOMO electron and two HOMO electrons, respectively. The electron density distribution of acetylene HOMO dominates in the perpendicular direction to the molecular axis which leads to larger ionization yield for perpendicular alignment, as shown in Fig. 2(a). For a fragmentation channel, an excited electronic state of a cation or a dication need to be reached via detaching one or two electrons from inner valence molecular orbital by the few-cycle laser pulses, which features independent alignment dependence due to special angle dependence of ionization rate from different molecular orbitals. With the advantage of KER resolved measurements, as shown in Fig. 2(c,d), different pathways reaching the same fragmentation channel C_2H^+/H^+ show different alignment dependence due to ionization from different molecular orbital or different ionization mechanism (e.g. sequential double ionization vs. non-sequential double ionization induced by electron recollision). To obtain a more quantitative picture, we have performed time-dependent density functional theory calculations for different laser intensities and orientations. The simulated results confirm the experimental observations and the interpretation based on removing certain electrons from different molecular orbitals.

In conclusion, we introduced molecular alignment as a novel control tool for steering molecular dynamics in intense laser fields on the ultrashort time scale. We have shown that channel selective control over molecular fragmentation reactions can be realized via molecular alignment.

References

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