

Molecular isomerization and fragmentation of polyatomic molecules controlled by inner-valence recollision-ionization

X. Xie¹, K. Doblhoff-Dier², S. Roither¹, M. Schöffler¹, D. Kartashov¹, H. Xu^{1,3}, T. Rathje^{4,5},
G.G.Paulus^{4,5}, A. Baltuška¹, S. Gräfe², M. Kitzler^{1,*}

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

² Institute for Theoretical Physics, Vienna University of Technology, A-1040 Vienna, Austria

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

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

⁵ Helmholtz Institute Jena, D-07743 Jena, Germany

Synopsis Control over various fragmentation reactions of a series of polyatomic molecules (acetylene, ethylene, 1,3-butadiene) by the optical waveform of intense few-cycle laser pulses is demonstrated experimentally. We show both experimentally and theoretically that the responsible mechanism is inelastic ionization from inner-valence molecular orbitals by recolliding electron wave packets.

Selective control of isomerization and fragmentation pathway(s) through the shape of the optical waveform of strong few-cycle laser pulses, as determined by the carrier-envelope phase (CEP), has been demonstrated for diatomic molecules [1,2].

In this submission we present CEP control of fragmentation pathways of polyatomic molecules (acetylene, ethylene, 1,3-butadiene) [3]. Given the increased number of participating nuclei and a vastly more complex valence electron dynamics and the structure of energy surfaces, it is noteworthy that the CEP dependence of fragmentation pathways still survives in polyatomic molecules. We argue both experimentally and theoretically, that this is due to the existence of a universal attosecond mechanism of quasi-single-cycle fragmentation of large molecules, namely the field control of the tunneled-out electronic wave packet that is steered by the optical waveform before its recollision with the parent ion.

The process is sketched in Fig. 1(a) for the example of the acetylene molecule: The first ionization step takes place through field-induced tunnel ionization. After that the released electron is accelerated in the optical field, and subsequently driven back to its parent molecule where upon recollision it may knock out a second electron from an inner-valence orbital. This puts the molecule into an electronically excited ionic state from where the molecule might dissociate.

In our experiments we measured the yields of several two-body fragmentation pathways of acetylene, ethylene and 1,3-butadiene molecules as a function of the CEP of ~4.5 fs laser pulses using

COLTRIMS in combination with a phase-meter [3]. Fig. 1 shows the measured strong modulation of the fragmentation yield exemplarily for three different pathways of acetylene fragmentation. The results obtained for the other molecules are similar.

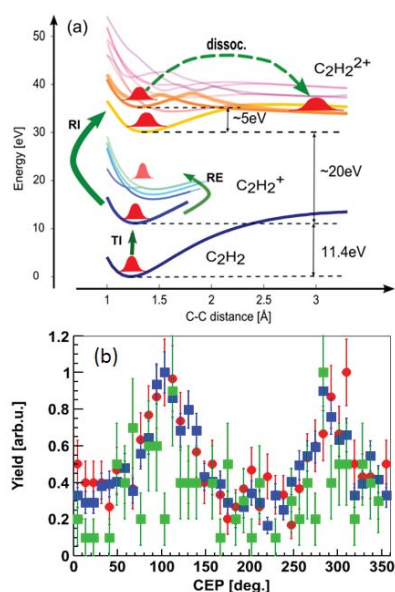


Figure 1. (a) Electronic energy levels of the neutral, cation, and dication of acetylene as a function of C-C distance. TI, RI and RE denote tunnel ionization, recollision ionization, and recollision excitation, respectively. (b) Measured fragmentation yields, normalized to 1, over CEP for the three channels $C_2H_2^{2+} \rightarrow H^+ + C_2H^+$ (blue), $C_2H_2^{2+} \rightarrow CH^+ + CH^+$ (red), $C_2H_2^{2+} \rightarrow C^+ + CH_2^+$ (green).

References

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*E-mail: markus.kitzler@tuwien.ac.at