

Electronic pre-determination of ethylene fragmentation dynamics

Xinhua Xie^{1,*}, S. Roither¹, E. Lötstedt², M. Schöffler¹, D. Kartashov¹, G.G. Paulus^{3,4},
A. Iwasaki², A. Baltuška¹, K. Yamanouchi², M. Kitzler^{1,#}

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

²Department of Chemistry, School of Science, The University of Tokyo, Tokyo 113-0033, Japan

³Institute of Optics and Quantum Electronics, Friedrich-Schiller-University Jena, D-07743 Jena, Germany, EU

⁴Helmholtz Institute Jena, D-07743 Jena, Germany, EU

*xinhua.xie@tuwien.ac.at, #markus.kitzler@tuwien.ac.at

Abstract: We demonstrate, using ethylene, that controlling lower-valence ionization and field-driven excitation dynamics with ultrashort, intense laser pulses allows steering fragmentation reactions of polyatomic molecules along a certain pathway towards a specific set of fragment ions.

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Strong laser fields can be used to both initiate and drive electronic dynamics in a polyatomic molecule on their natural, i.e., sub-femtosecond, time-scale. This potentially opens up the feasibility of controlling molecular fragmentation processes by influencing the intra-molecular dynamics of the electron cloud with strong laser-electric fields. Indeed, it was shown that the outcome of fragmentation processes in polyatomic molecules can be affected by the shape of the laser electric field [1]. In general, the key to controlling fragmentation and accompanying isomerization processes in molecular ions is to prepare them in specific dissociative states from which the reaction proceeds through a desired fragmentation *pathway* on multi-dimensional potential energy surfaces towards a certain set of final fragment products, called a *channel*. This can be achieved either during the ionization process, but also by subsequent excitation processes during the interaction with the laser field.

Here, we report experiments on the polyatomic molecule ethylene, C₂H₄, dedicated to disentangling the contributions of the ionization step and the subsequent field-driven excitation dynamics to different fragmentation pathways from the doubly charged ion. In particular, we show how these two excitation mechanisms that pre-determine the fragmentation reactions of the molecule, depend on laser pulse intensity and duration.

We observe that the relative importance of contributions to the fragmentation probability of a given *channel*, either from the ionization step or from field-driven excitations, strongly depends on both laser intensity and pulse duration. Moreover, we show that not only the probability of a given channel, but even the specific *pathways* that can be taken along the multitude of dissociative electronic states towards this channel, are dependent on the laser pulse parameters. Thus, by properly choosing pulse intensity and duration it becomes possible to steer the molecular dynamics along a desired pathway in the phase-space spanned by the nuclear coordinates and momenta towards a certain set of final fragment ions. This opens up new possibilities for controlling the outcome of fragmentation reactions of polyatomic molecules in that it may allow to selectively enhance or suppress individual fragmentation channels, which was not possible in previous attempts of controlling the fragmentation behaviour of polyatomic molecules [1].

In our experiments, we measured in coincidence the three-dimensional momentum vectors of fragment ions resulting from the interaction of sub-5 fs and 25 fs (FWHM) laser pulses with an ethylene molecule using a COLTRIMS setup. By coincidence analysis of the measured data we identified for all pulse parameters the following two-body fragmentation channels of the ethylene dication:



We can qualitatively explain our experimental results for channel (1) using the potential energy surfaces (PESs) of excited ionic states of the ethylene dication [Fig. 1(a)] and the kinetic energy release (KER) spectra for different intensities [Fig. 1(b)]. Results for channel (2) will be presented at the conference. It can be clearly seen that with

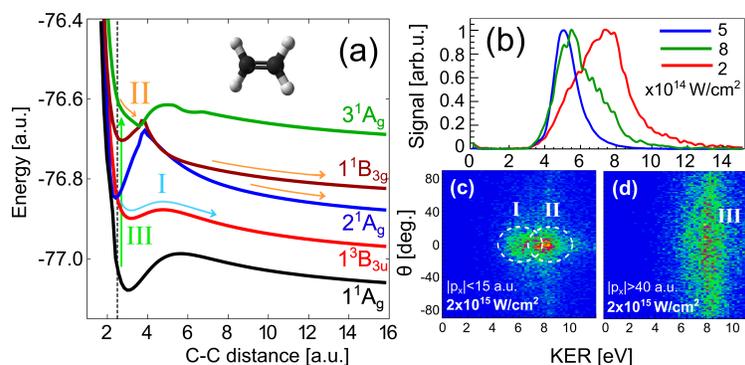


Fig. 1. (a) Calculated PESs of ground (1^1A_g , black line) and selected excited ionic states of the ethylene dication. The 3^1B_{3u} state is formed by removing one HOMO electron and one HOMO-2 electron, the 1^1B_{3g} by removing one HOMO-1 electron and one HOMO-2 electron, and the 2^1A_g and 3^1A_g states are formed by removing two HOMO-1 electrons and two HOMO-2 electrons, respectively. The vertical black dashed line indicates the C-C equilibrium distance of 2.53 a.u. The coloured arrows (labelled by I, II and III) refer to the three fragmentation pathways of channel (1), as discussed in the text. (b) Normalized KER spectra of fragmentation channel (1) for three different laser intensities as indicated. (c,d) Selections of the angular distributions over KER of CH_2^+ fragments from channel (1) measured at the indicated laser intensities for $|p_x| < 15$ a.u. (c) and $|p_x| > 40$ a.u. (d).

increasing laser intensity the mean value of the KER of the fragmentation increases from around 5 eV up to 7 eV. The dependence of the KER of fragmentation channel (1) on laser intensity indicates that the fragmentation of the C-C bond takes place via different pathways for different laser pulse parameters. As discussed above, this may involve the population of different initial dissociative (excited) states by ionization from different lower-valence orbitals, and/or field-induced excitations to other excited states by the action of the laser pulse. Three pathways to (1) (marked I, II and III in Fig. 1) are possible: Removal of one HOMO-2 electron and one HOMO electron prepares the dication in the 1^1B_{3u} state, dissociative along C-C direction [pathway I, marked by a cyan arrow in Fig. 1(a)]. The KER of this pathway is estimated from the theoretical potential energy curves as about 5 eV, in very good agreement with the measured KER of region I. Removal of two electrons from the HOMO-2 can put the ethylene dication onto the 3^1A_g state. From there it will dissociate through crossings with the 2^1A_g and 1^1B_{3g} states [Fig. 1(a)]. Theory predicts values of 8 eV and 9 eV, respectively, for dissociation along these states, which fits the measured KER energy range for recorded events in region II very well [Fig. 1(c)]. The fragments in region III [Fig. 1(d)], finally, show a KER distribution located around 8 eV, but their angular distribution is isotropic, indicating that the fragmentation starts from an excited ionic state formed by removal of electrons from the HOMO or HOMO-1. This would prepare the ion into the meta-stable ground state or a low excited state, which will not lead to breaking of the C-C center bond. Thus, the pathway leading to the fragment ions in region III must involve a field-induced excitation to the higher excited state 3^1A_g induced by the laser pulse. From there it dissociates along the same PESs as the pathway II leading to fragments with almost the same high KER as pathway II.

In conclusion, we demonstrated that the relative importance of the different molecular pathways along different dissociative electronically excited states, by which a particular set of final fragmentation products can be reached, strongly depends on the parameters of the laser pulse. Our work shows that selective population of excited ionic states by controlling intra-molecular electronic processes (in particular electron removal from lower-valence orbitals and non-adiabatic population transfer) with strong non-resonant laser fields is an efficient and general method for selectively enhancing or suppressing individual fragmentation channels.

References

1. Xinhua Xie *et al.* Attosecond-Recollision-Controlled Selective Fragmentation of Polyatomic Molecules. *Phys. Rev. Lett.* **109**, 243001 (2012).