

Electronic pre-determination of ethylene fragmentation dynamics using intense, ultrashort laser pulses

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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.

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. Sub-5 fs pulses were generated by spectral broadening of 25 fs laser pulses from a titanium-sapphire chirped-pulse laser amplifier system in a hollow-core glass capillary and subsequent temporal re-compression by chirped mirrors. By coincidence analysis of the measured data we identified for all pulse parameters the following two-body fragmentation channels of the ethylene dication:



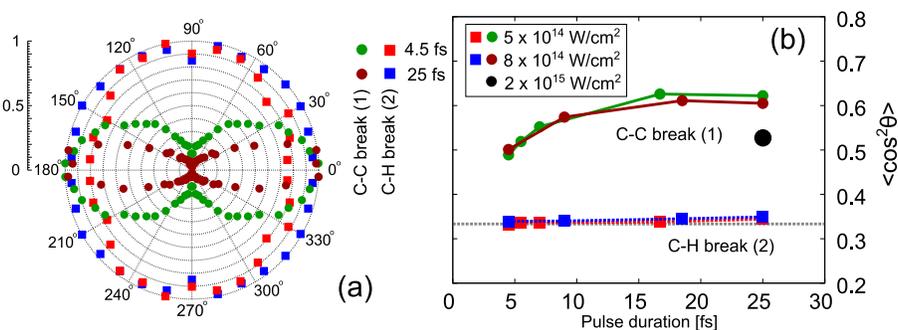


Fig. 1. (a) Normalized angular momentum distributions for channels (1) and (2). Polarization direction horizontal. (b) $\langle \cos^2 \theta \rangle$ over pulse duration for channels (1) and (2).

Fig. 1(a) shows measured angular distributions of fragment ions from channels (1) and (2). A clear observation is that the angular momentum distribution of channel (1) is anisotropic and peaks along the laser polarization direction, whereas that of channel (2) is isotropic. According to MO-ADK theory, the ionization rate from a certain orbital strongly depends on the relative orientation of the molecular orbital to the laser polarization direction and follows the shape of the electron density distribution of the respective orbital [2]. As a consequence, the anisotropic angular momentum distribution of channel (1) indicates, firstly, that the fragmentation process takes place from an excited ionic state of the ethylene dication formed by ionization of at least one HOMO-2 electron. Secondly, the strong anisotropy indicates that the fragmentation happens fast as compared to the rotational period of $C_2H_4^{2+}$ [3]. The isotropic angular momentum distribution of channel (2), in contrary, suggests molecular rearrangement after ionization in the course of the separation of two fragments, which takes much longer than the laser pulse duration. The fragmentation dynamics of channels (1) and (2), thus, take place apparently on different time-scales.

Our experimental results can be qualitatively explained by the potential energy surfaces (PESs) of excited ionic states of the ethylene dication. Cuts through PESs along the C-C distance calculated by GAMESS are shown in Fig. 2(a). The PESs reveal that the lowest electronically excited state that leads to C-C bond breaking is the $^3B_{3u}$ state, which is formed by removing one HOMO-2 electron together with one HOMO electron. Since the electron density of HOMO-2 is mainly distributed along the C-C axis, MO-ADK theory predicts that, among the randomly oriented molecules in the gas sample, those molecules with their C-C axis aligned with the laser polarization direction are much more likely to become doubly ionized through removal of at least one HOMO-2 electron. This explains the anisotropic angular momentum distribution of channel (1) observed in the experiment.

As a cross-check for our interpretation, we show in Fig. 1(b) the measured anisotropy of the angular distributions of the two channels (1) and (2), characterized by the value $\langle \cos^2 \theta \rangle$, as a function of pulse duration for different laser intensities. The observed independence of the angular momentum distribution of channel (2) on both intensity and pulse duration confirms our explanation that the fragmentation happens long after the laser pulse has faded, with enough time for molecular rearrangement after the double ionization. The observed increase of $\langle \cos^2 \theta \rangle$ with pulse duration for channel (1) is due to post-ionization alignment [4]. As the intensity is increased, the value $\langle \cos^2 \theta \rangle$ at 25 fs pulse duration decreases from 0.61 to 0.52 [see Fig. 1(b)]. However, with higher laser intensity, the post-ionization alignment effect should be stronger, which in turn should lead to a larger $\langle \cos^2 \theta \rangle$. To obtain insight into the reasons for this observation, we analyzed the kinetic energy release (KER) spectrum of channel (1) for different intensities [Fig. 2(b)]. It can be clearly seen that with 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. 2) are possible: Removal of one HOMO-2 electron and one HOMO electron prepares the dication in the $1B_{3u}$ state, dissociative along C-C direction [pathway I, marked by a cyan arrow in Fig. 2(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. 2(a)]. As the initial state is

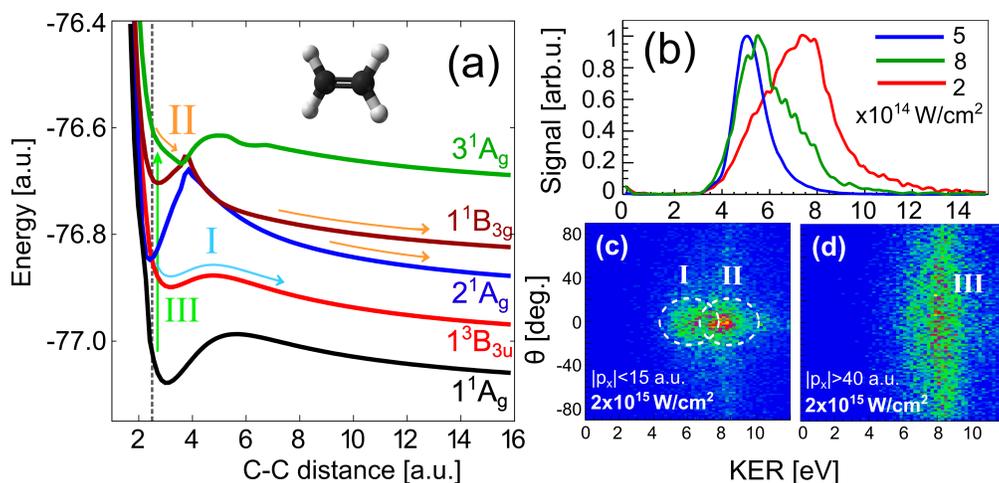


Fig. 2. (a) Calculated PESs of ground (1^1A_g , black line) and selected excited ionic states of the ethylene dication. The $^3B_{3u}$ state is formed by removing one HOMO electron and one HOMO-2 electron, the $^1B_{3g}$ by removing one HOMO-1 electron and one HOMO-2 electron, and the 2^1A_g and 3^1A_g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

populated by ionization from the HOMO-2, the angular distribution of the fragment ions will still be narrow along the laser polarization direction. However, fragmentations along this pathway II [orange arrows in Fig. 2(a)] will lead to a higher KER. Theory predicts values of 8 eV and 9 eV, respectively, for dissociation along the $^1B_{3g}$ and 2^1A_g states, which fits the measured KER energy range for recorded events in region II very well [Fig. 2(c)].

The fragments in region III [Fig. 2(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.

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