PAPER

Formation of fragment ions (H$^+$, H$_3^+$, CH$_3^+$) from ethane in intense femtosecond laser fields – from understanding to control

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The dissociative ionization of ethane in intense femtosecond laser fields has been investigated as a function of the laser pulse shape by systematically varying the quadratic spectral phase, *i.e.* the linear chirp. A very pronounced effect of the sign of the chirp is observed for the parent ion and all fragment ion yields, all ion yields being strongly favored by negative chirp of the laser field. The ratio of the H$_3^+$ ion yield to H$^+$ ion yield can also be manipulated by changing the linear chirp, the maximum being observed for a significantly smaller chirp value than that for the individual ion yields. Since the H$^+$ ions and the H$_3^+$ ions predominantly originate from the dication of ethane, this indicates control of fragmentation within one charge state of the ethane. Additional experiments performed with d$_3$-ethane demonstrate that the control is operative prior to the statistical scrambling of hydrogen atoms, further supporting the concept of intra-charge-state control. In the case of formation of CH$_3^+$ ions two different ensembles occur, one from the monocation, another from the dication. The ratio of these ensembles can again be controlled by means of the linear chirp parameter implying control between the two different charge states (inter-charge-state control).

Introduction

The dissociative ionization of small organic molecules has attracted considerable interest in recent years.[1–4] Depending on the laser pulse parameters, in general, formation of monocations but also multiple ionization as well as excessive fragmentation can be observed. A well investigated molecular system in this respect is the ethane molecule.[4–8] The dissociative ionization of ethane leads *e.g.* to the formation of H$^+$, H$_2^+$, CH$_n^+$(n = 0–3) and C$_2$H$_m^+$(m = 0–5). Yet, much of the attention dedicated to the dissociative ionization of ethane and, in fact, our own interest are connected to the formation of a rather intriguing fragment ion, the H$_3^+$. Its equilibrium geometry is that of an equilateral triangle, the binding energy

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with respect to $H_2 + H^+$ is in the order of 4.6 eV.[9] The H_3^+ ion is observed in the dissociative ionization of ethane as well as several other organic molecules. There, its formation involves not only the breaking of three C–H-bonds and the formation of one three-center-two-electron bond but also ultrafast hydrogen migration.[6–8,10,11] H_3^+ itself has first been reported by J. J. Thomson in a discharge experiment.[12] Today H_3^+ receives considerable attention in fields connected, *e.g.*, to kinetics[13–15] and interstellar chemistry.[16,17] In fs-laser ionization the first observation of H_3^+ was most likely accomplished by Xia *et al.*[5] In that work signal at mass-to-charge ratio $m/z = 3$ was assigned to C^{4+}, but in the light of today's knowledge it probably was rather H_3^+.

In the following we first review past attempts to understand the molecular dynamics involved in the dissociative ionization of ethane and some related molecules, before turning our attention to the goal of the current work, *i.e.* the attempt to control these dynamics.

The importance of ultrafast hydrogen migration in femtosecond laser ionization processes was emphasized in a systematic study about different hydrocarbons with and without methyl groups[7] as well as in H_3^+ formation experiments looking at methanol and partially deuterated methanol (CD_3OH).[10,18] To the best of our knowledge the first complete reaction path for the formation of H_3^+ in the dissociative fs-laser ionization of ethane was reported by Kraus *et al.* in a combined theoretical and experimental study.[6] In this study, quantum chemical calculations and supporting measurements of kinetic energy releases (KER) allowed to identify a reaction path, which involves a doubly charged $C_2H_6^{2+}$ ion evolving over a transition state (TS) leading to the formation of $H_3^+ + C_2H_3^+$. The most stable structure of $C_2H_6^{2+}$ can be described as a donor–acceptor complex of a planar methane dication (CH_4^{2+}) and a carbene (CH_2) which is consistent with the results of previous studies.[19] The calculated structure of the transition state (TS) consists of a neutral H_2 molecule which is attached to a $C_2H_4^{2+}$ entity, nevertheless this TS does not correlate to the $H_2^+ + C_2H_4^+$ or $H_2 + C_2H_4^{2+}$ channel but exclusively to $H_3^+ + C_2H_3^+$. A similar TS ($C_3H_2^{2+}\cdots H_2$) was proposed theoretically for the dissociation of the allene dication.[20] There, a hydrogen molecule was discussed to roam around the $C_3H_2^{2+}$ dication consequently leading either to the loss of a neutral H_2 or to the formation of H_3^+, the latter, however, *via* another TS.

The pathway indicated above as well as the kinetic energy releases were later confirmed in a photoion–photoion coincidence (PIPICO) experiment detecting coincidences between H_3^+ and $C_2H_3^+$ from ethane (CH_3CH_3).[8] Additional experiments performed for partially deuterated ethane (CD_3CH_3) allowed to analyze the yield ratios of $H_3^+ : H_2D^+ : HD_2^+ : D_3^+$ as $(8.01 \pm 1.20) : (43.0 \pm 5.4) : (43.1 \pm 0.3) : (5.89 \pm 0.10)$, which clearly show significant, almost statistical H-D scrambling through hydrogen migration.[8]

In the current work we present an attempt to go beyond understanding the dissociative ionization of ethane toward control of ion yields in this dissociative ionization. The control of fragmentation ratios in optically driven molecular dynamics has received enormous attention in the last decades and is in fact also the topic of the current Faraday Discussion meeting.[21] While the overall state of this field may be regarded as mature, several specific challenges remain. A common challenge is connected to the question in which charge state of the molecular system the control is operative. The other challenge pertains to the approach, with which the control is achieved. There are examples where control

has been achieved by employing genetic algorithms,[22] but also examples where the shape of the laser pulses has been systematically varied (*e.g.*, linear chirp).[23] The question of which of these approaches is to be preferred is almost philosophical in nature. The former in general leads to the "optimum" field for maximizing the fitness of a specific objective (*e.g.*, the ratio of two product yields). The latter in general leads to a local maximum of that objective in parameter space which may be more descriptive and easier to interpret.

In this contribution we describe the control of fragmentation channels employing a systematic variation of the laser pulse shape. Recent work employing the same concept includes systematic variation of the linear chirp[24–27] as well as binary pulse shaping.[28,29] Itakura *et al.*[24] reported on the dissociative ionization of ethanol in chirped laser fields finding that nuclear dynamics can be controlled on the singly charged state. However, positive and negative chirp led to the same fragment ratios, *i.e.* the control originated from laser intensity variation. Marthur *et al.*[25] investigated the dissociative ionization of methane in chirped laser fields reporting fragment ion yields as a function of the linear chirp parameter α. The results indicated a predominantly intensity-driven ion yield, superimposed on which a small sign effect of the chirp parameter was observed. Ultimately, the yields of H^+ and H_2^+ – presumably originating from dissociation of dications – were favored by a positive chirp. Our group has reported the control of the dissociative ionization of DCl by linearly chirped fs-laser pulses, where a positive chirp favored the formation of D^+ while a negative chirp favored the formation of Cl^+.[26] On one hand, it appears important to add further experimental studies hoping to lay a foundation for future theoretical work. On the other hand the observation of linear chirp effects in dissociative ionization has obvious applications in chemical analytics, that is, it is possible to distinguish structural isomers, *e.g.* *o*-xylene and *p*-xylene by ionization employing either linearly chirped[27] or binary shaped[28] fs-laser pulses.

The current work will concentrate on the dissociative ionization of ethane with particular attention on the formation of H^+, H_3^+ and CH_3^+. We will attempt to control total ion yields as well as ratios of ion yields by means of linearly chirping fs-laser fields. From previous work we know that formation of H_3^+ proceeds on the dicationic potential energy surface (PES). The H^+ formation most likely proceeds from a different conformational region of the same dicationic PES. These data will be complemented by a study of CH_3^+ formation, which may either occur on the monocationic or the dicationic PES. A major part of the studies will deal with normal ethane (C_2H_6). Additional experiments performed for d_3-ethane (CD_3CH_3) will shed light on the question whether control is operative prior to or after hydrogen scrambling.

Experimental

The dissociative ionization of ethane has been investigated *via* systematic variation of the linear chirp of fs-laser pulses. These fs-laser pulses were generated in a chirped pulse amplifier (ODIN, Quantronix, repetition rate 1 kHz) seeded by a Ti:Sapphire oscillator (SYNERGY, Femtolasers). The pulses were phase corrected using a spatial light modulator (SLM-S640, Jenoptik) inside a 4f-shaper setup, resulting in nearly Fourier-limited pulses with a typical pulse duration of 45 fs, a central wavelength of 810 nm and a typical pulse energy up to 140 μJ. These pulses

were linearly chirped by application of a quadratic spectral phase onto the spatial light modulator. We have also studied quadratically chirped laser pulses by applying a cubic spectral phase to the SLM, however this will not be at the focus of the current work. The corresponding Taylor parameter is $\alpha = 1/2!\cdot\partial^2\varphi/\partial\omega^2$ for linear chirp ($\beta = 1/3!\cdot\partial^3\varphi/\partial\omega^3$ for quadratic chirp), where φ is the spectral phase and ω is the central angular frequency. Note that imprinting a linear chirp onto the laser field is equivalent to stretching the pulse in the time domain according to the relation $\tau^2 = \tau_0^2 + \left(8\ln 2\, \alpha / \tau_0 \right)^2$,[30] with τ_0 being the pulse duration of an unchirped laser pulse.

The laser pulses were characterized using a frequency-resolved optical gating technique (GRENOUILLE, Swamp Optics). After pulse-shaping the beam is transmitted through two 1 mm thick optics; one being a beam splitter to couple into the GRENOUILLE and one being a quartz glass window of a vacuum chamber. The shaped and characterized laser pulses were focused *via* a cylindrical mirror ($f = 75$ mm) into the ion source of a home build Wiley McLaren time-of-flight mass spectrometer leading to the ionization of ethane under space focus conditions.[31] Ethane or d$_3$-ethane was effusively introduced into the reaction chamber at typical pressure values of 3×10^{-5} mbar. Ethane pressure tins with 99.95% purity were purchased from Fluka and used without further purification. Deuterated ethane was purchased from CDN Isotopes (99.3atom% D).

Ion yields of the parent and fragment ions were recorded as a function of the chirp parameter of interest. The experiments were performed for a range of laser pulse energies between 15 μJ and about 130 μJ. The corresponding peak intensities are 6.6×10^{12} W cm^{-2} and 5.7×10^{13} W cm^{-2}, respectively, both numbers referring to the shortest laser pulses employed, *i.e.* about 45 fs. Typically 10 000 mass spectra were averaged for each set of laser pulse parameters.

Results and discussion

In the following we will first present typical time of flight mass spectra (TOF-MS) of normal h$_6$-ethane as well as d$_3$-ethane. We will then discuss the ion yields as well as ratios of ion yields as a function of the linear chirp parameter α for h$_6$-ethane. In a third section we will demonstrate the influence of the laser pulse energy on the ability to control molecular dynamics. Finally, we will present the corresponding data for d$_3$-ethane.

Time of flight mass spectra

The TOF spectra of normal h$_6$-ethane and deuterated d$_3$-ethane have been recorded as a function of the linear chirp of the fs-laser pulses. Typical TOF spectra for both ethane species are presented in Fig. 1. Major signals arise from the C$_2$H$_m$ (m = 0–6) group and the CH$_n^+$ (n = 0–3) group for ethane and the corresponding C$_2$H$_p$D$_q^+$ (p,q = 0–3; $p + q \leq 6$) and CH$_p$D$_q^+$ (p,q = 0–3; $p + q \leq 3$) groups for d$_3$-ethane. Of particular interest in the current study is the formation of the hydrogen ions H$^+$, H$_2^+$ and H$_3^+$ in the case of ethane. The corresponding ion signals appearing at m/z equal to 1, 2, and 3, respectively, are unique under all conditions investigated. The corresponding hydrogen ions in the case of d$_3$-ethane are H$_3^+$, H$_2$D$^+$, HD$_2^+$ and D$_3^+$. In that case ion signals are observed
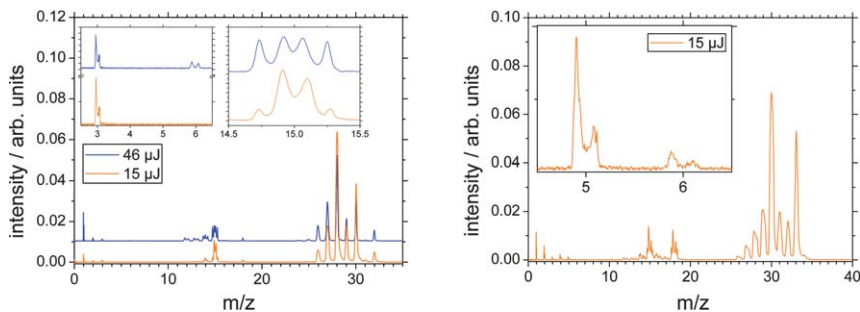
Fig. 1 TOF-MS of C_2H_6 for 46 μJ (blue) and 15 μJ (orange) at 6.0×10^{-6} mbar and 3.0×10^{-5} mbar, respectively (left). TOF-MS of CH_3CD_3 for 15 μJ (right). All mass spectra were recorded for negatively chirped laser pulses.

at $m/z = 1$ (H^+), 2 (H_2^+, D^+), 3 (H_3^+, HD^+), 4 (H_2D^+, D_2^+), 5 (HD_2^+) and 6 (D_3^+), as has been reported in previous studies.[8] Thus, the ion signals at m/z equal to 2, 3 and 4 are not unique, but those at m/z equal to 5 and 6 are, provided that contributions from the doubly charged carbon ion C^{2+} ($m/z = 6$) can be ruled out. As Fig. 1 shows, normal ethane does not show any signal at $m/z = 6$ at laser pulse energies of 15 μJ. Consequently, we assume that d_3-ethane experiments performed at the same laser pulse energy should also be free from contributions of C^{2+}. Note that normal ethane experiments can still be analyzed at considerably higher pulse energies, as long as C^{4+} ($m/z = 3$) can be excluded, which is the case for all pulse energies discussed here. The mass spectra in general contain contaminations from oxygen ($m/z = 32$) and water ($m/z = 18$), however they do not interfere with any of the interpretations.

Control of ion yields and ratios of ion yields from ethane *via* linear chirping

In Fig. 2 (left) the ion yields of the parent ion and the fragment ions CH_3^+, H_3^+, and H^+ from ethane are shown as a function of the pulse duration τ (lower axis) and the corresponding linear chirp parameter α (upper axis) at a pulse energy of
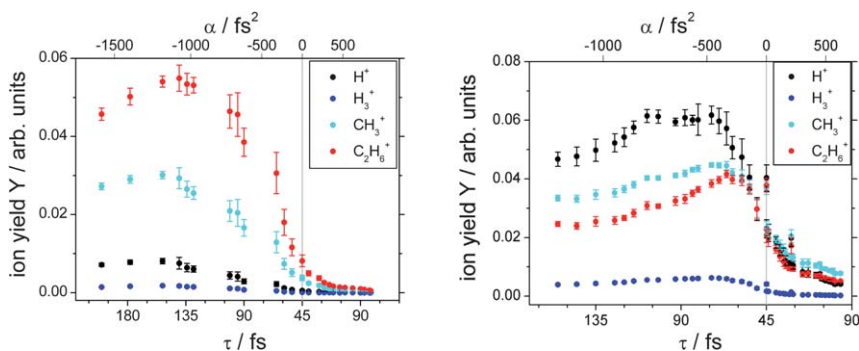
Fig. 2 Ion yields Y of the parent ion ($C_2H_6^+$), as well as the fragment ions CH_3^+, H_3^+ and H^+ from ethane as a function of the pulse length (FWHM, τ) and the linear chirp parameter α for a pulse energy of 15 μJ (left) and 46 μJ (right).

15 µJ. Evidently, all ion yields, including the parent ion yield are rather small for positive chirp, but increase significantly with increasing negative chirp. The ion yields appear to reach a maximum for negative chirp parameters around -1200 fs^2 before decreasing again with decreasing α. Thus, these data demonstrate a highly pronounced asymmetry of the ion yields for different signs of α, *i.e.* the formation of ions is not simply driven by the laser peak intensity. Even the yield of the parent ion is not maximized for the shortest pulses ($\tau = 45$ fs, $\alpha = 0$ fs^2), but rather for pulse durations of approximately 110–153 fs and negative α. This observation holds true for the total ion yield (not shown), which is maximized for ($\tau = 153$ fs, $\alpha = -1186$ fs^2).

In Fig. 2 (right) the corresponding ion yields are shown at a slightly higher laser pulse energy of 46 µJ. Several features deserve to be emphasized. First, the most intense ion (among the four ions shown) is now the H$^+$ ion. This indicates that the amount of fragmentation increases with increasing laser pulse energy. Second, the overall sign effect of the chirp control persists. However, the chirp parameter for which specific ion yields are maximized is clearly shifted to smaller α values. While at 15 µJ for positive chirp basically all ion signals vanish – making any further analysis numerically difficult – the data at 46 µJ have the advantage that finite signal intensities are also observed for positive chirp values. We will come back to these aspects below.

The fact that the yield of a parent ion is maximized for a pronounced negative chirp, implying a rather long laser pulse, is quite remarkable as the parent ions of methane[25] or ethanol[24] and several aromatic molecules[23,24,27] were shown to be maximized for the shortest laser pulse. To the best of our knowledge, this is the first observation of such a pronounced influence of the sign of the chirp on the ionization efficiency of an organic compound such as ethane. One important difference between the current work and the studies cited above (apart from that for xylene[27]) lies in the laser pulse intensity. While the literature work cited has been performed in the regime of 10^{15} to 10^{16} W cm^{-2}[23-25] our intensity was on the order of 10^{13} W cm^{-2}. As we will show below – in particular for the H$_3^+$ formation – most of the control effects depending on the sign of α tend to be smeared out at higher laser pulse energies.

The very pronounced increase of the parent ion yield for negatively chirped pulses suggests that we are dealing with a control of ionization efficiency for ethane and d$_3$-ethane *via* the laser field, more specifically the linear chirp parameter. In order to gain further insight at which point of the dissociative ionization the control is operative we have analyzed various ratios of ion signals, in particular those involving fragment ions. To this end, Fig. 3 addresses the ratio of the parent ion yield to the total ion yield. While the parent ion yield is not maximized for the shortest pulses the ratio of parent to total ion yield shows a maximum for the shortest pulse. Since the ratio decreases with increasing chirp, we conclude that fragmentation is enhanced for longer pulses, which is in agreement with literature reports.[23,24] The data shown in Fig. 3 suggest that there might be an effect of the sign of the chirp on the amount of fragmentation. However, the data for positive chirp have large error bars, since ion signals are vanishing there.

Clearly, both the enhancement of ionization efficiency and the enhancement of fragmentation with increasing negative chirp parameter are operative. The question remains: which part is more important for which molecular process. If
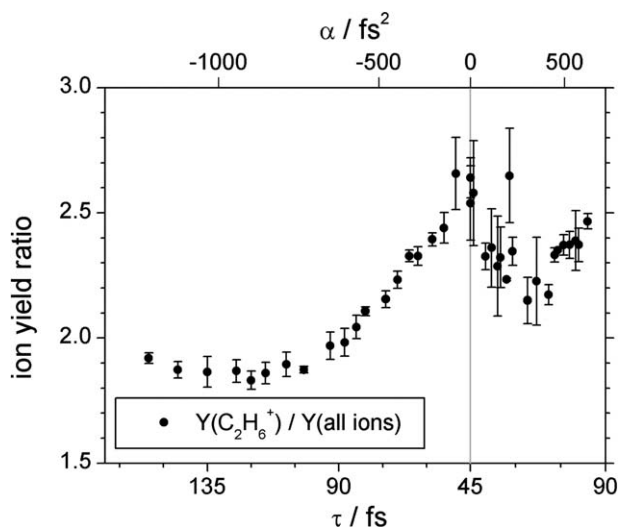
Fig. 3 Ratio of the parent ion yield to the total ion yield of ethane at 46 μJ. All fragments have been taken into account.
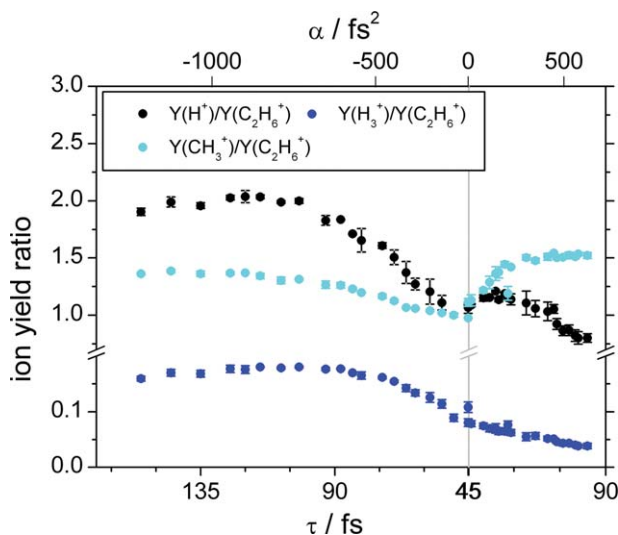
Fig. 4 Several fragment to parent ion yield ratios as a function of pulse duration and corresponding linear chirp parameter. Data taken at 46 μJ.

we assumed the fragmentation to be only dependent on the pulse duration, we would expect no dependency on the sign of the linear chirp parameter for a plot of a specific fragment ion yield normalized to the parent ion yield. As shown in Fig. 4 for different fragment ion to parent ion yield ratios this is not the case. Evidently, all normalized fragment ion yields shown (H^+, H_3^+, CH_3^+) exhibit pronounced sign effects of the linear chirp. The formations of H^+, H_3^+ and CH_3^+ all appear to be favored by negative chirp, the formation of CH_3^+ is also favored by positive

chirp, at least at 46 μJ. Since large chirp parameters α correlate with increased laser pulse duration, one might consider the possibility that enhanced ion yields might be influenced by charge resonance enhanced ionization (CREI).[32] On one hand, we do not easily see that CREI would depend on the sign of the chirp parameter. On the other hand, e.g. for the formation of H_3^+ on the dicationic PES there is no corresponding accessible region on the monocationic PES from which CREI could effectively start.

Note that there are literature reports of influence of the sign of the linear chirp for the generation of fragments, e.g. for NO_2^+ ions ($m/z = 46$) from p-nitrotoluene[23] and for the H_2^+ formation from methane,[25] all resulting from highly charged precursors. Further, the fluorescence intensity of N_2^+ ions can be enhanced by applying a negative chirp in the multiphoton ionization of N_2.[33] The selective population of dressed electronic states of an atom can also be controlled by means of linear chirp.[34]

In the following we discuss further characteristics of these ion yields, in particular ratios of fragment ion yields as a function of the linear chirp parameter. First, we show the ratio of ion yields $Y(H_3^+) / Y(H^+)$ as a function of the linear chirp parameter and the corresponding pulse duration in Fig. 5. Evidently, the ratio $Y(H_3^+) / Y(H^+)$ goes through a maximum in the region of negative chirp for both laser pulse energies displayed. The maximum in the yield ratio occurs around $\alpha = -750$ fs^2 for 15 μJ and is shifted toward $\alpha = -300$ fs^2 at 46 μJ. With further increasing negative chirp the ratio $Y(H_3^+) / Y(H^+)$ decreases, i.e. the H^+ channel is favored. For positive chirp – as mentioned above – the ion signals are so small at 15 μJ that it is impossible to extract reliable information from the ion yield ratios due to the large error bars. In fact, this is part of the reason why also data for a larger pulse energy are presented. Here, very clearly the error bars are reasonable and we conclude that the ratio of $Y(H_3^+) / Y(H^+)$ decreases in going to positive chirp parameters.
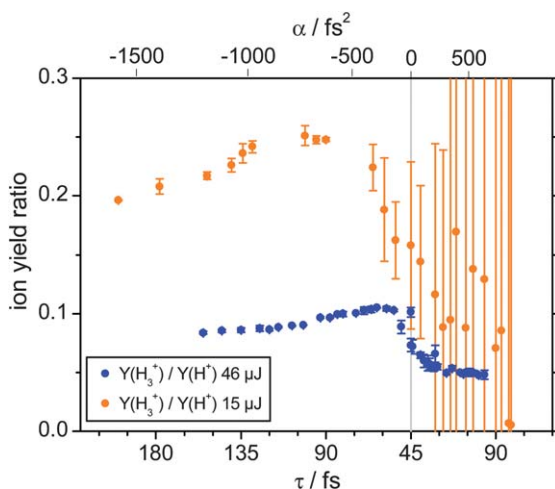

Fig. 5 Ion yield ratio of $Y(H_3^+) / Y(H^+)$ ion as a function of pulse duration and the corresponding linear chirp. Data taken at 15 μJ and 46 μJ.

While the origin of the H_3^+ is clear from previous work – it originates from a decay of the ethane dication[8] – the origin of the H^+ requires additional discussion. Assuming this H^+ might also originate from the dication one would first expect coincidences between H^+ and $C_2H_5^+$. However, Kanya et al. observed very few coincidences between H^+ and $C_2H_5^+$.[8] The angular distribution for the H^+ coincidence signal was strongly anisotropic, implying that its precursor has a lifetime shorter than the rotational period of the precursor (about 700 fs). The angular distribution of the H_3^+ coincidences on the other hand was isotropic implying that the lifetime of the precursor was larger than the rotational period. Yet, another puzzling detail was that the yield of H^+ was significantly larger than that of H_3^+. Further in the current work we find that the average kinetic energy of the H^+ is on the order of 6 eV at a pulse energy of 15 μJ, not compatible with the decay of a monocation, but only with Coulomb explosion. A possible solution to this mystery is offered in a paper by Eland, where it was shown that a significant amount of H^+ signal is observed in coincidence with the $C_2H_3^+$ ion![35] Possible mechanisms are a concerted three-body dissociation of $C_2H_6^{2+}$ or a consecutive mechanism in which either the H^+ comes off first with subsequent decay of the $C_2H_5^+$ into $C_2H_3^+ + H_2$, or the neutral H_2 comes off first with the intermediate $C_2H_4^{2+}$ ion subsequently breaking up into $H^+ + C_2H_3^+$. The analysis by Eland suggests that the latter process dominates. We note the average kinetic energy of the H^+ ion is on the order of 6 eV which is compatible with the conclusion above. Kraus et al. reported that the Coulomb energy expected from the dissociation of the dication in the eclipsed conformation of neutral ethane is 6.4 eV.[6] In fact, there are different conformations representing local minima on the dicationic PES that do not only differ in nuclear coordinates but also in electron density. Thus, the control of H_3^+ versus H^+ yields contains elements of electron density control. The results presented and discussed above provide evidence that we are able to control the fragmentation ratio of two reaction channels taking place on the same dicationic PES.

We now turn to the CH_3^+ ion signal, which exhibits a very peculiar TOF structure (cf. Fig. 1). Clearly, there are two different ensembles of CH_3^+ ions formed, a slow one with an average energy of 0.7 eV (inner two peaks) and a fast one with 2.7 eV (outer two peaks). Most likely the former ensemble originates from a decay of the monocation, the latter is due to the Coulomb explosion of the dication leading to $CH_3^+ + CH_3^+$. As shown in the inset of Fig. 1 (left) the relative amount of the slow and the fast CH_3^+ ions changes significantly as the laser pulse energy is increased, the fast component being favored by higher pulse energy. However, the relative amount of slow and fast CH_3^+ ions also depends on the linear chirp parameter. We demonstrate this in Fig. 6 by plotting the ratio of the slow to the fast CH_3^+ ions as a function of the linear chirp parameter α for laser pulse energies of 15 μJ and 46 μJ. At 15 μJ the relative fraction of slow CH_3^+ is significantly higher than at 46 μJ. At both pulse energies this ratio exhibits an S-shaped characteristic. At 15 μJ a maximum occurs around -500 fs^2, a minimum in the region of the transform limited pulse. At 46 μJ a maximum occurs around -500 fs^2, but the minimum is now shifted toward positive α around $+250$ fs^2. Concentrating on the negative chirp regime, where the signals are strongest, we conclude that increasing negative chirp appears to favor the formation of dications versus that of monocations. We interpret this as an example of inter-charge-state control.
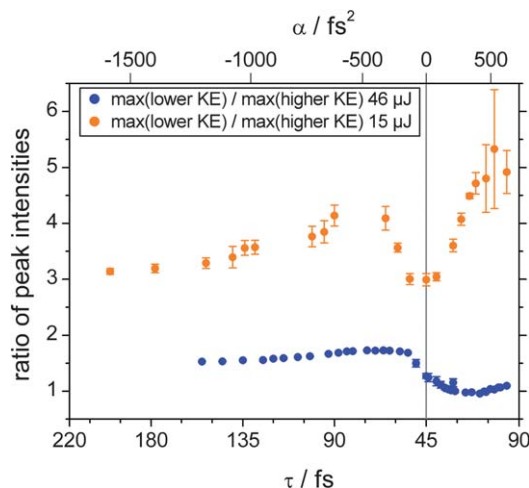
Fig. 6 Ratio of the peak intensities for the slow CH_3^+ divided by that of the fast CH_3^+ as a function of the pulse duration, respectively the chirp parameter.

The role of the laser pulse energy

In the following we discuss the H_3^+ formation from ethane as a function of the laser pulse energy. In Fig. 7 (left) normalized ion yields of H_3^+ are shown as a function of α and τ for different laser pulse energies. With higher laser pulse energies the value of α for the largest H_3^+ yield decreases. Consequently, for the highest pulse energy of 130 μJ we observe the highest ion yields for a vanishing chirp. Still, the ion yields depend on the sign of the chirp, and are higher for negatively chirped pulses as compared to positively chirped pulses.

On the right part of Fig. 7 the α values for which maximized H_3^+ yields are observed are shown as a function of laser pulse energy. This again serves to illustrate that this $\alpha(Y(H_3^+)_{max})$ decreases with increasing pulse energy. Note that
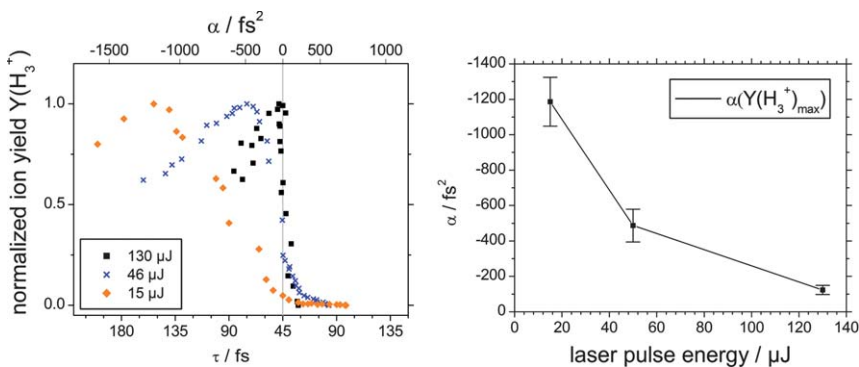

Fig. 7 Normalized ion yields of H_3^+ for different laser pulse energies from 130 to 15 μJ (left); α values, for which a maximum of H_3^+ ion yield is observed, as a function of the laser pulse energy (right). The connecting line serves to guide the eye.

in several chirp dependent experiments the relevant chirp effects observed were more pronounced at lower laser pulse energies.[27,36]

Formation of HD_2^+ and D_3^+ from d_3-ethane

We have demonstrated above that in the case of the CH_3^+, control of population is possible between different charge states (inter-charge-state control). For the ratio of H_3^+ to H^+ we demonstrated the possibility to control ion yield ratios within the dicationic state (intra-charge-state control). At this point the question remains whether the control affects the hydrogen scrambling known to dominate the statistical part of the dissociation dynamics leading to the formation of H_3^+ and $C_2H_3^+$.[8] Kanya *et al.* employed deuterium labeling of the ethane in order to resolve the issue of hydrogen scrambling. d_3-ethane with all three deuterons connected to the same carbon atom (CD_3CH_3) form four different $(H,D)_3^+$ species, *i.e.* H_3^+, H_2D^+, HD_2^+, and D_3^+ with a ratio of $8.01 \pm 1.20 : 43.0 \pm 5.4 : 43.1 \pm 0.3 : 5.89 \pm 0.10$, resembling almost statistical hydrogen scrambling prior to passing the relevant TS for $(H,D)_3^+$ formation. Here, we have also performed systematic chirp studies on d_3-ethane. Fig. 8 illustrates the impact of the linear chirp on the parent ion of d_3-ethane as well as fragment ions at $m/z = 1$ (H^+), 3 (H_3^+, HD^+), 4 (H_2D^+, D_2^+), 5 (HD_2^+), and 6 (D_3^+). The linear chirp dependence is very similar to normal ethane for all ions (Fig. 2). As indicated ion signals at $m/z = 3$ and 4 are not unique because they can originate from a three-atomic and a two-atomic species. However, the ion signals at $m/z = 5$ and 6 are unique. If the chirp dependent control influences the hydrogen scrambling, then the ratio of HD_3^+ yield to D_3^+ yield should exhibit marked variations.

As shown in Fig. 9 the ratio $Y(HD_2^+) / Y(D_3^+)$ is in fact independent of the linear chirp parameter between values of -1600 fs^2 and about -250 fs^2. The value of this ratio is about 6 : 1, very close to the experimental ratio reported by Kanya *et al.*[8] Thus, we conclude that the control between H_3^+ and H^+ discussed above for normal ethane is operative prior to the hydrogen scrambling. In fact, this is not surprising, since we would not expect coherent control for a statistical process.
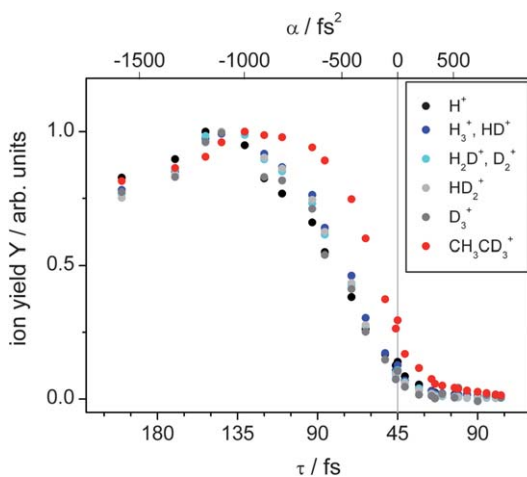
Fig. 8 Normalized ion yields of several ions generated form d_3-ethane at 15 µJ. All ion yields are normalized to their maximum value.

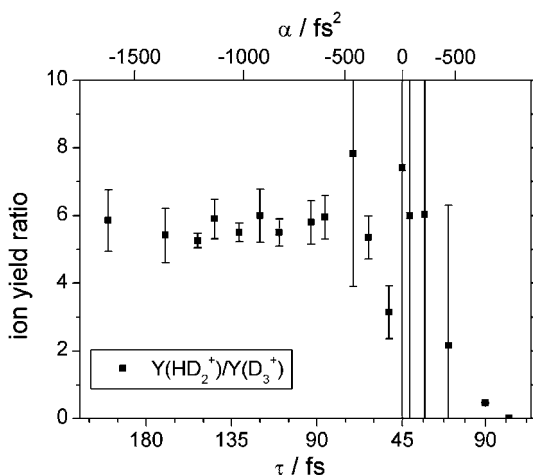**Fig. 9** Dependence of the ion yield ratio $Y(HD_2^+)$ / $Y(D_3^+)$ for d_3-ethane.

Summary and conclusions

We have investigated the dissociative ionization of h_6-ethane and d_3-ethane by means of shaped fs-laser pulses. Particular attention was given to the yields of the monocationic parent ion and the fragment ions H^+, H_3^+ and CH_3^+. Their yields have been recorded as a function of the linear chirp parameter α. A very pronounced sign effect of the chirp parameter is observed for all ion yields, a maximum of the yields being observed for negative chirp around -1000 fs^2. The position of this maximum shifts toward $\alpha = 0$ as the laser intensity is increased. Thus, for larger laser pulse energies the dynamics become more and more intensity driven.

The ratio of H_3^+ ion yields to H^+ ion yields can be controlled by means of the linear chirp parameter. Since there is evidence that both fragmentation channels occur on the dicationic PES this represents a case of control of dissociation dynamics within one charge state. The results shed new light on the complex PES of dicationic ethane with conformations not only differing in the nuclear coordinates but most of all also in the electron density. Ultimately, the ability to control the ratio H_3^+ to H^+ may be connected to the control of electron density.

On the other hand, the TOF spectra for CH_3^+ ions clearly indicate two different ensembles, one originating from the monocationic, the other from the dicationic channel. The ratio of these two channel yields can be manipulated by changing the laser pulse energy. This might be considered a trivial case of control. More interestingly, the ratio of the two CH_3^+ ensembles can also be controlled by the linear chirp parameter. There again a sign effect of α is observed implying that the control is not merely based on laser intensity variation. These results demonstrate that we are able to control the formation of different charge states *via* the linear chirp parameter α.

The current work appears to be one of the rare cases where very pronounced sign effects for parent ion and fragment ion yields are reported in dissociative fs-laser ionization. Lozovoy *et al.* reported on systematic chirp investigations for a number of organic molecules.[23] In most cases no significant sign effects were

observed, the exemption being the formation of NO_2^+ from *p*-nitrotoluene, which was also strongly favored by negative chirp.

For the future we hope that the current experimental results stimulate further theoretical work which would have to take into account strong field ionization dynamics as well as dissociation dynamics of a monocation and a dication within the same conceptual approach. This still appears to be a challenge for the time being.

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