



Controlling H_3^+ Formation From Ethane Using Shaped Ultrafast Laser Pulses

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OPEN ACCESS

Edited by:

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Specialty section:

This article was submitted to
Physical Chemistry and Chemical
Physics,
a section of the journal
Frontiers in Physics

Received: 06 April 2021

Accepted: 10 June 2021

Published: 30 June 2021

Citation:

Townsend T, Schwartz CJ, Jochim B,
P. KR, Severt T, Iwamoto N,
Napierala J L, Feizollah P, Tegegn SN,
Solomon A, Zhao S, Carnes KD,
Ben-Itzhak I and Wells E (2021)
Controlling H_3^+ Formation From Ethane
Using Shaped Ultrafast Laser Pulses.
Front. Phys. 9:691727.
doi: 10.3389/fphy.2021.691727

An adaptive learning algorithm coupled with 3D momentum-based feedback is used to identify intense laser pulse shapes that control H_3^+ formation from ethane. Specifically, we controlled the ratio of D_2H^+ to D_3^+ produced from the D_3C-CH_3 isotopologue of ethane, which selects between trihydrogen cations formed from atoms on one or both sides of ethane. We are able to modify the $D_2H^+:D_3^+$ ratio by a factor of up to three. In addition, two-dimensional scans of linear chirp and third-order dispersion are conducted for a few fourth-order dispersion values while the D_2H^+ and D_3^+ production rates are monitored. The optimized pulse is observed to influence the yield, kinetic energy release, and angular distribution of the D_2H^+ ions while the D_3^+ ion dynamics remain relatively stable. We subsequently conducted COLTRIMS experiments on C_2D_6 to complement the velocity map imaging data obtained during the control experiments and measured the branching ratio of two-body double ionization. Two-body $D_3^+ + C_2D_3^+$ is the dominant final channel containing D_3^+ ions, although the three-body $D + D_3^+ + C_2D_2^+$ final state is also observed.

Keywords: coherent control, molecular dynamics, bond rearrangement, laser physics, imaging, ultrafast science

1 INTRODUCTION

The intramolecular migration of hydrogen continues to be an active area of investigation in ultrafast science [1–11] with implications for topics ranging from combustion [12] to peptide dissociation [13] and characterizing conformational differences in molecules [14, 15]. In some cases the migration of hydrogen leads to the formation of new molecular ions, such as H_3^+ [5, 16–21], by processes such as H_2 roaming or double hydrogen migration [18, 19, 22, 23].

The formation of H_3^+ is usually a multi-step process that often involves the association of hydrogen atoms from different sites of the parent molecule. In allene (C_3H_4), at least one hydrogen migration to the other side of the molecule is required [24, 25]. Even in molecules that contain a methyl group with three hydrogen atoms close together, there are H_3^+ formation pathways that involve hydrogen atoms from other parts of the parent molecule. Methanol is perhaps the best studied example of this behavior [5, 16–21, 26–29]. In methanol (CH_3OH), there is clear evidence that H_3^+ may form when a roaming H_2 from the methyl side abstracts the hydroxyl proton in addition to alternative mechanisms that only involve the methyl side. For ethanol (CH_3CH_2OH) and several slightly longer alcohol molecules, multiple pathways to H_3^+ formation exist that involve hydrogen migration, although the relative importance of these pathways decreases as the carbon chain length increases [19, 20].

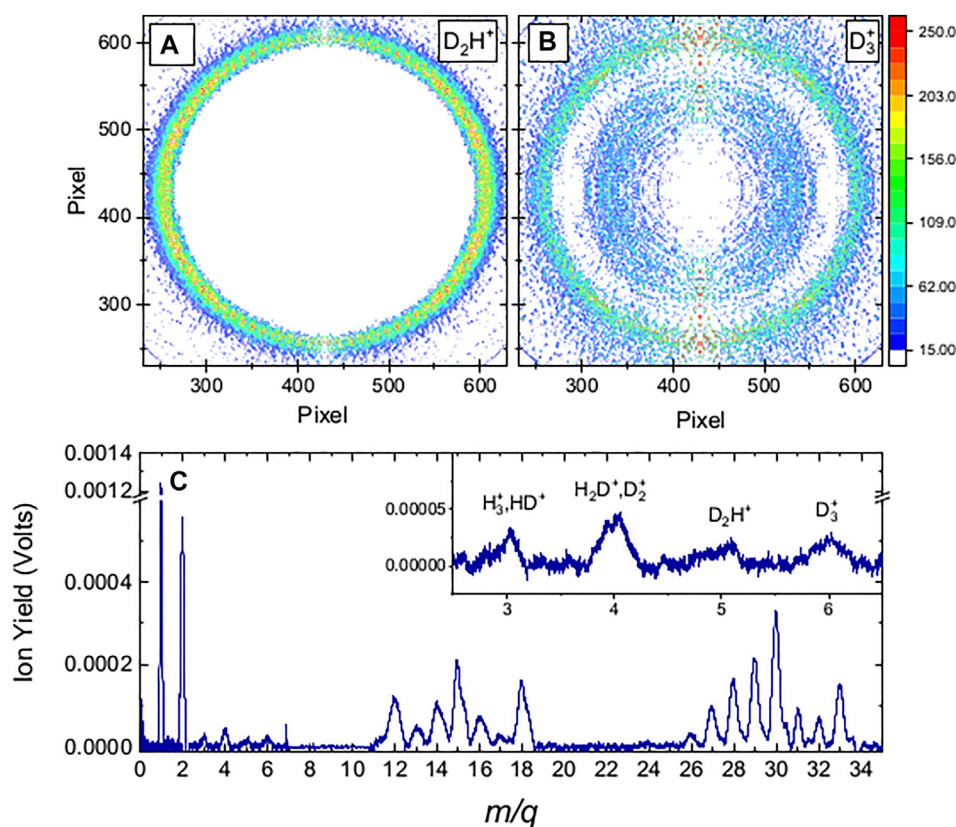


FIGURE 1 | Molecular fragmentation data obtained with 35 fs FWHM, 1.3×10^{14} W/cm² pulses centered at 785 nm, the conditions used in the closed-loop experiment. **(A)** Inverse Abel transformed VMI of D_2H^+ ions. **(B)** Inverse Abel transformed VMI of $m/q = 6$, which contains D_3^+ and $C_2H_2^+$ ions. At this intensity, the two features are separated, with the $C_2H_2^+$ ions inside the D_3^+ ring. The laser polarization is vertical for the VMI data. **(C)** Current mode time-of-flight (shown as a function of m/q) showing that the integrated yield of the $m/q = 5$ and $m/q = 6$ peaks are similar. When only the yield from the higher momentum feature in the $m/q = 6$ is considered, the ratio of D_2H^+ to D_3^+ is approximately 7:1, in agreement with the results of Kanya et al. [32]. The laser polarization is perpendicular to the time-of-flight axis in **(C)**.

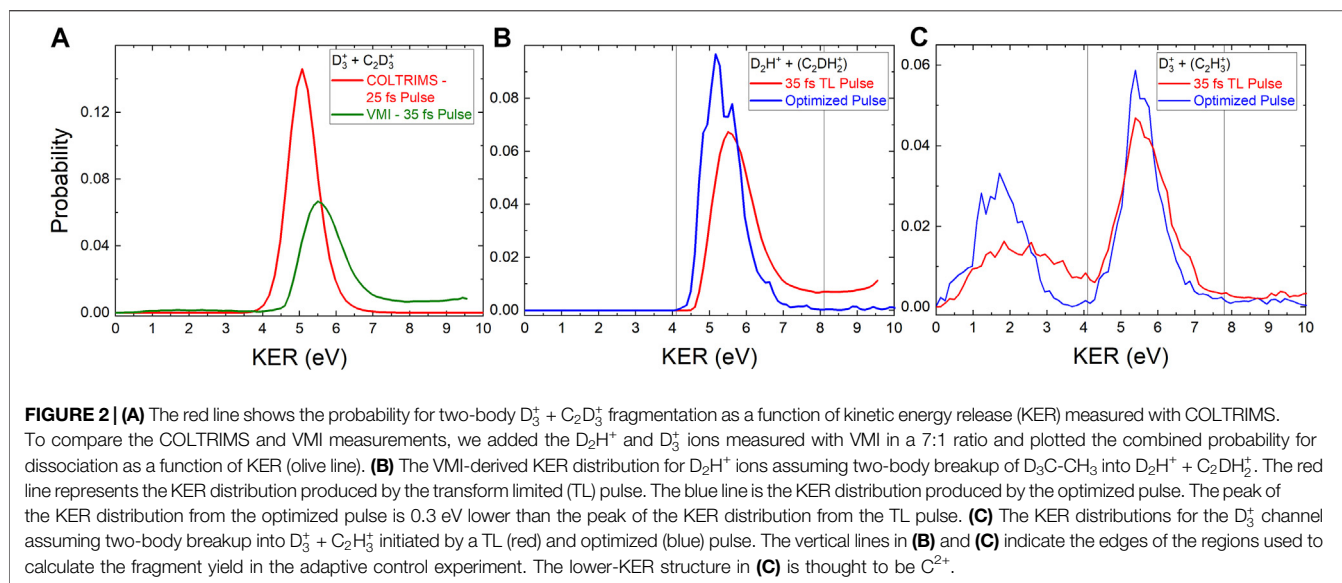
Ethane (C_2H_6) is composed of two back-to-back methyl groups, and thus it is an excellent baseline system for examining hydrogen-related bond rearrangement. H_3^+ formation following double ionization of ethane has been examined in several previous experimental and theoretical studies [16, 30–35]. Kraus and co-workers theoretically identified a minimum-energy-path transition state with a neutral hydrogen molecule attached to a $C_2H_4^{2+}$ ion that led to the $H_3^+ + C_2H_3^+$ final state [31]. Their calculations were in good agreement with the measured kinetic energy release (KER) of these final products, in which the KER is essentially the reverse activation energy along the proposed reaction path. Kanya et al. showed, using different isotopologues of ethane, that hydrogen atoms are statistically scrambled between the initial and final states following double ionization [32]. In a later study, Boran et al. proposed a pathway that begins with hydrogen elimination ($H + C_2H_5^+$) and continues through a sequence of transition states leading to a neutral hydrogen molecule attached to a $C_2H_3^{2+}$ ion followed by dissociation into $C_2H_2^+ + H_3^+$ [34]. Recent electron impact studies by Zhang et al. suggest the presence of an additional roaming-induced isomerization pathway that leads

to H_3^+ formation on a longer timescale than the transition-state pathways [35].

Motivated by significant H_3^+ yields from the dissociation of ethane dications, the suggestions of multiple pathways that lead to H_3^+ formation following double ionization of ethane, and the sensitivity of the H_3^+ production to laser pulse parameters reported by Schirmel and co-workers [33], this article reports our efforts to manipulate the formation of H_3^+ using shaped ultrafast laser pulses.

2 EXPERIMENTAL METHOD

The experimental techniques applied in this study have recently been discussed elsewhere [21, 36], and in this section we will only highlight a few key points. Two different approaches are used to examine the interactions of intense laser pulses with ethane gas: First, the laser pulses are shaped using an acousto-optic programmable dispersive filter (AOPDF) [37] and the ethane reaction products are measured using velocity map imaging (VMI) [38, 39]. Second, COLd Target Recoil Ion Momentum



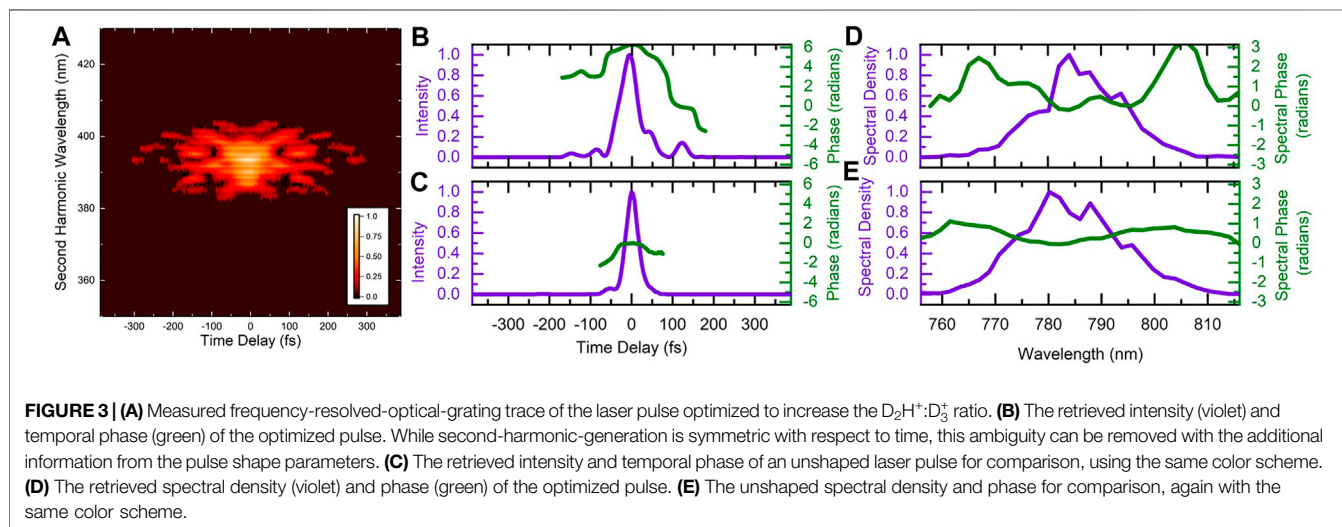
Spectroscopy (COLTRIMS) [40, 41] characterizes the dissociation dynamics of the ethane molecule following strong-field ionization.

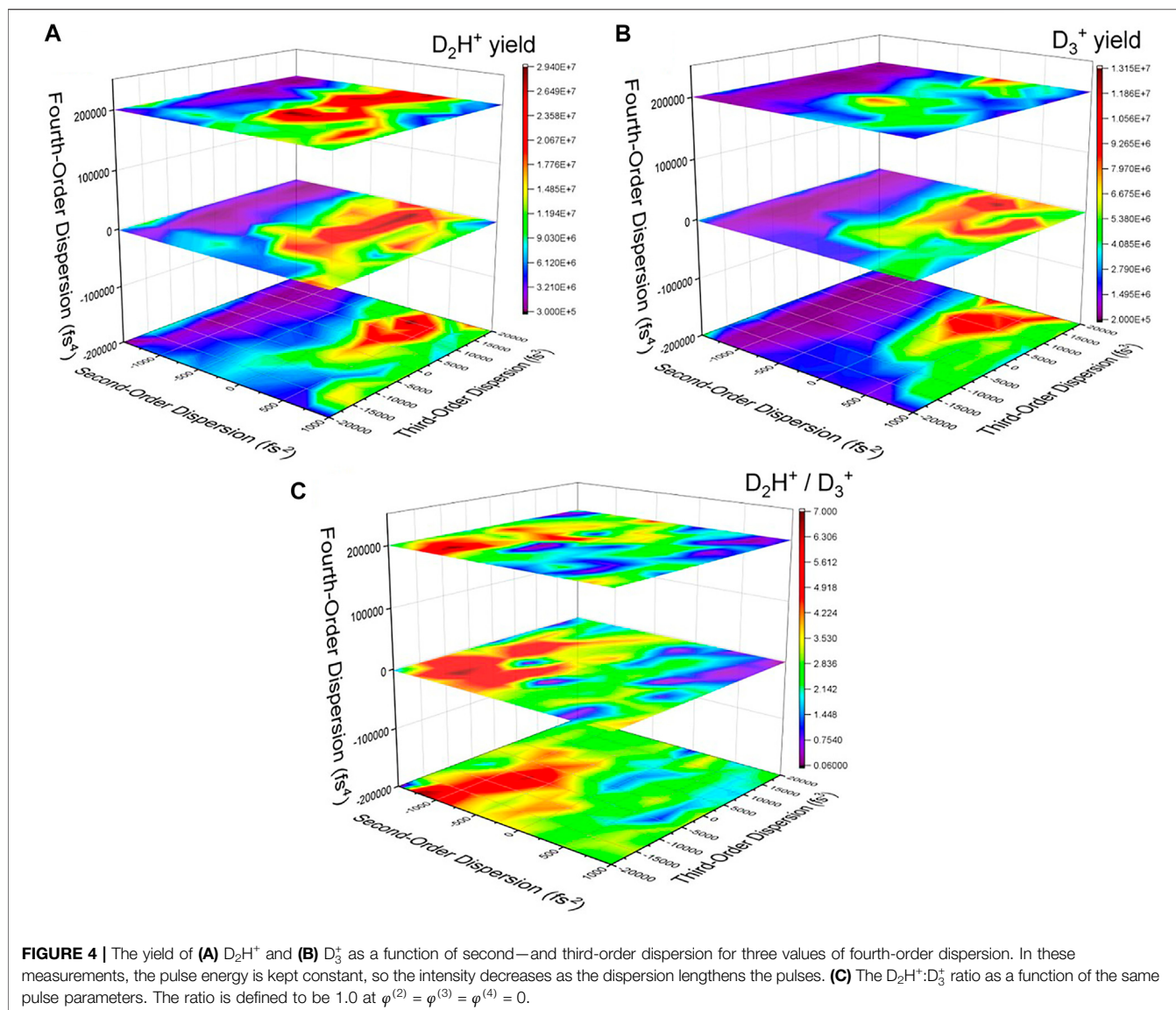
2.1 Shaped Pulses and Velocity Map Imaging

In the shaped pulse/VMI portion of the experiment linearly polarized pulses with a duration of 35 fs full-width at half-maximum (FWHM) in intensity and a center wavelength of 785 nm are generated at 1 kHz by a Ti:Sapphire laser system named KLS. In this laser system, the compressor grating pair is in the Treacy configuration [42] while the stretcher gratings are in the Martinez configuration [43]. The amplified pulse energy of about 1.5 mJ was attenuated to the levels needed in the experiment. These near-Fourier-transform limited pulses will be denoted as TL pulses in this article. The acousto-optic programmable dispersive filter [37] was placed between the

laser oscillator and multi-pass amplifier. In this experiment, we controlled only the spectral phase of the laser pulse. Pulse characteristics were determined using a second-harmonic-generation frequency-resolved-optical-grating (SHG-FROG) [44] device. Our version of VMI [45–47] integrates the momentum image of a given m/q time-of-flight peak over many laser shots by fully powering the detector within a specific time window. For a typical trial pulse, we collected VMI data for 5,000 laser shots for D_2H^+ and 35,000 laser shots for D_3^+ in order to obtain similar statistics for each ion. While our VMI approach does not measure correlated information about all the products from a specific laser-molecule interaction, it enables rapid data acquisition, making adaptive control experiments possible [48, 49]. Typical VMI data obtained with the online inversion method [47] are shown in Figures 1A,B.

In the closed-loop adaptive control approach, ion-specific three-dimensional momentum information provides the





feedback to drive a genetic algorithm that optimizes the pulse shapes to a control objective [46, 47]. The raw VMI data is inverted on-the-fly to recover a slice through the center of the three-dimensional momentum distribution using a modified “onion-peeling” algorithm as described by Rallis et al. [47]. The yield within user-defined regions of interest on the momentum plot is then evaluated, resulting in a numerical value that defines the “fitness” of the laser pulse being examined. The adaptive search parameterizes the pulse characteristics in terms of the spectral phase, which is broken into 16 evenly spaced segments between 734 and 830 nm. Since a portion of this range is beyond the pulse bandwidth, the effective number of search parameters is somewhat smaller than 16. Linear interpolation fills in the values between the adjacent phases. The algorithm is allowed to adjust each phase value between 0 and 2π .

To complement the closed-loop studies, systematic scans of the second- and third-order pulse dispersion were made for a few values of fourth-order dispersion. In this pulse-parameterization

scheme [21, 50, 51], we describe the spectral phase, $\varphi(\omega)$, as a Taylor series expansion [52]:

$$\varphi(\omega) = \varphi^{(0)} + \frac{\varphi^{(1)}(\omega - \omega_0)}{1!} + \frac{\varphi^{(2)}(\omega - \omega_0)^2}{2!} + \frac{\varphi^{(3)}(\omega - \omega_0)^3}{3!} + \frac{\varphi^{(4)}(\omega - \omega_0)^4}{4!} + \dots \quad (1)$$

2.2 Coincidence Momentum Imaging

In the COLTRIMS [40, 41] measurement, the laser pulses are produced by the PULSAR laser [53] at 10 kHz, with 25-fs (FWHM in intensity) pulse duration, a central wavelength of 790 nm, and maximum pulse energy of 2 mJ. The laser pulses were again characterized with SHG-FROG. The pulses are focused by a $f = 7.5$ -cm spherical mirror onto randomly oriented target molecules in the supersonic molecular beam of the COLTRIMS apparatus. Following the laser-molecule interaction within the electric field of the spectrometer, all the

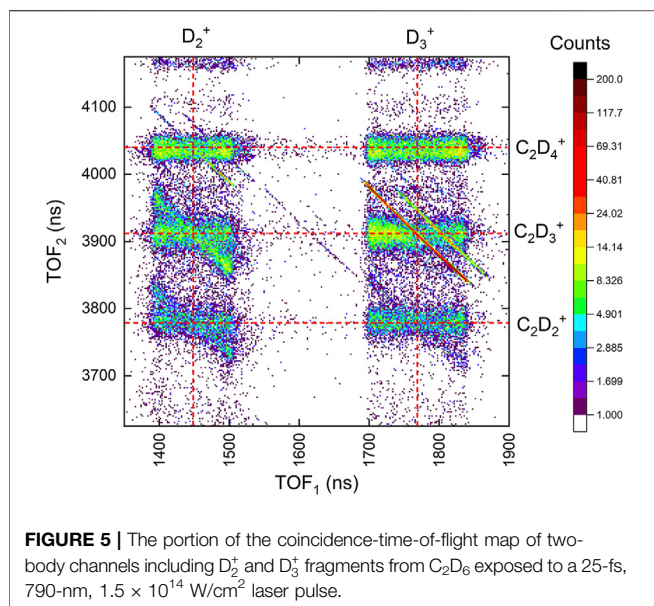


FIGURE 5 | The portion of the coincidence-time-of-flight map of two-body channels including D_2^+ and D_3^+ fragments from C_2D_6 exposed to a 25-fs, 790-nm, 1.5×10^{14} W/cm² laser pulse.

TABLE 1 | Ethane (C_2D_6) branching ratios for two-body double ionization by 25-fs, 1.5×10^{14} -W/cm² laser pulses centered at 790-nm.

Dissociation channel	Branching ratio (%)
$D^+ + C_2D_5^+$	1.00 ± 0.03
$D_2^+ + C_2D_4^+$	4.91 ± 0.08
$D_3^+ + C_2D_3^+$	69.80 ± 0.15
$CD_2^+ + CD_4^+$	1.01 ± 0.04
$CD_3^+ + CD_3^+$	23.27 ± 0.71

charged ethane photofragments are directed toward a time- and position-sensitive detector where they are measured in coincidence. The base pressure in the spectrometer region was below 2×10^{-10} Torr. Since the charged fragments are recorded on an event-by-event basis, we can use the measured time and position of all the charged fragments along with conservation of momentum to determine the three-dimensional momentum distributions.

3 RESULTS AND DISCUSSION

The experiments on D_3C-CH_3 (1,1,1- d_3 ethane, 98% pure) with shaped pulses and VMI detection used both an adaptive search strategy and a systematic search of pulse parameters. With this target, D_3^+ fragments must originate from only one side of the parent molecule, while D_2H^+ fragment formation must involve both sides of the parent molecule. While the D_3C-CH_3 target allows us to determine which hydrogen atoms participate in the bond rearrangement process, the $m/q = 6$ channel contains both the D_3^+ channel of interest and C^{2+} fragments [30]. At laser intensities that did not have a significant yield of C^{2+} ions (around 8×10^{13} W/cm²), for which we could assume there was no C^{2+} signal, the D_3^+ signal rate was too low for adaptive control experiments.

As the intensity was increased, the VMI of the $m/q = 6$ ions began to have two features, as shown in **Figure 1B**. The outer

feature, corresponding to a KER of around 5 eV, remained at that KER as the intensity increased. In contrast, both the signal size of the inside feature relative to the ≈ 5 eV feature and the radius of the inner feature in **Figure 1B** increased with intensity. We assume this inner feature, which is more aligned with the laser polarization at higher intensities, is caused by C^{2+} ions. At 1.3×10^{14} W/cm², the total yields of $m/q = 5$ and $m/q = 6$ are similar, as shown in **Figure 1C**. Using the VMI information, we can separate the two features in momentum space. The range of interest is shown by the vertical lines in **Figures 2B,C**. After separation of the C^{2+} from the D_3^+ and correction for different image exposure times, the ratio of D_2H^+ to D_3^+ is approximately 7:1, as expected from the time-of-flight studies performed by Kanya et al. on different isotopologues of ethane [32].

3.1 Pulse Shaping and Control

We were able to increase the $D_2H^+:D_3^+$ ratio by a factor of 3.2 ± 0.7 using adaptive control. With phase-only shaping the pulse energy is kept constant at around 11 μ J/pulse, which corresponds to a peak intensity of 1.3×10^{14} W/cm². Experiments at slightly higher pulse energy also resulted in a $D_2H^+:D_3^+$ ratio higher than obtained with a TL pulse, but we observed significant overlap between the C^{2+} and D_3^+ fragments making it difficult to evaluate these results. When attempting to optimize the inverse $D_3^+:D_2H^+$ ratio, we did not observe any improvement over the TL 35-fs pulse.

Figure 2 shows the KER distributions obtained for the D_2H^+ and D_3^+ fragments with the optimized pulses and TL pulses. For the VMI data, we calculate the KER by assuming a two-body breakup of the D_3C-CH_3 parent molecule into an ion pair. For comparison, the KER distribution of $C_2D_6^{2+} \rightarrow D_3^+ + C_2D_3^+$ directly measured with COLTRIMS is shown in **Figure 2A**. The KER distributions are similar, although the COLTRIMS measurement is slightly lower. This could be due to small differences in the respective momentum/energy calibration or the slightly different pulse characteristics. As described in the introduction, Kraus et al. [31] and Boran et al. [34] have examined the dissociation pathways leading to H_3^+ formation from ethane and found KER values peaked between 5.2 and 5.5 eV. Zhang and co-workers have observed a slightly lower KER in recent electron-impact studies and suggested a different dissociation pathway [35].

Notably, the D_2H^+ KER distribution obtained with the pulse optimized to increase the $D_2H^+:D_3^+$ ratio is shifted about 0.3 eV lower than the KER distribution obtained with the TL pulse. The corresponding KER distribution for the D_3^+ yield, which is in the denominator of the control objective, shows no significant shift. In addition, the increase in the $D_2H^+:D_3^+$ ratio was due to an increase in D_2H^+ yield, not a reduction of D_3^+ yield. In some similar experiments, this combination of indicators has been a signature of a barrier-suppression mechanism [46]. Several of the theoretical efforts with ethane [31, 34, 35] identified one or more transition states in the dissociation process. If the energy of the transition state was modified by the field at an appropriate time, it could promote D_2H^+ production.

The characteristics of the optimized pulse are shown in **Figure 3**. While there is indeed a trailing secondary pulse around 125 fs after the main pulse, there are other features of

the pulse shape that could be significant. To try and determine which pulse parameters are important for the manipulation of the control objective, we systematically scanned the linear chirp and third-order dispersion for three values of fourth-order dispersion. During these systematic scans we recorded the D_2H^+ and D_3^+ yields, shown in **Figure 4**, using the same gates on the VMI data as in the adaptive control experiment.

From a time-domain perspective, the second- and fourth-order dispersions lengthen the pulse symmetrically, while the third-order dispersion adds a pedestal either before or after the main pulse (see, e.g., Ref. 50). Thus, some of the temporal characteristics of the optimized pulse (**Figure 3**) can be reproduced, but the secondary pulse would be more difficult to construct using dispersive pulse parameters. As shown in **Figure 4C**, there are a number of combinations of pulse parameters that reach nearly the same level of effectiveness at manipulating the $D_2H^+:D_3^+$ ratio as the optimized pulse. The highest values of the $D_2H^+:D_3^+$ ratio are seen at negative values of both $\varphi^{(2)}$ and $\varphi^{(3)}$. In this region of parameter space, the yield of the individual channels have both been reduced by roughly a factor of 10. Therefore, while the adaptive and systematic search strategies can both find pulses that improve the control objective, and thus distinguish between formation of trihydrogen cations from one side of the parent molecule or both sides of the parent molecule, the adaptive search result maintains the overall yield better than the systematic search. This result is similar to the observations in a recent methanol experiment [21].

One curious element of the dispersion scan is the comparison to the previous work of Schirmel et al., who also examined H_3^+ , D_2H^+ , and D_3^+ yields from various isotopologues of ethane as a function of second-order dispersion (linear chirp) [33]. Our results match the results of Schirmel et al. in the sense that

the sign of the linear chirp matters in the production of H_3^+ . This is somewhat unusual, since dissociation rates rarely seem to depend on the sign of the chirp [54]. Our results show increases in D_2H^+ and D_3^+ yields, as well as an increasing $D_2H^+:D_3^+$ ratio, for positive linear chirp, with a maximum around $\varphi^{(2)} = +250 \text{ fs}^2$. This is in direct contrast to the result of Schirmel and co-workers who reported that negative linear chirp increases the yield of H_3^+ and other fragments from ethane, with a maximum at $\varphi^{(2)} \approx -1000 \text{ fs}^2$. They also report an essentially constant $D_2H^+:D_3^+$ ratio as a function of chirp.

One possible explanation for the seemingly conflicting results is that different intensities lead to different dissociation dynamics. The TL intensity of $1.3 \times 10^{14} \text{ W/cm}^2$ used in this experiment is higher by about a factor of two than the highest intensity pulses used by Schirmel et al. [33]. In both our scans of the dispersion parameters and those of Schirmel et al., the pulse energy was kept constant. Schirmel et al. also noted that as the pulse energy increased in their experiments, the value of linear chirp that produced the most fragmentation became closer to zero (more positive). It is possible that our results simply continue this trend, although if the intensity is becoming the dominant factor in the dynamics it is unclear why zero dispersion does not produce a maximum or a minimum. We note that our D_2H^+ and D_3^+ yields also increased for $\varphi^{(3)} > 0$ and changing $\varphi^{(4)}$ had limited effect. Additional work, including a more detailed study of how dispersion and intensity combine to influence the dissociation dynamics, is needed to resolve these issues.

3.2 Branching Ratio

Another factor potentially confounding our understanding of how the production of H_3^+ can be manipulated with shaped laser pulses is the likelihood that more than one dissociation pathway

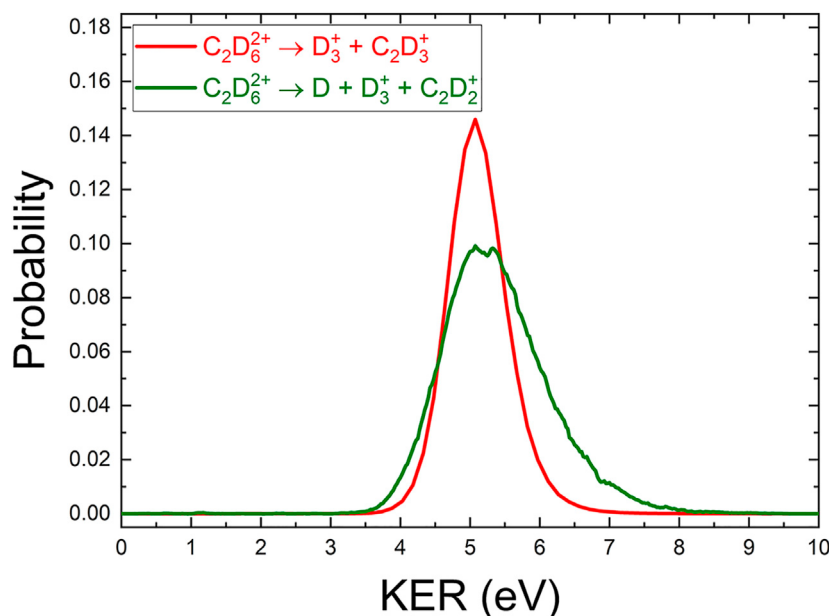


FIGURE 6 | A comparison of the (COLTRIMS-derived) KER spectrum of $D_3^+ + C_2D_3^+$ (red) and $D + D_3^+ + C_2D_2^+$ (olive) produced by 25 fs, $1.5 \times 10^{14} \text{ W/cm}^2$ laser pulses centered at 790 nm.

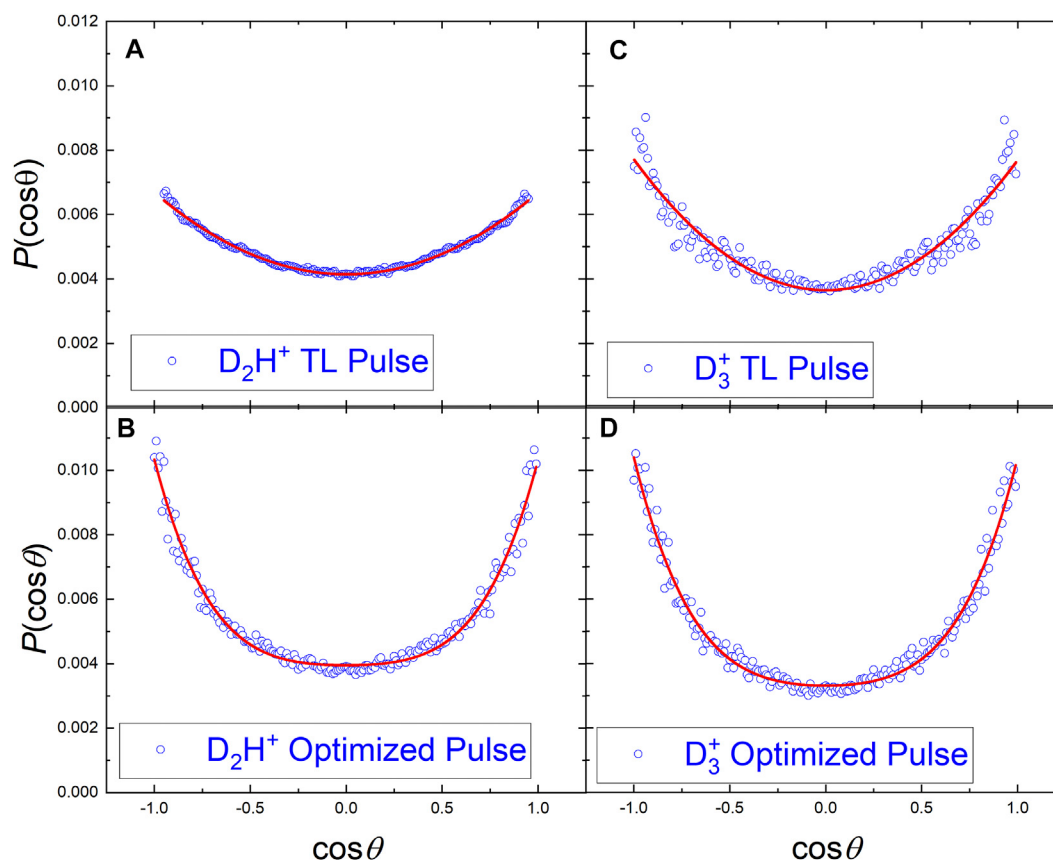


FIGURE 7 | The angular distributions of D_2H^+ and D_3^+ from VMI measurements of D_3C-CH_3 dissociation. **(A)** D_2H^+ fragments from a TL pulse. **(B)** D_2H^+ fragments produced from pulses optimized to increase the $D_2H^+:D_3^+$ ratio. In the right column are the same distributions for D_3^+ fragments by the **(C)** TL and **(D)** optimized pulses. The molecular ions forming the angular distributions are from within the areas of interest shown in **Figure 2**. The angle θ is between the laser polarization direction and the fragment dissociation direction. The solid lines in each panel are fits of the data to a Legendre polynomial in $\cos\theta$. The fit coefficients are shown in **Table 2**.

TABLE 2 | Legendre polynomial coefficients, a_n , obtained by fitting the probability of dissociation of D_2H^+ and D_3^+ as a function of $\cos\theta$.

Dissociation channel	Pulse type	a_0	a_2	a_4
D_2H^+	TL	0.0050	0.0017	-
D_2H^+	Optimized	0.0054	0.0038	0.0012
D_3^+	TL	0.0050	0.0027	-
D_3^+	Optimized	0.0050	0.0043	0.0012

is active. To partially address this issue, we performed COLTRIMS measurements of laser-induced dissociation of C_2D_6 . We selected C_2D_6 as a target because D_3C-CH_3 was financially prohibitive for use in a supersonic jet without a buffer gas. While the peak intensities were similar in the COLTRIMS and VMI measurements, the pulse duration in the COLTRIMS measurements was 25 fs, i.e., significantly shorter than the 35 fs in the VMI case. As an approximate guide, we note that the Keldysh parameter [55] is approximately 0.9 for $1.3 \times 10^{14} \text{ W/cm}^2$ pulses and the 11.52 eV ionization potential of ethane [56]. When the pulses are lengthened by pulse shaping the corresponding decrease in intensity raises the Keldysh parameter. The quasi-static approximation used in tunnel

ionization is therefore not clearly valid in any of the experiments described here. **Figure 5** shows the relevant portion of the coincidence-time-of-flight (CTOF) plot. Following the procedure outlined in Ref. 36 for removing false coincidences, we use this data to obtain the two-body double-ionization branching ratio reported in **Table 1**.

We also analyzed the three-body $D + D_3^+ + C_2D_3^+$ channel. While the $D_3^+ + C_2D_2^+$ ion pair is visible in **Figure 5**, the momentum carried by the neutral deuterium atom smears out the corresponding island in the CTOF plot compared to the sharp two-body channels. The detailed corrections needed to reach the level of precision given in **Table 1** for three-body channels is time-consuming because of contributions from three-body channels containing three ions. By making some simplifying assumptions about which channels provide the most significant background, however, we estimate the $D + D_3^+ + C_2D_2^+$ yield is 16 times smaller than the main $D_3^+ + C_2D_3^+$ channel.

Using momentum conservation to deduce the contribution from the deuterium atom gives a KER distribution for this three-body channel, shown in **Figure 6**. The KER distribution is similar to the $C_2D_6^{2+} \rightarrow D_3^+ + C_2D_3^+$ KER distribution shown in **Figure 2C**

and also the prediction of Boran et al. [34] for a $C_2D_6^{2+} \rightarrow D + C_2D_5^+ \rightarrow D + D_3^+ + C_2D_2^+$ process.

In addition, we did not find any significant evidence for D_3^+ production from the monocation, that is, $D_3^+ +$ neutral fragments. Such a process would typically have low KER and there are negligibly few D_3^+ ions at low kinetic energy. Thus, we can conclude that we observe two, and only two, final channels that result in D_3^+ ions: two-body $D_3^+ + C_2D_3^+$ and three-body $D + D_3^+ + C_2D_2^+$. Of these, the two-body channel has the larger yield. When considering the results of our control experiments, it is likely that the main channel involved is a two-body double ionization process.

3.3 Angular Distributions

Since the control experiments with the D_3C-CH_3 isotopologue of ethane are designed to distinguish between the involvement of the hydrogen atoms on one or both sides of the molecule, the angular distributions from the VMI data might provide information about the dissociation dynamics beyond the KER shift shown in **Figure 2B**. Since the angular COLTRIMS data can be readily corrected using available experimental symmetries [36], we compared the COLTRIMS-measured $D_3^+ + C_2D_3^+$ angular distribution to the weighted sum of the D_2H^+ and D_3^+ VMI angular distributions to derive a function that ensured uniform detection efficiency across the VMI detector.

The angular distributions of the D_2H^+ and D_3^+ ions are shown in **Figure 7** for both TL and optimized pulses. These angular distributions were fit using a Legendre polynomial in $\cos\theta$, and the resulting coefficients are shown in **Table 2**. The most notable difference between the TL and optimized pulses is that the latter pulses produce a D_2H^+ distribution that is much more aligned with the laser polarization direction than the TL pulses. This trend is also apparent in the D_3^+ results, although to a lesser extent. In addition, both of the optimized pulses yield angular distributions that are better fit to 4th-order Legendre polynomials, while adding a 4th-order term does not improve the fit of the angular distributions produced by TL pulses.

The optimized pulse, therefore, is observed to have a significant impact on the yield, KER, and angular distribution of the D_2H^+ ions. In contrast, the D_3^+ ions display relatively similar dynamics for the optimized and TL pulses. A close comparison of **Figures 4A,B** shows that while the D_3^+ yield changes by a factor of 65 over the range of the dispersion scan, the D_2H^+ yield changes by a factor of 122 over the same parameter space. The relative stability of the D_3^+ formation process under the range of laser conditions may be a result of the limited combinations of atoms that could be involved. The greater multiplicity available for D_2H^+ formation might make that process more flexible and therefore more susceptible to the influence of the laser pulse changes.

4 SUMMARY

By using the D_3C-CH_3 isotopologue of ethane we were able to separate two different types of dissociation processes leading to

the formation of trihydrogen cations: D_3^+ formation which involves atoms from only one side of the molecule and D_2H^+ that involves atoms from both sides of the molecule. Using shaped laser pulses, we increased the $D_2H^+:D_3^+$ ratio by a factor of up to three. The laser pulses optimized with an adaptive search strategy were more effective at improving the $D_2H^+:D_3^+$ ratio while maintaining the overall ion yield than the most effective pulses found with a systematic scan of pulse dispersion parameters. Using coincident ion detection available in a COLTRIMS measurement of C_2D_6 , we verified that while three-body $D + D_3^+ + C_2D_3^+$ is observed, two-body $D_3^+ + C_2D_3^+$ is the dominant fragmentation channel containing D_3^+ ions. The pulse optimized with an adaptive search produces D_2H^+ fragments with a lower KER and an angular distribution more strongly peaked along the laser polarization direction than the TL pulse. This could be a signature of a barrier suppression mechanism. A multiple-pulse experiment probing the time dependence of H_3^+ formation in this process could be informative, as could further theoretical investigation of the timescales of some of the proposed H_3^+ formation mechanisms.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

TT and TS led the analysis of the COLTRIMS measurements, while CS led the VMI analysis with assistance from TT, NI, and ST. BJ led the adaptive control experiments and KP led the dispersion scan experiments with assistance from NI, CS, JN, AS, TS, PF, ST, and EW. TS, BJ, SZ, KC, IB-I, and EW carried out the COLTRIMS experiment. IB-I and EW mentored the students and postdocs. EW wrote the manuscript with assistance from TT, TS, BJ, KP, KC, and IB-I. All authors reviewed the manuscript prior to submission.

FUNDING

Augustana University personnel and equipment are supported by the National Science Foundation grant PHYS-2011864. JR Macdonald Laboratory personnel and equipment are supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Science, Office of Science, United States Department of Energy under award #DE-FG02-86ER1349.

ACKNOWLEDGMENTS

We thank Charles Fehrenbach for assistance with the PULSAR laser and the members of Vinod Kumarappan's group for assistance with the KLS laser.

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