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Strong-field control of H_3^+ production from methanol dication: Selecting between local and extended formation mechanisms

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ABSTRACT

Using the CD_3OH isotopologue of methanol, the ratio of D_2H^+ to D_3^+ formation is manipulated by changing the characteristics of the intense femtosecond laser pulse. Detection of D_2H^+ indicates a formation process involving two hydrogen atoms from the methyl side of the molecule and a proton from the hydroxyl side, while detection of D_3^+ indicates local formation involving only the methyl group. Both mechanisms are thought to involve a neutral D_2 moiety. An adaptive control strategy that employs image-based feedback to guide the learning algorithm results in an enhancement of the D_2H^+/D_3^+ ratio by a factor of approximately two. The optimized pulses have secondary structures 110–210 fs after the main pulse and result in photofragments that have different kinetic energy release distributions than those produced from near transform limited pulses. Systematic changes to the linear chirp and higher order dispersion terms of the laser pulse are compared to the results obtained with the optimized pulse shapes.

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I. INTRODUCTION

Controlling chemical reactions with lasers has been a goal of chemists and physicists since lasers became widely available to the research community.^{1,2} Several pioneering control methods work by producing, guiding, and interfering wavepackets on the potential energy surface (PES) with laser pulses.^{3–6} A drawback of these methods is that they require detailed knowledge of the system to be controlled, which is not always possible for complex molecules and intense, broadband, laser pulses. Closed-loop feedback methods⁷ using modern techniques for shaping ultrafast lasers pulses^{8–14} circumvented the necessity of finding an appropriate control pulse

from first principles and have been widely implemented.^{15–24} Ultrafast pulse shaping also allows systematic parameterizations of the laser pulse shape, thereby providing a method to, for example, probe the dynamics of laser–molecule interactions,^{25–29} manipulate charge oscillations,³⁰ produce pulse sequences for spectroscopy,³¹ or unravel quantum pathways.³²

Laser-induced unimolecular reactions involving bond cleavage and formation processes are an active area of study because they can reveal insights into the ways molecules rearrange to form new products.^{33–53} Unimolecular decompositions and reactions have traditionally been understood using a transition state on the multi-dimensional potential energy surface (PES) that may affect the rate

of a process. A standard example is a dissociation process that has to overcome a potential barrier associated with the transition state, although this is not the only application of the idea.⁵⁴ Usually, a reduced-dimension reaction coordinate links the initial state to the final state via a minimum energy path that goes through the transition state. This approximation has the advantage of dispensing with large portions of phase space, thereby making calculations much more tractable.

Implementation of closed-loop control in the strong-field regime^{55–57} introduces Stark shifting of the PES to the control toolbox, thereby providing the ability to directly alter the reaction coordinate and the transition state. Despite persistent problems with developing a general strategy for discerning the underlying control mechanisms,⁵⁸ the use of an adaptive search algorithm in combination with intense laser pulse shaping remains popular because it allows for a near-arbitrary manipulation of the PES and therefore many possible routes to control.²³ For example, the isomerization reaction $C_2H_2^{2+} \rightarrow C^+ + CH_2^+$ was enhanced by suppressing the barrier between the acetylene-like initial state and the vinylidene-like final state at the appropriate time.⁵⁹

Another way a bond-rearrangement reaction can occur in a polyatomic molecule is via the roaming mechanism.^{60–70} In the roaming process, a transient neutral atomic or molecular fragment explores the region of the parent molecule before reacting to form the final product. Roaming typically occurs when molecules are highly excited and thus are not restricted to minimum energy pathways.⁷¹ These highly excited states are easily accessed with exposure of the molecule to an intense laser pulse, and therefore, roaming is thought to be a common phenomenon that may have a role in such situations.^{61,72} In contrast to the numerous studies of roaming in excited neutral species, observations of roaming in polyatomic ions have only recently been predicted⁷³ and observed.^{74–76} From the coherent control perspective, manipulating the roaming motion offers a different way to control these reactions. In excited molecular species, this could be a useful alternative to manipulation of the minimum energy pathway.

In this article, we examine the application of strong-field control to the formation of H_3^+ from methanol, which is pictured in Fig. 1. The recent experimental and theoretical work of Ekanayake *et al.*⁷⁴ attributed the formation of H_3^+ in methanol to roaming of the H_2 moiety following double ionization. In this process, which is schematically illustrated in Fig. 1, a neutral hydrogen molecule from the methyl side of the parent molecule roams around the methanol dication until it captures an additional proton to form H_3^+ . The proton can come either from the methyl side of the dication, which we will call “local” roaming, or from the hydroxyl side, which we will call “extended” roaming. Earlier theoretical work by Nakai *et al.*⁴⁰ supports an interpretation similar to the one presented by Ekanayake *et al.*⁷⁴ The observation of nearly isotropic ejection of H_3^+ fragments^{33,34} was also taken as evidence that the CH_3OH^{2+} does not dissociate on a time scale much shorter than the rotational period of the molecule. Ekanayake and co-workers⁷⁴ used pump-probe experiments to estimate that the extended roaming process has a time constant of 244 ± 25 fs or about 2.5 times longer than the local formation process involving only the methyl side of the dication.

Yamanouchi and co-workers^{49,77} performed a different set of investigations into H_3^+ production from methanol, with the aim of

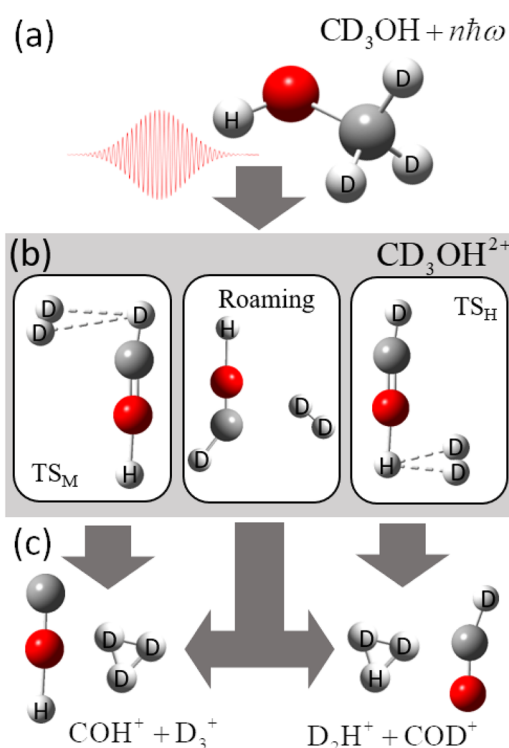


FIG. 1. A schematic illustration of the process explored in our experiment. Following double ionization of the neutral methanol by the ~ 40 fs laser pulse (a), the trihydrogen monocation may form. Panel (b) shows several proposed routes to trihydrogen monocation formation (see text). The goal of the experiment is to select between the two final products, shown in panel (c): D_3^+ or D_2H^+ . Recent coincidence COLTRIMS measurements show that these fragments are predominantly associated with the $D_3^+ + COH^+$ and $D_2H^+ + COD^+$ dissociation channels, respectively.⁷⁴ Depending on how the intermediate steps are viewed, this is equivalent to selecting between TS_M and TS_H or influencing the roaming dynamics.

using the time-dependent H_3^+ yield to probe the vibrational modes of the methanol monocation. In this pump-probe approach, the pump pulse drives single ionization and the probe pulse ionizes the monocation to the $H_3^+ + COH^+$ channel of the dication just above the H_3^+ appearance energy. As in the roaming scheme described in the previous paragraph, the creation of a neutral H_2 moiety leads to the formation of H_3^+ , but in this case, the reaction passes through one of two possible transition states: the lower transition state TS_M leads to the formation of H_3^+ from the methyl side of the dication (local), while the 0.31 eV higher transition state (TS_H) results in the neutral H_2 capturing a proton from the hydroxyl side of the dication (extended).

These two sets of experiments describe different routes to H_3^+ formation: through excited states of the dication⁷⁴ and through ionization of the monocation to lower-lying transition states in the dication.^{49,77} In addition, Wu *et al.*⁷⁸ recently demonstrated a monocation-only route to the formation of H_3^+ and neutral COH fragments, although we do not measure trihydrogen ion fragments in our experiment with the ~ 1 eV kinetic energy release (KER) they

observed. Regardless of the details of the intermediate step, illustrated in Fig. 1(b), we can experimentally distinguish between the local and extended mechanism by using the CD_3OH isotopologue of methanol, since detection of D_3^+ indicates local roaming or passage through TS_M , while detection of D_2H^+ signifies extended roaming or passage through TS_H . This point is illustrated schematically in Fig. 1(c).

Using the ratio of D_2H^+ to D_3^+ as our figure of merit, we explored the effect of the laser pulse shape on the relative amounts of local and extended H_3^+ formation mechanisms. In one set of measurements, we used an adaptive control scheme^{7,23,59,79} that couples feedback from velocity map imaging (VMI) to a learning algorithm, which seeks a pulse shape to enhance or suppress the D_2H^+ to D_3^+ ratio. In a second set of measurements, we systematically explored the ratio of D_2H^+ to D_3^+ as a function of the linear chirp and higher order dispersion terms of the laser pulse. Both sets of measurements showed variations in the D_2H^+ to D_3^+ ratio, although the adaptive control method identified the pulses that were most effective at manipulating the ratio. These optimized pulses, which have some similar time-domain structures, produce small changes in the momentum of the D_2H^+ and D_3^+ fragments. We examine the optimized pulse shapes and the associated photofragments for clues to how the control is accomplished.

II. EXPERIMENTAL METHOD

This experiment uses shaped laser pulses to ionize gas-phase methanol and initiate H_3^+ formation. Velocity map imaging (VMI) is used to detect the resulting photofragments. The goal of the experiment is to find a pulse shape that enhances the relative production of trihydrogen cations via local (D_3^+) or extended (D_2H^+) processes in CD_3OH .⁸⁰ In one approach, the laser pulse shapes are optimized using three-dimensional momentum based feedback derived from the VMI data to drive an adaptive learning algorithm.^{59,79} In a second approach, the laser pulse shape is systematically scanned through a reduced set of parameters, while the $\text{D}_2\text{H}^+/\text{D}_3^+$ ratio, obtained from the VMI data, is monitored.

The shaped ultrafast laser pulses are produced using an amplified Ti:sapphire laser, where an acousto-optical programmable

dispersive filter (AOPDF⁹) is placed between the oscillator and multi-pass amplifier. We only use the AOPDF to control the spectral phase of the laser. To produce the near-Fourier-transform-limited (TL) laser pulse, we apply a phase to compensate for higher-order dispersion accumulated during the propagation to our experimental chamber. The typical TL pulses used in the experiment had a pulse energy of 0.015 mJ following attenuation, a duration of 38–43 fs full-width at half-maximum (FWHM) in intensity, and a center wavelength of approximately 765 nm. After focusing by a $f = 75$ mm spherical mirror, the peak intensity was approximately 5×10^{14} W/cm² for the TL pulse with 0.015 mJ. Pulse characteristics were determined using a second harmonic generation frequency-resolved optical grating (SHG FROG).⁸¹

Methanol is introduced into the vacuum system (base pressure 1×10^{-10} Torr) through an effusive jet⁸² following a few freeze–pump–thaw cycles. The microchannel plates that detected the photofragments emerging from the VMI spectrometer^{79,83,84} were fully powered only for times that corresponded to the mass-to-charge ratio of the photofragment of interest. For each trial pulse, separate images of the D_2H^+ and D_3^+ ions are acquired. The raw VMI data are inverted 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.*⁷⁹ Background subtraction and image inversion are done “on-the-fly” as the images are recorded. Both D_2H^+ and D_3^+ form shells in momentum space and thus rings on the inverted VMI slice, as shown in Fig. 2. By defining regions of interest on the inverted momentum slice and evaluating the yield within those regions, the figure of merit used for feedback is obtained. Since the D_2H^+ channel is less likely than the D_3^+ channel (see Fig. 3), the data acquisition time for the D_2H^+ ions was set to be ten times longer than for the D_3^+ ions so that similar statistics were obtained for both ions before the evaluation of the $\text{D}_2\text{H}^+/\text{D}_3^+$ ratio.

As the pulse intensity is increased beyond the region for which we report data, we see additional features appearing in the ion distributions. As higher charge states of the parent are involved, both C^{2+} and O^{3+} could overlap the mass-to-charge ratio of D_2H^+ or D_3^+ , respectively. The TL intensity is kept low enough to minimize these

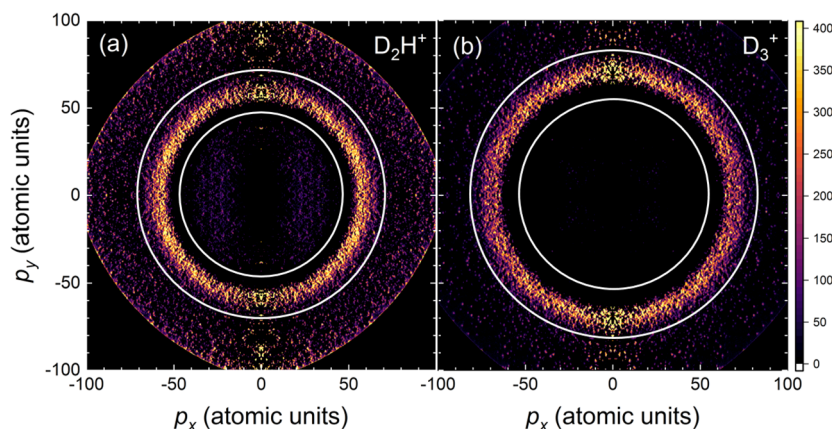


FIG. 2. A slice through the momentum distributions of (a) D_2H^+ and (b) D_3^+ obtained with TL pulses at an intensity of 4×10^{14} W/cm². The circles indicate the region from which the ion yield, and thus the $\text{D}_2\text{H}^+/\text{D}_3^+$ ratio, was evaluated. The laser polarization is in the y -direction in both figures. These images were obtained with exposure times of 9 s for D_3^+ and 90 s for D_2H^+ , which mimics the conditions used in the control measurements. The linear color scale expresses ion yield in arbitrary units.

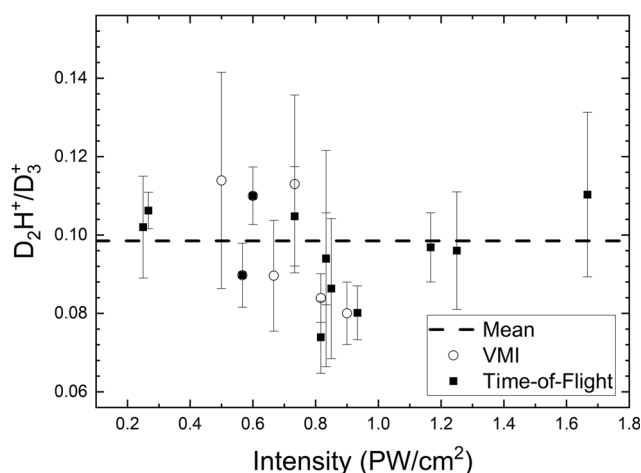


FIG. 3. The measured ratio of D_2H^+/D_3^+ as a function of intensity. For the points labeled VMI (open circles), the ratio is obtained during the adaptive control experiment. Specifically, after each generation of trial pulses, a TL pulse is loaded and the D_2H^+/D_3^+ ratio is measured. The error bars represent the standard deviation of this set of TL measurements. However, for the case of the points labeled time-of-flight (filled squares), specific single measurements of D_2H^+/D_3^+ were made by evaluating the ion yield at $m/q = 5$ and $m/q = 6$. Here, the error bars represent the statistical uncertainty in the ion yields.

contributions, and the ability to angularly resolve the fragmentation, as shown in Fig. 2, further allows us to see when any C^{2+} and O^{3+} begin to contribute to the spectra. Specifically, at the lower intensities used in the measurements, both the D_2H^+ and D_3^+ fragments have no strong angular dependence, which is consistent with the CD_3OH^{2+} parent being long-lived compared to its rotational period.^{33,34,85} In contrast, when higher charge states of other ions appear, such as C^{2+} , these ions tend to be ejected along the laser polarization direction.

In the closed-loop control scheme, the D_2H^+/D_3^+ ratio is used as the control objective, and this ratio is evaluated for an initial population of random pulse shapes. The pulse shapes are then optimized using a genetic algorithm, as described in previous publications.^{59,79} In the present experiment, the pulse was parameterized in the frequency domain and controlled via 16 spectral phase “genes” spread over the oscillator bandwidth. The number of genes was selected to keep the search space reasonably sized. Spectral phases between adjacent “gene” values were filled in using linear interpolation. Generations consisted of 30–50 trial pulses and the searches usually lasted from 10 to 20 generations. To penalize situations with large control objectives but small signal size, an offset was added to the denominator of the D_2H^+/D_3^+ ratio. The size of the offset was set to 10% of the D_3^+ yield measured with TL pulses.

After the closed-loop routine completed, the optimized pulse was characterized using SHG FROG. Since SHG FROG cannot determine the time-order of the pulse, we use our knowledge of the phases applied by the AOPDF to resolve any ambiguity about the time direction in the retrieved FROG data.^{81,86}

An alternative approach to finding a useful pulse shape is to conduct a systematic search over the phase space of the pulse characteristics (see, e.g., Lev *et al.*⁸⁷ or Nairat *et al.*⁸⁸). This is only practical if the parameter space is reduced. The electric field of the laser can

be characterized in the time domain as¹²

$$E(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{E}(\omega) e^{-i\omega t} d\omega, \quad (1)$$

where $\tilde{E}(\omega) = A(\omega)e^{-i\varphi(\omega)}$ is the complex electric field in the spectral domain defined in terms of the spectral amplitude, $A(\omega)$, and the spectral phase, $\varphi(\omega)$. This phase can be expanded as a Taylor series about ω_0 , the central frequency of the laser pulse, as

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

While $\varphi^{(0)}$ is an overall constant and $\varphi^{(1)}$ is a time delay for all the frequencies in the pulse, the higher order terms are associated with pulse dispersion. The $\varphi^{(2)}$ term corresponds to the second-order dispersion (i.e., linear chirp). Third-order dispersion, $\varphi^{(3)}$, causes a pedestal either before or after the main pulse, depending on the sign, and the fourth-order dispersion, $\varphi^{(4)}$, results in a pedestal appearing on both sides of the main pulse.^{87,88} In this systematic search, we scanned the linear chirp and third-order dispersion for three values of fourth order dispersion, recording the D_2H^+/D_3^+ ratio for each set of phase parameters. To verify that the applied pulse shapes match our expectations for particular values of $\varphi(\omega)$, we measured a few of these pulses with the same SHG FROG as used to characterize the pulses optimized using the closed-loop approach.

III. RESULTS AND DISCUSSION

Previous studies determined that H_3^+ formation from methanol predominantly occurs following double ionization,^{36,40,49,74,89} although the double ionization may be either direct^{40,74} or sequential.⁴⁹ As shown in Fig. 3, our measurements of the D_2H^+/D_3^+ ratio, taken with ~40 fs FWHM TL pulses, had a mean value of 0.099 ± 0.015 over the range of intensities measured. Note that this ratio, which is based on a mass-specific yield from our VMI data or ion-yields taken directly from a current-mode time-of-flight measurement, is not as rigorously defined as can be done in a coincidence experiment, where a charge-state specific branching ratio may be obtained. Still, the present result is consistent with the previously reported coincidence (COLTRIMS⁹⁰) measurements for pulses with slightly shorter durations and similar intensity.⁷⁴ The D_2H^+/D_3^+ ratio shown in Fig. 3 is reasonably close to the theoretical ratio of $D_2H^+/D_3^+ = 0.12$ predicted by Nakai *et al.*⁴⁰ More importantly, the D_2H^+/D_3^+ ratio is essentially unchanged with pulse intensity, and thus any observed changes are not the result of this “trivial”⁵⁵ parameter.

The results of adaptive control optimization trials are displayed in Table I for different pulse energies. We characterize the effectiveness of the control using the quantity,

$$\alpha = \frac{[D_2H^+/D_3^+]_{opt}}{[D_2H^+/D_3^+]_{TL}}, \quad (3)$$

where $[D_2H^+/D_3^+]_{opt}$ is the maximum value of the control objective obtained with the adaptive learning algorithm and $[D_2H^+/D_3^+]_{TL}$ is

TABLE I. Results of the adaptive control searches. For each pulse energy, the optimized ratio D_2H^+/D_3^+ is compared to the same ratio obtained with a TL pulse [α in Eq. (3)]. The third column shows a measure of the significance of the result and is calculated as the difference between the optimized and TL ratios divided by the standard deviation of the measurement of the TL ratio, as given by Eq. (4) (see text).⁹¹

Pulse energy (mJ)	α	δ
0.015	2.1 ± 0.5	4.5 ± 0.8
0.017	1.9 ± 0.2	9.9 ± 0.8
0.018	2.0 ± 0.1	14.9 ± 0.8
0.020	2.0 ± 0.3	6.3 ± 0.8
0.027	2.4 ± 0.2	14.1 ± 0.8

the average of the control objective obtained with TL pulses measured between generations of the optimization. On average, the optimized pulses increased the value of the control objective by $\alpha = 2.1 \pm 0.2$ times compared to the TL value. In other words, the extended mechanism for trihydrogen monocation formation was increased by a factor of about two compared to the local mechanism. The significance of these results with respect to fluctuations in the control objective over the course of the experiment is characterized using

$$\delta = \frac{[D_2H^+/D_3^+]_{opt} - [D_2H^+/D_3^+]_{TL}}{\sigma_{TL}}, \quad (4)$$

where σ_{TL} is the standard deviation of the control objective as measured with TL pulses between each generation of trial pulses. As shown in Table I, δ is generally smaller for lower pulse energies, a factor that is linked to the overall signal size and statistical uncertainties. While the statistics of smaller signals can be compensated for by using longer exposure times for each trial pulse, eventually this compensation is limited by the long-term stability of the laser.

We also attempted to optimize the inverse control objective (i.e., the D_3^+/D_2H^+ ratio), but the maximum value of $\beta = \frac{[D_3^+/D_2H^+]_{opt}}{[D_3^+/D_2H^+]_{TL}}$ we obtained was approximately 1.0 within statistical uncertainties. In these cases, pulses that optimized β were very similar to TL pulses, and thus, we conclude that a shorter duration pulse tends to favor D_3^+ production over D_2H^+ .

Most of the remainder of this article will focus on efforts to increase the D_2H^+/D_3^+ ratio. As stated earlier, we determine the value of the control objective based on the ion yield within the areas identified on the momentum distributions shown in Fig. 2, and so we can only comment on the angular- and energy-resolved trihydrogen cations and not on any associated molecular fragments. Thus, multiple dissociation pathways with similar kinetic energy release (KER) and angular distributions might contribute to the observed yield. For example, we have no way of distinguishing trihydrogen cations produced from different ionization states of the parent methanol molecule or to know if the D_3^+ and D_2H^+ ions result from two-, three-, or four-body breakup of the parent molecular ion.

Previous work at a variety of laser parameters,^{36,40,49,74,89} however, suggests that the primary channel for the production of H_3^+ from CH_3OH is $CH_3OH^{2+} \rightarrow H_3^+ + COH^+$. Furthermore, only

two-body breakup of the methanol dication leads to significant formation of the trihydrogen monocation at laser intensities similar to those used in this work.⁷⁴ In addition, the data in Fig. 4 do not contain any fragments with a KER distribution peaked around 1.0 eV, which would match what Wu *et al.*⁷⁸ reported for single ionization leading to $H_3^+ + COH$. Our results, shown in Figs. 3 and 4, also agree with the D_2H^+/D_3^+ ratio^{33,74,85} and the KER for two-body breakup^{49,74} from previous measurements of $CH_3OH^{2+} \rightarrow H_3^+ + COH^+$ at similar laser intensities. Collectively, it seems likely that we are also mostly observing either the $CD_3OH + n\omega \rightarrow CD_3OH^{2+} \rightarrow D_3^+ + COH^+$ or the $CD_3OH + n\omega \rightarrow CD_3OH^{2+} \rightarrow D_2H^+ + COD^+$ processes, which are distinguished from each other by the detection of D_2H^+ or D_3^+ ions.

A. Analysis of photofragment dynamics

While we can identify the final states that are associated with local or extended trihydrogen formation processes, experimentally distinguishing roaming of D_2 in an excited dication from sequential ionization leading to a minimum energy transition state dissociation pathway is difficult. For example, in order to confirm that the roaming mechanism was responsible for the anomalous⁶⁰ dissociation of formaldehyde⁹² (H_2CO), the energy carried by the products⁶⁰ had to be measured following a specific laser-induced excitation. In the present experiments, we do not have the ability to precisely define the initial state of the methanol dication.

Furthermore, although the initial ionization step and amount of dication excitation are different in the previous works,^{49,74} once the dication state is reached, the two explanations for the formation of trihydrogen cations^{49,74} differ mainly in the details of the dynamics associated with the neutral D_2 moiety. In both previous studies, these details were explored theoretically. In the transition state view,⁴⁹ the D_2 remains weakly bound to the $DCOH^{2+}$ through the charge induced dipole moment of the D_2 , and the two transition states (TS_M and TS_H) represent different geometrical structures, with TS_H located 0.31 eV above TS_M . In the roaming picture,⁷⁴ the dication also evolves through a geometry that has two methyl-side hydrogen atoms close together, forming D_2 . The D_2 then roams around the remaining $DCOH^{2+}$, abstracting a proton from one side or the other. Importantly, in this roaming picture, the final state is determined by kinematics rather than thermodynamics.⁷⁴

While we cannot observe the dynamics of the intermediate D_2 moiety directly, if the control occurs due to the strong-field modification of the transition states, the results might be visible as changes in the photofragment KER distribution, as observed in previous control experiments with acetylene.⁵⁹ On the other hand, changing the D_2H^+/D_3^+ ratio by altering the trajectory of the excited D_2 during the roaming process need not produce different KER distributions from the TL and optimized pulses. As a result, the fragment KER distributions may reveal if the observed control of the D_2H^+/D_3^+ ratio occurs due to the influence of the roaming process or manipulation of the transition state energies. The ion yields as a function of KER from our measurements are shown in Fig. 4. Since we do not measure ions in coincidence, the KER is calculated assuming two-body fragmentation of the transient CD_3OH ion.

Unfortunately, from an interpretation perspective, the KER distributions shown in Fig. 4 do not uniformly shift in a manner

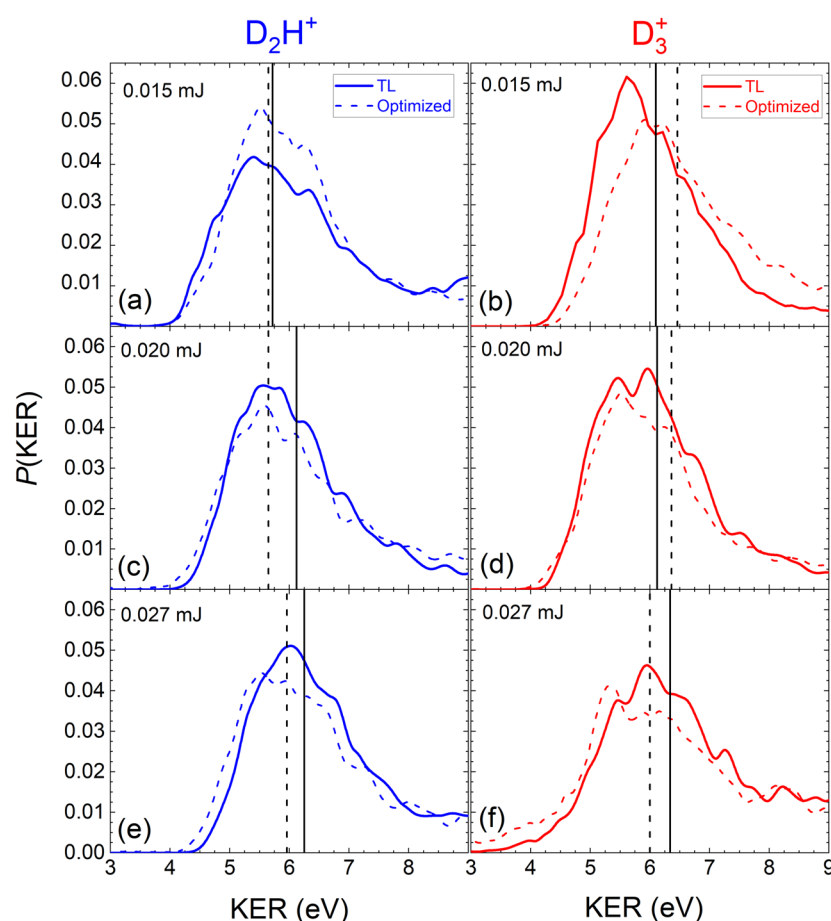


FIG. 4. Comparison of measured probability of dissociation as a function of KER for TL (solid) and optimized (dashed) laser pulses for different pulse energies as labeled on the panels. The KER value is calculated from the VMI data assuming two-body fragmentation. The left (blue) column shows D_2H^+ ions, and the right (red) column shows D_3^+ ions, presumably resulting from $CD_3OH + n\omega \rightarrow CD_3OH^{2+} \rightarrow D_2H^+ + COD^+$ and $CD_3OH + n\omega \rightarrow CD_3OH^{2+} \rightarrow D_3^+ + COH^+$, respectively. The solid (TL) and dashed (optimized) black vertical lines mark the values of the average KER.

consistent with a simple potential barrier suppression picture. For the D_2H^+ KER distributions shown in the left column of Fig. 4, the average KER from TL pulses is always higher than the average KER measured from the optimized pulses. The difference becomes larger at 0.020 mJ and 0.027 mJ than at 0.015 mJ pulse energy, where the TL and optimized pulses produce nearly the same average KER. The difference in the observed KER could be a signature of a time-dependent energetic suppression of the transition state leading to D_2H^+ , and thus a different KER. In contrast, for the D_3^+ (right column) measurements, the lower two pulse energies produce smaller average KER values with TL pulses than the optimized pulses. This can be interpreted as showing the local pathway must overcome a higher barrier when the optimized pulse is present. This relationship, however, flips at the highest pulse energy.

In conclusion, these small differences in the KER distributions might be hints that the local vs extended control of H_3^+ formation occurs via manipulation of the energy of the transition states, but the collective results do not present a uniform picture. The effects are particularly suggestive of transition state manipulation at the two lower pulse energies, where the optimized pulses raise the average KER for the D_3^+ ions while simultaneously lowering the average KER for D_2H^+ ions. At lower pulse energy, it is more likely

that lower-lying states of the dication might be populated, making manipulation of the transition states more effective than when the D_2 moiety is highly excited. We also note that drawing a direct comparison between pulse energy and the amount of possible PES modification is difficult due to the complexities of the optimized pulses and the associated field strengths.

B. Analysis of optimized pulse characteristics

In addition to analyzing the photofragment dynamics, we can also inspect the optimized pulse characteristics for clues about the observed control. We note that previous pulse shaping results⁵¹ have shown that the presence of a $3\pi/4$ spectral phase step can influence the H_3^+ yield from methanol. Since those studies used the CH_3OH isotopologue of methanol, they were not focused on differentiating the local and extended mechanisms leading to H_3^+ formation. Figure 5 shows a representative SHG FROG trace of a pulse optimized to enhance the D_2H^+/D_3^+ ratio. The temporal and spectral intensities and associated phases obtained from the measured SHG FROG trace are shown in Fig. 6. In the frequency domain [Fig. 6(b)], the optimized pulses had little similarity beyond the general envelope of the spectral bandwidth associated with the laser. For each individual optimized pulse, the measured spectral phases were

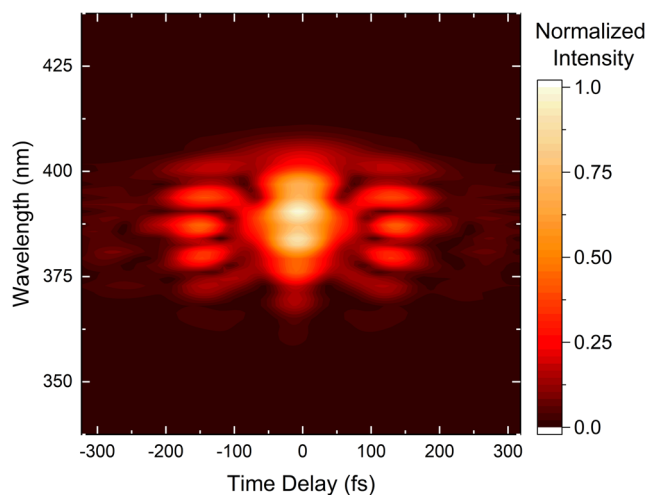


FIG. 5. The retrieved SHG FROG trace for a pulse optimized to increase the D_2H^+/D_3^+ ratio at a pulse energy of 0.018 mJ.

complex and different in all cases. In contrast, the time-domain characteristics have some similar features across the pulses, as shown in Fig. 7.

The two most notable similarities in the optimized pulses are the extended duration of the main pulse (45–60 fs FWHM in intensity) and the presence of a secondary pulse trailing the main pulse. The secondary pulse was displaced from the peak of the main pulse by about 110–210 fs. While some of the pulses [see Figs. 7(b) and 7(c)] have a leading structure as well, all of the observed optimized pulses have the trailing structure.

How might control due to the secondary pulse structure be rationalized using either a roaming or a transition state picture

of the trihydrogen formation? When control is exerted by manipulating the transition state, the secondary pulse could be timed to selectively drive population through one transition state or the other. To control the roaming mechanism, the pulse would need to influence the D_2 trajectory. We examine each of these possibilities below.

In the roaming case, the first step of the process is the double ionization of methanol. The electronic structure calculations done by Ekanayake *et al.*⁷⁶ show that the double ionization leads to a localization of charge near the oxygen atom, which tends to shift the electron density away from the methyl group, thus lengthening the C–D bonds. Nakai *et al.*⁴⁰ reported a similar elongation in their theoretical work, which assumes that the electronic ground state of CD_3OH^{2+} was populated via a vertical transition onto an undistorted potential energy surface. This elongation can lead to the formation of a neutral D_2 moiety. From this point, another deuteron is removed from the methyl side, forming D_3^+ , or a proton is removed from the hydroxyl side, forming D_2H^+ .

This situation results in complex trajectories, which sometimes encounter the proton/deuteron needed to form either D_2H^+ or D_3^+ . Previous work⁷⁴ has shown that a longer roaming duration is more likely to be associated with the extended roaming leading to the formation of D_2H^+ . The difference in roaming times can be interpreted as a consequence of the initial configuration of the molecule; the D_2 is simply in closer proximity to the methyl-side deuterium than the hydroxyl-side hydrogen atom and so local formation of D_3^+ occurs on a shorter time scale than extended formation of D_2H^+ . Similarly, the pulses that maximize the D_2H^+/D_3^+ ratio have a longer duration than the TL pulses that maximize the D_3^+/D_2H^+ ratio. As will be discussed in Sec. III C, the optimized pulses have structure that appears important to their ability to enhance the D_2H^+/D_3^+ ratio. A rationale relating the roaming process and the pulse structure is not evident, although we speculate that the presence of the laser field could allow the recombination of the roaming D_2 and

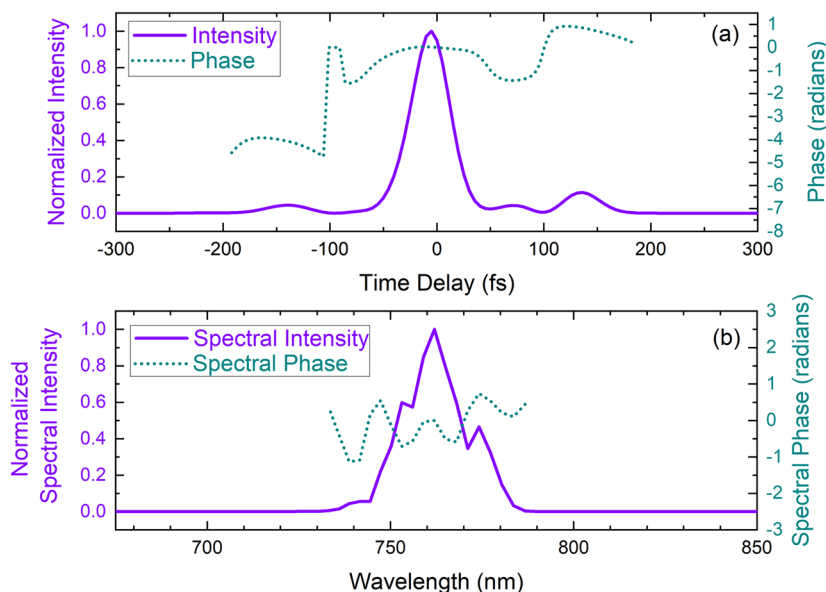


FIG. 6. The temporal intensity and phase (a) and spectral intensity and spectral phase (b) extracted from the SHG FROG measurement shown in Fig. 5.

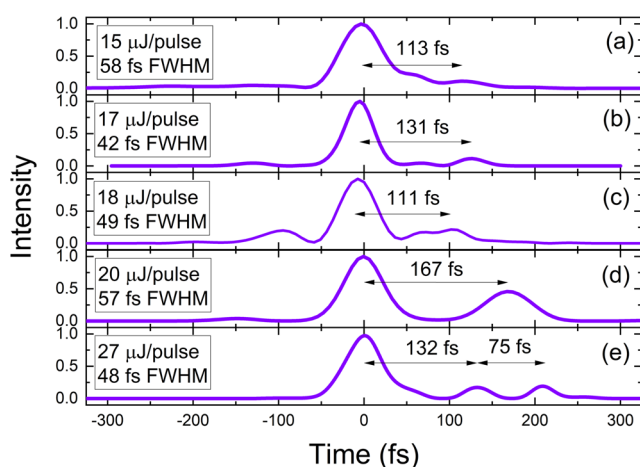


FIG. 7. Measured intensity vs time for a selection of the optimized pulses listed in Table I. As discussed in the text, the spacing of the secondary pulse seems to be similar to multiples of the C–O stretching period. The FWHM reported on these figures is for the main pulse.

a free hydrogen atom. Additional study is needed to explore this question.

As described previously, controlling the extended to local trihydrogen formation ratio through manipulation of transition states might be related to the population of lower-lying dication states. The process explored by Ando *et al.*⁴⁹ starts when the neutral methanol is singly ionized with a few-cycle near-IR pulse, launching a vibrational wavepacket on the CH_3OH^+ surface. A second few-cycle near-IR pulse then ionizes the monocation further, populating the $\text{CH}_3\text{OH}^{2+}$ dication that eventually dissociates to form H_3^+ passing through either TS_M or TS_H . They found that the H_3^+ yield showed periodic enhancements starting at 58 fs and repeating every 38 fs thereafter for hundreds of femtoseconds. They note that this can be related to the vibrational frequency of the C–O stretch in CH_3OH^+ of 895 cm^{-1} , which corresponds to a period of 37.2 fs.⁹³ In their explanation,⁴⁹ when the second ionization occurs near the inner turning point of the C–O stretch, lower-lying states of $\text{CH}_3\text{OH}^{2+}$ are preferentially populated, leading to enhanced H_3^+ production. The major point of their work was that the time-dependent H_3^+ yield could be used to explore the vibrational modes of the monocation.

In our experiment, we are interested in how the optimized pulses might take advantage of these timings to influence the $\text{D}_2\text{H}^+/\text{D}_3^+$ ratio. Three of the pulses [Figs. 7(b), 7(d), and 7(e)] have secondary peaks that would be near the inner turning point of the C–O stretch (relatively more population of lower-lying channels of $\text{CD}_3\text{OH}^{2+}$). While Ando *et al.*⁴⁹ showed that this leads to more overall formation of trihydrogen monocations, since TS_M is lower than TS_H by 0.31 eV, it seems unclear how increased overall population of these states enhances the $\text{D}_2\text{H}^+/\text{D}_3^+$ ratio. Conversely, the other two pulses, shown in Figs. 7(a) and 7(c), have secondary peaks at locations very near the outer turning point of the C–O stretch, which should preferentially populate higher-lying channels of $\text{CD}_3\text{OH}^{2+}$ and decrease the overall amount of trihydrogen monocation production. Since TS_H is higher than TS_M , one could argue that D_2H^+

might be enhanced relative to D_3^+ for the pulses in Figs. 7(a) and 7(c), but this would be inconsistent with the timings in Figs. 7(b), 7(d), and 7(e).

There are other inconsistencies that arise when trying to relate the timing of the C–O stretch to our optimization results. First, the C–O stretch in CD_3OH is 985 cm^{-1} , which corresponds to a period of 34 fs.⁹⁴ This period does not match our results as well as the longer period of CH_3OH , although it is not clear how the ionic nature of the molecule might alter the C–O stretch frequency. Second, the few-cycle pulses used by Ando and co-workers provide better time resolution than our longer pulses in which several cycles near the peak will have similar intensity. In light of this, the close match between the C–O stretch period and the observed peak structure seems unusual. Finally, in our results, the secondary pulses are much smaller in amplitude than the main pulse. This leads one to believe that double ionization seems more likely to occur during the main pulse rather than an initial ionization followed by a second ionization at the time of the secondary pulse.

In summary, while the appearance of a secondary pulse at times when the C–O vibration is near a turning point seems to be a consistent feature of our pulses, it is unclear how this feature might enhance the $\text{D}_2\text{H}^+/\text{D}_3^+$ ratio, the timings do not match the C–O stretch frequency for CD_3OH^+ exactly, and the differences in the pulse amplitudes are suggestive of direct double ionization rather than sequential ionization. Despite these points, the time structure remains intriguing and cannot be entirely discounted as an element of a control process within the transition state picture. If the secondary pulses are influencing the $\text{D}_2\text{H}^+/\text{D}_3^+$ ratio through manipulation of transition state(s), it may be that there is a temporal relationship between the initial double ionization step and subsequent transition state alteration(s) related to the half periods of the C–O stretch. Further exploration of the role of the secondary pulses may require additional theoretical work.

C. Analysis of systematic pulse shape changes

Since the FWHM duration of the main portion of the pulses that optimize the $\text{D}_2\text{H}^+/\text{D}_3^+$ ratio, shown in Fig. 7, is longer than the TL pulses, it is possible that this extended duration is the control parameter rather than just a consequence of the increased pulse complexity. To examine this possibility, we reduced the bandwidth of the pulse before the AOPDF, thereby lengthening the TL pulse (to ~60 fs FWHM in intensity) and reducing the complexity of any optimized pulse the algorithm might identify. If the duration of the roaming mechanism is the main factor influencing D_2H^+ formation, then a longer pulse duration might be as effective as the pulses obtained in the previous optimization with a spectral bandwidth of ~30 nm.

The results of this reduced bandwidth adaptive search are shown in Fig. 8. Here, the optimized pulse is essentially TL with a FWHM of 60 fs and does not contain any notable secondary peaks. Furthermore, as shown in the inset, the adaptive search cannot find any pulse shapes that significantly improve on $\alpha = 1$. This suggests that the higher values of α obtained via optimization of the full-bandwidth pulses owe their effectiveness to some combination of the complicated phase and the associated time-domain

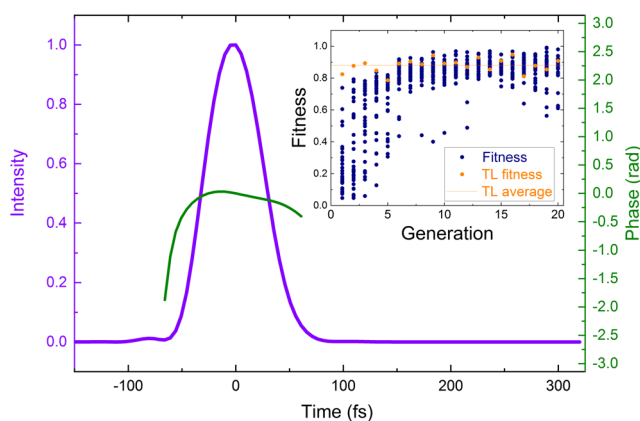


FIG. 8. The intensity and phase of a pulse optimized to enhance D_2H^+/D_3^+ . In this optimization trial, the TL bandwidth is reduced to ≈ 20 nm from the usual ≈ 30 nm. The result is an optimized pulse that has essentially the same characteristics as the TL pulse. The inset shows the progress of the adaptive control algorithm as a function of the generation of the trial pulses. The blue points are the value of the D_2H^+/D_3^+ ratio for each trial pulse, and the orange points represent the same ratio measured with a TL pulse.

structure observed in Figs. 5 and 7, and not simply to the pulse duration. Stated in traditional coherent-control language, the increased bandwidth allows for additional pathways to indistinguishable final states, allowing more possibilities for interference to influence the outcome.

In adaptive strong field control,²³ the search algorithm has a great deal of freedom to change the pulse characteristics and therefore can arrive at high levels of pulse complexity. In our case, this is accomplished by manipulation of the spectral phase of the pulse.

An alternative approach is to parameterize the spectral phase in terms of some discrete parameters that might capture some of the important pulse characteristics and relate them to the control objective. Following this approach, we systematically scanned the second-, third-, and fourth-order dispersion [see Eq. (2)] while recording the D_2H^+/D_3^+ ratio in the same manner described for the adaptive control study. These results are shown in Fig. 9.

Systematic addition of dispersion to the laser pulse increases the D_2H^+/D_3^+ control objective from the TL value. The maximum value of the control objective measured in the scan of the dispersion parameters is again approximately a factor of two greater than the D_2H^+/D_3^+ ratio measured with the full bandwidth TL pulse. This maximum value occurs at the edges of our scan, where both the second- and third-order dispersion are either both negative or both positive. When the fourth-order dispersion is set to zero, we are able to scan the second- and third-order dispersion further without exceeding the AOPDF capabilities. In this case, the same trend continues as far as we are able to probe. This symmetric nature of the dispersion results suggests that the sign of the dispersion is not as important as the duration of the pulse. Changing the fourth-order dispersion influences how rapidly the ratio increases as the second- and third-order dispersion moves away from zero but has little effect on the overall magnitude of the change of the D_2H^+/D_3^+ ratio.

As indicated by Fig. 9, choosing specific values of the pulse dispersion can increase the D_2H^+/D_3^+ control objective as much as the adaptive search strategy. However, if the overall signal size is considered, the dispersion scan is less effective than the adaptive control. Figure 10 displays a comparison between the overall D_2H^+ and D_3^+ yield in the adaptive search and the dispersion scan. This illustrates that the D_2H^+/D_3^+ ratio increases as both the individual D_2H^+ and D_3^+ yields decrease, but the D_3^+ yield decreases more than the D_2H^+ yield in some areas, leading to an increase in the D_2H^+/D_3^+ ratio. In

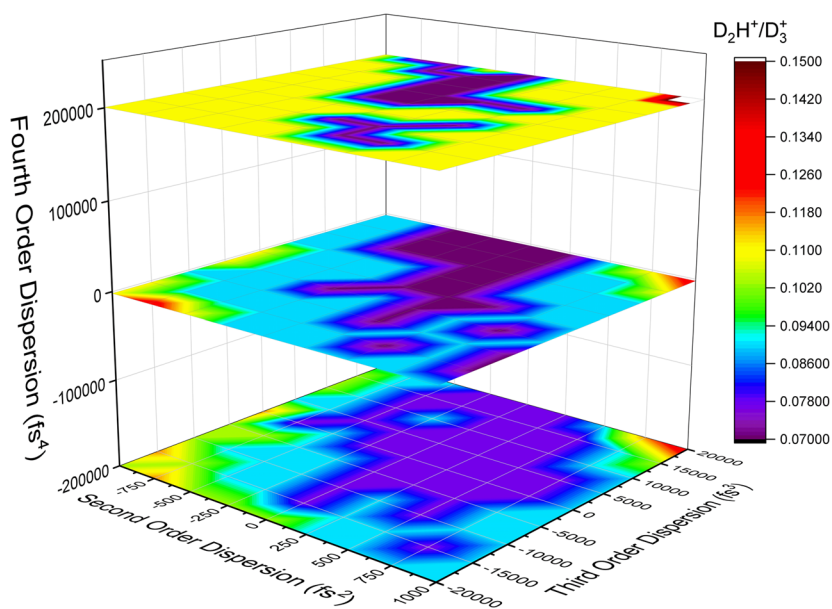


FIG. 9. The D_2H^+/D_3^+ ratio as a function of second- and third-order dispersion for three values of fourth-order dispersion. The spectral phase parameters are described using the Taylor series given in Eq. (2). The $(0 \text{ fs}^2, 0 \text{ fs}^3, \text{ and } 0 \text{ fs}^4)$ point on the plot corresponds to the dispersion parameters that give the shortest pulse in the experimental chamber.

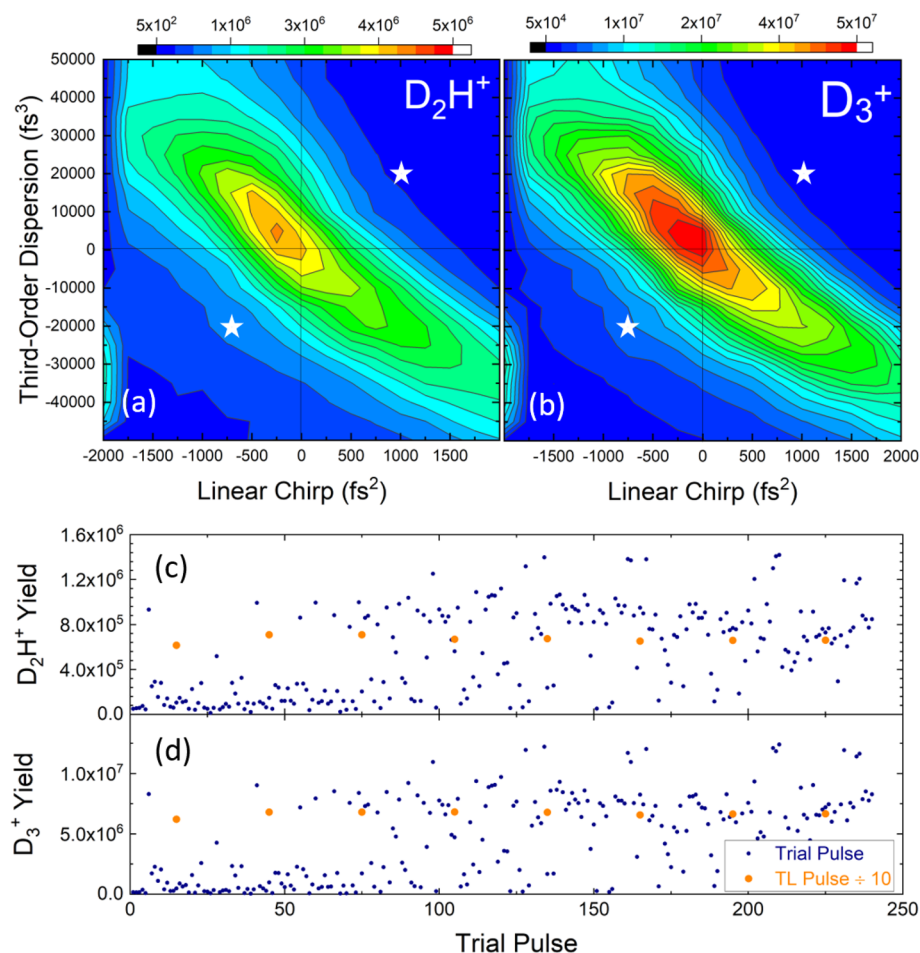


FIG. 10. The yield of D_2H^+ (a) and D_3^+ (b) fragments as a function of second- and third-order dispersion at zero fourth order dispersion. This contains the yields used to make the middle distribution of Fig. 9 but shows a larger range of linear chirp and third-order dispersion. The horizontal and vertical lines mark the location of the TL pulse in this representation. The peak of the D_2H^+ yield is further away from the transform limited value and drops more slowly than the D_3^+ yield, showing why the maximum of the D_2H^+/D_3^+ ratio peaks at the edges of the scan shown in Fig. 9, at locations marked by the white stars. At these points, the D_2H^+ and D_3^+ yields have dropped by about a factor of 20. The yields of D_2H^+ (c) and D_3^+ (d) as a function of the trial pulses used in an optimization run. By the eighth generation of optimization (starting around pulse 225), these pulses produce yields at or above 10% of the TL pulse for both ions.

contrast, as illustrated in Figs. 10(c) and 10(d), while the initial trial pulses in an adaptive search result in small signal, after several generations the signal size has reached 10% of the TL size for D_2H^+ and D_3^+ where the signals tend to remain for the rest of the search.

Thus, we can conclude that the secondary pulse observed when the control objective is maximized using an adaptive search (Fig. 7) is more effective at increasing the control objective while simultaneously preserving the overall yield than the results from the dispersion scan (Fig. 9). Both the dispersion scan and the reduced bandwidth adaptive search suggest that simply lengthening the pulse duration does not produce pulses that are as effective as the adaptive search results. The most consistent feature of the optimized pulses is the secondary pulses, which cannot be entirely reproduced by the higher order dispersion terms. A different choice of parameters for the systematic scan, such as ones that were designed to reproduce multiple pulse structures, might have been more effective. The collective results described in this article illustrate the experimental choice that must be made between a systematic search of a small pulse parameter space vs guided searches of a large pulse parameter space. Understanding how to better parameterize pulses for different control objectives would be a useful advance for these sorts of control problems.

While the optimized pulses all have complex spectral features, these spectral traits are not consistently expressed and show considerable variation from pulse to pulse. It remains possible that these spectral features are important for the control. Principal component analysis (PCA) is a tool that, when applied to the results of an adaptive search,^{95–97} can potentially simplify the description of the optimized pulse by expressing the pulse parameters in a different basis. When PCA is applied to the optimization trials reported in Table I, seven to nine of the possible 15 eigenvalues are relatively large, indicating that the pulse characteristics cannot be expressed in a simple manner using one or two orthogonal control directions. This suggests a complexity to the optimized pulses beyond the observed temporal structure.

IV. SUMMARY

Control of site-specific trihydrogen monocation formation following ionization of the CD_3OH isotopologue of methanol is demonstrated using two different pulse shaping approaches. While both an adaptive search strategy and a systematic scan of pulse dispersion parameters can increase the ratio of extended (associated with D_2H^+) to local (associated with D_3^+) formation of

trihydrogen cations by a factor of approximately two, the adaptive search is more efficient at changing the ratio while maintaining the overall trihydrogen monocation yield. The optimized pulse shapes have a similar secondary pulse trait in the time domain that is associated with the increase in the D_2H^+/D_3^+ control objective. Simply extending the pulse duration does not replicate the increase in the D_2H^+/D_3^+ control objective observed from the optimized pulses with a secondary pulse in the time-domain.

While the optimized pulses have clear advantages over the pulse shapes arrived at by other means, the question of how these optimized pulses selected between the formation of trihydrogen cations solely from the methyl side of the methanol parent or trihydrogen formation involving both the methyl and hydroxyl sides of the methanol parent cannot be definitively resolved by this experiment. It is possible, especially given the role of focal volume averaging, that more than one control process is at work. Theoretical investigations or pump-probe experiments with shaped pulses might provide more insight into the control mechanism.

AUTHOR'S CONTRIBUTIONS

N.I. and C.J.S. contributed equally to this work.

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REFERENCES

- M. Shapiro and P. Brumer, *Quantum Control of Molecular Processes* (Wiley VCH Verlag GmbH, 2011).
- M. Wollenhaupt, T. Bayer, and T. Baumert, "Control of ultrafast electron dynamics with shaped femtosecond laser pulses: From atoms to solids," in *Ultrafast Dynamics Driven by Intense Light Pulses: From Atoms to Solids, from Lasers to Intense X-Rays*, edited by M. Kitzler and S. Gräfe (Springer International Publishing, Cham, 2016), pp. 63–122.
- D. J. Tannor and S. A. Rice, *J. Chem. Phys.* **83**, 5013 (1985).
- D. J. Tannor, R. Kosloff, and S. A. Rice, *J. Chem. Phys.* **85**, 5805 (1986).
- P. Brumer and M. Shapiro, *Chem. Phys. Lett.* **126**, 541 (1986).
- K. Bergmann, N. V. Vitanov, and B. W. Shore, *J. Chem. Phys.* **142**, 170901 (2015).
- R. S. Judson and H. Rabitz, *Phys. Rev. Lett.* **68**, 1500 (1992).
- A. M. Weiner, *Rev. Sci. Instrum.* **71**, 1929 (2000).
- F. Verluise, V. Laude, Z. Cheng, C. Spielmann, and P. Tournois, *Opt. Lett.* **25**, 575 (2000).
- T. Brixner and G. Gerber, *Opt. Lett.* **26**, 557 (2001).
- M. Wollenhaupt, M. Krug, J. Köhler, T. Bayer, C. Sarpe-Tudoran, and T. Baumert, *Appl. Phys. B* **95**, 245 (2009).
- A. Monmayrant, S. Weber, and B. Chatel, *J. Phys. B: At., Mol. Opt. Phys.* **43**, 103001 (2010).
- A. M. Weiner, *Opt. Commun.* **284**, 3669 (2011).
- C. Schwarz, O. Hütter, and T. Brixner, *J. Opt. Soc. Am. B* **32**, 933 (2015).
- A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, and G. Gerber, *Science* **282**, 919 (1998).
- B. J. Pearson, J. L. White, T. C. Weinacht, and P. H. Bucksbaum, *Phys. Rev. A* **63**, 063412 (2001).
- J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, and M. Motzkus, *Nature* **417**, 533 (2002).
- N. Damrauer, C. Dietl, G. Krampert, S.-H. Lee, K.-H. Jung, and G. Gerber, *Eur. Phys. J. D: At., Mol. Opt. Phys.* **20**, 71 (2002).
- C. Daniel, J. Full, L. González, C. Lupulescu, J. Manz, A. Merli, v. Vajda, and L. Wöste, *Science* **299**, 536 (2003).
- T. Brixner, G. Krampert, T. Pfeifer, R. Selle, G. Gerber, M. Wollenhaupt, O. Graefe, C. Horn, D. Liese, and T. Baumert, *Phys. Rev. Lett.* **92**, 208301 (2004).
- T. Laarmann, I. Shchatsinin, A. Stalmashonak, M. Boyle, N. Zhavoronkov, J. Handt, R. Schmidt, C. P. Schulz, and I. V. Hertel, *Phys. Rev. Lett.* **98**, 058302 (2007).
- D. G. Kuroda, C. P. Singh, Z. Peng, and V. D. Kleiman, *Science* **326**, 263 (2009).
- C. Brif, R. Chakrabarti, and H. Rabitz, *New J. Phys.* **12**, 075008 (2010).
- L. Levin, W. Skomorowski, L. Rybak, R. Kosloff, C. P. Koch, and Z. Amitay, *Phys. Rev. Lett.* **114**, 233003 (2015).
- V. V. Lozovoy, X. Zhu, T. C. Gunaratne, D. A. Harris, J. C. Shane, and M. Dantus, *J. Phys. Chem. A* **112**, 3789 (2008).
- P. Hockett, M. Wollenhaupt, C. Lux, and T. Baumert, *Phys. Rev. Lett.* **112**, 223001 (2014).
- K. Misawa, *Adv. Phys.: X* **1**, 544 (2016).
- X. Xing, R. R. de Castro, and H. Rabitz, *J. Phys. Chem. A* **121**, 8632 (2017).
- T. Bayer, D. Gräfin, S. Kerbstadt, D. Pengel, K. Eickhoff, L. Englert, and M. Wollenhaupt, *New J. Phys.* **21**, 033001 (2019).
- T. Bayer, H. Braun, C. Sarpe, R. Siemering, P. von den Hoff, R. de Vivie-Riedle, T. Baumert, and M. Wollenhaupt, *Phys. Rev. Lett.* **110**, 123003 (2013).
- S. Roeding and T. Brixner, *Nat. Commun.* **9**, 2519 (2018).
- S. Mueller, J. Lüttig, P. Malý, L. Ji, J. Han, M. Moos, T. B. Marder, U. H. F. Bunz, A. Dreuw, C. Lambert, and T. Brixner, *Nat. Commun.* **10**, 4735 (2019).
- Y. Furukawa, K. Hoshina, K. Yamanouchi, and H. Nakano, *Chem. Phys. Lett.* **414**, 117 (2005).
- T. Okino, Y. Furukawa, P. Liu, T. Ichikawa, R. Itakura, K. Hoshina, K. Yamanouchi, and H. Nakano, *Chem. Phys. Lett.* **419**, 223 (2006).
- T. Okino, Y. Furukawa, P. Liu, T. Ichikawa, R. Itakura, K. Hoshina, K. Yamanouchi, and H. Nakano, *Chem. Phys. Lett.* **423**, 220 (2006).
- K. Hoshina, Y. Furukawa, T. Okino, and K. Yamanouchi, *J. Chem. Phys.* **129**, 104302 (2008).
- B. Jochim, A. Lueking, L. Doshier, S. Carey, E. Wells, E. Parke, M. Leonard, K. D. Carnes, and I. Ben-Itzhak, *J. Phys. B: At., Mol. Opt. Phys.* **42**, 091002 (2009).
- K. Hoshina, H. Kawamura, M. Tsuge, M. Tamiya, and M. Ishiguro, *J. Chem. Phys.* **134**, 064324 (2011).
- P. M. Kraus, M. C. Schwarzer, N. Schirmel, G. Urbasch, G. Frenking, and K.-M. Weitzel, *J. Chem. Phys.* **134**, 114302 (2011).
- K. Nakai, T. Kato, H. Kono, and K. Yamanouchi, *J. Chem. Phys.* **139**, 181103 (2013).
- N. Schirmel, N. Reusch, P. Horsch, and K.-M. Weitzel, *Faraday Discuss.* **163**, 461 (2013).
- N. Kotsina, S. Kaziannis, and C. Kosmidis, *Chem. Phys. Lett.* **604**, 27 (2014).
- H. Ibrahim, B. Wales, S. Beaulieu, B. E. Schmidt, N. Thiré, E. P. Fowe, É. Bisson, C. T. Hebeisen, V. Wanie, M. Giguère, J.-C. Kieffer, M. Spanner, A. D. Bandrauk, J. Sanderson, M. S. Schuurman, and F. Légaré, *Nat. Commun.* **5**, 4422 (2014).
- T. Ando, A. Shimamoto, S. Miura, K. Nakai, H. Xu, A. Iwasaki, and K. Yamanouchi, *Chem. Phys. Lett.* **624**, 78 (2015).
- N. Kotsina, S. Kaziannis, and C. Kosmidis, *Int. J. Mass Spectrom.* **380**, 34 (2015).
- H. Wu, S. Zhang, J. Zhang, Y. Yang, L. Deng, T. Jia, Z. Wang, and Z. Sun, *J. Phys. Chem. A* **119**, 2052 (2015).
- M. Kübel, R. Siemering, C. Burger, N. G. Kling, H. Li, A. Alnaser, B. Bergues, S. Zhrebtsov, A. Azzee, I. Ben-Itzhak, R. Moshhammer, R. de Vivie-Riedle, and M. Kling, *Phys. Rev. Lett.* **116**, 193001 (2016).
- C. Burger, N. G. Kling, R. Siemering, A. S. Alnaser, B. Bergues, A. M. Azzee, R. Moshhammer, R. de Vivie-Riedle, M. Kübel, and M. F. Kling, *Faraday Discuss.* **194**, 495 (2016).

- ⁴⁹T. Ando, A. Shimamoto, S. Miura, A. Iwasaki, K. Nakai, and K. Yamanouchi, *Commun. Chem.* **1**, 7 (2018).
- ⁵⁰S. Xu, H. Zhao, X. Zhu, D. Guo, W. Feng, K.-C. Lau, and X. Ma, *Phys. Chem. Chem. Phys.* **20**, 27725 (2018).
- ⁵¹M. J. Michie, N. Ekanayake, N. P. Weingartz, J. Stamm, and M. Dantus, *J. Chem. Phys.* **150**, 044303 (2019).
- ⁵²S. Zhao, B. Jochim, P. Feizollah, J. Rajput, F. Ziaee, K. Raju P., B. Kaderiya, K. Borne, Y. Malakar, B. Berry, J. Harrington, D. Rolles, A. Rudenko, K. D. Carnes, E. Wells, I. Ben-Itzhak, and T. Severt, *Phys. Rev. A* **99**, 053412 (2019).
- ⁵³N. G. Kling, S. Díaz-Tendero, R. Obaid, M. R. Disla, H. Xiong, M. Sundberg, S. D. Khosravi, M. Davino, P. Drach, A. M. Carroll, T. Osipov, F. Martin, and N. Berrah, *Nat. Commun.* **10**, 2813 (2019).
- ⁵⁴P. Pechukas, *Annu. Rev. Phys. Chem.* **32**, 159 (1981).
- ⁵⁵R. J. Levis, G. M. Menkir, and H. Rabitz, *Science* **292**, 709 (2001).
- ⁵⁶C. Trallero-Herrero, D. Cardoza, T. C. Weinacht, and J. L. Cohen, *Phys. Rev. A* **71**, 013423 (2005).
- ⁵⁷B. J. Sussman, D. Townsend, M. Y. Ivanov, and A. Stolow, *Science* **314**, 278 (2006).
- ⁵⁸S. J. Glaser, U. Boschain, T. Calarco, C. P. Koch, W. Köckenberger, R. Kosloff, I. Kuprov, B. Luy, S. Schirmer, T. Schulte-Herbrüggen, D. Sugny, and F. K. Wilhelm, *Eur. Phys. J. D* **69**, 279 (2015).
- ⁵⁹E. Wells, C. Rallis, M. Zohrabi, R. Siemering, B. Jochim, P. Andrews, U. Ablikim, B. Gaire, S. De, K. Carnes, B. Bergues, R. de Vivie-Riedle, M. Kling, and I. Ben-Itzhak, *Nat. Commun.* **4**, 2895 (2013).
- ⁶⁰D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, and J. M. Bowman, *Science* **306**, 1158 (2004).
- ⁶¹N. Herath and A. G. Suits, *J. Phys. Chem. Lett.* **2**, 642 (2011).
- ⁶²J. M. Bowman and B. C. Shepler, *Annu. Rev. Phys. Chem.* **62**, 531 (2011).
- ⁶³J. M. Bowman, *Mol. Phys.* **112**, 2516 (2014).
- ⁶⁴R. Fernando, A. Dey, B. M. Broderick, B. Fu, Z. Homayoon, J. M. Bowman, and A. G. Suits, *J. Phys. Chem. A* **119**, 7163 (2014).
- ⁶⁵B. Joalland, Y. Shi, A. Kamasah, A. G. Suits, and A. M. Mebel, *Nat. Commun.* **5**, 4064 (2014).
- ⁶⁶N. D. Coutinho, V. H. C. Silva, H. C. B. de Oliveira, A. J. Camargo, K. C. Mundim, and V. Aquilanti, *J. Phys. Chem. Lett.* **6**, 1553 (2015).
- ⁶⁷S. Maeda, T. Taketsugu, K. Ohno, and K. Morokuma, *J. Am. Chem. Soc.* **137**, 3433 (2015).
- ⁶⁸P. L. Houston, R. Conte, and J. M. Bowman, *J. Phys. Chem. A* **120**, 5103 (2016).
- ⁶⁹F. A. L. Mauguère, P. Collins, S. Stamatiadis, A. Li, G. S. Ezra, S. C. Farantos, Z. C. Kramer, B. K. Carpenter, S. Wiggins, and H. Guo, *J. Phys. Chem. A* **120**, 5145 (2016).
- ⁷⁰D. V. Cofer-Shabica and R. M. Stratt, *J. Chem. Phys.* **146**, 214303 (2017).
- ⁷¹J. M. Bowman and P. L. Houston, *Chem. Soc. Rev.* **46**, 7615 (2017).
- ⁷²J. M. Bowman and A. G. Suits, *Phys. Today* **64**(11), 33 (2011).
- ⁷³A. M. Mebel and A. D. Bandrauk, *J. Chem. Phys.* **129**, 224311 (2008).
- ⁷⁴N. Ekanayake, M. Nairat, B. Kaderiya, P. Feizollah, B. Jochim, T. Severt, B. Berry, K. R. Pandiri, K. D. Carnes, S. Pathak, D. Rolles, A. Rudenko, I. Ben-Itzhak, C. A. Mancuso, B. S. Fales, J. E. Jackson, B. G. Levine, and M. Dantus, *Sci. Rep.* **7**, 4703 (2017).
- ⁷⁵N. Ekanayake, M. Nairat, N. P. Weingartz, M. J. Michie, B. G. Levine, and M. Dantus, *J. Chem. Phys.* **149**, 244310 (2018).
- ⁷⁶N. Ekanayake, T. Severt, M. Nairat, N. P. Weingartz, B. M. Farris, B. Kaderiya, P. Feizollah, B. Jochim, F. Ziaee, K. Borne, K. Raju P., K. D. Carnes, D. Rolles, A. Rudenko, B. G. Levine, J. E. Jackson, I. Ben-Itzhak, and M. Dantus, *Nat. Commun.* **9**, 5186 (2018).
- ⁷⁷T. Ando, A. Iwasaki, and K. Yamanouchi, *Mol. Phys.* **117**, 1732 (2019).
- ⁷⁸H. Wu, Y. Xue, J. Wen, H. Wang, Q. Fan, G. Chen, J. Zhu, F. Qu, and J. Guo, *RSC Adv.* **9**, 16683 (2019).
- ⁷⁹C. E. Rallis, T. G. Burwitz, P. R. Andrews, M. Zohrabi, R. Averin, S. De, B. Bergues, B. Jochim, A. V. Voznyuk, N. Gregerson, B. Gaire, I. Znakovskaya, J. McKenna, K. D. Carnes, M. F. Kling, I. Ben-Itzhak, and E. Wells, *Rev. Sci. Instrum.* **85**, 113105 (2014).
- ⁸⁰Our CD₃OH sample was purchased from Cambridge Isotope Laboratories and had a listed purity of 99.5%.
- ⁸¹R. Trebino, *Frequency-Resolved Optical Gating* (Kluwer Academic Publishers, 2000).
- ⁸²O. Ghafur, W. Siu, P. Johnsson, M. F. Kling, M. Drescher, and M. J. J. Vrakking, *Rev. Sci. Instrum.* **80**, 033110 (2009).
- ⁸³B. Jochim, R. Averin, N. Gregerson, J. McKenna, S. De, D. Ray, M. Zohrabi, B. Bergues, K. D. Carnes, M. F. Kling, I. Ben-Itzhak, and E. Wells, *Phys. Rev. A* **83**, 043417 (2011).
- ⁸⁴N. G. Kling, D. Paul, A. Gura, G. Laurent, S. De, H. Li, Z. Wang, B. Ahn, C. H. Kim, T. K. Kim, I. Litvinyuk, C. L. Cocke, I. Ben-Itzhak, D. Kim, and M. F. Kling, *J. Instrum.* **9**, P05005 (2014).
- ⁸⁵T. Okino, Y. Furukawa, P. Liu, T. Ichikawa, R. Itakura, K. Hoshina, K. Yamanouchi, and H. Nakano, *J. Phys. B: At., Mol. Opt. Phys.* **39**, S515 (2006).
- ⁸⁶N. X. Truong, J. Tiggesbäumker, and T. Döppner, *Meas. Sci. Technol.* **21**, 085303 (2010).
- ⁸⁷U. Lev, L. Graham, C. B. Madsen, I. Ben-Itzhak, B. D. Bruner, B. D. Esry, H. Frostig, O. Heber, A. Natan, V. S. Prabhudesai, D. Schwalm, Y. Silberberg, D. Strasser, I. D. Williams, and D. Zajfman, *J. Phys. B: At., Mol. Opt. Phys.* **48**, 201001 (2015).
- ⁸⁸M. Nairat, V. V. Lozovoy, and M. Dantus, *J. Phys. Chem. A* **120**, 8529 (2016).
- ⁸⁹J. Eland and B. Treves-Brown, *Int. J. Mass Spectrom. Ion Processes* **113**, 167 (1992).
- ⁹⁰J. Ullrich, R. Moshammer, A. Dorn, R. Dörner, L. P. H. Schmidt, and H. Schmidt-Böcking, *Rep. Prog. Phys.* **66**, 1463 (2003).
- ⁹¹The uncertainty in δ is the same in each case because the camera was adjusted to acquire the maximum unsaturated signal for each ion. As a result, the statistical error turns out to be nearly identical for each ion species.
- ⁹²R. D. van Zee, M. F. Foltz, and C. B. Moore, *J. Chem. Phys.* **99**, 1664 (1993).
- ⁹³L. Karlsson, R. Jadrny, L. Mattsson, F. T. Chau, and K. Siegbahn, *Phys. Scr.* **16**, 225 (1977).
- ⁹⁴M. Mollabashi, *Int. J. Infrared Millimeter Waves* **21**, 1061 (2000).
- ⁹⁵J. L. White, B. J. Pearson, and P. H. Bucksbaum, *J. Phys. B: At., Mol. Opt. Phys.* **37**, L399 (2004).
- ⁹⁶E. Wells, K. J. Betsch, C. W. S. Conover, M. J. DeWitt, D. Pinkham, and R. Jones, *Phys. Rev. A* **72**, 063406 (2005).
- ⁹⁷E. Wells, M. Todt, B. Jochim, N. Gregerson, R. Averin, N. G. Wells, N. L. Smolnisky, N. Jastram, J. McKenna, A. M. Saylor, N. G. Johnson, M. Zohrabi, B. Gaire, K. D. Carnes, and I. Ben-Itzhak, *Phys. Rev. A* **80**, 063402 (2009).