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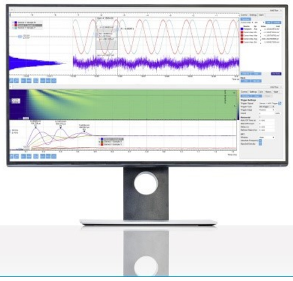

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Interaction of toluene with two-color asymmetric laser fields: Controlling the directional emission of molecular hydrogen fragments

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The interaction of toluene with strong asymmetric two-color laser irradiation of 40 fs duration is studied by means of Time of flight mass spectrometry. Highly energetic H_2^+ and H_3^+ fragment ions are produced through an isomerization process taking place within transient multiply charged parent ions. Comparative study of deuterium labeled toluene isotopes enables the discrimination between molecular hydrogen fragments formed exclusively within the CH_3- part from those that require hydrogen atom exchange between the former and the phenyl moiety. It is demonstrated that by manipulating the relative phase of the $\omega/2\omega$ field components the selective ionization of oriented toluene molecules can be used as a tool to control the directional emission of the H_2^+, H_3^+ species. *© 2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4895097]

INTRODUCTION

Strong laser matter interaction leads to a variety of interesting phenomena associated to multiple ionization and deformation of molecular structure. In some cases, the latter proceeds through isomerization processes, involving the migration of protons or neutral hydrogen atoms, between different cites of transient multiply charged parent ions. A plethora of recent publications have demonstrated that the related phenomena may take place in quite different timescales.

Yamanouchi and co-workers have studied hydrogen migration within singly charged methanol formed by its interaction with an ultra-fast pump laser pulse and interrogated by an equivalent probe at 800 nm using CMI detection techniques (coincidence momentum imaging).[1] It was shown that the migration from the CH_3- to the OH- part leading to H_2O^+ fragment formation, occurs partially in a timescale similar to the laser pulse duration (∼38 fs) and in a post-pulse timescale as well (∼150 fs). The same group proposed that the required time for H_2^+ or H_3^+ ions ejection from $[P^{2+}]$ methanol equals roughly the molecular rotational period, i.e., a few hundreds of fs, as it is indicated by their almost isotropic angular distributions.[2] Following a similar approach Hishikawa *et al.* have shown that acetylene (C_2D_2) to vinyldene isomerization involving a migration of a D atom from one C to the other takes place in 90 fs after the initial 9 fs excitation pulse, while the vinyldene transient state lives roughly 280 fs before it relaxes back to the initial structure.[3]

At the same time, several researchers have attempted a step further towards the control of hydrogen migration, following different experimental techniques.[4–7] For the case of acetylene isomerization, Wells *et al.* demonstrated an enhancement of the migration efficiency by orders of magnitude by optimizing the laser pulse characteristics. The novel experimental technique employs an adaptive control scheme, where the feedback variable is the ratio of the CH^+ fragments (coming from the two-body dissociation of the doubly charged acetylene: $[C_2H_2]^{2+} \rightarrow CH^+ + CH^+$) to CH_2^+ cations (formed by the dissociation of doubly charged vilyldene: $[C_2H_2]^{2+} \rightarrow CH_2^+ + C^+$), which are recorded in each step by VMI (velocity map imaging).[4] Schirmel *et al.* demonstrated intra-charge state control of H_3^+/H^+ ratio for ethane and its deuterium labeled isotopes by varying the intensity and chirp of the laser pulse.[5] It was shown that H_3^+ fragment ions production follows a reaction pathway through a transient state of $[P^{2+}]^*$ with a lifetime longer than the molecular rotational period. Thus, the process is too slow to be coherently controlled and all the H atoms of ethane are contributing in a statistical manner in H_3^+ formation. Xu *et al.*, studied the dependence of hydrogen migration within a doubly charged methanol on the characteristics of the fs laser pulse (intensity, duration, polarization). It was shown that as the laser intensity is increased the ratio of the migration to non-migration pathways decreases, while the opposite trend is observed for longer durations.[6] Finally, Xie *et al.* have shown that isomerization process taking place from doubly charged parent ions ($[P^{2+}]$) of polyatomic hydrocarbons can be manipulated by few cycle carrier envelope phase controlled pulses.[7] The controlling mechanism is based on fine tuning the ponderomotive energy of the rescattering electron released after single ionization, in order to excite different dissociative states in the $[P^{2+}]$ ionic manifold. The isomerization channels producing H_2^+ ions can be manipulated up to 50% of the maximum signal depending on the phase of the CEP controlled pulse.

Finally, our research group demonstrated for the first time the applicability of a two-color asymmetric field on the efficient control of the directional emission of $[P^{2+}]$ methanol fragments, formed through dissociation channels involving H migration.[8] In the present work, we investigate the applicability of the same technique on the photo-chemical processes leading to highly kinetic H_2^+ ionic fragments from toluene, which can be used as prototype case representative of asymmetric aromatic hydrocarbons. The amplitude and the direction of the combined laser electric field is controlled by fine tuning the phase between an 800 nm ultra-fast pulse and its second harmonic (400 nm). It has been established that the technique provides control on the directional emission of fragments, which is based on the orientation dependence of molecular ionization with respect to the asymmetric laser field, for the case of asymmetric targets or/and the control of electron localization within different sites within a dissociating molecular ion, studied experimentally and theoretically for diatomic molecules and ions [CO, D_2, H_2, $H_2{}^+$, $I_2{}^+$].[9–19] The related literature concerns mainly diatomic and recently triatomic molecules[20,21] and only a few cases of polyatomic ones have been investigated.[8,22,23]

EXPERIMENT

The experiments were performed at the Central Laser Facility of the University of Ioannina. An ultra-fast Ti:Sapphire laser is used with characteristics: 800 nm central wavelength, 5 mJ energy/pulse, and 1 kHz repetition rate. The second harmonic was produced in a 250 μm thick β-barium borate (BBO) crystal, which is a polarization axis perpendicular to that of the fundamental. Due to different refractive indexes in the various traversed media, a time difference is introduced between the two pulses which can be corrected using a calcite plate (2.4 mm thick, cut angle 55°) placed into their common path. A second calcite plate of 1.6 mm thickness, which is mounted in a high precision rotational stage, is utilized for phase adjustment of the $\omega/2\omega$ field. Finally, a dual waveplate ($\lambda/2$ at 400 nm, λ at 800 nm) rotates the 2ω polarization making it parallel to the ω one and the time of flight (ToF) mass spectrometer axis. The homemade ToF-mass spectrometer (1.4 m length), operating in a Wiley-MacLaren configuration with dual stage acceleration, is used to record the molecular mass spectrum with a high mass resolution (m/Δm:1200 at 100 D). The toluene molecules (Sigma-Aldrich, 99.998% purity) were effusively introduced in the reaction chamber through a needle valve and the pressure in the interaction region was kept below 5×10^{-7} Torr to avoid space charge effects. The interaction region is pumped by a diffusion pump (2400 l/s) equipped with a liquid nitrogen trap and the rest of the chamber was pumped by a turbo-molecular pump (100 l/s) resulting in a stagnation pressure bellow 10^{-7} Torr. The ionic signal was detected by a chevron type micro-channel detector and recorded by an Ultrafast Multiscaler card (FASTComTec, Model ToF P7888: 1 ns time resolution). The rotation stage adjusting the $\omega/2\omega$ field phase was controlled by a personal computer.

RESULTS AND DISCUSSION

Mass spectra of $C_6H_5CH_3$, $C_6D_5CH_3$, and $C_6D_5CD_3$

In Fig. 1, the $\omega/2\omega$ mass spectra of toluene and two different deuterium labeled isotopes ($C_6D_5CH_3$, $C_6D_5CD_3$) recorded at 2×10^{14} W/cm^2, with the laser polarization parallel to the ToF axis, are depicted. Typically, the mass spectra recorded are the average of 3×10^5–2×10^6 single pulse acquisitions. In the insets of Fig. 1, a magnified representation of the m/z: 15–18 regions is given and the same stands for the m/z: 2–6 regions in the lower part of Fig. 1. Ionic fragments with m/z = 2 and m/z = 3 are clearly observed in the mass spectra of C_7H_8, which correspond to $H_2{}^+$ and $H_3{}^+$ ionic fragments.

The observation of these peaks could be related to the presence of water contamination in the vacuum chamber, i.e., the m/z:3 peak could be attributed to HD^+ originating from deuterated isotope of water HDO. However, the natural abundance of D atoms is orders of magnitude lower than the recorded ionic signal ratios of the m/z = 2 peak with respect to the H^+ and that of m/z = 3 with respect to the m/z = 2 and therefore the observed mass spectra peaks cannot be attributed to water fragmentation.

The peak profiles of the atomic and molecular hydrogen fragments consist of different components, which originate

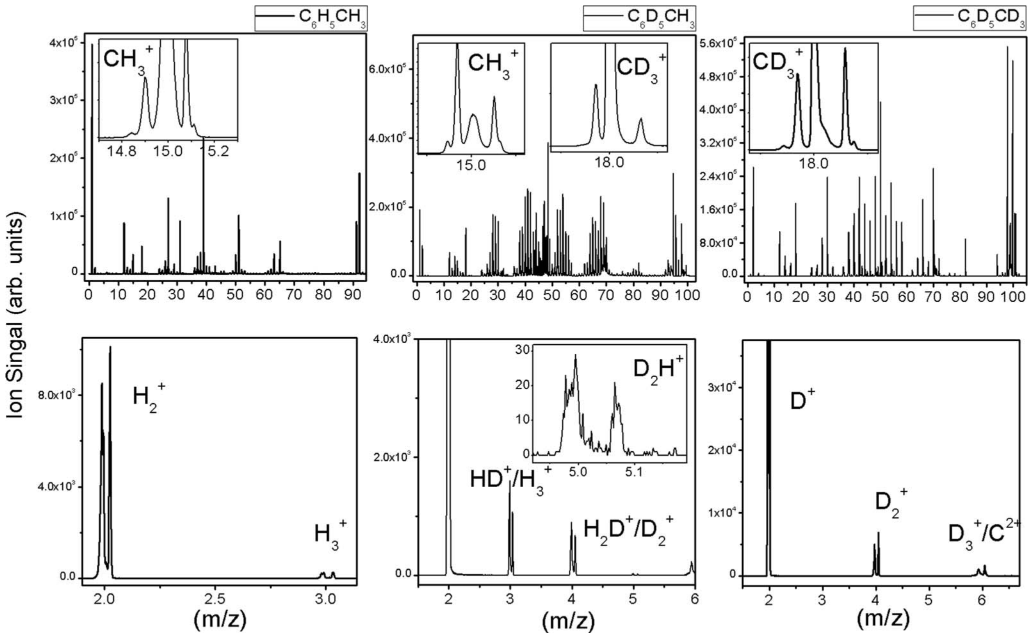

FIG. 1. Time-of-flight mass spectra of C_7H_8, $C_6D_5CH_3$, and C_7D_8 recorded at ~2×10^{14} W/cm^2, 40 fs.

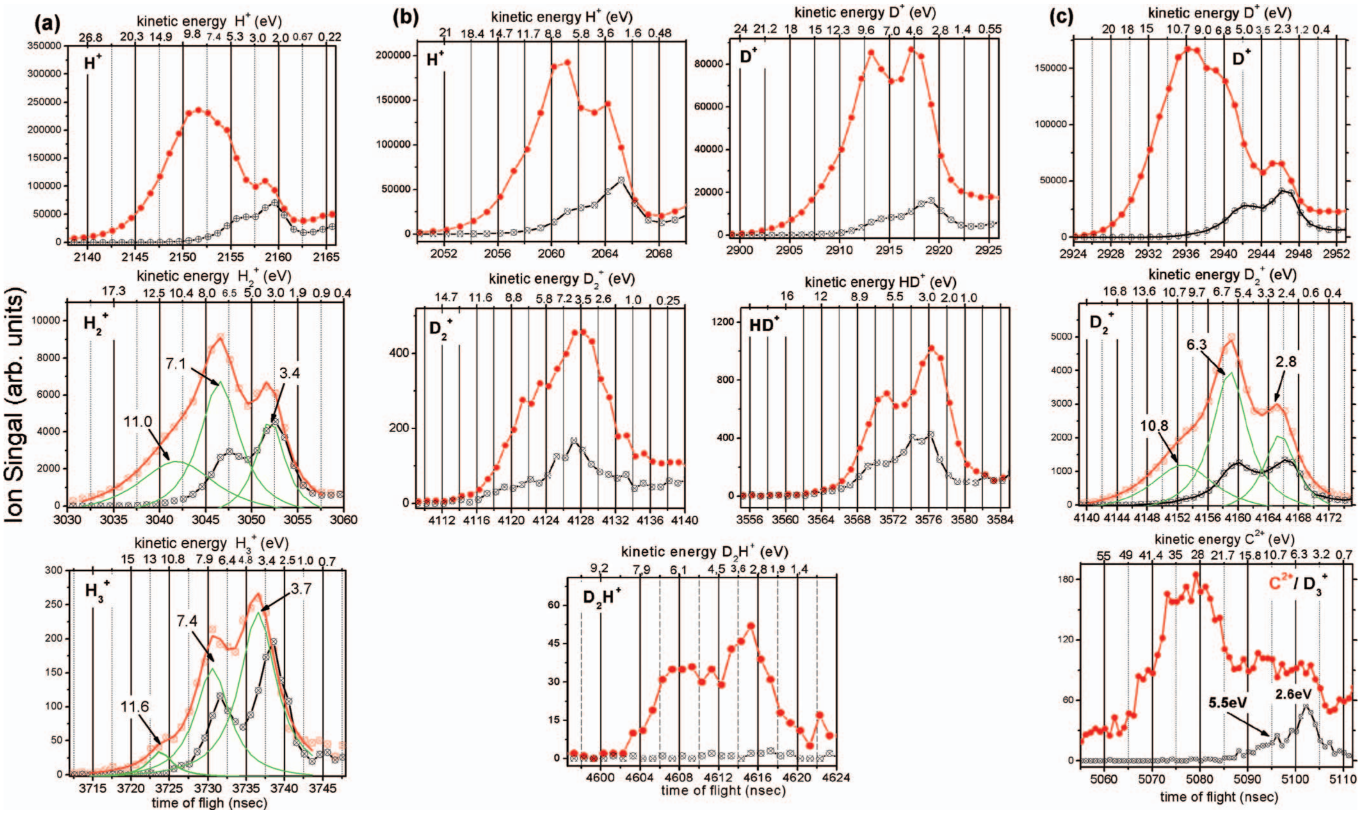

FIG. 2. The forward component of the ToF-MS peaks of atomic and molecular hydrogen ions at two-different laser intensities 1.5 × 10^{14} W/cm^2 (red solid line) and 8 × 10^{13} W/cm^2 (black solid line). The (a)–(c) sections correspond to C_7H_8, $C_6D_5CH_3$, and C_7D_8, respectively. The data points of H_2^+, H_3^+ in (a) and D_2^+ in (c) (open circular symbols) of C_7H_8 and C_7D_8, respectively, are fitted (red solid line) with the sum of three Lorentzian components (green solid lines).

from ions ejected towards the detector (forward component) or to the opposite direction (backward component) and, therefore, present different time-of-flights. In fact, the difference in the ToF of the forward-backward components can be used to calculate the kinetic energy of these fragments.[24] The results of calculations for the kinetic energy values of the H^+, H_2^+, and H_3^+ fragments are found to be in agreement with ToF simulations, performed with Simion 8.0, and they are presented in Fig. 2.

The C_7H_8 case

The H^+, H_2^+, and H_3^+ fragment ions present a broad distribution of kinetic energies spanning from values lower than 1 eV and up to 20 eV for the H^+ case and roughly 15 eV for the H_2^+ and H_3^+ molecular fragments. The broad kinetic energy distributions are indicative of Coulomb explosion channels and the formation of a variety of transient multiply-charged parent ion precursors. Defining the precursors exact charge state is by no means an easy problem to resolve and it calls for the application of advanced coincidence techniques, which, on the other hand, are usually applied in cases of ionization-dissociation channels producing a relatively small number of fragments. Quite recently, Bubin *et al.*[25] reported the first application of coincidence momentum imaging in the investigation of polyatomic hydrocarbons interacting with strong laser fields and proposed that H^+ ions with E_{kin} ∼ 20 eV or more are a result of a sudden all-at once fragmentation, where ionization is followed by simultaneous ejection of H^+ fragments.

In the present work, the E_{kin} of H_2^+ and H_3^+ fragments present at least three dominant components centered at values: 3.3 ± 0.3, 6.8 ± 0.3, and ∼11 eV. The lower kinetic energy values are comparable to those reported for benzene,[26] ethane,[27] and a series of hydrocarbons,[28] under 800 nm laser irradiation of similar intensity and pulse duration. In the latter case, the H_2^+ and H_3^+ were attributed to the fragmentation of doubly charged parent ions. However, the higher kinetic energy H_2^+ and H_3^+ ions (∼11 eV) are reported for the first time for hydrocarbons under strong laser irradiation and they are obviously correlated with parent ions of higher charge multiplicities. This result is somewhat unexpected since the formation of molecular hydrogen ions and hydrogen migration channels are described in the related literature as processes competitive to multiple ionization.[3,6,26,29] In order to evaluate the relative contribution of hydrogen atoms originating from the CH_3- or the phenyl (C_6H_5-) moieties we recorded the mass spectra of two deuterium labeled isotopes of toluene ($C_6D_5CH_3$, $C_6D_5CD_3$) at similar irradiation conditions.

The $C_6D_5CH_3$ case

For the $C_6D_5CH_3$ target, mass spectra peaks corresponding to m/z: 1, 2, 3, 4, 5, 6 are observed as shown in Figs. 1 and 2. These peaks can be attributed to H^+, H_2^+/D^+, H_3^+/HD^+, H_2D^+/D_2^+, D_2H^+, and D_3^+/C^{2+}. Taking into account the ratios of peaks with m/z: 2, 3, 4, 5 over that of H^+ plus D^+ (64%, 0.66%, 0.43%, and 0.01%, respectively) and the ratios of H_2^+/H^+ and H_3^+/H^+ (3.5%, 0.11%) observed for C_7H_8 we can safely conclude that the m/z = 2 and 3 peaks consist mainly of D^+ (>94%), HD^+ (>80% of total m/z = 3 peak) rather than H_2^+, H_3^+. On the other hand, the m/z = 4 may be attributed to a D_2^+ ion rather than H_2D^+, making the reasonable assumption (in terms of H/D stoichiometry) that the latter has a formation probability equivalent to that of D_2H^+. The m/z = 5 peak is unambiguously attributed to D_2H^+ providing along with the presence of HD^+ clear evidence that the migration of hydrogen atoms between the CH_3- and C_6D_5- moieties takes place within multiply charged parent ions prior to their dissociation.

The kinetic energy of the HD^+ and D_2H^+ peaks present a bimodal profile similar to that observed for the H_2^+ and H_3^+ fragments of C_7H_8 suggesting that the migration process between the two moieties takes place within parent ions of similar charge states for both toluene isotopes. On the contrary, the HD^+ and D_2H^+ kinetic energies do not present the high kinetic energy peak component (~11 eV for H_2^+, H_3^+ fragments of C_7H_8) and the same is valid for the peak profile of D_2^+/H_2D^+. The results indicate that the migration process between the CH_3- and C_6D_5- and the D migration within C_6D_5- is outcompeted by the dissociation rate of the corresponding transient parent ion. At the same time, the results point towards an ionization-dissociation mechanism forming high kinetic energy H_2^+, H_3^+ fragments exclusively from hydrogen atoms within the CH_3- moiety. Nevertheless, these conclusions are drawn under the assumption that the deuterium labeled target interacts with the irradiation field in a similar manner as the C_7H_8 case and that there is no isotopic effect in the ability of deuterium atoms to form molecular fragments. Both of the assumptions can be crosschecked by recording the mass spectra for the fully deuterated isotope of toluene (C_7D_8).

The C_7D_8 case

Mass spectra peaks with m/z: 2, 4, and 6 are presented in Figs. 1 and 2, which are attributed to D^+, D_2^+, and D_3^+/C^{2+} ions depending on the laser intensity conditions. The kinetic energy of the D^+ and D_2^+ (3.0 ± 0.3, 6.5 ± 0.3, ~11 eV) are quite similar to those for the H^+ and H_2^+ fragments of C_7H_8. The atomic hydrogen fragments and their kinetic energy are considered as a sensitive probe of the ionization efficiency for hydrocarbons under strong laser irradiation.[25,30] Therefore, the similar E_{kin} values for H^+ and D^+ of toluene and its deuterium labeled isotopes suggest a similar ionization efficiency for the two cases or at least no indication of an isotopic effect is apparent. To some extent, this is anticipated since the 40 fs pulse duration of the composed field is long enough to avoid any important contribution to the ionization process from differences in the nuclear dynamics along the C–H and C–D coordinates. Roither *et al.*[31] recently proposed an enhanced ionization mechanism for hydrocarbons, where the efficient elongation of C–H bonds along the laser electric field strongly affects the ionization efficiency. Moreover, their results support that the minimum pulse duration required for enhanced hydrocarbons ionization is ~17 fs at intensities similar to those used in the present work.[32]

Finally, the D_2^+ kinetic energy values shown in Fig. 2 contain a strong contribution from high kinetic energy fragments (~11 eV) providing clear evidence that the absence of the same component from the HD^+ and D_2^+ fragments of $C_6D_5CH_3$ is not due to a strong H/D isotopic effect and that the highly kinetic molecular hydrogen fragments are formed exclusively within the CH_3- part. Therefore, it can be concluded that their formation within CH_3- follows a faster timescale than that involving migration of hydrogen atoms between the different cites of the molecular structure. It should be noted that for the D_3^+ case the high kinetic energy component cannot be safely discriminated from C^{2+} fragment ions, due to the fact that both species present similar appearance intensities. Nonetheless, at low laser intensities (8×10^{13} W/cm^2, see Fig. 2) the E_{kin} of D_3^+ shows similar characteristics with the H_3^+ case.

RESULTS ON THE DIRECTIONAL EMISSION OF TOLUENE FRAGMENTS CONTROLLED BY $\omega/2\omega$ ASYMMETRIC FIELD

In order to investigate the dissociative-ionization of toluene under two color fields and the possibility of using the asymmetric irradiation to control the directional photochemical process leading to H_2^+ and H_3^+ formation, the ToF-mass spectra were recorded as function of the $\omega/2\omega$ phase difference. Moreover, in order to determine the absolute phase of the composed electric field the asymmetric fragmentation of carbon monoxide is recorded simultaneously with the toluene data, since the CO has been studied extensively under asymmetric irradiation, which makes it an ideal gas for phase assignment.[10]

Control over the directional emission of fragments is achieved by changing of the relative amplitude of the forward vs backward mass spectra peaks, i.e., ions ejected towards or away from the detector (see Figs. 3(a)–3(c)), while manipulating the direction of the $\omega/2\omega$ field. This is clearly demonstrated for several fragments of the molecules under study (H_2^+, H_3^+, CH_3^+) as shown in Fig. 3, where the corresponding peaks are compared for two different values of the $\omega/2\omega$ phase ($\varphi = 0$ and π), i.e., for laser electric field pointing towards the detector or the opposite direction, respectively. It should be noted that similar trends are observed for the methyl fragment ions for all the deuterium labeled isotopes under study as it is clearly demonstrated in Figs. 3(a)–3(c).

These results, in accordance to our recent report on methanol,[8] are a manifestation of the applicability of the $\omega/2\omega$ asymmetric field on controlling the directional emission of photo-products requiring the breakup of C–H bonds and the formation of new H–H ones. To a first approach, the results could be attributed to a selective ionization mechanism of oriented molecules, achieved under the particular laser irradiation conditions. It is highly unlikely that a dynamic orientation process is contributing to the observed asymmetries, since the 40 fs laser pulse is negligible compared to the rotational timescale of toluene (~tens of ps).[33] In other words, the asymmetric laser field interacts preferentially with those

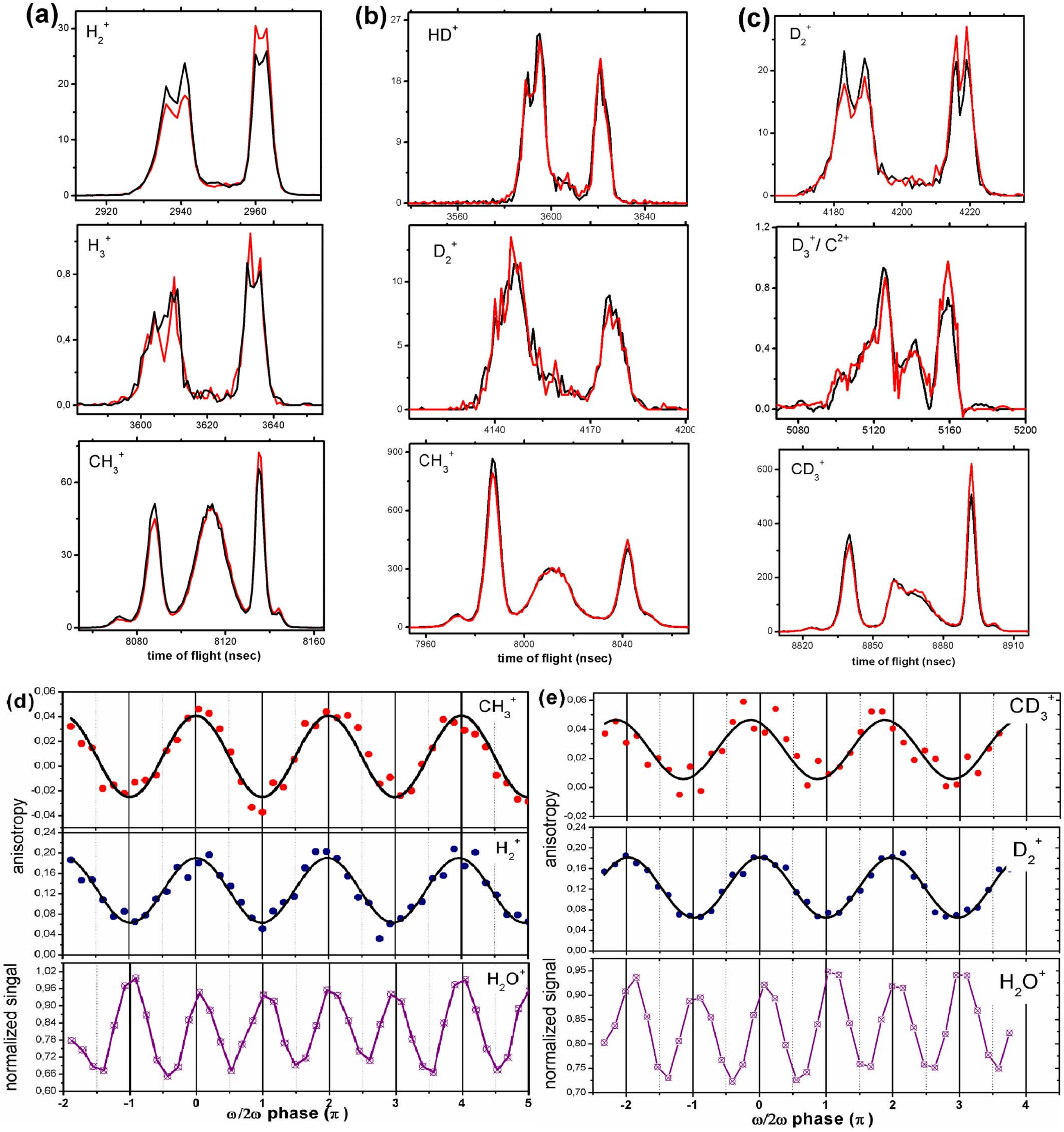

FIG. 3. (a)–(c) ToF-MS peak profiles of fragment ions of C_7H_8, $C_7D_5H_3$, and C_7D_8, respectively, recorded at 8×10^{13} W/cm^2. Black and red lines correspond to $\varphi = 0$ and π, respectively, where φ the phase between ω and 2ω pulses. (d) and (e) Anisotropy parameter of C_7H_8 and C_7D_8 fragments and the normalized to unity H_2O^+ signal as a function of the relative phase of the $\omega/2\omega$ field components.

molecules that have their electron cloud already oriented to the laser polarization (geometric orientation).

Provided that the dissociation process is faster than the rotational timescale, the directionality of produced fragments is an indirect measure of the asymmetric ionization. The latter is supported by angular distribution measurements, where strong anisotropies are confirmed at ~10^{14} W/cm^2 for all the atomic and molecular hydrogen species, the C^{2+} ions and $CH_3{}^+$ molecular fragments (see the supplementary material[34]). In all cases, the angular distributions present a maximum along the laser electric field polarization implying the dominant contribution of ionization processes from molecular orbitals, where the electron cloud is preferentially distributed along the phenyl-CH_3 axis,[35] according to the MO-ADK model.[10,22,36]

In order to quantify the observed anisotropies and to facilitate the comparative evaluation of the results for the different toluene isotopes, we estimate the beta parameter versus the variation of the phase φ of the laser field. The beta parameter represents the ratio:

$$\beta = \frac{Y_f - Y_b}{Y_f + Y_b},$$

where Y_f, Y_b stand for the integrated forward signal and the backward one, respectively. In Fig. 3(d), the beta parameters are presented for the H_2^+ and CH_3^+ fragments. The presented data correspond to an intensity of 8 × 10^{13} W/cm^2. The ratio of the intensity of the 800 and 400 nm laser beams is an important experimental factor for the recorded asymmetric fragmentation, since it defines the spatial asymmetry of the combined laser field. In the present case, the intensity of the 800 and 400 nm fields used are calculated to be 6.5 × 10^{13} W/cm^2 and 1.5×10^{13} W/cm^2, respectively, which provide a ratio ($E_{400\,nm}/E_{800\,nm}$) of the electric fields close to ∼0.5. At low laser intensities 8 × 10^{13} W/cm^2 the beta plots present a maximum for phase values $\varphi = 0, 2\kappa \times \pi$ (k is an integer number) for both fragments, which corresponds to an enhanced ionization process when the asymmetric laser field points towards the CH_3- part of the molecule, while the H_2O^+ peak follows the expected $\varphi = \kappa \times \pi$ sinusoidal behavior. Therefore, the observed orientation dependence of ionization is in accordance with the MO-ADK model, since the toluene HOMO presents a higher electronic cloud distribution around the phenyl moiety and the electrons should be extracted more efficiently via tunneling ionization from this side of the molecule.[10,22,36] The present work provides another case of a polyatomic molecule where the orientation dependent ionization follows qualitatively the MO-ADK tunneling ionization model, even though non-adiabatic multielectron effects may as well contribute to the involved ionization/dissociation processes.[23]

Anisotropy measurements were performed for different laser intensities and the amplitude of the "beta" parameter oscillation for each fragment is stronger close to the corresponding appearance intensity. For example, the H_2^+ and D_2^+ ions recorded for the C_7H_8 and C_7D_8 targets, respectively, present a modulation of the ratio of forward to backward fragmentation of ∼23% ± 2% at a laser intensity ∼5 × 10^{13} W/cm^2 (see the supplementary material[34]). The results indicate that the $\omega/2\omega$ asymmetric field is indeed a promising alternative experimental tool to control efficiently the involved isomerization.

Moreover, it is important to note (see Figs. 3(d) and 3(e)) that there is no H/D isotope effect observable on the "beta" parameter amplitude or the phase values corresponding to "beta" maxima or minima. This result could be attributed to the 40 fs pulse duration of the $\omega/2\omega$ field, which seems to be too slow to follow any difference in timescale for the formation of the aforementioned peaks for D or H atoms within the CH_3- part of the molecule. To some extent the results are comparable to that reported on the directional emission of H^+ and D^+ fragments from H_2 and D_2 molecules applying a 45 fs $\omega/2\omega$ laser field, where similar asymmetries are observed,[19] in contradiction to a strong isotopic effect observed for CEP-control laser pulses of 5 fs duration.[18]

Finally, it is important to note that the $\omega/2\omega$ asymmetric field does not provide any apparent control on the directional emission of HD^+, D_2^+ ions from $C_6D_5CH_3$ (contrary to the C_6D_5–CH_3 bond break up and the CH_3^+ ejection), since the particular species present no phase dependence and almost isotropic angular distributions (see the supplementary material[34]). Actually, the HD^+ fragments present a small anisotropic contribution which is less than 10% of its total signal. This would be somewhat contradicting to the fact that the aforementioned ions present similar kinetic energies with the H_2^+, D_2^+ (coming from C_7H_8 and C_7D_8) excluding the high kinetic energy component (∼11 eV). To a first approach, the results could be attributed to a much slower dissociation timescale (longer than the rotational period of toluene) for the HD^+ and D_2^+ precursors. However, the slower timescale scenario is not compatible with the similarity in the kinetic energy release, because it would provide enough time for sufficient internal vibrational relaxation processes to take place and, therefore, at least partial transfer of the excitation energy, associated with the ionization process, to different vibrational degrees of freedom.[37] Alternatively, the absence of angular or $\omega/2\omega$ phase dependence may be related to the fact that the D atoms are distributed almost symmetrically along the plane of the molecule at least in the ground state geometry. Therefore, the HD^+ and D_2^+ fragment ions might present an anisotropic emission with respect to the molecular plane and not a specific direction. This scenario would require that the migration occurs within a transient species geometry not far from that of the ground state. That would be in accordance with our previous work with single color pulses at 800 nm and 27 fs duration on C_6H_6, 1,2-$C_6H_4D_2$, and 1,6-$C_6H_4D_2$, where a strong dependence of the formation of HD^+, D_2^+, and H_2D^+ on the position of the participating H and D atoms in the ground state structure of the benzyl ring was verified.[26]

CONCLUSIONS

In the present work, we attempt to use an asymmetric two-color laser field to control the isomerization process taking place within multiply charged states of toluene, which leads to the directional emission of highly kinetic molecular hydrogen fragments.

Using deuterium labeled isotopes of toluene we conclude that highly energetic H_2^+ and H_3^+ (∼11 eV) fragments, reported for the first time in the hydrocarbon related literature, are formed exclusively from H atoms originally bonded on the CH_3- moiety. The recorded phase dependent directional emission of the molecular hydrogen and CH_3^+ fragments are in accordance with the MO-ADK model predicting enhanced ionization when the asymmetric laser field direction points towards the CH_3- part. An appreciable controlling efficiency (∼23% ± 2%) of the photo-chemical process leading to H_2^+, H_3^+ species formed within the CH_3^+- moiety is demonstrated for irradiation conditions close to their appearance intensity. The technique could be potentially used on ''cold molecular targets'' along with field-free dynamic orientation techniques (terahertz, $\omega/2\omega$)[38,39] aiming for an improved control of the photo-chemical process. On the contrary, at similar laser intensities no dependence on the $\omega/2\omega$ asymmetric field is manifested for molecular hydrogen fragments (D_2^+, HD^+)

requiring hydrogen migration between different sites of the $C_6D_5CH_3$ isotope.

Finally, the same controlling efficiency is verified for toluene and the corresponding fully deuterated sample (C_7D_8) indicating that the 40 fs laser pulse duration is too slow to discriminate any H versus D isotope mass effect on the nuclear dynamics. Therefore, the prospect of a similar experimental study on the C_7H_8 and C_7D_8 targets at shorter timescales using CEP controlled few cycle pulses seems promising.

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