Carrier-envelope phase dependence of the directional fragmentation and hydrogen migration in toluene in few-cycle laser fields

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The dissociative ionization of toluene initiated by a few-cycle laser pulse as a function of the carrier envelope phase (CEP) is investigated using single-shot velocity map imaging. Several ionic fragments, CH_3^+, H_2^+, and H_3^+, originating from multiply charged toluene ions present a CEP-dependent directional emission. The formation of H_2^+ and H_3^+ involves breaking C-H bonds and forming new bonds between the hydrogen atoms within the transient structure of the multiply charged precursor. We observe appreciable intensity-dependent CEP-offsets. The experimental data are interpreted with a mechanism that involves laser-induced coupling of vibrational states, which has been found to play a role in the CEP-control of molecular processes in hydrocarbon molecules, and appears to be of general importance for such complex molecules. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4941601]

I. INTRODUCTION

The interaction of molecules with intense laser fields of ultra-short duration has been the subject of numerous publications over the last few decades. Under intense laser irradiation ($\geq 10^{14}$ W/cm^2), several electrons may be stripped from the molecule, forming transient molecular ions which can later fragment. The possibility of controlling the fragmentation products, or their directional emission, has been investigated, where different pulse parameters are used as control knobs, such as intensity, duration, chirp,[1,2] pulse shape,[3] and, more recently, spatially asymmetric laser fields (phase-dependent two-color laser fields in the multi-cycle regime[4–6] or broadband, few-cycle pulses[7,8]).

Current state-of-the-art ultrashort laser pulses are close to the single-cycle limit, where the oscillatory carrier electric field becomes an important parameter, in addition to the pulse envelope. This offset between the carrier and envelope is described by the carrier envelope phase (CEP) of the pulse. Several groups have demonstrated control over the directional emission of molecular fragments as a function of the CEP.[7–18]

To a good extent, the related theoretical (see, e.g., Refs. 19–22) and experimental research (see, e.g., Refs. 7, 17, and 18) is focused on H_2 and D_2 molecular targets. These studies suggest that the directional emission of H^+/D^+ ions stems from an electron localization effect, taking place at different optical cycles of the laser electric field. The coupled electron-nuclear dynamics can be observed in real-time using pump-probe schemes with attosecond resolution.[23] For slowly evolving systems (such as T_2^+), simulations suggest that femtosecond resolution may be sufficient.[24] This effect is the result of electron-nuclear coherence,

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namely, population transfer between bound and dissociative states of parent ions within the duration of the laser pulse. For the case of asymmetric molecules, the interpretation of the experimental results is more challenging due to the contribution of the orientation dependence of the ionization process.[5,25] In spite of the complexity of ionization, which in general is intensity and molecular target dependent, the use of few-cycle pulses has provided promising results with potential applications for controlling the fragmentation process, even though the latter takes place on longer timescales compared with the duration of the pulse (see, e.g., Refs. [8], [25], and [26]).

In the present work, we use a few-cycle pulse covering the range of peak intensities from 8×10^{13} to 1.5×10^{14} W/cm^2 to investigate the directional emission of H_2^+, H_3^+, and CH_3^+ fragments from toluene as a function of the CEP.

II. EXPERIMENTAL METHODS

The experimental setup has been discussed in detail in Ref. [27]. A beam of 25 fs pulses at 790 nm with a repetition rate up to1 kHz (Ref. [28]) is sent to a rare-gas filled hollow-core fiber for spectral broadening and then compressed by chirped mirrors. The resulting 4 fs pulses, with a central wavelength of 720 nm, are divided into two parts by a 20/80 broadband beam splitter. The weaker beam is sent to the stereo-above threshold ionization (ATI) phasemeter for single-shot CEP detection, while the stronger beam is focused into a single-shot velocity map imaging (VMI) spectrometer, where it intersects with an effusive molecular beam of toluene. The laser intensity is tuned by a rotatable neutral density filter, and the polarization can be switched from linear to circular using a broadband quarter-wave-plate. Vaporized toluene (>99.8% purity, Sigma-Aldrich) enters the vacuum in a differentially pumped chamber. It then passes through a skimmer with an opening of 500 μm before it reaches the interaction region within the VMI.

After the laser-target interaction, the resulting fragment ions are projected by the electro-static field of the VMI onto a microchannel plate (MCP)/phosphor assembly. The fluorescence of the phosphor screen is recorded by a complementary metal-oxide semiconductor (CMOS) camera. The VMI images and CEP are recorded in parallel for each laser shot. In the post-analysis, the VMI images for a CEP range of 2π are divided into 20 bins. There is a constant phase offset between the measured CEP and the absolute CEP, which can be calibrated by measuring the directional electron emission from Xe (under the same experimental conditions) and comparing it to simulations.[18,29] The VMI images are Abel-inverted[30] to extract the central slice of the 3D momentum distribution in the plane of the detection, for the data sets using linearly polarized pulses.

III. RESULTS AND DISCUSSION

A. Angular and kinetic energy distributions

In Fig. 1, the CEP averaged 2D-momentum maps and the corresponding kinetic energy distributions of the H_2^+, H_3^+, and CH_3^+ fragments are presented. The CH_3^+ fragment is studied along with the molecular hydrogen fragments, providing a reference for a simple C-C bond breaking process, occurring without the involvement of an isomerization or hydrogen migration step. However, this stands only for a part of the CH_3^+ distribution, which exhibits a bimodal profile, consisting of two E_{kin} components centered at ~1.7 and 4.0 eV (Fig. 1(d)). The 1.7 eV component is attributed to the well-studied two-body dissociation channel involving a metasta-ble dication state, leading to isotropic ejection of CH_3^+ fragments on a microsecond time-scale.[31] Moreover, it involves complete scrambling of the hydrogen atoms, originally bonded to the phenyl- or methyl moiety, and, therefore, it is obviously far from being a simple dissocia-tion process. In contrast, the 4.0 eV component consists of ions ejected preferentially along the laser polarization axis suggesting a "fast" dissociation process—at least as compared with the rotational timescales for toluene (~tens of ps). Identifying the precursor state of the particular channel is not crucial, provided that the dissociation process is fast enough to exclude hydrogen
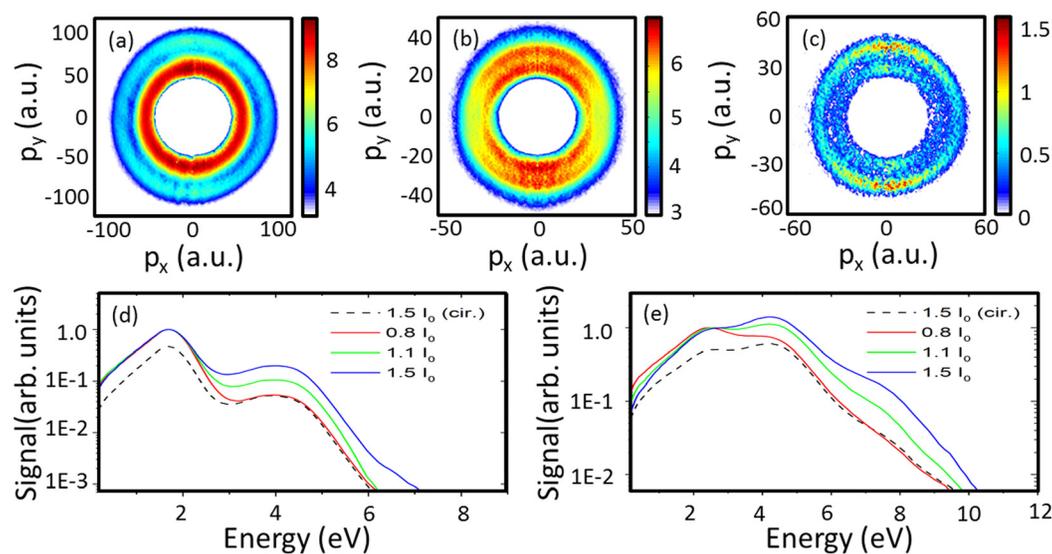
FIG. 1. CEP-averaged momentum distributions of (a) CH_3^+, (b) H_2^+, and (c) H_3^+ ions in a 4 fs laser field at an intensity of $(0.8 \pm 0.1) \times 10^{14}\,W/cm^2$. The color bar indicates the signal strength on a logarithmic scale. Kinetic energy spectra for (d) CH_3^+ and (e) H_2^+ ions for linear polarization at intensities: $(0.8 \pm 0.1, 1.1 \pm 0.1,$ and $1.5 \pm 0.1) \times 10^{14}\,W/cm^2$. I_0 in the legend represents $1 \times 10^{14}\,W/cm^2$. The spectra are normalized to the lower kinetic energy peak ($\sim 2\,eV$). The dashed line corresponds to a measurement at the highest intensity with circular polarization. Note that in this case, the data are not inverted and the spectrum is obtained from projection along p_z.

scrambling or migration phenomena. This indeed is the case, as it is consistent with a recent study of the $C_6D_5CH_3$ isotope interacting with asymmetric two-color fields at similar laser intensities with the present work.[26] In particular, the fast dissociation process is verified in the CH_3^+ mass spectra peak components. In those studies, the 4.0 eV component is completely absent from the energy spectra corresponding to the CD_3^+ and CHD_2^+ fragments, which are necessarily formed through processes involving hydrogen and deuterium exchange. Therefore, the CH_3^+ fragments with $E_{kin} \sim 4.0\,eV$ seem to originate from precursors that dissociate with a rate that out-competes hydrogen migration.

In regard to the H_2^+ and H_3^+ fragments, their E_{kin} distributions consist of a pair of components centered at around 2.4 and 4.2 eV, while for the H_2^+ case some higher E_{kin} fragments $\sim 7.5\,eV$ are also observed (see Figs. 1(b) and 1(e)). Identifying the exact ionization/ dissociation channel producing the aforementioned fragments is by no means a trivial task, especially for the channels which result in several ionic fragments. In any case, the observed kinetic energy values can be compared with those reported in the literature for a series of polyatomic targets for multi-cycle pulses at similar intensities.[32] The corresponding reported values are in the range of 3.5–5 eV and they are attributed to the Coulomb explosion of doubly charged parent ions. Although the energies observed in the present work are quite similar, their range is certainly broader. In particular, the H_2^+ fragments with higher $E_{kin} \sim 7.5\,eV$ imply the formation of parent ions of higher multiplicities ($[C_6H_5CH_3^{n+}]$, $n > 2$). This is supported by the fact that the relative contribution of the high kinetic energy component is enhanced as the intensity increases (Fig. 1(e)). Measurements with circular polarization, with twice the intensity as the linear case ($0.8 \times 10^{14}\,W/cm^2$), are shown as dashed lines in Figs. 1(d) and 1(e) and indicate similar spectral structure, especially for the highest energy peaks.

Moreover, the CEP averaged 2D-momentum distributions of the H_2^+ and H_3^+ fragments, shown in Figs. 1(b) and 1(c), present anisotropic angular distributions. The degree of anisotropy is increased along with the fragment kinetic energy suggesting a shorter lifetime for the corresponding precursors and/or a multiple ionization process, which is feasible for molecules having their C-CH_3 bonds confined within a smaller range of angles with respect to the laser electric field.

B. The CEP dependence of CH_3^+, H_2^+, and H_3^+ fragment ions

The CEP dependence of the directional fragment ion emission is visualized in terms of asymmetry maps that are depicted in Figs. 2(a)–2(c) at a laser intensity $\sim 1.1 \times 10^{14} \, \text{W/cm}^2$. Here, the asymmetry is defined as

$$A(E_{kin}, \varphi) = \frac{N_+(E_{kin}, \varphi) - N_-(E_{kin}, \varphi)}{N_+(E_{kin}, \varphi) + N_-(E_{kin}, \varphi)}, \tag{1}$$

for a kinetic energy E_{kin}, laser CEP φ, and for yields N_+ and N_- in the up and down directions along the polarization axis, respectively.

Asymmetric fragmentation is observed for all cases, with asymmetry amplitudes ranging from 1.5% to 3.0%. It should be noted that a CEP dependent directional emission of H_3^+ (from allene) was reported for the first time only recently[33] and is not easily achieved, since its formation requires the breakup of two C-H bonds and the formation of a new H_3^+ moiety within a multiply charged precursor prior to its dissociation. The possibility of an intermolecular process involved in the H_3^+ or H_2^+ formation or the contribution of clusters, can be excluded at the employed experimental conditions, where a continuous pure toluene beam is used without carrier gas and the pressure in the differential pumping chamber is kept below 10^{-5} mbar during data acquisition.

We have integrated the asymmetry maps over selected energy windows (see Figs. 2(d)–2(f)), corresponding to the peaks observed in the spectra of the fragment species. The asymmetries for the high-energy peaks of all fragment ions have similar maxima and minima with respect to the CEP, indicating a common mechanism for their generation. Only a slight tilt of the asymmetries with energy is observed. The asymmetry maps for H_2^+ and H_3^+ show gradual changes in both asymmetry amplitude and phase offset, as further shown in Fig. 2(e) and 2(f), whereas for CH_3^+, we find a sudden jump in the phase between the low- and high-energy contributions, at about 4 eV(see Fig. 2(d)).

In order to quantify the asymmetry oscillations, a fitting function: $A(\varphi) = A_o \cdot \cos(\varphi + \varphi_o)$, where A_o is the asymmetry amplitude and φ_o is the intensity dependent phase offset, is applied to the energy integrated asymmetry oscillations. The results of the fitting for different species and energy windows are presented in Table I for the H_2^+ and CH_3^+ fragments.

With increasing laser intensity $(0.8 \text{ to } 1.5) \times 10^{14} \, \text{W/cm}^2$, further changes in the asymmetry amplitudes and phase offsets become evident. Noteworthy is a decrease in the phase offset for
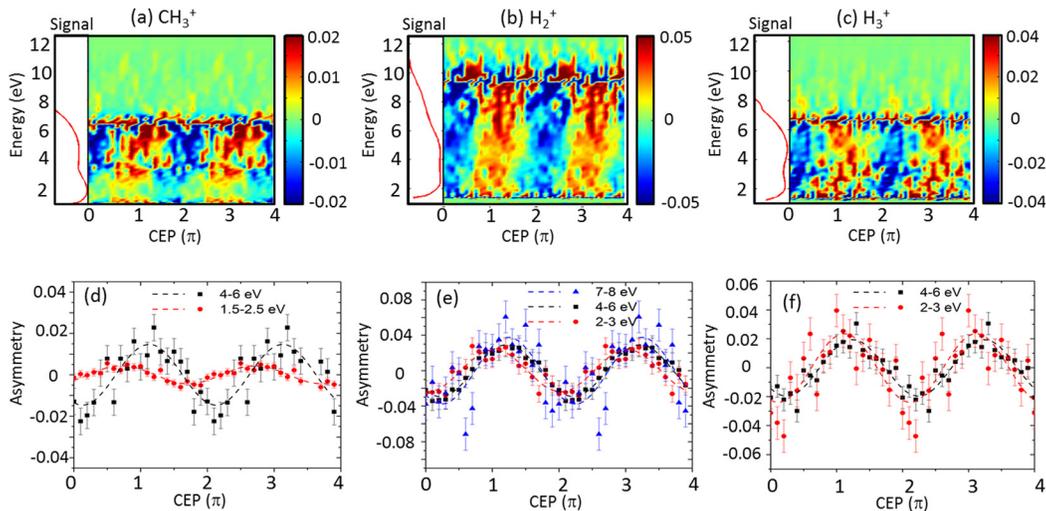

FIG. 2. The asymmetries for (a) CH_3^+, (b) H_2^+, and (c) H_3^+ fragment emission recorded at $(1.1 \pm 0.1) \times 10^{14} \, \text{W/cm}^2$ as a function of kinetic energy and CEP. The asymmetry for (d) CH_3^+, (e) H_2^+, and (f) H_3^+ is obtained via integration of the indicated kinetic energy ranges of the asymmetry maps shown in (a), (b), and (c), respectively.

TABLE I. The results of fitting the function $A(\varphi) = A_o \cdot \cos(\varphi + \varphi_o)$ to the CEP-dependent asymmetries of the CH_3^+ and H_2^+ fragments for the indicated energy windows and intensities.

Intensity ($\times 10^{14}$ W/cm^2)		0.8 ± 0.1		1.1 ± 0.1		1.5 ± 0.1	
Fitting results		A_o (%)	φ_o (rad)	A_o (%)	φ_o (rad)	A_o (%)	φ_o (rad)
H_2^+	(2–3)eV	2.4 ± 0.2	3.1 ± 0.1	2.0 ± 0.2	3.0 ± 0.1	1.1 ± 0.3	2.3 ± 0.2
	(4–6)eV	3.1 ± 0.2	2.6 ± 0.1	2.2 ± 0.1	2.4 ± 0.1	1.4 ± 0.1	1.8 ± 0.1
	(7–8)eV	4 ± 1	2.7 ± 0.2	4.9 ± 0.7	1.8 ± 0.1	2.9 ± 0.5	1.5 ± 0.2
CH_3^+	(1.5–2.5)eV	0.7 ± 0.1	3.7 ± 0.1	0.5 ± 0.1	3.7 ± 0.2	0.2 ± 0.1	2.7 ± 0.3
	(4.5–6)eV	2.7 ± 0.3	2.8 ± 0.1	2.1 ± 0.3	2.44 ± 0.1	0.70 ± 0.01	2.64 ± 0.2

the highest energy peak (7–8 eV) of H_2^+ from 2.7 to 1.8 rad when the intensity is increased from (0.8 to 1.1) $\times 10^{14}$ W/cm^2, whereas the other peaks appear less affected by the slight increase in intensity, and only noticeably shift for the highest intensity is reported in this study. For CH_3^+, the high-energy peak shows no discernible trend in its phase offset with intensity.

In order to shed some light on which pathways are involved in the observed asymmetric fragment ion emissions, we discuss the various mechanisms that are known to produce such asymmetries.

(1) In the simplest case, selective ionization of molecules with orientation dependent ionization rates can lead to an asymmetry. Here, an asymmetric laser field ionizes only a subset of randomly oriented molecules in the chamber. Such a mechanism was discussed, e.g., for the dissociative ionization of DCl[14] and CO.[16,34]

(2) Recollisional excitation/ionization of the molecular ion can create an asymmetric fragment emission through, e.g., energy dependent population of the higher-lying states.[8]

(3) Laser-induced coupling of electronic states with suitable symmetry can lead to electron localization, which in turn creates a CEP-dependent asymmetry. In photon representation, pathway interference which involves different n-photon channels has been introduced as a general interpretation for the CEP dependence of any system which consists of two suitable levels.[35] The laser-induced coupling of electronic states was made responsible for observations of asymmetric fragment emission from dissociation of molecular hydrogen[4,11,12,15,17] and some diatomic molecules (such as CO[13,16]).

(4) Laser-induced coupling of vibrational states by directly setting the sign in the superposition with the CEP can lead to a controlled directionality in a molecular reaction. This mechanism was identified in the CEP control of the directional H-emission from hydrocarbon molecules[3] and recently also for hydrogen migration reactions.[33]

If only mechanism 1 was at work for the toluene reactions described here, we would expect energy and intensity-independent phase dependence. On the contrary, we observe some small, but nonetheless unambiguous, phase offsets in the CEP-dependent asymmetry oscillations of the fragments between low and high energy. The tilt in the asymmetry maps shown in Figs. 2(b) and 2(c) would also not be explainable with mechanism 1. We have tested the importance of recollisional excitation, regarding mechanism 2, by using circular polarization (see dashed lines in Figs. 1(d) and 1(e)). Circular polarization is expected to omit recollisional excitation/ionization.[36,37] It appears that none of the peaks observed for linear polarization vanish for circular polarization. We therefore rule out a large importance of mechanism 2. Interestingly, simulation work has predicted that by combining co-rotating or counter-rotating pairs of circularly polarized pulses, electron recollision could be preserved.[38] Studies with such pulses have not been conducted here, but might lead to new insight into the strongly coupled electron-nuclear dynamics in the future.

So far, mechanism 3 has only been observed for small diatomic molecules, largely due to the fact that the populated electronic states would need to superimpose in a suitable way to

create significant electron localization. With increasing number of populated states (i.e., for more complex and larger molecules) such as in the case of toluene,[39–42] this becomes less feasible and was in fact also ruled out as a dominant mechanism in recent studies on hydrocarbons.[3,33]

For the reasons outlined above, we thus expect mechanism 4 to be responsible for the observed control of the directionality of the fragmentation of toluene and the migration reactions that produce H_2^+ and H_3^+ fragments. Mechanism 4 has been shown to be a general scheme for steering deprotonation and hydrogen migration in small hydrocarbons.[33,43] Extensive theoretical work will have to be carried out to verify the contribution of this mechanism, which requires knowledge of the potential energy surfaces, and the propagation of wavepackets on those surfaces. Due to the complexity of toluene for the required computations, they were out of scope for the current paper, but we expect the theoretical capabilities to improve significantly over the next years, such that it can be verified if mechanism 4 is responsible for the observed control shown in Fig. 2.

IV. CONCLUSIONS

In the present work, the directional emission of CH_3^+, H_2^+, and H_3^+ fragments from toluene interacting with intense ($\sim10^{14}$ W/cm^2), few-cycle (4 fs) pulses is studied as function of the CEP. Molecular hydrogen fragments with high kinetic energy, and a broad distribution (2.0 to 9.0 eV), are recorded. Their formation involves an intramolecular isomerization process within multiply charged precursor toluene molecules, requiring the break-up of C-H bonds and the formation of bonds between the hydrogen atoms. By varying the CEP of the laser pulses, we show that the directional emission of the CH_3^+, H_2^+, and H_3^+ ionic fragments can be steered. We expect a mechanism involving laser-induced coupling of vibrational states to be responsible for the observed asymmetry in the directional fragment emission. Our experimental work indicates the general importance of this mechanism in the control of the directionality of molecular reactions of larger molecules.

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