The ejection of triatomic molecular hydrogen ions $H_3^+$ produced by the interaction of benzene molecules with ultrafast laser pulses

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The ejection process of triatomic molecular hydrogen ions produced by the interaction of benzene with ultrafast laser pulses of moderate strong intensity ($\sim 10^{14}$ W/cm$^2$) is studied by means of TOF mass spectrometry. The $H_3^+$ formation can only take place through the rupture of two C–H bonds and the migration of hydrogen atoms within the molecular structure. The $H_3^+$ fragments are released with high kinetic energy (typically 2–8 eV) and at laser intensities $\geq 10^{14}$ W/cm$^2$, well above that required for the double ionization of benzene, suggesting that its formation is taking place within multiply charged parent ions. The relative ejection efficiency of $H_3^+$ molecular hydrogen ions with respect to the atomic ones is found to be strongly decreasing as a function of the laser intensity and pulse duration (67–25 fs). It is concluded that the $H_3^+$ formation is only feasible within parent molecular precursors of relatively low charged states and before significant elongation of their structure takes place, while the higher multiply charged molecular ions preferentially dissociate into $H^+$ ions. The ejection of $H_2^+$ ions is also discussed in comparison to the production of $H_3^+$ and $H^+$ ions. Finally, by recording the mass spectra of two deuterium label isotopes of benzene (1,2-C$_6$H$_5$D$_2$, 1,4-C$_6$H$_4$D$_2$) it is verified that the ejection efficiency of some molecular fragments, such as $D_3H^+$, $DH^+$, is dependent on the specific position of hydrogen atoms in the molecular skeleton prior dissociation. © 2009 American Institute of Physics. [doi:10.1063/1.3246832]

I. INTRODUCTION

The interaction of polyatomic molecules with strong laser fields is known to lead to variety of interesting phenomena associated with their multiple ionization, such as the rearrangement of the molecular ions prior to their fragmentation. In some cases, it has been proven that the molecular rearrangement can in fact result in the production of “unexpected” molecular fragments such as the diatomic and triatomic molecular hydrogen ions, with the latter having attracted the interest of several research groups, which resulted in an appreciable number of recent related publications.$^{1-3}$ The triatomic molecular hydrogen is of importance for experimental and theoretical chemical physics (it is the simplest polyatomic molecular system), while its participation in the interstellar chemistry as a proton donor is considered as crucial, especially in ion-molecule reactions leading to complex molecules formation.$^4$

The triatomic molecular hydrogen $H_3^+$ ions have been observed in the mass spectra of several polyatomic molecules induced by strong femtosecond laser pulses, while the majority of the related literature is referring to molecules containing methyl groups, such as alcohol molecules and their deuterium labeled isotopes. Yamanouchi and co-workers, by using the ion-coincidence momentum imaging technique, have proven that the formation of $H_3^+$ from methanol proceeds through different rearrangement channels within the doubly charged molecular ion in competition to the C–O bond fragmentation.$^5$ Moreover, the same authors have shown that the rearrangement can either take place within the CH$_3$-part of the molecule or through a hydrogen atom transfer process from the –OH to the methyl part, while the hydrogen transfer is a fast process taking place within the duration of ultrafast laser pulses, sometimes as short as 60 fs. It has been proposed that the hydrogen migration within different sites of the molecule is a tunneling process that is actually facilitated by the presence of the strong laser field, due to the distortion of the molecular potential surfaces and the lowering of the barriers that restrict hydrogen mobility.$^2-5$

The same mechanism has been proposed for hydrogen migration in laser induced multiple ionization of alkyl halide molecules, leading to the ejection of $H_3^+$ ionic fragments.$^7$

However, some experimental results on the ejection of $H_3^+$ from polyatomic molecules interacting with few-cycle laser pulses and with high kinetic energy ions or electrons suggest that the presence of a strong laser field is not a mandatory condition for the migration of hydrogen atoms. In particular, for the case of the acetylene molecule interacting with moderate strong few-cycle laser pulses (9 fs), hydrogen migration takes place within doubly charged molecular ions and it was concluded that the time for the field free process is about 90 fs.$^8$ Moreover, it was also observed that by stretching the pulse duration to 35 fs the efficiency of the migration process was greatly enhanced.$^9$ Another example is that of the $H_3^+$ ions being observed in the mass spectra of some...
alkenes (CH₄, C₂H₆, C₃H₈) induced by few cycle pulses. The short laser pulse suppresses the possibility of the alternation of the molecular structure during the pulse duration, implying in that way the process of hydrogen migration and the formation of H₃⁺ ions may actually take place in the absence of a strong laser field. Finally, the same is also supported by the fact that the H₃⁺ ion can also be produced by the ionization and fragmentation of different molecules due to their interaction with high kinetic energy cations or electrons. It should be noted that the b-alanine is the first case of molecules noncontaining a methyl group that was proven to eject H₃⁺ fragments. However, during the processes of the research leading to the results shown in the present work, the investigation of H₃⁺ formation has been expanded to additional molecular targets that do not contain methyl groups.

Nevertheless, despite the numerous publications concerning molecular hydrogen ejection there are still important questions that need to be addressed such as the dependence of H₃⁺ ejection efficiency on the parameters of the laser beam, namely, its intensity and the pulse duration. In the present work we present the experimental investigation of the H₃⁺ ion ejection due to the interaction of benzene molecule with fast laser pulses (25–67 fs) by means of time of flight (TOF) mass spectrometry. In the case of the benzene molecule the formation of the H₃⁺ ionic fragment can only take place through the rupture of at least two C–H bonds and the intramolecular migration of two hydrogen atoms within the benzene molecule. It is also of importance to explore if there is any dependence of H₃⁺ ion formation on the specific position of hydrogen atoms in the molecular skeleton prior dissociation. In order to investigate this, two deuterated benzene molecules (1,2-C₆H₅D₂ and 1,4-C₆H₅D₂) have been studied too.

II. EXPERIMENTAL DETAILS

The experimental setup used in the present study includes the laser system and the interaction chamber, which is equipped with an ion-mass TOF mass spectrometer and an electron-energy analyzer. The light source is provided by an amplified Ti:sapphire laser delivering pulses with up to ~0.8 mJ energy per pulse, ~25 fs pulse duration at a repetition rate of 1 kHz, with central wavelength set at 793.7 nm.

The ions that were produced in the molecule-laser interaction are detected and discriminated according to their mass-to-charge ratio using a TOF mass spectrometer. The TOF spectrometer is equipped with three molybdenum disks where dc extraction fields up to 250 V/cm are applied for efficient charge collection. The ions are accelerated and enter the field-free zone of the spectrometer through the apertures of the second and third molybdenum plates, which in both cases are of 2-mm-diameter. The flight tube is a 35-cm-long, gold-plated, copper cylinder with a diameter of 5 cm. In order to prevent external magnetic field effects, a coaxial μ-metal cylinder encloses both the flight tube and the interaction region. A microchannel plate assembly placed at the end of the field-free zone detects the ions. The time-resolved signal is amplified and shaped by a fast constant fraction discriminator and sent to a fast multiscaler personal computer board with ~0.5 ns time resolution. Finally the data are stored in a personal computer and analyzed. The mass resolution was typically 330 at 50 Da. The laser beam is directed and focused into the interaction region by an f = 25 cm plane-convex lens. The laser intensities achieved at the focus were also checked through comparison with the intensities required to produce multiply charged argon ions.

The background pressure of the system was 2×10⁻⁷ Torr, while the molecular vapor was allowed to expand through a needle valve into the interaction region. The pressure in the chamber was kept below 5×10⁻⁷ Torr, depending on the laser intensities conditions, with the view to suppress the possibility of the recorded mass spectra being impaired by space charge effects. The three benzene isotopes (C₆H₆, 1,2-C₆H₄D₂, and 1,4-C₆H₄D₂) purchased by CDN isotopes had a purity better than 99.5% and it was used after several repeated freeze-thaw-degassing cycles under vacuum. Special care is given in order to accurately measure the laser pulse duration in the interaction region. In order to achieve this, the laser beam is reflected by a flipping mirror to a commercial second-order interference-autocorrelator (Femtometer-FEMTOLASERS). This secondary path includes the same optical elements as those of the beam path to the interaction region. The signal from the autocorrelator is monitored in a PC where the data are stored.

III. RESULTS AND DISCUSSION

A. Mass spectra of C₆H₆, 1,2-C₆H₄D₂, and 1,4-C₆H₄D₂

In Figs. 1 and 2 the mass spectra of benzene and two different deuterium labeled isotopes, 1,2-C₆H₄D₂ and 1,4-C₆H₄D₂, recorded at ~8×10⁻¹⁴ and 3×10⁻¹⁴ W/cm², with the laser polarization parallel to the TOF axis, are depicted. Typically, the mass spectra recorded are the average of 3×10⁵ to 4×10⁶ single laser pulse mass spectra. In the inserts of Figs. 1 and 2 the magnified part of the spectrum in the m/z regions from 2 to 6 and from 12 to 18 are also presented. Ionic fragments with m/z=2 and m/z=3 are clearly observed in the mass spectra of C₆H₆, which correspond to H₂⁺ and H₃⁺ ionic fragments. In the past, the observation of these peaks was related to the presence of water contamination in the vacuum chamber and it has been proposed, especially for the case of m/z=3, that it can be attributed to HD⁺ fragment originating from the dissociation of the deuterated isotope of water HDO. Obviously, a similar explanation could be undertaken for the presence of the m/z =2 mass spectra peak. However, this interpretation can be ruled out in the case of the present work, despite of the presence of a strong H₂O⁺ ion peak in the recorded mass spectra, because the relative abundance of the ionic signal of the m/z=2 peak with respect to the H⁺ and that of m/z=3 with respect to the m/z=2 is found to be about 1.6% and 10% at 3×10⁻¹⁴ W/cm², respectively, which is orders of magnitude bigger than that expected by the relative abundance of H and D in nature (0.015%). Moreover, the mass spectra coming from water contamination have been recorded at the same laser intensity region and under similar

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data acquisition conditions as for the case of the presented benzene results. There was no observation of \( m/z = 3 \) ions peak, while \( H^+ \), \( H_2^+ \), and/or \( D^+ \) \( (m/z = 2) \) and \( OH^+ \) \( (m/z = 17) \) have been recorded. In fact, by using the recorded ratios of \( H^+ / H_2O^+ \) and \( H_2^+ / H_2O^+ \) from the background spectra and the amplitude of the \( H_2O^+ \) peak in the mass spectra of \( C_6H_{16} \), it is concluded that the contribution of \( H_2O \) in the \( H^+ \) and \( H_2^+ \) peaks of the latter is less than 3% and 5%, respectively. Finally, it should be noted that the \( m/z = 3 \) ion peak cannot be attributed to \( C_4^+ \) ions because of the relatively low laser intensities used in the present work, for which no \( C_5^+ \) ion peak can be detected in the mass spectra of \( C_6H_6 \). Therefore, the particular peaks can unambiguously be attributed to the \( H_2^+ \) and \( H_3^+ \) ions formed due to the interaction of the benzene with strong laser pulses of fs duration.

The formation \( H_2^+ \) ionic fragment, through a possible dissociation pathway of benzene trication, has been discussed theoretically.\(^{19,20}\) On the contrary, to the best of the authors knowledge, there has been no experimental observation of \( H_3^+ \) ion for the case of \( C_6H_6 \) or a theoretical prediction of its formation due to the interaction of benzene with strong laser fields.

In order to avoid clustering formation of benzene molecules and the possibility of intermolecular collisions within the laser-molecule interaction region, which could be a plausible origin of the particular molecular hydrogen fragments,
the pressure in the TOF chamber has been kept lower than $4 \times 10^{-7}$ Torr, during data acquisition. At this pressure regime and even up to $8 \times 10^{-7}$ Torr it has been confirmed that the total recorded ionic signal presents a linear dependence on the working pressure.

For the case of the atomic and molecular hydrogen fragments, their mass spectra peaks exhibit a complicated profile consisting of different components which originate from the ejection of ions, with sufficient kinetic energy, toward (forward component) or to the opposite direction (backward component) with respect to the detector and therefore present different time of flight. The forward part of the particular peaks consists of well discriminated components while the backward part presents a relatively sharp single peak profile and at the same time its area is much smaller in comparison to that of the forward one. The diversity observed in the peak profiles of the forward and backward components has been reported in the past\textsuperscript{37,38} in the mass spectra ionic peaks produced by the multiple ionization of aromatic molecules by strong laser fields with broad kinetic energy distribution and it can be attributed to the difference in the acceptance angle for the forward and backward ejected ions. Nevertheless, the kinetic energy of the ions produced from the dissociation of different multiply charged precursors can be estimated by taking into account the difference in the TOF of the corresponding components with respect to the backward one.\textsuperscript{23}

The estimated kinetic energy values for the case of the H$_2^+$ molecular hydrogen ions are presented in the insert of Fig. 1(a). As it is depicted, the forward part of the H$_2^+$ mass spectra peak consists of two well discriminated components with kinetic energy values centered on the values: 2.9 and 6.5 eV, which are high enough to indicate that these ions are generated from two dissociation channels taking place within multiply charged states of C$_6$H$_6$. The same is also implied by the fact that the H$_3^+$ could only be detected for intensities ($\approx 10^{14}$ W/cm$^2$), well above that required for the production of [P$^{2+}$] molecular ions and even the CH$_3^+$ fragments [Fig. 2(a)], which are known to originate from excited states of the doubly charged molecular ion.\textsuperscript{24,25} Finally, the estimated values are similar to those measured by Yamanouchi and co-workers\textsuperscript{4} for H$_3^+$ fragments of doubly charged molecular ions of hydrocarbon molecules. The exact ionization/dissociation pathway leading to the production of H$_2^+$ is by no means trivial problem to resolve. This in fact is also true for most cases of the photoinduced fragmentation of polyatomic molecules calling for the use of more advanced detection techniques such as the ion-coincidence momentum imaging. However, this technique has been applied so far in the study of fragmentation dynamics of molecules into a relatively small number of fragment ions due to experimental difficulties.\textsuperscript{26}

For the elucidation of the hydrogen atom sites from where the H-migration becomes probable, the TOF mass spectra of two deuterium labeled isotopes of benzene (1,2-C$_6$H$_4$D$_2$ and 1,4-C$_6$H$_4$D$_2$) have been recorded [Figs. 1(b), 1(c), 2(b), and 2(c)] under similar laser irradiation conditions. The migration processes related to the formation of molecular hydrogen ions can be investigated by observing the mass spectra of the benzene isotopes in the $m/z$ area from 2 to 5. As it is depicted in the inserts of Figs. 1(b) and 1(c), the corresponding mass spectra peaks can be recorded for both cases of the deuterium labeled benzene isotopes. The $m/z=5$ peak can be attributed to the D$_2$H$^+$ ionic fragment, while those observed at $m/z=2$, 3, and 4 can be attributed to H$_2^+$ and/or D$^+$, H$_3^+$, and/or DH$^+$, and D$_2^+$ and/or DH$_2^+$, respectively. In order to investigate the dependence of the ejection efficiency of the molecular hydrogen fragments on the site of the migrating atoms, their relative abundance with respect to the C$^+$ is compared for the benzene isotopes under study. The C$^+$ was chosen as a normalization factor of the number of molecules within the interaction region since all the isotopes have the same number of carbon atoms per molecule. Obviously, the particular approach is valid under the assumption that the ionization/dissociation processes of the benzene molecules are not strongly dependent on the presence of the deuterium atoms. It should be noted that the C$^+$ peak was chosen as a normalization factor instead of that of H$^+$ due to the contribution from water contamination, which varies for different sets of measurements. Even though, the H$^+$ ionic signal can be corrected indirectly by taking into account the abundance of the H$_2$O$^+$ and OH$^+$ ions in each mass spectrum, the normalization of the mass spectra peaks abundance with respect to that of H$^+$ is evidently less accurate than the use of C$^+$ ion peak.

As it is depicted in Fig. 3, for the case of the $m/z=2$ fragment ions, their relative abundance with respect to C$^+$ is the same for the deuterated isotopes, while it is much stronger than in the case of C$_6$H$_6$ implying that these ions are mainly D$^+$. Similar trends have been confirmed for the ratio of the H$^+/C^+$ ratios after carefully subtracting the contribution of water contamination in the H$^+$ ions peak. On the contrary, the $m/z=3$ peak is clearly more abundant in the mass spectra of 1,4-C$_6$H$_4$D$_2$ and 1,2-C$_6$H$_4$D$_2$ than the H$_3^+$ for the case of C$_6$H$_6$, which implies that at least a large part of the peak is DH$^+$. The fact that the abundance of this peak is higher in the case of 1,4-C$_6$H$_4$D$_2$ indicates that the efficiency of the formation of the DH$^+$ presents a site specificity related to the position of the deuterium atoms within the molecular structure. Obviously, for the case of 1,4-C$_6$H$_4$D$_2$ for each of the D atoms there are two H atoms situated in the
neighboring positions in contrast with the case of the 1,2-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2} isotope. The recorded DH\textsuperscript{+} ions can be roughly attributed to two different possible pathways: one involving migration of hydrogen atoms bonded at neighboring carbon atoms and one involving the migration between hydrogen atoms positioned at more distant positions within the benzene molecular structure. In the case of the 1,4-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2} the possibility of the first mechanism contributing to the recorded DH\textsuperscript{+} ion signal is twice that of the 1,2-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2}, while the second pathway is profoundly more probable in the latter case. Therefore, the stronger DH\textsuperscript{+} ionic signal observed in the case of 1,4-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2} in comparison to that of the 1,2-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2} indicates indirectly that the formation efficiency of the diatomic molecular hydrogen depends on the distance between the migrating hydrogen atoms. The same is also confirmed for the ejection efficiency of the D\textsubscript{2}H\textsuperscript{+} ions, by comparing their relative abundance with respect to C\textsuperscript{+} under similar irradiation conditions. In particular, the D\textsubscript{2}H\textsuperscript{+}/C\textsuperscript{+} ratio was found to be \(2.1 \pm 0.3\) \times 10\textsuperscript{-4} for the 1,2-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2} isotope and \(1.3 \pm 0.2\) \times 10\textsuperscript{-4} for the 1,4-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2} at a laser intensity \(\sim 8 \times 10^{14}\) W/cm\textsuperscript{2}. These results are compatible with the interpretation of hydrogen migration as a tunneling process through a hydrogen transfer barrier. The larger the distance between the initial and the final site of the migrating hydrogen the smaller the probability of the tunneling process to take place.

The above approach is based on the assumption that during the H-migration the benzene molecule preserves its basic molecular structure, which implies that the H\textsubscript{3}\textsuperscript{+} formation is a faster process compared to those leading in changes of the molecular skeleton. Nevertheless, the molecular skeleton can be modified as a result of the interaction with the laser beam. The rupture of C–C bonds can lead to different molecular geometries. Typically, these processes are expected to take place after the end of the femtosecond laser pulse. Even though some fragment ions, for instance the CH\textsubscript{3}\textsuperscript{+}, could act as precursors for the recorded H\textsubscript{3}\textsuperscript{+} ions and this possibility should be explored. This assumption is based on the fact that the literature includes numerous examples where the laser induced fragmentation of molecules into H\textsubscript{3}\textsuperscript{+} ions has been associated with the presence of a CH\textsubscript{3}-part within their molecular structure. The particular ions have been recorded in the mass spectra of benzene \(m/z=15\) of Figs. 1 and 2, while the corresponding ions CD\textsubscript{3}H\textsuperscript{+} are observed at \(m/z=17\) in both cases of the deuterium labeled benzene isotopes. The profile of these peaks consists of two (backward and forward) components of similar amplitude, in contradiction with the ones of the molecular hydrogen fragments. The middle mass spectra peak at \(m/z=17\) is observed for all cases of isotopes of benzene and is attributed to OH\textsuperscript{+} coming from the fragmentation of water contamination in the TOF mass spectrometer chamber. The discrepancy in the peak profiles is attributed to the fact that the CH\textsubscript{3}\textsuperscript{+} ions are released through a dissociation channel of the doubly charged molecular ion with a narrow distribution of kinetic energy. In particular, the kinetic energy of the CD\textsubscript{2}H\textsuperscript{+} peak along with the CH\textsubscript{3}\textsuperscript{+} and the \(m/z=16\) one (CD\textsubscript{H}\textsubscript{2}\textsuperscript{+}) is estimated to be \(2.5 \pm 0.2\) eV, which is in accordance to that reported previously.\textsuperscript{27} From Fig. 3, it is clear that the relative abundance of the CD\textsubscript{H}\textsubscript{2}\textsuperscript{+} with respect to the C\textsuperscript{+} is the same for the 1,2-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2} and 1,4-C\textsubscript{6}H\textsubscript{4}D\textsubscript{2}, and therefore in this case the rearrangement process is independent on the distance between the migrating hydrogen atoms which, as stated above, is found to be valid for H\textsubscript{3}\textsuperscript{+} ion production. This result implies that the CH\textsubscript{3}\textsuperscript{+} fragments are not the precursors of the H\textsubscript{3}\textsuperscript{+} ions or at least an additional more efficient mechanism is involved in their formation. In order to have more insight on the mechanism involved in the ejection of molecular hydrogen ions, the dependence of the mass spectra of C\textsubscript{6}H\textsubscript{6} has been recorded for different laser intensities.

B. Dependence on laser field intensity

In Figs. 4(a) and 4(b) the dependence of the ionic signal of H\textsubscript{3}\textsuperscript{+} and H\textsubscript{2}\textsuperscript{+} divided by that of H\textsuperscript{+} is presented. In Figs. 4(c)–4(e) the peak profiles of the molecular and atomic hydrogen ions are presented for different laser intensities. The horizontal axis is the estimated values of the kinetic energy of the fragments. The normalized peak profiles are presented for laser intensities up to \(5.4 \times 10^{14}\) W/cm\textsuperscript{2} in order to suppress the possibility of them being impaired by space charge effects. As it can be observed, the relative ejection efficiency of the molecular hydrogen ions with respect to the atomic ones is decreasing rapidly as the laser intensity increases (for example the H\textsubscript{2}\textsuperscript{+}/H\textsuperscript{+} drops from \(1.7 \times 10^{-3}\) to \(2.6 \times 10^{-3}\) for laser intensities \(3.7 \times 10^{14}\) and \(8.5 \times 10^{14}\) W/cm\textsuperscript{2}, respectively). Within the same laser intensity range, the kinetic energy distribution of the H\textsubscript{3}\textsuperscript{+} and H\textsubscript{2}\textsuperscript{+} ions is found to be independent on the intensity in contrast with that of the H\textsuperscript{+} ion. This experimental result implies that the charge states of the molecular precursors of the H\textsubscript{3}\textsuperscript{+} and H\textsubscript{2}\textsuperscript{+} ions and also their structure (the internuclear distance) are independent on the intensity. It should be noted that the same observation is valid for the case of CH\textsubscript{3}\textsuperscript{+} fragments, originating from the dissociation of [P\textsuperscript{2+}] benzene molecules, which serves also as a confirmation that the estimated kinetic energies are not apparently affected by space charge effects.

On the contrary, in this laser intensity range, the H\textsuperscript{+} fragments are produced with increasing kinetic energies, which implies that they are generated from the Coulomb explosion of molecular precursors of higher charged states. This is especially evident for ions ejected with kinetic energy higher than 10 eV. Therefore, the observed dependence on the laser intensity of the relative ionic signal abundance of the molecular hydrogen ions (H\textsubscript{3}\textsuperscript{+}, H\textsubscript{2}\textsuperscript{+}) with respect to the atomic ones (H\textsuperscript{+}) can be attributed to the relative increase of higher multiply charged benzene molecular ions that favorably dissociate into high kinetic energy H\textsuperscript{+} ions in comparison to the lower charge states that dissociate partly into H\textsubscript{2}\textsuperscript{+} and H\textsubscript{+}\textsuperscript{3}. These results are consistent with the interpretation of the hydrogen migration as a tunneling process through hydrogen transfer barriers (which are suppressed by the laser field), taking place within multiply charged molecular ions, as it was proposed previously for the H\textsubscript{3}\textsuperscript{+} elimination from alkyl iodide molecules.\textsuperscript{7} As the charge states increase, the possibility of tunneling through the transfer barriers is expected to be reduced due to the fact that highly charged molecular ions experience strong repulsive forces leading to a fast elonga-
tion of the molecular skeleton. Moreover, these results are in consistence with the study of $H_3^+$ formation from methanol\textsuperscript{28} according to which the hydrogen transfer is a competitive process to the breaking of the C–O bond.

Therefore, it is reasonable to assume that the precursors of the recorded $H_3^+$ and $H_2^+$ ions could actually be the bound multiply charged states of benzene ($P_n^{m+}$, $n=2–3$) and/or some higher multiply charged states with relatively slow dissociation rate with respect to the 25 fs pulse duration. This is also in accordance with the observed kinetic energy distributions of the $H_3^+$ and $H_2^+$ on the laser intensity. The above argument would also be consistent with that reported for the case of $N_2$ interacting with few cycle pulses (10 fs), where the fragmentation channel $N^{2+}+N^{2+}$ is found to take place from internuclear distances that depend strongly on the laser intensity. This was attributed to the fact that the $[N_2^{3+}]$ has the time to stretch out before its ionization to $[N_2^{5+}]$. On the contrary, the fragmentation channels of the lower charged states are taking place from the equilibrium internuclear distance and therefore present the same kinetic energy release for different laser intensities.\textsuperscript{28}

Nevertheless, the recorded relative abundance of the molecular hydrogen fragments as a function of intensity could also be compatible with a different interpretation \textsuperscript{29} according to which the formation of these ions and their ejection from their molecular precursors are very fast processes taking place during the rise time of the laser pulse. In that case, the produced molecular hydrogen ions released in the rise time of the pulse could dissociate to hydrogen atoms by further interaction with the rest of the pulse. That, however, would only contribute to less than 3\% on the ion signal of $H^+$ ions provided that all the $H_2^+$ and $H_3^+$ fragment to $H^+$ and they are recorded with a quantum efficiency of 1, which is much less than the experimentally observed increase in the high kinetic energy component of $H^+$ (55\%). This approach is based on the assumption that the ejection dynamics of $H_3^+$ is orders of magnitude faster than the reported values for the case of CH$_3$OH (110–550 fs for $H_2^+$ and longer than 1.4 ps for $H_3^+$)\textsuperscript{3} and that of allene (1.2 and 1.9 ps for $H_3^+$ and $H_2^+$, respectively).\textsuperscript{5} According to the authors, for both cases, the precursor species of the $H_2^+$ and $H_3^+$ fragments are trapped in quasibound metastable states and, therefore, they are released long after the end of the laser pulse, while the related hydrogen migration process is actually taking place within the pulse duration (40–60 fs). On the other hand, Baker et al.\textsuperscript{29} using harmonic generation as a probe for the hydrogen motion in the presence of a strong field, concluded that the time scale for proton motion within the H$_2$ and CH$_4$ molecules is actually a few optical cycles. Therefore, it is interesting to investigate the dependence of the ejection efficiency of $H_3^+$ and $H_2^+$ on the laser pulse duration.

C. Dependence on laser pulse duration

In Fig. 5 the ratios of $H_3^+/H^+$ and $H_2^+/H^+$ and the kinetic energy distributions of the atomic and molecular hydrogen ions are presented for different pulse durations at the same peak intensity $4.7 \times 10^{14}$ W/cm$^2$. As it is depicted in Fig. 5(a) the ratios of molecular to atomic hydrogen ions are decreasing for longer pulse durations. Taking into account that the formation of $H_3^+$ and $H_2^+$ fragments can only take place through the migration of hydrogen atoms between different sites of the benzene molecule, the presented results are somewhat in contradiction with that reported on the pulse duration dependence of hydrogen transfer processes taking place within doubly charge states of CH$_3$OH and C$_2$H$_2$. For
both molecules, the hydrogen migration was proven to be more efficient when the pulse duration is increased from 30 to 60 fs for the case of methanol and from 9 to 35 fs for the case of acetylene.

In the present case, the observed dependence of the \( \text{H}_3^+ / \text{H}^+ \) and \( \text{H}_2^+ / \text{H}^+ \) ratios on the laser pulse duration is mainly a result of the increased probability for multiple ionization of benzene for pulses of longer duration. This is evident in the peak profile of the \( \text{H}^+ \) and \( \text{C}^{2+} \) ions presented in Figs. 5(d) and 5(e) for different laser pulse durations and at the same peak intensity. For the case of \( \text{H}^+ \) ion the mass spectra peaks have been normalized to the peak height of the low kinetic energy components. As the duration of the laser pulse is stretched the high kinetic energy component of the \( \text{H}^+ \) mass spectra peak is strongly increased in comparison with the lower kinetic energy ones, indicating the increase in the relative abundance of higher multiply charged molecular benzene ions with respect to the lower charged states. The same is also observed indirectly by the increase in the relative abundance of the \( \text{C}^{3+} \) ions and their kinetic energy distribution peaking at higher values as the laser pulse duration increases. The enhanced multiple ionization probability of benzene at longer pulse durations can be described as a process, where unstable multiply charged precursors, which tend to dissociate fast, are produced at the rise time of the laser pulse. The latter is certainly feasible at the intensity of \( 4.7 \times 10^{14} \) W/cm\(^2\), where the pulse duration dependence study was performed, since ions coming from the fragmentation of multiple charge states of benzene, such as \( \text{C}^{2+} \), are already recorded at lower intensities (\( \sim 10^{14} \) W/cm\(^2\)).

By stretching the laser pulse it is more probable that the metastable molecular ions have the time to reach elongated internuclear distances within the duration of the laser pulse, which are expected to be further ionized more efficiently than molecular ions at internuclear distances near their equilibrium structure. Therefore, as the pulse duration increases the ions produced by the fragmentation of molecular precursors of low charge states (\( \text{H}_2^+\), \( \text{H}_3^+ \)) are expected to decrease in comparison to those originating from higher multiply charged precursors (\( \text{H}^+\), \( \text{C}^{2+} \)), in agreement with the observed dependence of the \( \text{H}_3^+ / \text{H}^+ \) and \( \text{H}_2^+ / \text{H}^+ \) ions on the pulse duration. Similarly, as it shown in Fig. 5(f) the ionic signal of \( \text{CH}_3^+ \), which originates from metastable states of \( [P^2\pi] \), is found to be decreasing for longer pulse durations, while its kinetic energy distribution is independent on this parameter.

Obviously, the proposed interpretation of the enhanced multiple ionization probability is in terms of sequential ionization, which is expected to become more dominant as the laser pulse duration increases. In a recent study, Sharifi et al. proposed that the double ionization of benzene interacting with relatively longer laser pulses (175 fs) is taking place through nonsequential processes at low laser intensities, \( \sim 3 \times 10^{13} \) W/cm\(^2\). According to the same authors, the sequential ionization to higher charge states is becoming dominant at \( \sim 7 \times 10^{14} \) W/cm\(^2\), which is reasonably close to the laser peak intensity \( \sim 4.7 \times 10^{14} \) W/cm\(^2\) used in the present study, supporting in that way our interpretation of the experimental results in terms of sequential ionization.

At this point, the question that arises is whether the recorded relative abundance of \( \text{H}_2^+ \) and \( \text{H}_3^+ \) ions with respect to \( \text{H}^+ \) can be simply considered as a reflection of the abundance of their multiply charged molecular precursors. This simplified approach seems to be somewhat inconsistent with the experimental results: The total signal for \( \text{H}_2^+ \) and \( \text{H}_3^+ \) ions is reduced as the pulse duration is increased, but the reduction rate is not the same for their peak components. In order to facilitate the observation of this trend, the peak profiles of the \( \text{H}_2^+ \) molecular hydrogen ion have been normalized to the height of the smaller kinetic energy peak compo-

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**FIG. 5.** (a) The ionic signal of the \( \text{H}_3^+ \) and \( \text{H}_2^+ \) fragment ions of \( \text{C}_6\text{H}_6 \) with respect to that of \( \text{H}^+ \) as a function of the pulse duration. [(b)–(f)] The calculated kinetic energy of \( \text{H}^+\), \( \text{H}_2^+\), \( \text{H}_3^+\), \( \text{C}^{2+}\), and \( \text{CH}_3^+ \) ions at different laser pulse durations; \( \text{C}_2 \), \( \text{H}_2 \), \( \text{C}_2^+ \), and \( \text{CH}_3^+ \) ions corresponding to 27, 39, 59, and 67 fs, respectively.)
inent as it is depicted in Fig. 5(c). In the case of the \( \text{H}_3^+ \) peak the normalization was ineffective, since the corresponding experimental signal to noise ratio is much smaller than that for \( \text{H}_2^+ \) fragments, and, therefore, it was not applied. From Figs. 5(b) and 5(c) it is evident that, as the pulse duration is increased, the high kinetic energy component of the molecular hydrogen ions is reduced more intensively than the low kinetic energy one.

Making the reasonable assumption that the higher kinetic energy fragments are produced from higher multiply charged states than the lower kinetic energy ones, the dependence of their relative abundance on the laser pulse duration is in contradiction with the increased multiple ionization probability, which has been verified for the longer pulses. Although, the origin of the observed variation cannot be clarified unambiguously on the basis of the experimental results, it seems to indicate that the ionization/dissociation process leading to the \( \text{H}_2^+ \) and \( \text{H}_3^+ \) ejection (ionization to the precursor charge states-hydrogen migration—formation of \( \text{H}_3^+ \), \( \text{H}_3^+ \) ions—ejection of \( \text{H}_3^+ \), \( \text{H}_3^+ \) ions), or at least part of it, is actually taking place within the laser pulse duration.

A plausible interpretation can be proposed, assuming that the migration process of hydrogen atoms between different sites of the multiply charged precursors is taking place within the pulse duration, which, as mentioned earlier, has been shown in the past for the case of methanol and allene interacting with laser pulses of similar duration.\(^2\),\(^3\),\(^5\) Provided that the migration is indeed a tunneling process, and taking into account that its probability is dependent on the length of the hydrogen transfer barriers, the variation of the kinetic energy distribution of the \( \text{H}_2^+ \) and \( \text{H}_3^+ \) ions could be interpreted as a result of different dissociation rates of the precursor charge states. As the pulse duration is increased the precursors of the high kinetic energy components, due the stronger (in comparison to the low kinetic energy ones) repulsive forces, have the ability for extensive elongation within the pulse duration reducing in that way the probability of the hydrogen transfer process, while, at the same time, the competitive process of sequential ionization to higher charge states becomes more plausible. In other words, the formation of the molecular hydrogen ions is only feasible within parent molecular precursors before significant elongation of their structure takes place in agreement with the independence of the \( \text{H}_3^+ \) and \( \text{H}_3^+ \) kinetic energy values on the laser intensity and pulse duration.

However, the possibility that the high kinetic energy molecular hydrogen ions are ejected within the duration of the laser pulses, especially as the later increases, and dissociate further due to interaction with the laser field cannot be unambiguously ruled out on the basis of the current experimental results. A more thorough understanding of the dynamics of the underlying ionization/dissociation mechanism leading to the ejection of molecular hydrogen ions from benzene would be achieved by expanding the presented study to laser pulses of even shorter duration. It should be noted that a study of the dissociation pathways of the triply charged molecular ion of fully deuterated benzene under few cycle laser pulse irradiation has recently been reported by Matsuda et al.\(^32\) However, in the particular publication there is no reference related to the appearance of the hydrogen molecular fragments \( \text{D}_2^+ \), \( \text{D}_3^+ \), which is the central point of the present work.

IV. CONCLUSIONS

The ejection process of triatomic and diatomic molecular hydrogen ions produced by the interaction of benzene (\( \text{C}_6\text{H}_6 \)) with ultrafast laser pulses is studied by means of TOF mass spectrometry. The \( \text{H}_2^+ \) ions are recorded unambiguously for the first time in the mass spectra of benzene molecule. These fragments are released with high kinetic energy (typically 2.0–7.0 eV) and at laser intensities \( \approx \text{10}^{14} \text{ W/cm}^2 \), well above that required for the double ionization of benzene, suggesting that its formation is taking place within multiply charged parent ions. Similar kinetic energies have been recorded for the case of the diatomic molecular hydrogen ions. By comparing the mass spectra of two deuteron label isotopes of benzene (1,2-\( \text{C}_6\text{H}_4\)D\(_2\), 1,4-\( \text{C}_6\text{H}_4\)D\(_2\)) recorded at similar laser intensities, it is verified that the ejection efficiency of some fragments \( \text{D}_2\text{H}^+ \), \( \text{DH}^+ \) presents a site specificity and that the distance between the positions of the migrating hydrogen atoms is of importance.

The kinetic energy distributions of the \( \text{H}_3^+ \) and \( \text{H}_2^+ \) ions consist of two main components centered on values, which are found to be independent of the parameters of laser irradiation, namely, the intensity in the region from \( \approx 3 \times \text{10}^{14} \) to \( \approx 8 \times \text{10}^{14} \text{ W/cm}^2 \) and the pulse duration from 25 to 67 fs. These results indicate that the molecular hydrogen ions originate from multiply charged precursors of particular charge state and structure, before significant elongation of their internuclear distances takes place. The charge states of the \( \text{H}_4^+ \) and \( \text{H}_5^+ \) precursors cannot be univocally identified. However, the experimental results imply that as the charge state of the molecular ions increases they are preferentially fragmented to atomic hydrogen ions. This is based on the fact that the \( \text{H}_4^+ / \text{H}^+ \) and \( \text{H}_5^+ / \text{H}^+ \) ratios are decreasing strongly as the laser intensity increases, while, at the same time, the relative abundance of the high kinetic energy part (>10 eV) of the \( \text{H}^+ \) peak is increased.

The same experimental trends are recorded as the duration of the laser pulse is stretched from 25 to 67 fs, at constant peak intensity. These observations are attributed to the fact that the multiple ionization of benzene becomes more efficient for longer laser pulses as it has been securely verified on the basis of the experimental results. The enhanced multiple ionization probability is ascribed to a sequential mechanism. This implies that the multiply charged molecular ions formed during the rise time of the pulse tend to dissociate fast and, therefore, reach elongated internuclear distances, where the probability for further ionization is expected to increase.

Moreover, the same observations are somehow in contrast with that reported for hydrogen migration taking place within doubly charged states of methanol and allene, where an increase in the migration efficiency was achieved by stretching the pulse duration [from 30 to 60 fs (Ref. 30) and from 9 to 35 fs,\(^9\) respectively]. Although the irradiation conditions applied in the present work and that of Refs. 30 and 9.
are somewhat different, the observed discrepancy seems to indicate that the dynamics of the hydrogen transfer process and the formation of the $\text{H}_2^+$ and $\text{H}_3^+$ ions are dependent on the specific molecular target. This would be in accordance with the description of hydrogen migration as a laser induced tunneling process through hydrogen transfer barriers, since the efficiency of the process is expected to depend on the characteristics of the barriers (length, depth) and, therefore, on the actual structure of the molecules.

Finally, the relative abundance of the “high” kinetic energy component of the $\text{H}_3^+$ and $\text{H}_2^+$ hydrogen ions is found to be reduced for longer pulse durations with respect to the “low” kinetic energy one, which, in fact, suggests that the timescale of the process leading to the formation of the particular ions is comparable to the laser pulse duration used in the present study, i.e., in the order of tens of femtoseconds. However, in order to have a complete understanding of the dynamics of the $\text{H}_3^+$ and $\text{H}_2^+$ ejection process, further experimental work is required with laser pulses of shorter duration.

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