H₂ roaming chemistry and the formation of H₃⁺ from organic molecules in strong laser fields

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Roaming mechanisms, involving the brief generation of a neutral atom or molecule that stays in the vicinity before reacting with the remaining atoms of the precursor, are providing valuable insights into previously unexplained chemical reactions. Here, the mechanistic details and femtosecond time-resolved dynamics of H₃⁺ formation from a series of alcohols with varying primary carbon chain lengths are obtained through a combination of strong-field laser excitation studies and ab initio molecular dynamics calculations. For small alcohols, four distinct pathways involving hydrogen migration and H₂ roaming prior to H₃⁺ formation are uncovered. Despite the increased number of hydrogens and possible combinations leading to H₃⁺ formation, the yield decreases as the carbon chain length increases. The fundamental mechanistic findings presented here explore the formation of H₃⁺, the most important ion in interstellar chemistry, through H₂ roaming occurring in ionic species.
As one of the most abundant, yet simplest, triatomic cations in the universe, the trihydrogen cation \( \text{H}_3^+ \) plays a vital role in interstellar gas-phase chemistry by facilitating the formation of molecules such as water and hydrocarbons. Clues regarding the fundamental dynamics and mechanisms of these chemical processes may be obtained from laser-induced dissociation processes producing \( \text{H}_2^+ \). The production of \( \text{H}_2^+ \) from various organic molecules following excitation with intense femtosecond laser pulses has been reported previously\(^3\)–\(^13\). However, the exact mechanism(s), timescale(s), and yield(s) for this reaction have remained a mystery. In a recent study\(^14\), we provided experimental and theoretical evidence for the existence of two reaction pathways for the formation of \( \text{H}_2^+ \) from methanol under strong-field ionization. In brief, both reaction pathways are initiated by the ultrafast double ionization of the parent molecule and proceed through prompt formation of a roaming neutral \( \text{H}_2 \) moiety from the methyl site. By roaming, here we imply that a neutral fragment explores relatively flat regions of the potential energy surface far from the minimum energy path\(^15\)–\(^19\). In doubly ionized methanol, the roaming \( \text{H}_2 \) fragment abstracts a third proton from the methyl carbon or from the hydroxyl oxygen leading to the formation of \( \text{H}_3^+ \). Experimental findings for methanol and its isotopologues showed that the proton transfer is faster from carbon than from oxygen. In both these \( \text{H}_2^+ \) formation pathways, the multiple bond cleavage and bond formation processes, and the roaming of the neutral \( \text{H}_2 \) moiety, all occur within a 100–250 fs timescale in our experiments. This recent finding, associating neutral \( \text{H}_2 \) roaming with the formation of \( \text{H}_3^+ \) under strong-field excitation, inspired a series of additional experiments aimed at elucidating aspects of this novel chemical reaction mechanism.

The recent recognition of roaming mechanisms has deepened our understanding of certain exotic chemical reactions\(^15\)–\(^19\). Roaming has been widely observed in highly excited polyatomic molecules, for which photodissociation proceeds through trajectories other than the minimum energy pathway. Typically, roaming takes place on a flat region of the potential energy surface, thus allowing nascent reaction products to remain near each other long enough for further reactions to occur. Of particular interest to the work presented, recent studies have focused on roaming processes in small organic molecules such as acetaldehyde\(^20\)–\(^22\), acetone\(^23\), methyl formate\(^24\)–\(^26\), and propanone\(^27\). In most cases, the roaming pathway contributes a small fraction of the total yield. However, certain photodissociation pathways, such as the visible light-induced \( \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \) decomposition reaction, occur solely via a roaming mechanism\(^28\)\(^,\)\(^29\). Similarly, the roaming of a neutral hydrogen molecule is essential for \( \text{H}_3^+ \) formation from the methanol dication\(^14\).

While roaming mechanisms have been well established in neutral molecules, the same cannot be said about ionic species. Outside of our work, to the best of our knowledge there is only one theoretical prediction of \( \text{H}_2 \) roaming in the dissociative ionization of allene\(^30\). A theoretical analysis on the \( \text{H}_3^+ \) formation reaction from ethane identified a transition state with a \( \text{H}_2 \) molecule attached to a \( \text{C}_2\text{H}_2^+ \) ion\(^8\). However, in that study, no evidence was provided confirming \( \text{H}_2 \) roaming during the dissociation of the ethane dication. Based on the above background, together with our previous work\(^14\), one might speculate that all \( \text{H}_3^+ \) formation pathways originating from organic molecules require neutral \( \text{H}_2 \) roaming, regardless of whether such mechanisms are initiated by charged particles or intense femtosecond laser fields. While scientifically confirming or refuting the validity of such a general statement is beyond the scope of this work, a systematic study of \( \text{H}_3^+ \) formation reactions on a family of molecules can provide valuable information about this relatively unknown \( \text{H}_2 \) roaming mechanism in ionic species. Our work on the simplest alcohol cation\(^14\), and the follow-up experimental and theoretical work presented here on a series of alcohols, constitute most of what is known about \( \text{H}_2 \) roaming and \( \text{H}_2 \) migration mechanisms occurring in ionic species. Here the roaming \( \text{H}_2 \) molecule acts as a Bronsted–Lowry base\(^31\)\(^,\)\(^32\) accepting a proton from the highly acidic doubly-charged fragment ion.

As the initiator of many interstellar chemical reactions, \( \text{H}_3^+ \) is a catalyst for the formation of dense molecular clouds containing complex organic molecules\(^33\)\(^,\)\(^34\)\(^,\)\(^35\). The formation reaction\(^35\), existence in interstellar space\(^36\)\(^,\)\(^37\), and spectroscopic properties of the \( \text{H}_3^+ \) ion, as well as its importance in the ion chemistry of interstellar molecular clouds are well documented\(^38\)\(^,\)\(^39\)\(^,\)\(^40\). In interstellar media, an environment rich in molecular hydrogen, protonation of molecular hydrogen is initiated by cosmic radiation. As proposed by Hogness and Lunn\(^35\), a bimolecular reaction involving neutral and singly ionized hydrogen molecules yields \( \text{H}_3^+ \), i.e., \( \text{H}_2 + \text{H}_3^+ \rightarrow \text{H}_3 + \text{H} \). It is worth noting here that the proton abstraction by \( \text{H}_2 \) observed in methanol resembles the Hogness and Lunn reaction leading to the formal \( \text{H}_3^+ \). In addition to its formation through femtosecond laser excitation, \( \text{H}_3^+ \) has been observed from certain organic molecules via electron impact\(^42\)\(^–\)\(^44\), proton impact\(^45\)\(^–\)\(^47\), and highly-charged ion collisions\(^38\)\(^,\)\(^49\) under laboratory conditions. Most of what is known about \( \text{H}_3^+ \) chemistry comes from reactive scattering experiments and from ion-neutral reactions in flow drift tubes. These measurements, full collisions, provide reaction cross sections and in some cases angle-resolved product state distributions\(^50\)\(^–\)\(^52\). Unimolecular photodissociation reactions, half collisions\(^53\)\(^,\)\(^54\), proceed from a well-defined geometry and can be studied with femtosecond time resolution\(^55\). Here we apply the concept of half-collision to learn about the femtosecond dynamics of reactions involving \( \text{H}_3^+ \) produced from alcohols\(^56\) and their importance in astrochemistry in the formation of larger complex molecules through protonation\(^57\)\(^,\)\(^58\). Our study helps reveal dynamics and mechanistic details that are not measurable in reactive ion-neutral scattering studies. Furthermore, our findings are relevant to chemistry initiated by cosmic radiation including photons and electrons with energies in the 30–100 eV range. Given the abundance of hydrogen in organic compounds, solvents, and fuels, the neutral hydrogen roaming chemical reactions discussed in this work may be relevant to condensed-phase chemical reactions involving superacids\(^59\), soot formation in combustion chemistry\(^60\), charged particle-impact-induced chemical reactions\(^61\), and gas-phase acid/base reactions including those that formed the first organic compounds in the universe\(^2\).

In this article, we examine the involvement of \( \text{H}_2 \) roaming mechanisms in ionic species in the formation of \( \text{H}_3^+ \) from a series of alcohols under strong-field excitation and investigate the effect that longer carbon chains have on the yield of \( \text{H}_3^+ \). The formation pathways of \( \text{H}_3^+ \) via the roaming \( \text{H}_2 \) mechanism for methanol and ethanol, which are triggered by the strong-field double ionization of the corresponding parent molecule, are shown in Fig. 1. When comparing the doubly-charged structures to their neutral counterparts, one can clearly see the elongation of C–H bonds and the narrowing of the H–C–H angle on the α-carbon atom. Based on our previous study\(^14\), we consider that these intramolecular changes are the primary motions leading to the formation of neutral \( \text{H}_2 \) and eventually of \( \text{H}_3^+ \). Here we evaluate the validity of this mechanism and the influence of alkyl-chain length by extending our work to a series of primary alcohol molecules: methanol (\( \text{CH}_3\text{OH} \)), ethanol (\( \text{CH}_3\text{CH}_2\text{OH} \)), and 1-propanol (\( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)). Findings for a secondary alcohol, 2-propanol (\( \text{CH}_3\text{CH(OH)}\text{CH}_3 \)), and a tertiary alcohol, tert-butanol (\( \text{CH}_3\text{C(OH)}\text{CH}_3 \)), species that cannot react as proposed in Fig. 1, are then compared. Through in-depth experimental analysis of
product yields and timescales of formation at a peak laser intensity of $2.0 \times 10^{14}$ W cm$^{-2}$, we show that $\text{H}_3^+$ yield decreases as the primary carbon chain length increases. Furthermore, we reveal additional formation mechanisms available for the production of $\text{H}_3^+$ in small alcohols, particularly from ethanol.

Results
Experimental $\text{H}_3^+$ yields. In order to compare $\text{H}_3^+$ production from different alcohols upon ultrafast double ionization, we employed two distinct experimental setups and analysis methods. Using time-of-flight (TOF) mass spectrometry, we are able to compare the total yield of $\text{H}_3^+$ (i.e. the integral over that peak) for each of the different alcohols. Complete TOF mass spectra (TOF-MS) for methanol, ethanol, 1-propanol, 2-propanol, and tert-butanol are given as Supplementary Information Figs. 1–5. For these measurements we carefully controlled the laser excitation and the target density. In order to quantify the $\text{H}_3^+$ branching ratio following double ionization, we carried out coincidence TOF (CTOF) measurements where we directly counted the number of events leading to the $\text{H}_3^+$ formation relative to all dications produced. Further information regarding experimental techniques, setups, and parameter settings can be found in the Methods section.

Quantifying the CTOF branching ratio requires consideration of every coincidence ion pair associated with the production of $\text{H}_3^+$. Specifically, we determined the sum of all measured ion pairs containing $\text{H}_3^+$ (i.e. $\text{H}_3^+$ + $mX^+$) divided by the sum of all single ions and ion pairs originating from the parent dication (i.e. all dication products). Extraction of the pair coincidences is illustrated in Supplementary Fig. 6. The analytical expression for
the CTOF branching ratio is given in the Methods: Experimental setup section (Eq. 2). As explained in Supplementary Note 1, this method has the advantage that it allows a direct comparison of branching ratios among different molecules. While this accounting is relatively easy to do for methanol, it is challenging for ethanol, and very complicated and time consuming for larger molecules. The results from our measurements on a series of alcohols are presented in Fig. 2. The first column (purple) corresponds to the CTOF-determined branching ratio, the second column (light green) corresponds to the integrated \( \Sigma \left[ H_3^+ \right] / \left[ \text{all ions} \right] \), and the third column (dark green) corresponds to the \( H_3^+ \) TOF yield normalized by the total number of ions detected. For comparison, the TOF measurements have been normalized to the measured \( H_3^+ \) branching ratio of methanol obtained by CTOF measurements.

What is immediately visible in Fig. 2 is the reduction in the \( H_3^+ \) formation with increasing carbon chain length, regardless of the measurement technique or the normalization method. Formation of \( H_3^+ \) is most prominent from methanol, even though it has fewer hydrogen atoms per molecule than the other molecules of interest. In the case of ethanol, the production of \( H_3^+ \) is smaller by a factor of about 5 or 3 (for the CTOF and TOF data, respectively) compared to that of methanol. This observation seems counterintuitive; ethanol contains 50% more hydrogen atoms than methanol, suggesting that additional \( H_3^+ \) formation pathways might have been expected, resulting in a higher \( H_3^+ \) yield. To our surprise, upon further lengthening the carbon chain, i.e. in the case of 1-propanol, the total \( H_3^+ \) production drops by an additional factor of 11 or 2 (for CTOF and TOF measurements, respectively) compared to ethanol.

When expressed as a fractional yield, i.e. \( \left[ H_3^+ \right] / \left[ \text{all ions} \right] \) (dark green column in Fig. 2), the TOF results follow a similar trend as observed with total \( H_3^+ \) branching ratios for the smaller three molecules for which CTOF measurements are not too demanding. Though the fractional yield is proportional to the branching ratio for \( H_3^+ \) production, a derivation detailed in the Supplementary Note 1 indicates that the proportionality coefficient depends on the ratio of single to double ionization probabilities, denoted by \( \sigma_1 \) and \( \sigma_2 \), respectively. Explicitly this relation is given by

\[
\sum_j F_3(3,j) \simeq \left( \frac{\sigma_1}{\sigma_2} + 1 \right) \sum_k M(k),
\]

where \( F_3(3,j) \) is the branching ratio of \( H_3^+ + m_j^+ \) and \( M(i) \) is the number of counts measured in a specific TOF peak associated with mass \( m_i \) (assuming singly-charged for simplicity). In spite of the additional dependence on the ionization probabilities, the trend evaluated using the fractional \( H_3^+ \) yield is in reasonable agreement with the branching ratios evaluated directly from the CTOF measurements. This suggests that the \( \sigma_1 \) to \( \sigma_2 \) ratio, which can vary significantly from one molecule to another, varies slowly for the group of molecules in our study. The most likely explanation is that double ionization occurs predominantly from the oxygen atom in the hydroxyl group that is common in all these molecules.

Through our analysis, we learn that the TOF fractional \( H_3^+ \) production allows the discovery of \( H_3^+ \) formation trends, and that even a direct comparison of the measured TOF \( H_3^+ \) yield is consistent with the more complex and in-depth analysis-dependent CTOF method as long as one can maintain the experimental conditions between measurements on different molecules under tight control and the single to double ionization probability does not change significantly between molecules. It is worth noting here that the discrepancy in the CTOF and TOF data for 1-propanol could be attributed to the production of some \( H_3^+ \) from the mono-cation of 1-propanol (a more detailed error analysis is provided in Supplementary Note 2 and Supplementary Figs. 7–9). Having established the qualitative trends of both methods, and calibrated the TOF data with the best numbers obtained by CTOF on methanol, we are able to evaluate trends among the larger alcohols.

In Fig. 2, we observe that the integrated \( H_3^+ \) yield as well as the fractional \( H_3^+ \) yield from 1-propanol and 2-propanol, which have the same number of hydrogen atoms (and, most likely, have similar photoionization rates), is comparable within the measurement error. Clearly, the arrangement of hydrogen atoms within the molecules is significantly different; however, 2-propanol
possesses a single α-hydrogen atom, which plays a key role in H$_3^+$ formation as we discuss in a later section of this work. In the case of tert-butanol, which has three terminal methyl groups and no α-hydrogen atom in its structure, we expected a reduction in the H$_3^+$ yield. However, no such reduction is observed. The observation of H$_3^+$ formation from tert-butanol implies that an H$_3^+$ formation mechanism exists that primarily involves hydrogen atoms from terminal methyl groups, without an involvement of α-hydrogen atoms. This observation is in agreement with the formation of H$_3^+$ from acetone, in which hydrogen migration is not favorable and H$_3^+$ is solely produced from terminal methyl groups.

Electronic structure calculations. Ab initio electronic structure calculations play an important role in further explaining the observed yields and branching ratios. Further information regarding electronic structure calculations is provided in the Methods: Ab initio calculations and simulations section and in Supplementary Note 3. In methanol, upon instantaneously double ionization of the parent molecule, the positive charges that build up on the oxygen atom draw electron density from the methyl group, thus decreasing the electron density on the hydrogen atoms, as shown in the calculated Mulliken population analysis for the neutral and doubly-charged molecules (Supplementary Fig. 11). This results in weakening of the C–H bonds, causing elongation and favoring detachment of H$_2$ from the parent C atom (Supplementary Fig. 10), an essential step in initiating the roaming mechanism leading towards the formation of H$_3^+$. In the case of ethanol, the depletion of electron density on the α-carbon and the α-hydrogen atoms is partially compensated by the terminal methyl group. Therefore, the α-hydrogen atoms are less positively charged in the ethanol dication than in the methanol dication, as evident in the Mulliken population analysis of doubly-charged ethanol (Supplementary Fig. 11). One can also see that the positive charge on the β-carbon hydrogen atoms is smaller than the α-carbon ones; we therefore surmise that the β-carbon C–H bonds are less likely to favor H$_2$ detachment, resulting in a reduced yield of H$_3^+$. The further reduction in H$_3^+$ yield found for 1-propanol can be attributed to the fact that the electronic induction from the terminal ethyl group is higher than that of the methyl group (Supplementary Fig. 11).

New H$_3^+$ formation pathways. While Fig. 1 shows the primary mechanism for H$_3^+$ formation, the trends observed in Fig. 2 for the different alcohols indicate that other formation pathways exist. Here we address the different mechanisms for H$_3^+$ formation available to alcohols, focusing initially on the two-body fragmentation of ethanol. The complexity arising from having a larger number of hydrogen atoms is addressed by the judicious selection of partially deuterated ethanol isotopologues, which allows us to identify and clearly distinguish several different H$_3^+$ formation pathways.

Figure 3 presents CTOF spectra from dissociative ionization of (a) CH$_3$CD$_2$OD and (b) CD$_3$CH$_2$OH obtained at a peak laser intensity of 3.0 × 10$^{14}$ W cm$^{-2}$, in which four H$_3^+$ formation pathways were clearly identified. Each correlated pair of ions (two-body breakup channel) occurs as a narrow diagonal streak on the two-dimensional ion arrival time map as a result of momentum conservation, for example the ion pair D$_3^+$ and C$_2$H$_4$O$^+$. Data from an ion pair, with the second fragment having a lower mass (lower in the column) is associated with three-body dissociation involving neutral H or H$_2$, and because the neutral fragment carries some momentum, the diagonal streak is broadened. Data from an ion pair, with the second fragment having a higher mass (higher in the column), is associated with a 13C isotopic impurity in the sample (further details pertaining to interpreting the CTOF spectra can be found in Supplementary Information Note 4 and Supplementary Fig. 12). For simplicity, we focus our discussion only on two-body breakup channels leading to the formation of H$_3^+$, which are labeled on Fig. 3. In Fig. 3a, we observe a well-defined, strong coincidence channel that corresponds to the formation of D$_3^+$. As supported by ab initio simulations (described later), we consider that D$_3^+$ formation proceeds via dissociation of a neutral D$_2$ moiety from two deuterium atoms bound to the α-carbon followed by roaming and abstraction of the third proton from the hydroxyl group. This pathway is quite similar to what we observed in methanol, in which the neutral H$_2$ formed from the methyl group abstracts the hydroxyl proton to form H$_3^+$. The next prominent channel in Fig. 3a corresponds to the formation of HD$_2$+, likely resulting when a similar neutral D$_2$ moiety abstracts a β-hydrogen atom from the terminal methyl group. However, in our ab initio simulations, we observe that a roaming H$_2$ moiety can be formed from one α- and one β-hydrogen. Therefore, in the formation of HD$_2$+, we cannot exclude the possibility of an α-deuterium and a β-hydrogen atom migrating (as an HD fragment) and abstracting the oxygen-bound deuterium. Unfortunately, due to $m/z$ degeneracy, the remaining two channels shown in Fig. 3a, i.e. H$_2$D$^+$ (with D$_3^+$) and H$_3^+$ (with HD$^+$), do not provide conclusive evidence for any further pathways. However, as shown in Fig. 3b, by using CD$_3$CH$_2$OH we can isolate two additional channels for H$_3^+$ formation from ethanol, primarily involving β-deuterium atoms. The HD$_2$+ formation channel results from two β-deuterium atoms associating with a single α-hydrogen atom or the oxygen-bound hydrogen. The fourth pathway we identified from CD$_3$CH$_2$OH is D$_3^+$ formation, which only involves β-deuterium atoms from the terminal methyl group. As evident in the later described ab initio simulations, these latter two pathways are most likely initiated by the migration of an α-hydrogen to the terminal methyl site, which enables the ejection of β-hydrogens. Beyond the identification of the above four pathways, further analysis regarding the multiple H$_3^+$ formation mechanisms will be presented elsewhere, in order to maintain the focus of this Communication on comparisons found among different alcohol molecules.

Returning to Fig. 2, it is noteworthy that 1-propanol, 2-propanol, and tert-butanol have approximately the same H$_3^+$ yield, within experimental errors. For 1-propanol, one might expect H$_3^+$ formation paths similar to those described for ethanol, namely the primary pathway described in Fig. 1, and H-migration. However, for 2-propanol the primary mechanism as described in Fig. 1 is no longer available. Therefore, H$_3^+$ formation must follow migration of the α-hydrogen toward either of the methyl groups, or occur directly from hydrogens of the methyl groups. Perhaps having two terminal methyl groups instead of one compensates for the absence of two α-carbon bound hydrogen atoms. Direct formation of H$_3^+$ from a terminal methyl group seems to be the most probable mechanism available for tert-butanol, but having three such terminal methyl groups makes up for not having an H-migration pathway available.

H$_3^+$ formation timescales. The formation timescale of H$_3^+$ was experimentally obtained using a femtosecond pump-probe technique, which utilizes a strong pump pulse to generate the reaction precursor, the doubly-charged parent ion, and a weak probe pulse to interrupt the formation of H$_3^+$. Figure 4 presents the H$_3^+$ yield from methanol as a function of pump-probe time delay over a time period of 1.0 ps. A detailed description of time-dependent features of the complete transient (see Fig. 4 inset) can be found in our previous work. In brief, a strong pump pulse creates the
parent dication, which is then fragmented by the time-delayed weak probe pulse, thus preventing the formation of H$_3^+$+. For short delay times, the probe arrives prior to the formation of H$_3^+$+, the parent dication fragments and we observe a depletion in the H$_3^+$+ yield. The incremental time delay between pump and probe pulses results in an exponential rise that tracks the H$_3^+$+ formation time and reaches a plateau at long time delays > 500 fs. Using a mono-exponential fit given by $y = y_0 + A (1 - \exp(-t/\tau))$, where $A$ is the amplitude, $y_0$ is the offset, and $\tau$ is the time constant, we extracted the formation time of H$_3^+$+. Considering a 95% confidence level for the fit parameters, we observed a fast formation of H$_3^+$+ from methanol, specifically $\tau = 102 \pm 7$ fs, which is in good agreement with our previous work$^{14}$ ($\tau = 98 \pm 4$ fs). Furthermore, as observed in previously published ab initio molecular dynamics simulations$^{14}$, the measured value is in good agreement with the H$_3^+$+ formation time range of 50–150 fs for the mechanism involving the three hydrogen atoms from the methyl group.

Figure 5 presents the pump-probe transients of H$_3^+$+ yields as a function of applied time delay over a time period of 1.0 ps for ethanol, 1-propanol, and 2-propanol. Subsequent to a similar exponential fit described previously, ethanol and 1-propanol exhibit formation times a factor of 2.3 ± 0.2 longer than for methanol, while the formation time for H$_3^+$+ from 2-propanol only increased by a factor of 1.9. Our previous study$^{14}$ found that the roaming H$_2$ molecule abstracts the third proton from the methyl group.

**Fig. 3** H$_3^+$+ formation from ethanol. Truncated coincidence time-of-flight maps focused only on H$_3^+$+ production in two-body channels from dissociative ionization of a CH$_3$CD$_2$OD and b CD$_3$CH$_2$OH in a linearly polarized laser pulse centered about 790 nm, 23-fs long with a peak intensity of 3.0 × 10$^{14}$ W cm$^{-2}$. The labeled dashed lines indicate the two-body breakup ion pairs related to H$_3^+$+ formation from the ethanol dication. The logarithmic color scale depicts the number of ion pairs recorded.
same atom (carbon) faster (~100 fs) than from the adjacent atom (oxygen), due to the longer roaming time (and distance) of the neutral H₂ moiety. With no third α-hydrogen atom available in ethanol or 1-propanol, this latter, slower H₃⁺ formation channel is expected to dominate, as supported by our ab initio simulations. Here the roaming H₂ molecule forms from the α-hydrogens and then abstracts the third hydrogen from the adjacent hydroxyl group. In both molecules, the H₃⁻ formation mechanism takes over when the terminal methyl hydrogens must be involved.

Ab initio molecular dynamics simulations. An adequate first-principles molecular dynamics scheme for the fragmentation of ethanol requires a method that provides a balanced description across all potential closed and open shell fragments, such as the complete active space self-consistent field (CASSCF) method, which was implemented using an active space of 12 electrons in 12 orbitals. A summary of the final hydrogen dissociation products following ab initio molecular dynamics simulations of the photodissociation of doubly-ionized ethanol is reported in Table 1. We notice that the largest pathway is H⁺ formation, which is in agreement with the experimental yield as the H⁺ ion peak is the strongest. The H₂ and H₂⁺ channels were minimal compared to H⁺. H₃⁺ formation was not observed in our CASSCF trajectories due to the limited sampling afforded by these high-level calculations and the low H₂ formation yield.

Our main interest throughout the calculations is to understand and elucidate the H₃⁺ formation mechanism in ethanol and whether it proceeds through formation of a roaming neutral H₂ followed by abstraction of a proton to form H₃⁺ as found in methanol¹⁴. In hopes of observing H₃⁺ formation, we have also carried out molecular dynamics simulations with the electronic structure computed at the quadratic configuration interaction singles and doubles (QCISD) level, which can adequately describe 

### Table 1: Percentage of hydrogen species (summed over all channels) ejected from doubly-charged ethanol that are observed using CASSCF and QCISD ab initio molecular dynamics simulations

| Species        | CASSCF % yield | QCISD % yield |
|----------------|----------------|---------------|
| H⁺ formation   | 38.6           | 30.1          |
| H₂⁺ formation  | 0.5            | 0.0           |
| H₂ formation   | 2.6            | 0.0           |
| H₃⁺ formation  | 0.0            | 0.2           |

Fig. 4 Pump-probe transient for H₃⁺ production from methanol (CH₃OH). Normalized H₃⁺ yield (blue solid line) together with an exponential fit (red solid line) from dissociative ionization of methanol as a function of applied time delay between the pump and probe pulses. In the inset, the complete view of the normalized transient is shown where the dashed rectangle highlights the area of interest displayed in the main Figure. Normalization was performed such that the minimum value of the yield is 0 and the yield at large positive time delays (≥500 fs) is 1.

Fig. 5 Pump-probe transient for H₃⁺ production from alcohols. Normalized H₃⁺ transients from dissociative ionization of different alcohols as a function of applied pump-probe delay. Shown in the figure (in blue solid lines) are a H₃⁺ from ethanol, b H₃⁺ from 1-propanol, and c H₃⁺ from 2-propanol. Normalization was performed as described in Fig. 4 caption. Corresponding exponential fits are shown by red solid lines.
closed shell pathways, such as H₂ and H₃⁺ formation. Though this method surely overestimates the probability of neutral H₂ formation, it also likely provides a very accurate representation of the dynamics following the formation of neutral H₂. To support this assessment, we have benchmarked the validity of QCISD for the formation of H₃⁺ relative to our previous CASSCF calculations¹⁴ using methanol as shown in the Supplementary Note 5. In the benchmark study, we noticed that QCISD was incapable of predicting the formation of the open shell fragment H₂⁺, and at the same time QCISD was biased toward H₂ and H₃⁺ formation as can be deduced from their higher yields compared to the CASSCF results. The observed probability of H₃⁺ formation upon release of H₂ was comparable at the CASSCF and QCISD levels, and the qualitative mechanism was observed to be similar regardless of method (Supplementary Table 2). This mechanism commences with the formation of a neutral H₂ moiety from the α-hydrogen atoms that roams for a brief period until it abstracts a proton from the terminal methyl site or the hydroxyl site. Thus, QCISD is sufficient to understand the H₂ formation pathways as well as H₃⁺ production. Ethanol QCISD results are summarized in Table 1, which shows that H₂ formation is relatively high through which H₃⁺ formation is observed as well.

Two videos of representative H₃⁺-forming molecular dynamics trajectories are included in the online Supplementary Information (Supplementary Videos 1 and 2). These videos show that H₂ forms from the two α-hydrogens, then roams and abstracts a proton from the hydroxyl group to form H₃⁺ (snapshots of a trajectory are shown in Fig. 6). In our molecular dynamics simulations, all the observed H₂⁺ trajectories (4 events out of 2000 trajectories) followed the same mechanism, in which a neutral roaming H₂ formed from two α-hydrogens, then abstracts the hydroxyl hydrogen on timescales between 110 and 220 fs. This is in good agreement with our experimental observations for ethanol presented in a previous section of this study.

The molecular dynamics trajectories were sampled from the ground state minima, which correspond to geometries far from minima on the doubly-charged potential energy surface. The excess energy results in vibrational excitation of multiple bonds and the possibility for multiple bond breaking. Here we focus on bond breaking that results in the formation of a roaming H₂, which is the first step toward the production of H₃⁺. When tracing H₂ formation in ethanol we noticed three different pathways; the main pathway is from the two α-hydrogens, which accounts for about 65% from all the observed H₂ trajectories. The second pathway is initiated with the migration of an α-hydrogen to the β-carbon, followed by the formation of H₂ from one α- and one β-hydrogen. This second pathway was observed in about 29% of the H₂ trajectories. The remaining 6% of H₂ molecules were formed from two β-hydrogens. Interestingly, this pathway was initiated with the migration of an α-hydrogen to the β-carbon prior to the ejection of neutral H₂, i.e. α-hydrogen migration preceded the ejection of two β-hydrogens. Videos showing these three H₂ formation pathways are provided as Supplementary Videos 3-5.

**Discussion**

In summary, we have studied the reaction pathways and ultrafast dynamics associated with the formation of H₂⁺ from a series of alcohol molecules with varying primary carbon chain lengths and molecular structures. Ab initio electronic structure calculations and molecular dynamics simulations, together with in-depth experimental data analysis allow us to refine our understanding of the relatively unknown mechanisms that lead to hydrogen molecule formation, roaming, and H₃⁺ formation. The results presented in this Communication confirm the prevalence of roaming H₂ molecule mechanisms in the formation of H₂⁺. From our findings from methanol, ethanol, and 1-propanol, it is evident that the elongation of C–H bonds and narrowing of the H–C–H angle are the primary initial steps in the formation of neutral roaming H₂. Our key experimental finding, supported by ab initio calculations, indicates that the yield of H₂⁺ decreases as the carbon chain length increases from methanol to 1-propanol. The clear implication is that a mere increase in the number of hydrogen atoms does not necessarily result in increased H₂⁺ yield as H₂⁺ formation pathways are defined by unique features of the molecular structure, such as the prevalence of α-hydrogen atoms. Furthermore, through experimental evaluation of isotopically substituted ethanol, CH₃CD₂OD and CD₃CH₂OH, we unraveled four distinct H₂⁺ formation pathways for alcohol molecules with long primary carbon chain lengths. Observation of D₂⁺ from ethanol isotopologue CD₂CH₂OH, and formation of H₃⁺ from tert-butanol, together with our previous results from acetone¹⁴ point to the existence of a lower-yield pathway exclusively involving hydrogen atoms in a terminal methyl group.

The neutral H₂ roaming chemical reactions studied here provide insights into the exotic and hitherto unknown chemical processes occurring in our universe. Specifically, the combined experimental and theoretical work presented here explores the existence of roaming reactions occurring in ionic species, which have not been widely studied thus far. Based on time-resolved measurements following ultrafast double ionization of small alcohols and confirmed by molecular dynamics simulations, we observe that these H₂ roaming chemical reactions occur in the 100–260 fs timescale. Given that roaming fragments spend time in relatively flat regions of the potential energy surface, the dynamics of these reactions are much slower than those of direct unimolecular dissociation. These reactions take place following double ionization (27.0–30.5 eV) and involve hydrogen atoms, which are very light. Direct dissociation should be expected to be faster than 20 fs, especially because of the Coulombic repulsion within the small molecule. The measured reaction times (100–260 fs) are an order of magnitude slower than what one would expect if the reaction pathways did not involve roaming.

Details learned by studying the unimolecular photodissociation reactions, or “half collisions”²⁵,²⁶, presented in this study enhance our understanding of H₂⁺ reaction mechanisms (i.e. reactive

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**Fig. 6** Molecular dynamics trajectory for H₃⁺ formation. Snapshots at different times from a representative trajectory showing formation of H₃⁺ from ethanol calculated using QCISD ab initio molecular dynamics. The complete trajectory is provided as Supplementary Video 1.

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collisions). Most importantly, we find the H$_2$ roaming molecule behaves as a Brønsted–Lowry base, abstracting a proton to form H$_3$$. In turn, H$_3$$^+$ can behave as a Brønsted–Lowry acid, donating a proton in interstellar reactive collisions. These fundamental findings reveal an important aspect about molecular hydrogen formation from organic compounds under high-energy conditions, the chemistry mediated by the roaming hydrogen molecules, and improve our understanding of the chemical reactions that resulted in the organic compounds that likely led to life in the universe.

**Methods**

**Experimental setup.** A detailed description of experimental setups, parameter settings, and intensity calibration methods utilized in acquiring TOF-MS, pump-probe transients, and CTOF measurements can be found in our previous work$^{14}$. Some salient information relevant to reproducing the data presented in this study are briefly stated below.

Both TOF-MS and pump-probe transients were acquired using a 1-kHz CPA Ti:sapphire laser system delivering 1-mJ pulses with a transform-limited duration (full width at half maximum in intensity) of 38 ± 2 fs and a Wiley-McLaren mass spectrometer. In order to maintain high reliability and reproducibility of data across all molecules, we took great care to maintain crucial experimental parameters, such as laser pulse duration, pulse energy, beam pointing, sample density, and detector bias as close as possible among acquisitions. Occurrence of asymmetric ion yields in our previously published$^{14}$ mass spectra were eliminated by employing a circular slit with a diameter of 12.5 mm. Even though this change may have caused an increased volume effect, we did not observe any significant influence on the presented results. All liquid organic samples (with percent purity better than 99.9%) were first dehydrated for more than 24 h using an ample amount of 4-Å molecular sieve dessicants and outgassed using several iterations of freeze-pump-thaw cycles. During all the measurements carried out, the sample gas pressure inside the mass spectrometer was kept at (3.5 ± 0.5) x 10^{-7} Torr (corrected for Bayard–Alpert ion gauge sensitivity for the specific gas sample being measured, approximately three orders of magnitude higher than the typical base pressure. The intensity of the pump beam was kept at 2.0 x 10^{14} W cm^{-2} and the probe beam’s intensity was set to 1.0 x 10^{14} W cm^{-2}. Polarization of the pump beam was kept parallel to the TOF axis and that of the probe was set perpendicular to the pump. No long-lived doubly-charged parent ion, which is the essential precursor state needed for H$_3$$^+$ formation, was observed due to the pump-probe technique. During TOF measurements, all ions produced within the same laser shot were detected using a chevron micro-channel plate (MCP) detector assembly coupled to a 500 MHz, 2 Gza s^{-1} digital oscilloscope. The ion detection efficiency of the detector plates was not taken into account since in this configuration, the MCP detection efficiency was shown to exhibit a minimal m/z dependence$^{26,28}$. Each data point of a given pump-probe transient (e.g. Fig. 4) is an average value of more than 3 x 10^5 laser shots. The measured signal has an uncertainty lower than 5%. CTOF data were acquired using a Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS)$^{65}$ setup and a CPA Ti:sapphire laser system, known as PULSAR, operating at 1-kHz repetition rate delivering energies up to 2 mJ per pulse. The pulse duration was measured to be approximately 35 fs during the measurements presented in Fig. 2 and reduced to 23 fs for data shown in Fig. 3. High-purity liquid samples were introduced to the UHV chamber subsequent to thorough outgassing. The laser beam was focused to a peak intensity up to 2.0 x 10^{14} W cm^{-2} for CTOF measurements presented in Fig. 3 and directed into a skinned molecular beam created by a supersonic gas jet, producing doubly-charged parent precursors. The polarization of the incident laser beam was set parallel to the TOF axis. The event rate recorded by the detector was kept below 1 event/shot to reduce random coincidence events. In order to obtain statistically significant results, each acquisition lasted more than 10^8 laser shots. The algebraic analysis used for the evaluation of the total H$_3$$^+$ production branching ratios, derived in Supplementary Note 1, is given by

\[ F_{3b} = \sum \frac{M(3,j)}{\sum M(3,i)} \sum \frac{M(3,j)}{\sum M(3,i)} \] (2)

Observing in some previous published works that the C$^+$ yield at m/z=3 of the mass spectrum had been erroneously assigned to H$_3$$^+$ due to degeneracy in m/z, we took extra caution to confirm that there is no contribution from C$^+$ to the ion yield at m/z=3 in our data. In all acquired mass spectra (Supplementary Figs. 1-5), we observed no ions at m/z=4, which can be assigned to C$_2$$^+$, above our detection threshold, an essential precursor for formation of C$^+$$^+$. Thus, we conclude any contribution from C$^+$ yield to our data is insignificant.

**Ab initio calculations and simulations.** The structural rearrangements following ionization were assessed by performing geometry optimization calculations for the neutral and the doubly-charged structures of methanol and ethanol at the CCSD/aug-cc-PVZD level of theory. Mulliken population analysis was carried out at the EOM-CCSD/aug-cc-PVQZ level of theory for both the neutral and doubly-charged electronic configurations of the optimized neutral structures of each alcohol. All CCSD geometry optimizations were carried out using the Molpro 2012.1 software package$^{66,68}$ while the EOM-CCSD property calculations were performed using GAMESS$^{20}$. Ab initio molecular dynamics for the dissociation of doubly-charged ethanol were carried out using the CASSCF method employing 12 electrons in 12 orbitals as an active space. The 6-31G** basis set was used. We also carried out dynamics simulations using QCISD with the basis set 6-311G**$^{21}$. The validity of QCISD was benchmarked for methanol and compared with our previously reported CASSCF results$^4$. The trajectories’ initial positions and momenta were sampled from the vibrational Wigner distribution for the neutral ground state computed in the harmonic approximation at each of the aforementioned levels of theory. The dynamics were integrated up to 300 fs while utilizing the velocity Verlet integrator with a time step of 0.5 fs. A total of 2000 trajectories was computed for each method. CASSCF trajectories were calculated using a development version of TeraChem$^{72–74}$ while QCISD calculations were carried out using Molpro 2012.1$^{75}$. 

**Data availability**

The data that support the findings of this study are available within the Supplementary Information and upon reasonable request from the corresponding author.

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Author contributions

N.E. setup and performed the time-of-flight experiments and coordinated the overall project. T.S. lead the CTOF experiments and their analysis. M.N. performed ab initio calculations and molecular dynamics simulations under the guidance of B.G.L. and wrote relevant sections of the manuscript. N.P.W. and B.M.F. provided significant assistance in executing the time-of-flight experiments. Coincidence measurements were performed by T.S., B.K., P.F., B.J., F.Z., D.K., K.R.P., and K.D.C. under the supervision of D.R., A.R., and I.B.-I. CTOF data analysis, as detailed in Supplementary Notes 1 and 2, was conducted by T.S. under the guidance of I.B.-I. Many valuable insights and suggestions were provided by J.E.J. Final analysis, interpretation, and manuscript preparation were carried out by N. E. with contributions from other authors. M.D. conceived and supervised the project. All authors participated in the scientific discussions and in the revisions of the final manuscript.

Additional information

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