Time-resolving the ultrafast H₂ roaming chemistry and H₃⁺ formation using extreme-ultraviolet pulses

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The time scales and formation mechanisms of tri-hydrogen cation products in organic molecule ionization processes are poorly understood, despite their cardinal role in the chemistry of the interstellar medium and in other chemical systems. Using an ultrafast extreme-ultraviolet pump and time-resolved near-IR probe, combined with high-level ab initio molecular dynamics calculations, here we report unambiguously that H₃⁺ formation in double-ionization of methanol occurs on a sub 100 fs time scale, settling previous conflicting findings of strong-field Coulomb explosion experiments. Our combined experimental–computational studies suggest that ultrafast competition, between proton-transfer and long-range electron-transfer processes, determines whether the roaming neutral H₂ dynamics on the dication result in H⁺ or H₂⁺ fragments respectively.

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Trihydrgen (H$_3^+$) is one of the most abundant ions in the universe with an important role in the formation of complex molecules in the interstellar medium (ISM). The formation of H$_3^+$ and particularly its destruction in the ISM attracts a vast experimental and theoretical effort. While H$_3^+$ is typically formed by H$_2^+ +$ H$_2$ collisions, it is a ubiquitous product of organic-molecule ionization processes such as electron impact, fast ion bombardment, multi-photon strong-field laser ionization, as well as single extreme-ultraviolet (EUV) photon ionization. However, the mechanisms for H$_3^+$ formation, as well as for the related H$_2$ product, are still poorly understood. Early fragment imaging experiments using strong-field laser ionization by Yamanouchi and co-workers exhibited prolonged roaming lifetimes ranging from hundreds of femtoseconds to thousands of picoseconds. Interpretation of multi-photon strong-field laser ionization experiments poses intrinsic challenges due to co-existence of direct and indirect ionization mechanisms. This intrinsic ambiguity has previously been the source of surprising and controversial results—for example concerning the double-proton transfer in a DNA base-pair model, which assignment as a sequential process was challenged due to the co-existing direct and indirect strong-field ionization mechanisms. Furthermore, in the case of methanol, Itakura et al. demonstrated the non-linear sensitivity of the dication dissociation spectra and branching ratios to the exact strong-field laser parameters. Nevertheless, in a recent pump-probe study implementing consecutive strong-field (10$^{14}$ W/cm$^2$) laser pulses, Ekanayake et al. reported H$_3^+$ product signal appearance on an ultrafast (~100 fs) time scale. However, in another recent pump-probe study, also implementing strong-field lasers with similar peak intensities albeit with shorter pulse lengths, Yamanouchi and co-workers were able to observe a ~38 fs beating in the time resolved H$_3^+$ product signal, which time scale they assigned not to its formation dynamics on the final dication but rather to the vibrations of a singly-ionized intermediate. Evidently, strong-field double-ionization can proceed via different competing direct as well as indirect mechanisms, involving intermediate state dynamics that may mask the time evolution of the making and breaking of chemical bonds.

In addition to these experimental challenges, strong-field laser ionization experiments require for H$_3^+$ formation. This intrinsic ambiguity poses intrinsic challenges due to co-existence of direct and indirect ionization mechanisms. Theoretical simulations have paved the way for the experimental timing of the roaming H$_2$ dynamics that forms H$_3^+$ on the low lying states of the dication by excitation to higher lying states, which quench H$_3^+$ formation and enhance three-body fragmentation. The combined pump-probe measurements and the nonadiabatic AIMD trajectory simulations allows us to unambiguously conclude that H$_3^+$ formation in double-ionization of methanol occurs on an ultrafast sub 100 fs time scale, in direct competition with the H$_2^+$ formation channel, settling previous conflicting experimental findings.

**Results and discussion**

**Methanol dication dynamics.** Figure 1 shows the potentials of the low- and the high-lying energy states of the methanol dication as a function of the CO stretch. The dynamics in the latter case typically results in rapid dissociation, accompanied by cleavage of the C–O bond as well as a three-body breakup. In contrast, the dication formed in the low-lying states initially exhibits a potential charge imbalance that hinders direct CE due to the ~3 eV potential barrier indicated in Fig. 1. As a consequence dynamics on the low-lying states are prolonged and highly complex, involving the emergence of a roaming neutral H$_2$. Figure 2 compares the simulated branching ratios for the H$_3^+$ product of roaming H$_2$, with the combined branching ratio for the three-body breakup channels, calculated for each initial

**Fig. 1** The adiabatic potential curves for the C–O bond breaking channel of CH$_3$OH$^{+}$ using MS-CASPT2/(12e,10o)/aug-cc-pVTZ. As the C–O strech coordinate is extended away from the Frank-Condon geometry of the neutral methanol ground state, shown by the black curve, the dication potentials exhibit a ~3 eV barrier that prevents the C–O bond breaking on the low lying states. The potentials are calculated while keeping all other coordinates at their neutral methanol ground state value.
excitation of the methanol dication. Over 1/3 of the ground-state trajectories produce H$_3^+$, this compared with ~4% obtained in previous ground-state simulations that did not include the second order perturbation theory corrections\textsuperscript{26}. The high H$_3^+$ formation probability on the ground state, drops for the higher lying states and is completely quenched once the CO bond cleavage becomes possible above the third excited state. In contrast, the three-body breakup exhibits an opposite trend, which increases for higher-lying excited states.

These theoretical predictions provide a handle for the experimental time-resolved probing of the dynamics using a delayed nIR pulse, following excitation with the ultrafast EUV pulse. Where the time delayed probe will excite the transient dication to higher-lying states, consequently quenching H$_3^+$ formation and enhancing three-body breakup. However, once the excess internal energy is released in a successful CE, the product branching is expected to be less affected by the probe pulse.

In designing the probe pulse, we ensure that its peak intensity is kept well below the threshold for strong-field CE, such that at long negative time delays the branching ratios are identical to the ratios measured with the EUV pulse alone. In particular, the H$_3^+$ formation branching ratio is 6% and the three:two body ratio is 3 to 1. The effect of the nIR probe pulse delay (with respect to the EUV pulse) on the relative enhancement of the three:two body ratio is shown in Fig. 3a. The three:two body ratio increases by up to ~8% at positive time delays, as the nIR probe arrives shortly after the dication formation. This effect decays as the probe pulse arrives and positive time delays longer than ~70 fs. For comparison, Fig. 3b shows the enhancement of doubly-ionized Ne$_2^{2+}$ yield as a function of the nIR probe delay that reflects the instrumental response time. The full line in Fig. 3b represents a fit of the Ne$_2^{2+}$ yield, assuming photoionization of high lying Ne$_{e}^{+}$ cations by the time delayed nIR pulse, which rise time reflects the cross-correlation of the EUV and nIR pulses. The dashed red line represents the corresponding Gaussian cross-correlation function, in agreement with the <35 fs FWHM of our laser pulses. Figure 3c shows the time correlated relative change in the H$_3^+$ + COH$^+$ branching ratio, which exhibits up to ~12% suppression. The full lines in Figs. 3b and 3c show a model trace including an exponential ~70 ± 25 fs lifetime, convoluted with the instrumental time response directly determined based on the Ne$_2^{2+}$ data shown in Fig. 3b. While the three:two body ratio appears to return to its unperturbed value, the asymptotic H$_3^+$ formation remains suppressed by 2.5% even at long time delays. It should be mentioned that while the energy needed to dissociate the H$_3^+$ ground state is ~4.5 eV\textsuperscript{32}, nIR photodissociation of the highly vibrationally excited H$_3^+$ can still be expected\textsuperscript{33,34}. We therefore assign the residual H$_3^+$ depletion at long times to photodissociation of the vibrationally hot H$_3^+$ cations after the CE is completed.

To provide additional insight into the nIR probe mechanism we compare, in Fig. 4, the shapes of normalized KER distributions, collected at different pump-probe delays. The red line shows the KER measured for negative times, where the nIR probe arrives over 150 fs before the EUV pulse. Similar to the branching ratios, the KER spectrum at negative times is identical to the one measured with the EUV pulse only. The blue line shows the KER at positive delays longer than 150 fs, while the open circles show the KER during the transient suppression times. Thus, while the branching ratios reveal clear time dependence, the KER spectra are not significantly affected by the nIR pulse. We therefore conclude that the field of the nIR probe acts as a switch between H$_3^+$ formation and three-body breakup but does not significantly change transient dynamics leading to the specific channel, as suggested for other experiments implementing EUV pump and a
strong-field nIR probe\textsuperscript{27,35}. Photo-excitation of the transient time-evolving dication before the CE is expected to promote also competing C–O bond breaking channels and enhances fragmentation as predicted by the AIMD simulations. Interestingly, the C–O bond breaking branching ratio does not exhibit a clear time evolution within the experimental error bars (not shown), possibly due to its competing enhancement on the higher lying states and suppression by three-body fragmentation\textsuperscript{28}. For the less abundant CE channels of H\textsuperscript{+} + CH\textsubscript{3}O\textsuperscript{−}, H\textsuperscript{2}O\textsuperscript{+} + CH\textsubscript{3}\textsuperscript{+}, statistical errors limit the determination of their individual time evolving branching ratios.

Further dynamical insight can be obtained from analysis of the AIMD trajectories culminating in the formation of H\textsubscript{3}\textsuperscript{+}. Figure 5a shows the time evolving inter-fragment velocity, corresponding to the time derivative of the distance between the H\textsubscript{3}\textsuperscript{+} and COH\textsuperscript{+} products. Before dissociation occurs, the inter-fragment velocity exhibits oscillations between positive and negative values, reflecting the roaming H\textsubscript{2} motion away from and towards the HCO\textsubscript{2}\textsuperscript{+}, prior to the formation of H\textsubscript{3}\textsuperscript{+} as can be seen in the typical AIMD movies provided (see Supplementary Movie 1). Interestingly, Palaudoux et al proposed a possible concerted mechanism for H\textsubscript{3}\textsuperscript{+} ejection from a CH\textsubscript{3}Cl\textsuperscript{2+} dication\textsuperscript{8}. However, none of the trajectories simulated here could be attributed to a concerted ejection of H\textsubscript{3}\textsuperscript{+}. The arrow in Fig. 5a indicates the dissociation time assigned to the highlighted black trajectory, where for each trajectory the dissociation time is defined as the last point of attraction between two dissociating fragments, after which their relative velocity is monotonically increasing until reaching the asymptotic KER. The bars in Fig. 3d show the histogram of the total of 66 trajectories resulting in H\textsubscript{3}\textsuperscript{+} + COH\textsuperscript{+} dissociation, peaking at \textasciitilde100 fs. While explicit theoretical modeling of the nIR probe is beyond the scope of this paper, the experimental time resolved branching ratios can be compared with the simulated suppression time window that tentatively extends from the formation of each simulated dication until its dissociation time. The full line in Fig. 3d shows the average simulated suppression, constructed from the 66 trajectories that form H\textsubscript{3}\textsuperscript{+} and convoluted with the experimental instrumental response, in good agreement with the transient branching ratio measurements and an ultrafast sub 100 fs lifetime.

Previous simulations also showed similar roaming H\textsubscript{2} dynamics within the dication and ultrafast H\textsubscript{3}\textsuperscript{+} formation\textsuperscript{18,26}. However, to understand the ultrafast lifetime of the roaming H\textsubscript{2} it is important to consider also its other decay channels. Earlier AIMD simulations using CISD and CASSCF electronic potentials reported unbalanced charge dissociation of the methanol dication ground state to form H\textsubscript{2} + CHO\textsubscript{2}\textsuperscript{+}, with over 11% and 18% branching ratio respectively\textsuperscript{18,26}. In contrast, the non-adiabatic AIMD simulations using CASPT2 potentials indicate that the neutral H\textsubscript{2} cannot escape, it is polarized and bound by the CHOH\textsuperscript{2+} dication. Like the charge-transfer barrier preventing C-O bond cleavage with unbalanced charge, clearly visible in Fig. 1, the neutral H\textsubscript{2} cannot dissociate before charge is transferred and CE can proceed. In the H\textsubscript{3}\textsuperscript{+} formation mechanism the abstraction of a third proton from either methyl site or hydroxyl site allows dissociation by the transfer of a proton. This mechanism is in direct competition with the transfer of an electron that results in a H\textsubscript{2}\textsuperscript{+} + CHOH\textsuperscript{+} breakup. Figure 5b represents typical AIMD trajectories evolving towards H\textsubscript{3}\textsuperscript{+} formation, showing the inter-fragment velocity between the H\textsubscript{3}\textsuperscript{+} and CHOH\textsuperscript{+} products. The highlighted trajectory exhibits the "inverse harpooning" mechanism\textsuperscript{28}, observed in all the trajectories resulting in the H\textsubscript{3}\textsuperscript{+} + CHOH\textsuperscript{+} breakup. The star labeled arrow indicates the time at which a neutral H\textsubscript{2} molecule begins to separate from the CHOH\textsuperscript{2+} dication on the highlighted black trajectory. Although the relative velocity continues to be positive until the asymptotic dissociation limit is reached, the neutral H\textsubscript{2} is still bound by the CHOH\textsuperscript{2+} dication. This is evident from the deceleration of the relative velocity. Although reaching long inter-fragment distances, as high as 9 angstroms, no neutral H\textsubscript{2} escape. Eventually, at a time indicated by the second arrow, a long-range adiabatic electron transfer from the neutral H\textsubscript{2} to the CHOH\textsuperscript{2+} ignites a CE, producing H\textsubscript{2}. The charge transfer is evident both from the computed Mulliken charges as well as from the sudden transition to a long acceleration to a high asymptotic KER, typical of the long-range Coulomb repulsion. The open and full bars in Fig. 3e show histograms of the times assigned to the neutral H\textsubscript{2} separation and the inverse harpooning times respectively. Interestingly, the competing proton and electron transfer mechanisms that facilitate the release of the two molecular hydrogen ions proceed on comparable ultrafast time scales of \textasciitilde100 fs, in agreement with the measured H\textsubscript{3}\textsuperscript{+} suppression time window on the transient dication. This competition can be directly visualized in a selected trajectory
methanol were sampled from a 300 K AIMD simulation of neutral methanol, calorific understanding of the different pathways for H₂ was found to exhibit ultrafast competition between proton abstraction resulting in H₂⁺ and the “inverse harpooning”, a long-range electron transfer that results in the H₂⁺ + CHO⁻ → H₂ + COH⁺ CE channel. Further experimental and theoretical work on deuteron methanol as well as other organic systems will allow to provide a more detailed understanding of the different pathways for H₂⁺ formation, explored so far only by strong-field laser experiments. Such ultrafast roaming H₂ chemistry, accompanied by competing proton and electron transfer dynamics described here are expected to occur also in other ionized systems produced by ionizing radiation damage, e.g., by cosmic radiation in planetary and interstellar environments or manmade light sources for single-particle CE imaging experiments.15–38.

Methods

Experimental. The single-photon CE imaging setup has been described earlier. Briefly, basis-set experiments were performed using the BAGEL code interfaced with a modified version of the Newton-X program15 for carrying out the formation of H₂⁺. To facilitate the trajectory calculations, the system in adiabatic state n is allowed to hop only to the state m nearest in energy above or below it (i.e., we neglect the non-adiabatic coupling terms r̂mm unless |n−m| = 1). We modified the way Newton-X interfaces with the BAGEL code to enable this approximation. The time step for the NA-AIMD trajectories is 0.3 fs. The ab initio dynamics are typically followed until 300 fs or until the inter-fragment velocities are observed to reach an asymptotic monotonic behavior. At this stage, the effect of the residual long-range Coulomb repulsion on the final velocities is taken into account using the classical equations of motion applied to the center of masses of the cationic fragments. Once the asymptotic fragment identity is determined, the inter-fragment velocities are calculated as the time derivative of the distance between the fragment centers of mass. Data availability

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

Code availability

Simulations were performed using open source programs. Modified code files are available from the corresponding authors upon reasonable request.

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Author contributions
E.L., I.L., and K.G. had equal contributions, where E.L. performed the theoretical calculations and I.L. the experiments. K.G. joined the project after the experimental data was obtained and made important contributions to the data analysis and in the manuscript preparation stages. All authors participated in the writing and the joint analysis of the experimental and theoretical data, guided by R.B. and D.S.

Competing interests
The authors declare no competing interests.

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