DOI: 10.1002/ntls.10022

RESEARCH ARTICLE



Two pathways and an isotope effect in H_3^+ formation following double ionization of methanol

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Abstract

The trihydrogen ion has a central role in creating complex molecules in the interstellar medium. Therefore, its formation and destruction mechanisms in high photon energy environments involving organic molecules are drawing significant experimental and theoretical attention. Here, we employ a combination of time-resolved ultrafast extreme-ultraviolet pump and near-infrared probe spectroscopy applied to the deuterated CH₃OD methanol molecule. Similar to other double-ionization studies, the isotopic labeling reveals two competing pathways for forming trihydrogen: A) H_3^+ + COH⁺ and B) H_3^+ + HCO⁺. We validate our high-level ab initio nonadiabatic molecular dynamic simulations by showing that it closely reproduces the essential features of the measured kinetic energy release distribution and branching ratios of the two pathways of the deuterated system. The success of ab initio simulation in describing single photon double-ionization allows for an unprecedented peek into the formation pathways for the undeuterated species, beyond present experimental reach. For this case, we find that the kinetic energy release of pathway B shifts to lower energies by more than 0.6 eV due to a dynamical isotope effect. We also determine the mechanism for trihydrogen formation from excited states of the dication and elucidate the isotope effect's role in the observed dynamics.

KEYWORDS

AIMD, CASPT2, Coulomb explosion, double-ionization, dynamical isotope effect, HHG, methanol, roaming H2, ultrafast EUV

INTRODUCTION

The trihydrogen ion (H_3^+) is the simplest triatomic molecule. It is often found in many natural and human-made plasmas.¹⁻⁴ In particular, it plays a central role in the formation of complex molecules in the interstellar medium.⁵⁻¹¹ Hence, the reaction mechanisms that lead to its creation and destruction have received significant experimental and theoretical attention.¹²⁻²⁴ In the interstellar medium, trihydrogen is believed to form primarily by the $H_2^+ + H_2$ collisions.³

Nevertheless, it has been ubiquitously identified as a surprising product of many types of organic molecule ionization processes, including electron impact,^{25,26} fast-ion bombardment,^{27,28} multi-photon doubleionization (MPDI) by intense laser pulses,²⁹⁻³⁷ as well as single photon double-ionization (SPDI).³⁸⁻⁴² In particular, H⁺₂ formation from the simplest alcohol (methanol) received special attention due to its abundance in a wide range of interstellar environments.⁴³

H₃⁺ formation occurs on doubly ionized organic molecules and involves a highly nontrivial structural rearrangement of the hydrogen

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atoms.⁴⁴ This intricate process in the dication species occurs with the detachment of a neutral H₂ entity from the parent dication that exhibits roaming dynamics with insufficient energy to escape. Eventually, a proton capture by the roaming H₂ entity occurs, followed by a rapid explosion of the dication into two singly charged fragments that are repelled from each other by the long-range Coulomb force.⁴⁴ This type of H₂-roaming mechanism for trihydrogen formation has also been reported by ab initio molecular dynamics (AIMD) simulations of the dication system.^{29-31,40,41} Several studies found measurable scrambling of the methyl and hydroxyl hydrogens that was experimentally investigated by observing deuterated methanol systems,^{25,28,30-34,38} where to the best of our knowledge, Nakai et al. were the first to confirm simulation predictions and attribute the observed D₂H⁺ ion yields from the Coulomb explosion of CD₃OH to proton capture from the hydroxyl by a roaming neutral D₂.³⁰

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Yamanouchi and coworkers also conducted a series of studies on the H_3^+ formation in the methanol dication using MPDI by intense ultrafast laser pulses.^{30,35,36} Detailed MPDI Coulomb explosion imaging studies revealed the great sensitivity of the experimentally observed products to the precise value of the intense laser pulse parameters.^{30,33,35} The intense laser dynamics are further complicated by sequential ionization contributions to trihydrogen formation, revealed as vibrational beating of the intermediate singly ionized cation.³⁶ Furthermore, Kotsina et al. interpreted the asymmetry parameter dependence in two-color MPDI studies of CH₃OD as evidence for the dominance of an alternative route to trihydrogen formation involving migration of the D atom.³⁴ Subsequently, Dantus and coworkers determined the ultrafast time scale of trihydrogen formation using MPDI pump-probe studies with intense near-infrared (NIR) pulses.²⁹ Further still, MPDI studies explored the trihydrogen creation on larger alcohols,^{31,32} and on deuterated CD₃OH and CH₃OD systems that allow to experimentally distinguish between the hydrogen atoms originating from the methyl and hydroxyl sites based on the products charge to mass ratio.²⁹ Using MPDI, Dantus and coworkers also studied the two pathways A-d and B-d in deuterated CH₃OD methanol,²⁹ where we denote the two pathways in this deuterated system as A-d) H_2^+ + COD⁺ and B-d) H_2D^+ + HCO⁺. And concluded that pathway B involved considerably longer times than A, while releasing higher kinetic energy products (by ~0.5 eV). It was conjectured that the kinetic energy release (KER) difference in the two pathways can be attributed to the significant HCO⁺ and COH⁺ energy difference.²⁹

Toward overcoming the intrinsic challenges of MPDI studies, which are known to exhibit strong sensitivity to the laser parameters,⁴⁵⁻⁴⁸ Luzon et al.⁴⁰ performed Coulomb explosion imaging of methanol using SPDI with ultrafast extreme-ultraviolet (EUV) pulses that allow removing the masking effects of the intense laser field^{29,31,33} and contribution of dynamics on singly ionized states due to sequential photoionization.³⁶ The use of SPDI with low-field EUV pulses, produced by high-order harmonic generation,^{49–51} supplies experimentally measured branching-ratios, channel-resolved KER, and momentum correlation spectra. It also paves the way for time-resolved ultrafast EUV pump and NIR probe spectroscopy.^{52–54} A detailed and multifaceted comparison of the measured data confirmed that the



FIGURE 1 The potential energies of low-lying singlet states of the methanol dication as a function of CO bond extension, showing the barrier for direct Coulomb explosion that results in complex structural reorganization dynamics

nonadiabatic AIMD simulations successfully describe all the observed channels, including CO bond cleavage and H₂O⁺ formation that occurs only on the excited states of the dication.⁴⁰ On the ground state and low-lying excited states, shown in Figure 1, an ~3 eV barrier prevents the direct Coulomb explosion of the CO bond and results in the complex roaming H₂ dynamics. Livshits et al. have shown that excitation of the dication by a time-delayed NIR probe pulse, arriving before completion of the roaming H₂ dynamics, can supress trihydrogen formation and promote three-body breakup.41 Where the ultrafast nature of the roaming H_2 dynamics was attributed to a competing Coulomb explosion channel involving long-range electron transfer, termed inverse harpooning, resulting in H_2^+ formation.⁴⁰ Furthermore, Gope et al. recently confirmed that SPDI predominantly forms the singlet CH₃OH²⁺ states.⁴² The fact that theoretical simulations for these systems agree so well with the SPDI experiments allows us to use them to explore questions that cannot be directly resolved by experiments.

This paper aims to extend the study of trihydrogen formation pathways A-d and B-d in the *deuterated methanol* to pathways A and B of the *undeuterated methanol*, formerly experimentally indistinguishable due to the products' mass identity. For this purpose, we will use detailed nonadiabatic AIMD simulations, which we carefully check and validate using SPDI Coulomb explosion experiments of deuterated CH₃OD methanol. Where dications are prepared by absorption of a single photon from an EUV pump pulse and the time evolving dynamics are probed by a delayed femtosecond NIR pulse.

RESULTS AND DISCUSSION

Coincidence three-dimensional imaging of deuterated methanol (CH₃OD) by broad bandwidth EUV pulses shows that ~8% of the CH₃OD²⁺ dications culminate in trihydrogen production. Where similar to the undeuterated species, the other Coulomb explosion channels include CO bond dissociation with and without proton transfer, as well as many other three-body breakup channels.^{29,30} As the deuteration is localized on the hydroxyl cite, it is possible to



FIGURE 2 The relative change in *R*, the ratio of pathway B versus A yields, as a function of the NIR time-delay t_{NIR} . Blue markers indicate the measured ratio of the deuterated B-d and A-d pathways. The red curve represents the functional form of the AIMD-based theoretical response of pathways A and B in the undeuterated system, convoluted with the instrumental resolution function, where the modulations' amplitude was scaled to fit the data. The shaded region estimates the uncertainty due to the finite statistics of simulated AIMD trajectories

experimentally distinguish between the two trihydrogen formation pathways A-d yielding H₂⁺ + COD⁺, and B-d yielding H₂D⁺ + HCO⁺ by the coincident cation masses and their momenta correlations. The measured yield ratio of B-d versus A-d is R = 1: (7 ± 0.5), indicating that the explosion-igniting proton capture by the roaming H₂ occurs more readily from the carboxyl group than from the hydroxyl group. This measured value of R agrees with the simulated ratio of HCO^+ versus COH⁺ products R = 1.8, as well as with other calculated and measured estimates on similar systems. Where recent MPDI measurements by Dantus et al.,²⁹ Yamanouchi et al.,³⁰ electron impact,²⁵ and ion bombardment ionization²⁸ studies have reported R = 1.5, 1:8.5, 1:7.7, and 1:7, respectively. The potential contribution of the same-mass $HD^+ + CH_2O^+$, considered in MPDI studies as possible background to the H_2^+ + COD⁺ channel, can be neglected in the SPDI data, based on the significantly lower $\sim 2\%$ yield measured for twobody H_2^+ + HCOH⁺ observed in SPDI of the undertreated system.⁴⁰ Furthermore, the lack of H/D exchange between the hydroxyl and carboxyl moieties is reaffirmed by our AIMD simulations, including seven low-lying electronic states of the dication. Moreover, an experimental upper limit of < 0.1% for H/D scrambling probability in SPDI is inferred by comparing the vanishing yield of $CH_2D^+ + OH^+$ coincidences with respect to the predominant $CH_3^+ + OD^+$ channel.

Figure 2 shows the relative change in the measured value of the *R* ratio for the two competing channels as a function of a t_{NIR} time-delay of an NIR probe pulse with respect to the ultrafast EUV pump. Where the $t_{NIR} = 0$ time is independently determined based on the transient CH₃OD⁺ ion yield.⁴¹ At negative times, the probe arrives before the EUV pump and does not affect the dication dynamics. Similarly, at the long t_{NIR} limit, the probe arrives after completion of the Coulomb explosion dynamics and trihydrogen formation and does not signifi-

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cantly affect the ratio of the two pathways. At positive t_{NIR} , the probe suppresses the roaming of the H₂ dynamics, promoting three-body fragmentation instead of trihydrogen formation.⁴¹ When the probe appears in the intermediate range of ~ 150 – 300 fs, a lower value of *R* is observed, probably due to a faster proton capture in pathway A-d (completed on the ~ 100 fs time scale^{29,41}), while a longer pathway B-d can also be supressed at longer time delays. Thus, at intermediate times, the probe pulse generally induces suppression of pathway B-d as reflected in the measured lower *R* values that recover after Coulomb explosion via pathway B-d is mostly completed at t_{NIR} ~300 fs. Our SPDI data, therefore, support the conclusions of earlier strong-field time-resolved MPDI studies that reported τ ~ 100 fs for pathway A-d and τ ~ 240 fs for pathway B-d.²⁹

Although explicit inclusion of a time-delayed NIR probe pulse is beyond scope of the AIMD simulations presented here, trajectory analysis makes it possible to extract channel-resolved roaming times and estimate the time-resolved branching ratio. Figure 3 shows the dication ground-state dynamics of a representative trajectory of undeuterated pathway A, culminating in H_3^+ + COH⁺ formation (left panels) and pathway B, culminating in H₃⁺ + HCO⁺ formation (right panels). Panels A-1 (B-1) show the relative velocity of the center of mass of the three H atoms that eventually form the trihydrogen cation relative to the remaining atoms composing the COH+ (HCO⁺) fragment. The proton capture and resulting Coulomb explosion can be identified at ~150 fs (~260 fs) as the threshold time for a strong monotonic acceleration. After proton capture, the relative velocity rapidly grows due to the long-range Coulomb repulsion, reaching an asymptotic dissociation value measurable as the KER. In panels A-2 (B-2), we see that the onset of roaming can be identified at ~ 60 fs (~ 70 fs) where $R(C - H_2)$, the distance from the roaming H₂ to the carbon atom (dashed line), starts growing and a vibrational signature in R(H - H) (solid line) emerges at \sim 3600 ± 300 cm⁻¹ wavenumbers, typical of vibrationally excited H₂.

We have performed simulations initiated on the dication's excited states and found they exhibit decreasing H_3^+ probability with increasing electronic excitation.⁴⁰ Figure 4 shows a representative pathway A trajectory initiated on the third excited state of the dication, where the color of the trajectory curves encodes the instantaneous time-evolving electronic state. The trajectory shows that the system undergoes a series of surface-hopping events until it reaches the electronic ground state at ~160 fs before the onset of H_2 roaming dynamics at ~180 fs. We observed similar dynamics in all trihydrogen-forming trajectories initiated on excited states of the dication and therefore conclude that the roaming H2 develops primarily on the ground-state potential.

The representative excited state trajectory shown in Figure 4 reaches the ground state and starts roaming at relatively long times. Nevertheless, as shown in Figure 5a, the distribution of roaming onset times of trajectories initiated on excited states does not appear to exhibit a significant delay with respect to roaming onset of ground-state trajectories. Furthermore, within the finite statistics of simulated trajectories, no significant differences in roaming onset can be observed between the pathways A and B. In contrast, each pathway exhibits a different proton capture time distribution showed in Figure 5b. The time it takes for the roaming H₂ to capture a proton



FIGURE 3 Two typical AIMD trajectories corresponding to pathways A and B, occurring on the undeuterated dication ground state. (A-1) shows as a function of time the relative velocity of the center of mass of the atoms that eventually form the H_3^+ and COH^+ fragments. (B-1) shows the relative velocity of the center of mass of the atoms that eventually form the H_3^+ and HCO⁺ products. Panels (A-2) and (B-2) show corresponding distances of the roaming H_2 entity from the carbon atom (dashed line) and the H-H bond length (solid line). The simulations begin at the ionization time, under the Franck–Condon sudden approximation. The green-shaded regions mark the neutral H_2 roaming times, which onset and termination by proton capture are, respectively, identified by the intramolecular distances and relative fragment velocities



FIGURE 4 A representative AIMD trajectory initiated on the third excited state of the dication. Panel A-1 shows the relative velocity of the center of mass of the atoms that eventually form the H_3^+ and COH^+ products, where the color coding indicates the instantaneous electronic state. Panel (A-2) shows the corresponding distances of the roaming H_2 entity from the carbon atom (dashed line) and the H-H bond length (solid line). The green-shaded region marks the neutral H_2 roaming time, which starts shortly after the system reaches the electronic ground state and terminates in a Coulomb explosion



FIGURE 5 Panel (a) shows the similar probability distributions of simulated roaming onset times for trajectories initiated on the ground (open bars) and on excited states (full bars). The probability distributions of simulated proton capture times are shown in panel (b), indicating longer proton capture times for pathway B (red bars) than for pathway A (blue bars). In both panels, the probabilities are quoted from all the simulated trajectories on the seven lowest singlet states of the methanol dication

is, therefore, shorter when the donor is the nearby carboxyl than the more distant hydroxyl.

We can use the simulated proton capture times to produce a theoretical estimate of the functional form of the $R(t_{NIR})$, the ratio of the two pathway yields. For each trajectory, the NIR pulse is assumed to quench trihydrogen formation if it arrives before the proton capture time. After proton capture, the stable trihydrogen is assumed not be further affected by the NIR pulse. Thus, the time dependence of $\Delta R(t_{NIR})/R$ arises solely from the different dissociation time distributions of the two pathways shown in Figure 5b. The resulting functional form, convoluted with the experimental time resolution, is presented by the red curve in Figure 2 and compared with the experimental data. At early and "negative" time delays, when the NIR precedes the EUV pulse and when no trajectory could yet be stabilized by Coulomb explosion, $\Delta R/R$ is negligible. After the relatively rapid (on the order of 100 fs) formation of H_3^+ + COH⁺ via pathway A, the $\Delta R/R$ becomes negative for ~200 fs time window in which the competing H_3^+ + HCO⁺ forming trajectories via pathway B reach proton capture. At longer time delays, trihydrogen ions formed by both pathways are assumed to be similarly immune to the NIR probe pulse, and once again, $\Delta R/R$ is negligible. It is important to note that the quantitative estimate of NIR suppression is beyond the present theoretical analysis. We, therefore, scale the functional form of the simulated response to enable qualitative comparison with the experimental measurement. Furthermore, the simulated trajectories' finite statistics are reflected in the confidence region shown in Figure 2 by the shaded area around the theoretical curve.

The different dynamics of the two trihydrogen pathways are reflected not only in the time-resolved data, but also in the experimentally measured channel-resolved KER distributions. Figure 6a compares the measured KER distribution for pathway A-d, H_3^+ + COD⁺. and for pathway B-d, H_2D^+ + HCO⁺, which are, respectively, shown by the full blue and dashed red curves. The KER distributions of both channels overlap; however, the median KER of each distribution that are indicated by the vertical lines reveal an ~300 meV higher median KER in the longer hydroxyl pathway. This, in rough agreement with earlier strong-field MPDI measurements that report ~5 and ~5.48 eV KER, respectively.²⁹ Ekanayake et al.²⁹ attribute this shift to the over 1.6 eV energy difference between the dynamically favored COH⁺ product and the energetically more favorable HCO⁺.⁵⁵ Figure 6b compares the theoretical KER distributions for pathway A, H_3^+ + COH⁺, and pathway B, H_3^+ + HCO⁺, simulated for the undeuterated system. The median simulated KER for the shorter carboxyl pathway agrees with the experimentally measured KER. However, in contrast to the experimental data, the simulated longer hydroxyl pathway trajectories exhibit a shift toward lower KER. Thus, despite the excess ~1.6 eV potential energy available to the HCO⁺ formation via pathway B, the longer roaming times allow for greater energy redistribution into the products internal degrees of freedom and result in a lower KER.

The alleged discrepancy between the experimental and theoretical results makes it critical to resolve the possible isotope effect. The deuterated hydroxyl is not expected to affect the roaming H₂ dynamics; however, we may expect a difference in the H⁺/D⁺ capture process. We, therefore, performed an additional computational study to



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FIGURE 6 Kinetic energy release distributions of $H_3^+ + COD^+$ and $H_2D^+ + HCO^+$ from (a) CH_3OD^{2+} initiated by EUV experimentally and (b) nonadiabatic AIMD trajectories of CH_3OH (c) nonadiabatic AIMD trajectories of CH_3OD . The vertical lines are median of the distributions

explore dynamics initiated on the deuterated dication CH₃OD²⁺ system. Where dication dynamics were initiated from a slightly different distribution of Frank-Condon geometries that were sampled from ~300 K trajectories of the deuterated neutral system. Figure 6c shows the simulated KER distributions of pathway A-d forming $H_3^+ + COD^+$ and pathway B-d forming H_2D^+ + HCO⁺. As can be expected, the KER distribution of pathway A-d is similar to pathway A and is not affected by the deuteration of the hydroxyl. In contrast, pathway Bd exhibits an isotope shift toward higher KER, in which median value slightly exceeds that of pathway A-d, in agreement with the experimental data. We, therefore, attribute the experimentally measured higher KER in pathway B-d (vs. pathway A-d) not to the relative energies of the HCO⁺ and COH⁺ isomers, but to a dynamical isotope effect. Comparison of the simulated median KER of pathway B-d and pathway B indicates a +0.6 eV shift of the deuterated system. A similar isotope effect was previously reported to result in higher KER in D versus H abstraction reactions.^{56,57} The agreement with the experimental data indicates that the roaming H_2 and H^+/D^+ capture dynamics are successfully described by the nonadiabatic AIMD trajectory simulations performed on CASPT2 potential surfaces and the negligible role of tunneling to the proton capture and H_3^+ formation mechanism.



FIGURE 7 The experimental setup: schematically showing the paths of the EUV pump--near IR probe beams (red), the molecular beam (green) introducing the methanol sample, as well as the correlated cationic products ejected from a single methanol molecule and accelerated toward a 3D coincidence imaging detector

CONCLUSION

Two competing pathways of trihydrogen formation on the deuterated methanol dication were explored both experimentally and theoretically. Dication CH_3OD^{2+} dynamics are initiated by single photon double ionization with an ultrafast EUV pump pulse and probed by a timedelayed NIR pulse. The different formation time scales are probed by suppression of the roaming H₂ dynamics by the NIR pulse, and consequent time-resolved change of the measured Coulomb explosion yields ratio of pathway A-d products H_3^+ + COD⁺ and pathway B-d products $H_2D^+ + HCO^+$. The dominant shorter pathway, in which a roaming H_2 captures a proton from the carboxyl site, trihydrogen formation times peak on an ~100 fs time scale. The duration of longer pathway B of proton capture from the hydroxyl site is delayed and peaks at ~150 fs. The observed and simulated time scales are found to be in qualitative agreement with strong-field MPDI experiments on the deuterated system.³⁰ Detailed comparison of the measured and simulated KER spectra of both trihydrogen formation pathways reveals a dynamic isotope effect that results in a higher KER in trihydrogen formation from the deuterated hydroxyl site. In contrast, AIMD simulations of the undeuterated system predict that a proton capture via pathway B from the hydroxyl will result in a lower KER. Further theoretical investigations are required to quantitatively describe the MPDI studies as well as the EUV pump and NIR probe experiments. Additional experimental and theoretical effort is also required for accounting the role of the competing electron-transfer from the roaming H_2 to the HCOH²⁺ dication and formation of H_2^+ product.

EXPERIMENTAL AND COMPUTATIONAL METHODS

The experimental setup for single-photon Coulomb explosion imaging and theoretical nonadiabatic AIMD simulations has been described earlier.^{39-42,54,58} Figure 7 shows the experimental scheme, in which broad bandwidth ultrafast EUV pulses are produced by high-order harmonic generation (HHG) by focusing sub 35 fs NIR pulses, centered around 800 nm generated at a 1 kHz repetition rate in a semi-infinite neon gas cell.^{50,51}

The resulting EUV pulses are spatially filtered from the higher divergence NIR.⁵⁹ Additional 4.5 mJ of the Solstice laser output is time delayed, mildly focused to ~400 μ m and merged with the EUV pulse at a small ~1 degree angle at the center of a home built 3D coincidence imaging spectrometer, where both beams cross a skimmed effusive beam of commercially available CH₃OD samples. The cationic products are accelerated and their coincidence 3D momenta are imaged on a time and position sensitive detector.^{39,60} True Coulomb explosion events are disentangled from an overwhelming dissociative ionization background based on the total momentum conservation of two coinci-

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dent hits on the detector and any residual false coincidences are evaluated and subtracted based on the measured probabilities of single ion events.³⁹

Theoretical nonadiabatic AIMD simulations were performed using CASPT2 potentials.⁶¹⁻⁶⁶ Nonadiabatic dynamics were approximated using surface-hopping molecular dynamics trajectories,⁶¹ generated at the XMS-CASPT2/(8e,8o)/aug-cc-pVDZ level using the BAGEL electronic structure package.⁶² A more detailed description of the AIMD simulation is provided in our previous work concerning the Coulomb explosion dynamics on the singlet manifold of methanol dication states.⁴⁰ In order to determine the relative probability of different double-ionization product channels, we have initiated over 100 trajectories on each of the ground- and six low lying excited-states. Where the initial phase-space configurations were sampled from neutral ground-state AIMD simulations at 300 K, performed for the respective undeuterated and deuterated systems on the CASSCF level using the MOLCAS package.⁶⁴

The supplementary molecular dynamics movie shows the competing H_3^+ formation dynamics via pathway A and pathway B, simulated starting from two different geometries on the first excited state of the Methanol dictation. In both cases, roaming H_2 dynamics are observed to start after the system performs hopping to the ground-state potential energy surface (SI).

ACKNOWLEDGMENTS

We acknowledge European Research Council through grant number #306783 and ISF grant #1369/17 as well as equipment from the Wolfson foundation. RB acknowledges support from the Israel Science Foundation Grant number ISF- 800/19.

DATA AVAILABILITY STATEMENT

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

TRANSPARENT PEER REVIEW

The peer review history for this article is available at https://publons. com/publon/10.1002/ntls.10022.

COMPETING INTERESTS

The authors declare no competing financial interests.

AUTHOR CONTRIBUTIONS

Krishnendu Gope was involved in investigation; writing-original draft; writing-review and editing. Ester Livshits was involved in investigation; writing-review and editing. Roi Baer and Daniel Strasser carried out supervision; and were involved in writing-review and editing.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Gope K, Livshits E, Bittner DM, Baer R, Strasser D. Two pathways and an isotope effect in H_3^+ formation following double ionization of methanol. *Nat Sci.* 2021;1:e10022. https://doi.org/10.1002/ntls.10022