nature portfolio

Peer Review File

Factors Governing H_3^+ Formation from Methyl Halogens and Pseudohalogens

Corresponding Author: Professor Marcos Dantus

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Stamm et al. report on a study about the generation of H3+ ions from a series of methyl halogens and pseudohalogens through double-ionization by strong ultrafast laser pulses. The experiments are complemented by both static electronic structure calculations and simulations of the ionization-induced H3+ generation dynamics. They observe significant differences in the H3+ yield from 6 different investigated species. They formulate three criteria for efficient H3+ generation, based on the minimum geometry of the lowest doubly-ionized state in the molecules and the difference between the available energy to the molecules in the ionized state and the dissociation energy for H2 abstraction.

I have doubts about the relevance of the experimental part of the study to interstellar chemistry. The authors claim this relevance through the importance of the H3+ species and the need to understand its generation mechanism. The authors employ a double ionization mechanism through tunnel-ionization followed by rescattering of the ejected electron driven by the strong laser field. I find it questionable if any insight from investigating H3+ generation through such a process is transferrable to generation mechanism in interstellar space, where such strong, coherent electromagnetic fields are generally missing. It is well-demonstrated (see e.g. 10.1103/PhysRevLett.116.193001) that in the intensity regime employed in this experiment the electronic potentials for the nuclei of the molecule are substantially modified by the laser field. This can lead to field-induced dynamics, specifically for protons. The supplementary video shows that significant parts of the H3+ generation mechanism of CH3OH take place within the temporal envelope of the ionizing pulse. Therefore, I am not convinced that the authors can rule out the possibility that H3+ generation in the experiment is at least in part field-induced. I do not have any reason to doubt the simulations, which are performed on an impressive level of electronic structure theory. I just believe that the experiment is not a good match to benchmark the theory, specifically, since the theory neglects the influence of the laser field.

I have additional doubts about the impact of the conclusions from this study. Based on their results, the authors formulate three criteria for the efficient generation of H3+. Two of them are based on the minimum geometry of the molecules in the doubly-ionized state, particularly the proximity of two of the three CH3 hydrogens and their distance from the carbon. The third is based on the ratio of the available excess energy after relaxation in the dicationic state, termed as the adiabatic relaxation energy, and the required energy to abstract H2 from the dication (dissociation energy). Based on Fig. 6 in the manuscript, I cannot see the need for three criteria. The H3+ yield correlates well with the third criterium, the ratio of adiabatic excess energy and dissociation energy. Moreover, the authors mention simulations on the CH3F compound which cannot be explained by the established criteria. Therefore, I have serious doubts about the predictive power of the presented criteria.

Based on the points I outlined above, I cannot recommend publication of the manuscript in Nature Communications. I believe that an appropriately modified manuscript will be of interest to the strong field physics community.

I have further, more technical comments:
• Figure 1 suggests that the laser field only plays a role in the first step of the visualized process. I believe this is misleading. A significant part of the dynamics can be assumed to take place in the presence of the laser field.

• The researchers performed 800 nm strong field pump / 800 nm weak field probe experiments which they call disruptive probing. They observe a dependence of the H3+ yield on the pump-probe delay, but do not elaborate on the probing mechanism. It is unclear to me what exactly the nature of the probe interaction is. The authors seem to interpret it as a disruption of the generation mechanism of H3+ but do not elaborate how that would happen. I also do not understand the nature of the model underlying the function used in the fits to the experimental data. Therefore, it is unclear to me if and how the fit results can be compared to timescales extracted from the simulations.
• The dynamics simulations assume the reaction to take place in the respective lowest, field-free singlet state. I'm not sure if this assumption is strictly valid for the processes triggered in the experiment by strong-field ionization or even by other double ionization mechanisms. Could this be the reason for the large differences in simulated and experimental H3+ generation timescales?
• I am not convinced that the relaxed geometry in the dicationic state plays a major role in the reaction dynamics given the in part significant excess energy of the molecules (2.5 eV in case of methanol). Looking at the supplementary movie of methanol, the initial motion looks more like a frustrated abstraction of a single hydrogen than the suggested lengthening of two C-H bonds and a simultaneous approach of the two hydrogens.

Reviewer #2

(Remarks to the Author)
These comments are also included as an attached PDF.

Key Results:

The paper's overall theme is to evaluate the roaming process by which H3+ is produced from dications of the methyl halides and their analogues with formulae of the form CH3X, where X = OH, Cl, NCS, CN, SCN, and I. The authors aim to elucidate the criteria which determines the possibility and probability of this of this process occurring in these different species, and the timescale of formation.

The paper's results are split between experimental results and calculations, with a stronger focus on the latter.
To summarise the experimental scheme and results: time resolved, measurements of the ion yields were measured using an ultrafast, "disruptive probing" pump-probe scheme (described in detail in ref. [36] of the paper) where a strong infrared pulse is used to tunnel ionise the molecule followed by further ionisation by the recolliding electron to produce di-cations which dissociate. A weaker pulse probes the dissociation pathways by disrupting the product formation. The final ion states are measured with a Wiley-McLaren type mass resolving spectrometer. Static, pump-only measurements focus on the mass/charge region near m/q= 3.0 (with the two peaks at higher lower masses attributed to H3+ produced in the charge separation process $CH3X^{++} \rightarrow CX^{+} + H3^{+}$) with statistically meaningful quantities observed for X = OD, Cl, and NCS (the yield progressively decreasing), and little/no signal observed in the other species. Time-resolved measurements including the disruptive probe yielded timescales of formation, with the shortest of ~60 fs for Methanol and the longest of ~650 fs for Methyl chloride.

These results were supplemented by thoroughly comprehensive computations of the geometries and bond lengths of the ground state and dications of all six species, the vertical/adiabatic ionisation energies, and ab initio molecular dynamics simulations of chosen species. The authors use these results to define 3 key criteria that must be fulfilled to determine why H3+ is observed to be produced efficiently by some dicationic species but not others: (i) sufficient elongation of the CH bonds in the dication, (ii) that a pair of hydrogens in the dication become sufficiently close so as to be comparable to the internuclear separation of neutral H2 and (iii) that the adiabatic relaxation energy of the dication exceeds the dissociation energy of $CHX^{+} + H2$.

Suitability for publication:

Overall, I think the paper presents a comprehensive study with sufficient novelty and quality to justify eventual publication. The extensive supporting material, including the geometrical data and the movies of the AIMD simulations were extremely nice to see, and the paper is written such that the main text is broadly accessible to the general audience while also including extensive material in the supporting sections that would provide ample information for a specialist in the field. The included figures are, overall, clear and concise.

While some results with a similar scope have been previously reported for some of the studied molecules, the paper's unique selling point is the in-depth comparison between the entire set of molecules, and the criteria the authors have established in predicting the yields of H3+, which will prove useful in predicting the production of H3 in other species. Though I think these results will most likely be of primary interest to those in the atomic and molecular physics and chemical physics spheres, the authors have done a good job in their introductory and discussion sections in justifying the results' relevance to other, broader fields of interest, in particular astrophysical contexts and models of the primordial universe. Therefore, I think that the paper provides sufficient justification for its eventual publication in a broader interest journal like Nature Communications.

There are however some open questions with the paper I feel are necessary to address before I can wholeheartedly recommend that it should be accepted for publication. These, and some suggestions for improvements, are detailed below:

1) H3+ has also been observed to be produced by dications of unsaturated hydrocarbons such as ethylene, allene, and

larger alcohols [1-2]. The paper primarily focuses on the relevance of their results and established criteria purely in the context of modelling specifically the pseudohalides, but since some of the larger chain molecules (or close analogues) may also have astrophysical significance, I wonder if the authors can discuss if and to what extent their criteria might also apply to these larger systems (or to phrase it differently: how large can X be and their results still hold?) I think this would help to put their work in the broader context of H2+ and H3+ production by roaming mechanisms and further justify its publication in a broader-reach journal.

2) In the analysis of the ion yields presented in section 2.1 of the paper as I read it, it is implicitly assumed that all ions in the forwards and backwards peaks centred at m/q = 3 are H3+. While this must of course be true for any species that have only three H atoms in total, photoionization and particle impact studies show that there are charge separation fragmentation pathways of the methanol dication that produce H2+ via proton migration from the hydroxyl group [3-5], which would result in HD+ + CH2O+/CHO+. Since these pathways can also have similar kinetic energy releases to those that produce H3+, I don't think the paper as written sufficiently justifies why the charge separation peaks in the methanol ion spectra are purely H3+ as opposed to a mix of H3+/HD+.

I don't think any introduced uncertainty in the H3+ yield is likely to affect the qualitative conclusions of the paper since the HD yield would likely be a fraction of the H3+, so the overall trends reported in the paper would likely remain the same. However, since the H3+ yields of the other two species are normalised to the yield from methanol, an inaccuracy in the Methanol yield, if present, would have a knock-on effect in the quantitative accuracy of these reported yields. I think it is important that the paper explicitly states how the authors are sure that HD+ is not affecting the yield measurements, or if it is, to what extent this may be the case, as I don't think that using CH3OD is, by itself, enough to be certain of this. If possible, a PIPICO analysis or something similar would be strongly convincing, if this is possible to perform on the data.

3) I think the ion spectra presented in Figure 1 would be clearer if they were plotted as a series of vertically stacked 2D plots. The 3D perspective makes it harder to directly compare the series of spectra, especially those spectra that have weaker (or non-existent) features. I think it could also be useful to visually indicate the regions from which the H3+ yields were derived.

4) CH3Cl seems to have an additional small feature located between the two H3+ peaks, closer to the peak at longer flight times. Is the origin of this spectral feature known? Was it excluded from the yield calculations?

5) In Figure 4, according to the calculated fit functions, the probe seems to enhance H3+ product formation in CH3NCS in the limit of long probe delays (Yield ratio ~ 1.2), compared to the other species where a depletion (ratio 0.8 - 0.9) is observed. Based on my understanding of the disruptive probe technique, I would (perhaps naively) expect the trends to be broadly similar for the same final product ion produced by analogous processes under similar experimental conditions, thus can the authors illuminate on why the trend for CH3NCS differs in this respect? Is it simply the lower statistics introducing uncertainty to the fit?

6) Ref 36. also studied H3 production from methanol as a prototypical system of study as a demonstration of the methodology utilized in this paper. However, there the intensity of the pump was somewhat lower than that used in these experiments (3 vs 5e14 W/cm2) which would yield a sizeable difference in the electron re-collision energy. Can the authors elaborate on how (and why) these specific pump and probe intensities were chosen for these measurements? I gather from Ref 36 that the pump wants to be sufficiently high for efficient ionisation and below the saturation intensity, but it would be good if the authors and the paper explained briefly how these were set in practice.

[1] K. Hoshina et al, J. Chem. Phys. 129, 104302 (2008)
[2] V. Ideböhn et al., Phys. Chem. Chem. Phys., 24, 786 (2022)
[3] JHD Eland et al., International Journal of Mass Spectrometry and Ion Processes, 113 (1992) 167-176
[4] S. De et al., Phys. Rev. Lett. 97, 213201 (2006)
[5] Y Furukawa et al., Chem. Phys. Lett. 414 (2005) 117–121

Reviewer #3

(Remarks to the Author)
In this manuscript the authors report a joint theory-experimental work on H3+ formation from a series of doubly ionized methyl halogens and pseudo-halogens. Through a combination of experimental observation and computational simulation, the authors conclude that the different rates of H3+ formation for molecules in the series is dependent on dynamics that ensue following ionization within the manifold of low-lying doubly ionized electronic states. This study concludes that prompt H2 dissociation, and subsequent H3+ formation via a roaming mechanism, occurs on ultrafast (sub-ps) timescales. The computational results presented herein are used rationalize these results via a consideration of the structural relaxation that occurs following strong field ionization, and correlating the amount of internal energy imparted to the system relative to the relevant H2 dissociation barriers to the degree to which H3+ is observed. Ab initio molecular dynamics simulations are also performed and are consistent with the experimental results and static electronic structure computations, with H3+ formation being observed for only a subset of the molecules in the series.

This work employs appropriate and often state-of-the art experimental and theoretical approaches to present a compelling case for the conclusions drawn in this manuscript. The degree to which the various elements of this work present a self-consistent picture of the ionization and nuclear dynamics makes for a coherent and convincing account of H3+ formation in these molecules and will be of interest to a significant cross-section of readers in spectroscopy, dynamics, and interstellar chemistry. This work would be suitable for publication in Nature Communications following minor revision to improve the

presentation.

1. While it's reasonable to assume the formation of H2 should be energetically favorable in order to proceed on femtosecond timescales, the rate of H2 formation will be determined by the barrier to dissociation, which does not appear to be addressed in this work. Where these structures identified? As this is the more germane for the dynamics, can the barrier to H2 dissociation be estimated for these molecules?

2. That there is the possibility for "fwd" and "bwd" Coulomb explosion indicates that the strong ionization process prepares a highly anisotropic axis distribution of dicationic species. For much of the readership of Nature Comms, this may not be immediately obvious and should be explicitly stated and explained.

3. The authors do not comment on which electronic states are populated during the ionization process, even though they are included in the state electronic structure calculations in Figure 3. In the Methods section, it would appear that the AIMD simulations only involved the dynamics on the singlet dicationic states. In summary, it would seem the experiment will not be particularly sensitive to the multiplicity of the electronic states produced via ionization and this would be difficult to compute from first principles. Furthermore, based on the results in Figure 3 and subsequently rationalizaion of the results, the structural relaxation in the triplet manifold is perhaps not sufficient to lead to significant H2 dissociation. Firstly, is this the authors' understanding? Secondly, does the ratio of H3+ yield (which is assumed to be formed ultrafast, if formed at all from singlet channels) to all dicationic channels in Table I related to singlet/triplet yields in the ionization process? Whatever the answers to these questions, any discussion of electronic character of the dicationic states following ionization, and the relation to the pertinent observables, is currently absent in the manuscript and should be addressed.

4. Since the purpose of Figure 6 is to use computed quantities to predict reactive outcomes, the inclusion of CH3F (despite there being no experimental data) would be appropriate, particularly given the amount of discussion in the main body of the manuscript. In particular, the statement "but cannot be so large that other reactive mechanisms, such as the H–H bond breaking in the liberated H2 , may become dominant or the H2 molecule escapes" on page 13 would be better motivated via the inclusion of the CH3F results.

5. A few gridlines along the 'mass to charge' axis in Figure 1 would be helpful to aid the reader to show alignment in the H3/H2 peaks between different molecules.

6. On pg. 8, the repeated phrase "two degenerate HOMOS..." is confusing. There is a single HOMO orbital is that doubly-degenerate at C3v configurations.

Reviewer #4

(Remarks to the Author)
Review of manuscript titled H3+ Formation from Methyl Halogens and Pseudohalogens: Experiment Theory and Governing factors. By Stamm and co workers.

This manuscript describes and explains experiments whereH3+ is observed after CH3X molecules where X= OD, Cl, NSC, CN, SCN, I and F are doubly ionized with an intense non-resonant laser field. Despite the molecules being very similar some form H3+ easily and quickly and other not at all. The authors have done a lovely job in explaining the subtle differences between the systems that dictate whether the CH3X molecule will produce H3+. It seems that the doubly excited state needs for three things to be simultaneously true; 1) upon excitation two of the H bonds must lengthen and weaken 2) those two Hydrogen atoms must come close together so that their bond length is close to an H2 molecules and 3) the amount of internal energy put into the molecule by the vertical ionization process must exceed the dissociation energy. The authors make a very convincing experimental and theoretical case for this. I think this paper should definitely be published. I do however have a few issues with some of the presentation that I feel the authors should address before publication.

On page 10 they talk about the difference in the vertical versus adiabatic ionization energy being important and reference equations 3 and 4 but it is not till page 19 that equations 3 and 4 show up. Not sure why this obvious clumsy organization is here but please move the discussion on page 19 up to page 10 when one talks about those equations. In addition, equation 3 defines E as the "adiabatic relaxation energy". I think it would be clearer to the audience if it was labeled Einternal., or something like that, of course in these experiments the available energy for dissociation is this E plus the internal thermal energy that the molecule has as the experiments are done at room temperature. This is small but considering the small values of E for CH3CN it may be responsible for the small amount of H3+ that is observed in figure 2.

In Figure 4 why do the signals not come back to the one level, CH3OD asymptotes below one and CH3NCS above one?

Does the electron that rescatters have plenty of energy to make electronically excited states of the dication. If so is there any indication that excited electronic states play a role or would that just be a parasitic process lowering the quantum yield of H3+?

In conclusion this is a very nice manuscript and should be published. I have some small issues with the organization but none with the science.

David Chandler

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I commend the authors for their diligent response to my earlier comments. The revisions have certainly enhanced the manuscript. However, I remain concerned about the time-resolved studies, which I consider crucial to this work.
The employed time-resolved experiment, a degenerate 800nm pump/800nm probe setup, while relatively straightforward to implement, particularly with the high sensitivity of charged particle detection, yields data—the multiphoton-induced ion yield—that is notoriously challenging to interpret in terms of the underlying process. As the authors themselves noted in their response, the observed modulations in ion yield are likely due to higher electronic states shifting in and out of resonance with single or multiphoton excitation by the probe pulse. Consequently, these modulations do not directly reflect the dynamics of the dication on the ground state potential energy surface (i.e., the actual formation of H3+), but rather probe energy gaps between the ground state and various excited states of unknown character. How these energy gaps relate to the H3+ generation coordinate remains unclear. Thus, the insights into H3+ generation that can be gleaned from this particular experimental approach are inherently limited.
In light of this, the discrepancy between the timescales observed in the simulation and experiment is unsurprising. The two are fundamentally incommensurate: the simulation tracks product formation, whereas the experiment captures signatures of resonances between the initially populated state and higher-lying states during product formation. It's akin to comparing apples and oranges.
In light of these from my perspective inherent short comings of the study, I do not recommend publication in Nature Communications. The results are certainly interesting but should be published in a more targeted journal.

Reviewer #2

(Remarks to the Author)
The paper is a revision of the previously submitted manuscript NCOMMS-24-10836. The data and conclusions of the paper remain broadly the same as the previous iteration of the manuscript, but the authors have made several important additions and modifications to the manuscript, its figures, and to the supporting material. The authors have addressed the changes and provided rebuttals to the points raised by the four reviewers in an extremely comprehensive rebuttal letter. Cumulatively, I believe that these changes have significantly strengthened the paper and its conclusions.

I provide the following feedback to the rebuttals and changes presented by the authors that were specific to the six points I initially raised (numbered and ordered the same as in the rebuttal letter):

1. The inclusion of the preliminary hydrocarbon data and discussion of these in the broader context of their work strengthens the argument that that their criteria can be more generally applied to other systems and, in my opinion, significantly increases its justification for publication in a broader reach journal. i approve the explanation and additions/changes.

2. I think the changes to the text, which now explicitly explains that the central peak in the TOF data comes from HD+ produced by the monocation, is a welcome addition, but I am a bit less convinced by the following part of the added text. Adding the references that discuss the branching ratios of the two channels is a good step, but I think the sentence “the contribution of HD+ to the “fwd” and “bwd” peaks for CH3OD is expected to be minimal, having no significant effect on the reported H+ 3 yields.” would be improved further if they quantified what “minimal” means, since even by their own estimates, a 4.6 ratio derived from their work in Ref 36 would still correspond to more than a 20% contribution, which some readers may not class as “small”.

3. I wholeheartedly approve of the changes made to figure 2. The addition of the shaded regions indicating the areas used for yield calculations, the yield integrals on the second axis, and the addition of the “tick lines” suggested by reviewer 3 make for a much improved and comprehensible figure and a fine alternative to the stacked vertical arrangement I suggested. I approve and accept these changes.

4. I accept this explanation, and the addition of explicitly showing the integration regions in the figure removes any ambiguity as to what was treated as “signal”. I approve and accept these changes.

5. I approve of the explanation, and its inclusion in the text.

6. I welcome and approve of the inclusion of this additional information.

Addressing the manuscript as a whole: the additions/changes made to figure 1 and the surrounding discussion of the laser/field free dynamics is a welcome improvement, and better justifies the applicability of these results to more general scenarios/environments where double ionsation processes may arise (the interstellar environment in particular). Reviewer 3 also raised an important point (#2) regarding the origin of the fwd and bwd peaks in the time-of-flight data not being immediately obvious to someone outside of the field of ion time of flight spectroscopy, and the changes made by the authors do well to make the results more accessible to a broader audience. Overall, I also think that the authors have done well in addressing the other points raised by the three reviewers other than myself, and the substantial additions to the main text

have provided a wealth of additional context and discussion that only serves to strengthen the paper.

In summary, if the minor change I suggested (see point 2 above) is addressed, I would have no hesitation in recommending the manuscript (or a lightly edited form of it) being published in Nature Communications.

Reviewer #3

(Remarks to the Author)
The authors have satisfactorily addressed the comments raised in my previous report.

Reviewer #4

(Remarks to the Author)
I believe the authors have addressed all of the issues I have raised and the manuscript is now suitable for publication. The issues of time scale and the nature of the potential energy surfaces involved are very hard to be definitive about.

RESPONSES TO COMMENTS BY THE REVIEWERS

Comment by Reviewer #1:

Stamm et al. report on a study about the generation of H3+ ions from a series of methyl halogens and pseudohalogens through double-ionization by strong ultrafast laser pulses. The experiments are complemented by both static electronic structure calculations and simulations of the ionization-induced H3+ generation dynamics. They observe significant differences in the H3+ yield from 6 different investigated species. They formulate three criteria for efficient H3+ generation, based on the minimum geometry of the lowest doubly-ionized state in the molecules and the difference between the available energy to the molecules in the ionized state and the dissociation energy for H2 abstraction.

I have doubts about the relevance of the experimental part of the study to interstellar chemistry. The authors claim this relevance through the importance of the H3+ species and the need to understand its generation mechanism. The authors employ a double ionization mechanism through tunnel-ionization followed by rescattering of the ejected electron driven by the strong laser field. I find it questionable if any insight from investigating H3+ generation through such a process is transferrable to generation mechanism in interstellar space, where such strong, coherent electromagnetic fields are generally missing. It is well-demonstrated (see e.g. 10.1103/PhysRevLett.116.193001) that in the intensity regime employed in this experiment the electronic potentials for the nuclei of the molecule are substantially modified by the laser field. This can lead to field-induced dynamics, specifically for protons. The supplementary video shows that significant parts of the H3+ generation mechanism of CH3OH take place within the temporal envelope of the ionizing pulse. Therefore, I am not convinced that the authors can rule out the possibility that H3+ generation in the experiment is at least in part field-induced. I do not have any reason to doubt the simulations, which are performed on an impressive level of electronic structure theory. I just believe that the experiment is not a good match to benchmark the theory, specifically, since the theory neglects the influence of the laser field.

Our response:

We agree with the reviewer that further justification may be needed for the suitability of applying our results to interstellar molecular dynamics. Indeed, when it comes to highly energetic particle bombardment in the interstellar medium, the extremely broad range of particle energies will not necessarily yield the same results as those reported in our study. On the other hand, in the case of interactions between atoms and molecules with highly energetic particles and photons, the primary outcomes are secondary electrons with energies ranging from tens to hundreds of eV. It should also be noted that the interaction between a molecule and a high-energy particle depends on the energy of the particle and the impact parameter. One may, therefore, anticipate that there exists a broad range of energies over which the results presented in our work are relevant to astrochemistry. We would also like to emphasize that the tunnel-ionization and electron rescattering used in our experiments are just methods to generate CH_3X^{2+} dications. Once these dications are generated, their subsequent dynamics are independent of the method of their formation, *i.e.*, the mechanism, yields, and timescales of H_3^+ production from the doubly ionized CH_3X species reported in our

work generalize to other ways of generating CH_3X^{2+} dications, including those formed in the interstellar medium.

We also appreciate the reviewer's concern regarding the field of the 35-fs pulse possibly affecting the electronic potential energy surfaces while the dynamics are occurring. There are a few reasons why the effect of the laser field on the dynamics of H_3^+ can be considered minimal in our case:

1. Our results are consistent with time-resolved studies measuring the timescale of H_3^+ formation using one-photon extreme-ultraviolet (EUV) ionization, such as those reported in Ref. [11] cited in our manuscript. The results reported in Ref. [11] do not contain a field effect due to the short duration of the EUV pulse.
2. Most of the important dynamics of H_3^+ formation occur after the liberation of a neutral H_2 species. As mentioned in the Results: *Ab initio* molecular dynamics simulations section of our manuscript, H_2 is formed very fast, within ~30 fs from the double ionization event in the majority of our AIMD trajectories. Thus, the 35-fs pulse is over by the time the critical H_2 moiety is created, given that double ionization predominantly occurs at the peak of the pulse. The timescale of H_3^+ formation and its dependence on the molecular environment are dominated by the subsequent and much longer roaming dynamics, a process that is field free.

To reflect on the above remarks, we have added the following sentence in the last paragraph of the Introduction that begins with the words "In this article, we report …":

"While we chose tunnel-ionization and electron rescattering to generate CH_3X^{2+} dications in our experiments, which are illustrated in the upper half of Fig. 1 using methanol as an example, the dynamics of H_3^+ formation following the double ionization of CH_3X species via a roaming mechanism examined in the present study are not influenced by the electric field of the laser pulse once H_2 is formed. This also means that they do not depend on the specific method by which the CH_3X^{2+} dications are created."

Comment by Reviewer #1:

I have additional doubts about the impact of the conclusions from this study. Based on their results, the authors formulate three criteria for the efficient generation of H3+. Two of them are based on the minimum geometry of the molecules in the doubly ionized state, particularly the proximity of two of the three CH3 hydrogens and their distance from the carbon. The third is based on the ratio of the available excess energy after relaxation in the dicationic state, termed as the adiabatic relaxation energy, and the required energy to abstract H2 from the dication (dissociation energy). Based on Fig. 6 in the manuscript, I cannot see the need for three criteria. The H3+ yield correlates well with the third criterium, the ratio of adiabatic excess energy and dissociation energy. Moreover, the authors mention simulations on the CH3F compound which cannot be explained by the established criteria. Therefore, I have serious doubts about the predictive power of the presented criteria.

Our response:

While we agree with the reviewer that our H_3^+ yields correlate well with condition (iii) provided in the manuscript, we believe that conditions (i) and (ii) are important and useful for practical reasons. For example, as shown in Figure 6, the CH_3SCN and CH_3I molecules can be ruled out as producers of the trihydrogen cation based solely on the purely geometrical conditions (i) and (ii), thereby eliminating the need for the more laborious additional computational effort required to evaluate the third criterion, which involves determining the geometry and energetics of the CHX^{2+} dication and H_2 molecule, in addition to the doubly ionized CH_3X^{2+} species. Typically, an accurate determination of molecular energetics, including those needed to define the adiabatic relaxation and dissociation energies entering condition (iii), requires the use of higher-level quantum chemistry approaches, which are generally more expensive, whereas reasonably accurate geometries can often be obtained with relatively inexpensive lower-order methods. This is particularly useful in the case of our study, since the geometrical conditions (i) and (ii) are largely qualitative, *i.e.*, it is sufficient to run inexpensive low-order computations to determine if these two conditions are satisfied or not. This should be contrasted with the energetic condition (iii), whose examination requires the execution of multiple high-level quantum chemistry computations. It is, therefore, helpful to have simple, purely geometrical, and easy to verify conditions (i) and (ii) around, which at the very least allow us to quickly eliminate those CH_3X species that cannot produce H_3^+ after double ionization. Having conditions (i) and (ii), in addition to condition (iii), is also useful for a number of other reasons. For example, in the case of CH_3Cl^{2+} dication, which produces H_3^+ in its lowest singlet state, the contributions of the lowest triplet and second singlet states shown in Figure 3 to the yield of the trihydrogen cation can be immediately ruled out based on the first two geometrical conditions only, since the geometries of CH_3Cl^{2+} in its lowest triplet and second singlet states do not exhibit two substantially elongated C–H bonds and the H–H bond lengths in them are far from the internuclear separation in the isolated H_2 (see the new Supplementary Table 1 in the revised Supplementary Information document). For these and similar reasons, we consider the first two conditions (i) and (ii) as the useful initial filters that allow us to quickly exclude those doubly ionized CH_3X species that cannot form H_3^+, invoking the more elaborate condition (iii) only if the first two conditions are met. While Reviewer #1 has not asked about it, in response to point 1 by Reviewer #3, we have augmented the original condition (iii) with the additional requirement that the adiabatic relaxation energy should also be large enough to overcome the barrier(s) along the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ potential energy profile, including that corresponding to the $CHX^{2+} + H_2 \rightarrow CX^+ + H_3^+$ proton abstraction by the roaming H_2 (see our response to Reviewer #3 for further information).

The reviewer has expressed doubts regarding the predictive power of conditions (i)–(iii) presented in the Discussion section. This requires further clarification. We acknowledge that there may be additional factors influencing H_3^+ formation from the doubly ionized CH_3X compounds and that more elaborate criteria may have to be developed in the future. It is also important to recognize that our conditions (i)–(iii) do not apply to all mechanisms of H_3^+ formation one can think of. They should be treated as the specific criteria that must be simultaneously met in order for the doubly ionized CH_3X species to have the potential of generating H_3^+ via a roaming mechanism shown in Figs. 1 and 5, assuming that, as stated in condition (iii), the adiabatic relaxation energy is not too high. Given the observed consistency of our experiments with the high-level *ab initio* electronic structure and dynamics computations for several molecular examples, we have good reasons to

believe that our conditions (i)–(iii) are helpful and robust, allowing one to rationalize the formation of the trihydrogen cation from the doubly ionized CH_3X-type molecules or, at the very least, exclude those CH_3X species that cannot form H_3^+ via the roaming mechanism involving the generation of H_2 and subsequent proton abstraction from the CHX^{2+} moiety. To avoid further misunderstandings, and to make sure that our intentions are properly reflected on in our writing, we have replaced the more definitive fragment in the first paragraph of the Discussion section "the following three conditions must be simultaneously met in order for the doubly ionized CH_3X species to generate H_3^+" by the more precise "the following three conditions must be simultaneously met in order for the doubly ionized CH_3X species to have the potential of generating H_3^+". We have also replaced the word "predictive" in the last sentence of the abstract with "useful".

While we appreciate a comment made by the reviewer about CH_3F, we cannot agree with the opinion that our conditions (i)–(iii) do not apply to CH_3F^{2+}. Condition (iii), especially the latter part of it which states that the adiabatic relaxation energy (designated in the revised manuscript, in response to the request from Reviewer #4, as ΔE_{rlx}) cannot be so large that other reactive mechanisms and other ways of decomposing CH_3X^{2+} become dominant, is particularly relevant in this case. As shown in the new Supplementary Fig. 3, which is an extended version of Fig. 6 that includes the CH_3F^{2+} dication alongside the six CH_3X^{2+} species examined in our experiments, the adiabatic relaxation energy, *i.e.,* the energy released by the geometrical relaxation of CH_3F^{2+} after double ionization of CH_3F, is much higher than in the remaining CH_3X^{2+} species considered in our work and, as a result, redistributed very differently than in the CH_3OH^{2+}, CH_3Cl^{2+}, and CH_3NCS^{2+} dications that form H_3^+. This is illustrated by the new Supplementary Movie 3, which shows a typical trajectory obtained in our AIMD simulations for CH_3F^{2+} where, instead of the roaming mechanism observed, for example, in CH_3Cl^{2+}, the liberated, positively charged, H_2 fragment dissociates and the final products are CH_2F^+ and a proton. In a small number of trajectories for CH_3F^{2+}, the liberated H_2 fragment, having sufficiently large energy available to it, escaped the system, preventing H_3^+ formation as well. The enormous excess energy available to the CH_3F^{2+} system after its geometric relaxation, which is much higher than the adiabatic relaxation energies characterizing the remaining CH_3X^{2+} species examined in our study, results in other ways of decomposing CH_3F^{2+} than the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ process involving the generation of H_2 and subsequent proton abstraction from CHX^{2+}. We have added information about all of the above and improved our discussion of the behavior of the CH_3F^{2+} system, especially how our conditions (i)–(iii) apply to it, in the paragraph of the Discussion section that begins with the words "None of the remaining …". For consistency of our presentation, information about the new Supplementary Movie 3 has been added at the end of the Results: *Ab initio* molecular dynamics simulations section. We have also improved our description of the neutral and doubly ionized CH_3F species by performing the DIP-EOMCC(4h-2p)/cc-pVDZ calculations and the CCSD, DIP-EOMCC(3h-1p), and DIP-EOMCC(4h-2p) computations using the larger cc-pVTZ basis set, in addition to the previously considered CCSD/cc-pVDZ and DIP-EOMCC(3h-1p)/cc-pVDZ data, making the appropriate adjustments in Methods: Electronic structure calculations (by deleting the paragraph that begins with the words "To enrich our discussion …" and merging the information about the calculations for CH_3F and CH_3F^{2+} with those for the remaining CH_3X and CH_3X^{2+} species), Methods: *Ab initio* molecular dynamics simulations (in the middle of the paragraph forming this section), and the revised version of the Supplementary Information document. In the latter case, in the Supplementary Data section, we have provided the Cartesian coordinates and electronic

energies of the CH_3F and CH_3F^{2+} molecules resulting from the additional CCSD/cc-pVTZ, DIP-EOMCC(3h-1p)/cc-pVTZ, DIP-EOMCC(4h-2p)/cc-pVDZ, and DIP-EOMCC(4h-2p)/cc-pVTZ geometry optimizations, replaced Supplementary Figs. 1 and 2, which contain information needed to calibrate the CASSCF calculations exploited in our AIMD simulations, by their updated versions using the more accurate DIP-EOMCC(4h-2p)/cc-pVDZ results for CH_3F^{2+}, revised the original Supplementary Table 1 which, because of a new table in the Supplementary Information document labeled as Supplementary Table 1, is now called Supplementary Table 2 and which provides the most accurate values of the key bond lengths characterizing the neutral and doubly ionized CH_3F species and the most accurate values of ΔE_{rlx}, and ΔE_{diss} characterizing CH_3F^{2+} obtained in our study, and added the aforementioned Supplementary Fig. 3, which is an extended version of Fig. 6 in the main text that includes the CH_3F^{2+} dication alongside the six CH_3X^{2+} species examined in our experiments. The incorporation of Supplementary Fig. 3 in the Supplementary Information document has also been done in response to the request made by Reviewer #3 in his or her point 4. The new Supplementary Table 1, which shows the selected internuclear distances characterizing the low-lying states of a few doubly ionized CH_3X molecules and which has primarily been added to facilitate our response to point 3 in the report by Reviewer #3, contains information about the neutral and doubly ionized CH_3F species as well. Information about this new supplementary table has also been added to the Methods: Electronic structure calculations section (the last sentence of the third paragraph of that section).

Comment by Reviewer #1:

Based on the points I outlined above, I cannot recommend publication of the manuscript in Nature Communications. I believe that an appropriately modified manuscript will be of interest to the strong field physics community.

Our response:

We hope that our responses to the comments, questions, and suggestions made by the Reviewers, along with the revisions in our manuscript and Supplementary Information, are satisfactory, allowing the Editors of *Nature Communications* to continue processing our submission.

Comment by Reviewer #1:

I have further, more technical comments:
• Figure 1 suggests that the laser field only plays a role in the first step of the visualized process. I believe this is misleading. A significant part of the dynamics can be assumed to take place in the presence of the laser field.

Our response:

We are grateful to Reviewer #1 for this remark. We agree that the original version of Fig. 1 could be misleading. Thus, we have redesigned Fig. 1 to delineate between the field-influenced and field-free regimes and to better reflect on the timescales of the different processes leading to the formation of H_3^+ following the double ionization of CH_3X compounds via a roaming mechanism that involves the generation of H_2 and subsequent proton abstraction from the CHX^{2+} moiety (in

Fig. 1, X = OH). We have modified the figure caption accordingly. The upper half of the revised Fig. 1 illustrates the process of generating the CH_3X^{2+} dication and the lower half shows the formation of H_3^+ from the CH_3X^{2+} species, so in two places in the Introduction referring to these two parts of Fig. 1 (on pages 2 and 4), we have adjusted our text accordingly.

Comment by Reviewer #1:

• The researchers performed 800 nm strong field pump / 800 nm weak field probe experiments which they call disruptive probing. They observe a dependence of the H3+ yield on the pump-probe delay, but do not elaborate on the probing mechanism. It is unclear to me what exactly the nature of the probe interaction is. The authors seem to interpret it as a disruption of the generation mechanism of H3+ but do not elaborate how that would happen. I also do not understand the nature of the model underlying the function used in the fits to the experimental data. Therefore, it is unclear to me if and how the fit results can be compared to timescales extracted from the simulations.

Our response:

We agree that discussing the probing mechanism is important to justify our experimental results. As elaborated on in Ref. [38], when performing disruptive probing measurements, the probe pulse becomes sensitive to the wave packet motion due to one- or two-photon resonance with another electronic state (or states). As the geometry of the transient system, which in our case is the dynamically evolving CH_3X^{2+} dication, changes, the excitation by the probe can fall into or out of resonance with this other electronic state. As a result, if the probe successfully promotes an excitation of the transient system, it may induce a different fragmentation pattern relative to what would otherwise be observed if the probe was not present. This is what we think happens at short positive pump-probe delay times *t*, where we observe a depletion of the H_3^+ ion yield because the probe pulse can promote the transient CH_3X^{2+} system to some other electronic state that results in a reduced H_3^+ yield or does not produce H_3^+ at all. In a highly complex roaming reaction mechanism considered in our work, which involves the generation of H_2 and subsequent proton abstraction, the probe may, for example, mitigate the return of H_2 to the CHX^{2+} moiety, preventing H_3^+ formation. To reflect on these remarks, and to improve our description of the physics of disruption of the mechanism of H_3^+ generation by the probe pulse at short positive pump-probe delay times, in which we also refer to Ref. [38], we have replaced the sentence "This leads to a depletion of the H_3^+ ion yield at short positive pump-probe delay times *t*" in the last paragraph of the Results: Timescales of H_3^+ formation section by

"This leads to a depletion of the H_3^+ ion yield at short positive pump-probe delay times *t* because, as explained in Ref. [38], the probe pulse can promote the transient CH_3X^{2+} system to some other electronic state that results in a reduced H_3^+ yield or does not produce H_3^+ at all. For example, the probe may suppress the return of the roaming H_2 to the CHX^{2+} moiety, preventing H_3^+ formation. Since the probe accesses this other electronic state as the dynamics leading to the generation of H_3^+ is progressing, the timescale of recovery following the depletion of the trihydrogen cation yield matches the timescale of H_3^+ formation."

We also agree that the equations used to fit the experimental pump-probe delay dependent ion yields, which in the revised manuscript appear as Eqs. (3) and (4), should not be presented without justification or proper reference to where they come from. These equations originate from Ref. [38], where the model adopted in the present study to extract information about the timescales involved in H_3^+ formation from CH_3OD, CH_3Cl, and CH_3NCS has been discussed in detail. In response to the request by the reviewer to improve our description of the modeling procedure used to fit pump-probe delay dependent ion yields, we have replaced the sentence below Eq. (4) [in the original manuscript, Eq. (2)] that starts with the words "In the above equations …" by the following text:

"and t is a pump-probe time delay. The first term on the right-hand side of Eq. (3) describes the dependence of the ion yield on the Gaussian pump pulse, whereas the second and third terms are solutions of the differential rate equation described in Ref. [38] that accounts for changes in the populations of ion states by Gaussian pump pulses. In the case of the pump-probe experiments reported in the present study, we need two types of such solutions, $P_1(t, \tau_1)$ characterized by time constant τ_1 for a decay (τ_{decay}) of the ion signal and $P_2(t, \tau_2)$ using time constant τ_2 for the signal's rise (τ_{rise}). The parameters A in Eq. (3) and A_1 and A_2 in Eq. (4) are the respective amplitude factors and s is related to the full width at half maximum pulse duration (τ_{FWHM}) through the expression $\tau_{\mathrm{FWHM}} = 2s\sqrt{\ln 2}$."

Comment by Reviewer #1:

• The dynamics simulations assume the reaction to take place in the respective lowest, field-free singlet state. I'm not sure if this assumption is strictly valid for the processes triggered in the experiment by strong-field ionization or even by other double ionization mechanisms. Could this be the reason for the large differences in simulated and experimental H3+ generation timescales?

Our response:

The reviewer is raising a few questions here. The reasons why we believe the H_3^+ formation dynamics are not influenced by the electric field of the ionizing laser pulse have already been explained on page 2 of this document, as part of our response to the initial comments made by Reviewer #1 in the beginning of his or her report. We do appreciate the reviewer's concern that considering only the lowest singlet states of the CH_3X^{2+} dications may not be entirely valid, and we certainly agree that ionization by a strong-field laser can populate several excited states of the doubly ionized CH_3X species, but the previous AIMD simulations for methanol by Livshits *et al.*, reported in Ref. [11], clearly show that the probability of H_3^+ formation from CH_3OH^{2+} is the highest in its lowest singlet state, rapidly dropping down when higher excited states are examined. Quoting from Ref. [11] (see the left column of page 3 in Ref. [11]):

"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."

The follow-up study from the same groups, cited in our revised manuscript as Ref. [22], reinforces and further extends these findings by concluding that (quoting from Ref. [22])

"H_3^+ was not formed in any of the 700 trajectories simulated on the ground state and the first six excited states of the triplet manifold"

(the term "ground state" mentioned in the quoted fragment refers to the lowest state of the triplet symmetry [22]). It may also be worth mentioning again (see one of our earlier responses to Reviewer #1 on page 3) that of the three lowest electronic states of the CH_3Cl^{2+} dication, which is one of the three producers of H_3^+ examined in our study, only the singlet ground state satisfies the geometrical conditions (i) and (ii) laid down in the Discussion section. The geometries of CH_3Cl^{2+} in its lowest triplet and second singlet states do not exhibit two substantially elongated C–H bonds and the H–H bond lengths in them are far from the internuclear separation in the isolated hydrogen molecule (see the new Supplementary Table 1 in the revised Supplementary Information document). This prevents the formation of the H_2 precursor, shutting down the roaming mechanism explored in our study that leads to H_3^+ when the CH_3Cl^{2+} dication is in its lowest triplet or second singlet state. For this and all the other reasons listed above, the dynamics simulations reported in our work are single-state AIMD computations assuming that H_3^+ formation takes place on the lowest-energy, field-free, singlet state. While we do not want to discount the potential impact of some excited states of the CH_3X^{2+} dications on the dynamics of H_3^+ formation, which may require further study, we believe that the single-state AIMD simulations involving the lowest singlet states of the CH_3X^{2+} species reported in our work are sufficient to provide useful insights that help us understand the outcomes of our experiments. To reflect on these remarks in our paper, we have added statements explaining why we did not consider higher-lying states of the CH_3X^{2+} dications in our computations to our revised manuscript, citing Ref. [11]. They appear as the second sentence in section Results: *Ab initio* electronic structure calculations and as the second and third sentences in Results: *Ab initio* molecular dynamics simulations. In the latter case, to enrich our rationale why we have focused in our study on a single-state dynamics on the lowest-energy singlet potentials of the CH_3X^{2+} species, we have also added a remark about states belonging to triplet manifolds of these species, which are not conducive to the release of H_2 that could subsequently roam and abstract a proton from the CHX^{2+} moiety to form H_3^+, citing the new Ref. [22].

The reviewer suggests that the lack of quantitative agreement between our experimental and simulated timescales of H_3^+ formation might be a consequence of our assumption that the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ process proceeds on the lowest, field-free, singlet states of the CH_3X^{2+} dications. As implied by our responses above, the H_3^+ formation dynamics are not influenced by the electric field of the ionizing laser pulse and we also do not think that our reliance on the single-state AIMD simulations is the main reason for the observed discrepancies. The differences between the simulated and experimental timescales of H_3^+ formation could easily arise from other, in our view more important, factors, such as the quality of the statistical sampling, the duration of the computed trajectories, and the quality of the underlying potential energy surfaces and their curvatures. As explained in Methods: *Ab initio* molecular dynamics simulations, we computed 200 trajectories for each CH_3X^{2+} system, integrating every trajectory for 700 fs, and relied on the CASSCF/cc-pVDZ potential energy surfaces and gradients. While we made an effort to tailor our CASSCF calculations to the high-level DIP-EOMCC data available to us, and we did our best by computing as many trajectories as we could afford, running them for as long as feasible on the computers available to us, we realize that our AIMD simulations are not quantitative. For quantitative accuracy, we would have to use higher-level quantum chemistry methods than CASSCF and obtain many more trajectories, allowing longer simulation times, to ensure that the associated phase

spaces are accurately and thoroughly explored. Running nonadiabatic AIMD simulations in addition to all of the above improvements might help too but, given the number of systems included in our computations, which has no precedent in previous computational studies of H_3^+ formation from the doubly ionized CH_3X compounds, and taking into account intrinsic limitations in the hardware and software available to us, we can only do what has been reported in our paper. We believe that our AIMD simulations, while "only" qualitatively accurate, provide the most valuable microscopic insights into the mechanism, yields, and timescales of H_3^+ production. The qualitative nature of the agreement between the results of our AIMD simulations and experiment, which is all one can expect given the above explanations and established experiences, is clear in our writing (see, *e.g.*, the third paragraph of Discussion which begins with the words "As explained in Results and Methods, …"), so we only replaced the word "realistic" by "reasonable" in the sentence "To provide a realistic representation …" (now, "To provide a reasonable representation") in the Methods: *Ab initio* molecular dynamics simulations section.

Comment by Reviewer #1:

• I am not convinced that the relaxed geometry in the dicationic state plays a major role in the reaction dynamics given the in part significant excess energy of the molecules (2.5 eV in case of methanol). Looking at the supplementary movie of methanol, the initial motion looks more like a frustrated abstraction of a single hydrogen than the suggested lengthening of two C-H bonds and a simultaneous approach of the two hydrogens.

Our response:

The significant excess energy associated with the geometrical relaxation of the CH_3X^{2+} dications from their respective vertical ionization regions is initially converted into large-amplitude vibrations of the bonds in these ions, which may create an impression that the evolving CH_3X^{2+} molecules never pass near their equilibrium geometries, but this impression is false and is a result of the less–than–perfect way our original movies were produced. Our original movies were produced with a cutoff distance for the bond lengths which was too short to create an adequate visualization of the processes examined in our work. As a result, when the C–H bonds were stretched beyond the original cutoff while vibrating, the H atoms appeared to be prematurely detached from the C atom, resulting in a picture that did not properly represent the reality of the H_2 formation through a simultaneous elongation of two of the three C–H bonds prior to the roaming stage of the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ process. We have carefully reexamined all of our trajectories and it is clear that the trajectories illustrating the $CH_3Cl^{2+} \rightarrow CCl^+ + H_3^+$ and $CH_3OH^{2+} \rightarrow COH^+ + H_3^+$ reactions shown in our Supplementary Movies 1 and 2, which are representative of the roaming mechanism of H_3^+ formation investigated in our study, are fully consistent with the description of this mechanism in our manuscript, where the elongation of two of the three C–H bonds and formation of the H_2 fragment, as in the relaxed equilibrium geometries of the respective CH_3X^{2+} dications, prior to the roaming stage of the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ process, indeed takes place. To improve the visualization of all stages of the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ reactions, including the elongation of two of the three C–H bonds and formation of the H_2 fragment, in the revised versions of our movies, we have adjusted (increased) the cutoff distance for the bond lengths and paused the videos at the point where the geometry of a given CH_3X^{2+} dication is closest to its equilibrium structure, highlighting the importance of the dication minimum geometry in guiding

formation of the neutral H_2 fragment by the appropriate subtitle. As a result, it is now clear in our new Supplementary Movies 1 and 2 that the initial changes in nuclear geometries following the double ionizations of the CH_3Cl and CH_3OH molecules proceed in the direction of the minima on the lowest-energy singlet potentials of the corresponding dications. As already explained in our responses regarding the behavior of the CH_3F^{2+} dication, which does not produce H_3^+ (see page 4 of this document), we have augmented our movie set by the new Supplementary Movie 3, which shows a typical trajectory obtained in our AIMD simulations for CH_3F^{2+} where, instead of the roaming mechanism observed, for example, in CH_3Cl^{2+} and CH_3OH^{2+}, the liberated, positively charged, H_2 fragment dissociates and the final products are CH_2F^+ and a proton.

Comment by Reviewer #2:

Key Results:

The paper's overall theme is to evaluate the roaming process by which H3+ is produced from dications of the methyl halides and their analogues with formulae of the form CH3X, where X = OH, Cl, NCS, CN, SCN, and I. The authors aim to elucidate the criteria which determines the possibility and probability of this of this process occurring in these different species, and the timescale of formation.

The paper's results are split between experimental results and calculations, with a stronger focus on the latter.

To summarize the experimental scheme and results: time resolved, measurements of the ion yields were measured using an ultrafast, "disruptive probing" pump-probe scheme (described in detail in ref. [36] of the paper) where a strong infrared pulse is used to tunnel ionize the molecule followed by further ionization by the recolliding electron to produce di-cations which dissociate. A weaker pulse probes the dissociation pathways by disrupting the product formation. The final ion states are measured with a Wiley-McLaren type mass resolving spectrometer. Static, pump-only measurements focus on the mass/charge region near m/q= 3.0 (with the two peaks at higher lower masses attributed to H3+ produced in the charge separation process CH3X++ → CX+ + H3+) with statistically meaningful quantities observed for X = OD, Cl, and NCS (the yield progressively decreasing), and little/no signal observed in the other species. Time-resolved measurements including the disruptive probe yielded timescales of formation, with the shortest of ~60 fs for Methanol and the longest of ~650 fs for Methyl chloride.

These results were supplemented by thoroughly comprehensive computations of the geometries and bond lengths of the ground state and dications of all six species, the vertical/adiabatic ionisation energies, and ab initio molecular dynamics simulations of chosen species. The authors use these results to define 3 key criteria that must be fulfilled to determine why H3+ is observed to be produced efficiently by some dicationic species but not others: (i) sufficient elongation of the CH bonds in the dication, (ii) that a pair of hydrogens in the dication become sufficiently close so as to be comparable to the internuclear separation of neutral H2 and (iii) that the adiabatic relaxation energy of the dication exceeds the dissociation energy of CHX+ + H2.

Suitability for publication:

Overall, I think the paper presents a comprehensive study with sufficient novelty and quality to justify eventual publication. The extensive supporting material, including the geometrical data and the movies of the AIMD simulations were extremely nice to see, and the paper is written such that the main text is broadly accessible to the general audience while also including extensive material in the supporting sections that would provide ample information for a specialist in the field. The included figures are, overall, clear and concise.

While some results with a similar scope have been previously reported for some of the studied molecules, the paper's unique selling point is the in-depth comparison between the entire set of molecules, and the criteria the authors have established in predicting the yields of H3+, which will prove useful in predicting the production of H3 in other species. Though I think these results will most likely be of primary interest to those in the atomic and molecular physics and chemical physics spheres, the authors have done a good job in their introductory and discussion sections in justifying the results' relevance to other, broader fields of interest, in particular astrophysical contexts and models of the primordial universe. Therefore, I think that the paper provides sufficient justification for its eventual publication in a broader interest journal like Nature Communications.

There are however some open questions with the paper I feel are necessary to address before I can wholeheartedly recommend that it should be accepted for publication. These, and some suggestions for improvements, are detailed below:

1) H3+ has also been observed to be produced by dications of unsaturated hydrocarbons such as ethylene, allene, and larger alcohols [1-2]. The paper primarily focuses on the relevance of their results and established criteria purely in the context of modelling specifically the pseudohalides, but since some of the larger chain molecules (or close analogues) may also have astrophysical significance, I wonder if the authors can discuss if and to what extent their criteria might also apply to these larger systems (or to phrase it differently: how large can X be and their results still hold?) I think this would help to put their work in the broader context of H2+ and H3+ production by roaming mechanisms and further justify its publication in a broader-reach journal.

Our response:

We would like to thank the reviewer for a positive assessment of our work and its potential suitability for publication, in an appropriately revised form, in *Nature Communications*. Our manuscript focuses on the formation of H_3^+ from methyl halogens and pseudohalogens via the H_2 roaming mechanism, which we studied experimentally and theoretically, and we would like to retain this focus, but we are well-aware of the fact that, as the reviewer points out, there exist other organic species that can form H_3^+ following double ionization. A common feature of these other species that lead to H_3^+ formation is the presence of a neutral H_2 fragment forming a dative two-electron–three-center bond with a carbon atom in their dicationic structures, similar to the minima on the lowest singlet potentials of the H_3^+-producing CH_3X^{2+} systems obtained in our DIP-EOMCC computations. Among the best examples of compounds other than those examined in our work that illustrate this feature are the doubly ionized ethanol (see Refs. [10,43] in the revised manuscript or Refs. [7,8] in the revised Supplementary Information document) and the doubly

ionized ethane at an asymmetric $[CH_4–CH_2]^{2+}$ minimum on its lowest singlet potential resulting from hydrogen migration from one methyl group to another in a higher-energy $[CH_3–CH_3]^{2+}$ structure of $C_2H_6^{2+}$ (see Refs. [39,40] in the revised manuscript or Refs. [3,4,9-11] in the revised Supplementary Information document, which include additional older papers [9-11] about the $[CH_4–CH_2]^{2+}$ minimum). Both $C_2H_6^{2+}$ minima are shown in Supplementary Figs. 5 and 6, which have been added to the Supplementary Information document as part of this revision. They satisfy our geometrical conditions (i) and (ii), and if the condition (iii) is satisfied as well, the corresponding doubly ionized species are likely to produce H_3^+ in the roaming mechanism followed by proton abstraction similar to the CH_3OH^{2+}, CH_3Cl^{2+}, and CH_3NCS^{2+} dications examined in our work. This is illustrated in Supplementary Fig. 5 using the doubly ionized ethane, which produces H_3^+ [39-41] (in the revised Supplementary Information document, Refs. [3-5]), as an example. In this figure, we show the potential energy profile for the $C_2H_6^{2+} \rightarrow C_2H_3^+ + H_3^+$ reaction following double ionization of ethane obtained in the DIP-EOMCC computations discussed in the revised version of the Supplementary Information document. In this profile, the doubly ionized ethane molecule, after relaxing to the $[CH_3–CH_3]^{2+}$ minimum, designated in Supplementary Figs. 5 and 6 as Dication 1, in which two of the three C–H bonds at each carbon site are elongated and the distances between the associated hydrogens are close to that in H_2 (see Supplementary Table 3), undergoes hydrogen migration that leads to formation of the $[CH_4–CH_2]^{2+}$ structure, labeled as Dication 2. In analogy to the H_3^+-producing CH_3X^{2+} systems studied in our work, the $[CH_4–CH_2]^{2+}$ species is characterized by a substantial elongation of two of the four C–H bonds at one of the two carbon atoms and the presence of a neutral H_2 fragment which subsequently roams the $[C_2H_4]^{2+}$ moiety and abstracts the proton from it to form H_3^+. This is possible since, as shown in Supplementary Fig. 5, the vertical double ionization of ethane places it above the two minima, including the key $[CH_4–CH_2]^{2+}$ (Dication 2) structure, which meets our geometrical conditions (i) and (ii), and its higher-energy $[CH_3–CH_3]^{2+}$ (Dication 1) precursor, the transition state associated with the $[CH_3–CH_3]^{2+} \rightarrow [CH_4–CH_2]^{2+}$ hydrogen migration, the dissociation asymptote corresponding to the liberation of H_2, and the final transition state connecting the $[CH_4–CH_2]^{2+}$ structure with the $C_2H_3^+$ and H_3^+ products. This means that all three conditions (i)–(iii) are satisfied when the $C_2H_6^{2+} \rightarrow C_2H_3^+ + H_3^+$ roaming reaction following double ionization of ethane is examined. This is very different from the doubly ionized ethene, shown in Supplementary Fig. 7. As demonstrated in Supplementary Table 4, in this case, the minimum on the lowest singlet potential energy surface of $C_2H_4^{2+}$, which is characterized by rotation of one of the CH_2 groups without changing the C–H distances too much, obtained by the geometrical relaxation after double ionization, violates our conditions (i) and (ii). It has been shown in Ref. [42] (or Ref. [6] in the revised Supplementary Information document) that hydrogen migration between the two carbon centers can take place here too, producing a more favorable structure on the lowest singlet potential energy surface that may serve as a precursor for the roaming dynamics leading to H_3^+ formation, but, according to Fig. 3 in Ref. [42], this would require overcoming high-energy barriers which are at least twice as high as the adiabatic relaxation energy ΔE_{rlx} obtained in our DIP-EOMCC computations for the doubly ionized ethene reported in Supplementary Table 4. One would have to produce the $C_2H_4^{2+}$ dication in its high-lying excited electronic states located above these barriers and undergo nonadiabatic transitions to the lowest-energy singlet potential of $C_2H_4^{2+}$ in order for H_3^+ to form. This explains the very low yield of H_3^+ from the doubly ionized ethene observed experimentally [41,42] (in the revised Supplementary Information document, Refs. [5,6]), and is consistent with the fact that the $C_2H_4^{2+}$ dication violates our conditions (i)–(iii). The above considerations show that it is likely that the three conditions

laid down in the Discussion section are applicable to organic compounds of astrophysical significance outside the CH_3X family, such as hydrocarbons and larger alcohols, but additional factors may have to be considered as well. As implied by the above analysis of ethane, for example, doubly ionized hydrocarbons may require an additional migration of hydrogen between carbon sites to create structures having elongated C–H bonds and H–H distance close to the isolated H_2 that can serve as precursors to the roaming mechanism considered in our study. In the case of larger alcohols, we should keep in mind that the doubly ionized longer-chain saturated alcohol molecules examined in Ref. [10] (Ref. [7] in the revised Supplementary Information document) show a decrease in the H_3^+ yield due to an increase in the number of other competing fragmentation and energy-relaxation pathways. All of this means that this topic needs more study, but it is certainly interesting to observe that our conditions (i)–(iii), developed in the context of examining H_3^+ formation from the doubly ionized methyl halides and pseudohalides, apply to at least some organic compounds outside the CH_3X family.

We have incorporated the above analysis, along with the aforementioned Supplementary Figs. 5–7 and Supplementary Tables 3 and 4, in the revised Supplementary Information document as part of the new Supplementary Discussion section included in it. To reflect on these additions, we have also made two changes in the main text. First, after the last sentence of the Discussion section, we have added the following text:

"They also lead to interesting new questions. One such question is the generality of the geometrical and energetic conditions (i)–(iii) laid down in Discussion, *i.e.*, to what extent these three conditions apply to other organic compounds of astrophysical significance, such as hydrocarbons [39-42] and longer-chain alcohols [10,43], which may produce H_3^+ as well. Our preliminary examination of the doubly ionized ethane and ethene using the same CC and DIP-EOMCC methodologies as those employed in our calculations for the CH_3X systems, which are analyzed in greater detail in the Supplementary Discussion section of Supplementary Information, and our earlier studies of ethanol [10,43] suggest that our conditions (i)–(iii) may apply to organic compounds outside the CH_3X family, although additional factors may have to be considered as well. We will investigate to what extent these three conditions developed in the context of examining H_3^+ formation from the doubly ionized methyl halides and pseudohalides apply to other organic compounds in the future work."

Second, to inform the reader about our preliminary CC and DIP-EOMCC computations for ethane and ethene resulting in the above changes in Supplementary Information document, we have added the following text at the end of Methods: Electronic structure calculations:

"The details of our preliminary CC and DIP-EOMCC computations for the doubly ionized ethane and ethene species, which resulted in Supplementary Figs. 5–7 and Supplementary Tables 3 and 4 analyzed in Supplementary Discussion, can be found in Supplementary Information."

Comment by Reviewer #2:

2) In the analysis of the ion yields presented in section 2.1 of the paper as I read it, it is implicitly assumed that all ions in the forwards and backwards peaks centred at m/q = 3 are H3+. While this must of course be true for any species that have only three H atoms in total, photoionization and

particle impact studies show that there are charge separation fragmentation pathways of the methanol dication that produce H2+ via proton migration from the hydroxyl group [3-5], which would result in HD+ + CH2O+/CHO+. Since these pathways can also have similar kinetic energy releases to those that produce H3+, I don't think the paper as written sufficiently justifies why the charge separation peaks in the methanol ion spectra are purely H3+ as opposed to a mix of H3+/HD+.

I don't think any introduced uncertainty in the H3+ yield is likely to affect the qualitative conclusions of the paper since the HD yield would likely be a fraction of the H3+, so the overall trends reported in the paper would likely remain the same. However, since the H3+ yields of the other two species are normalised to the yield from methanol, an inaccuracy in the Methanol yield, if present, would have a knock-on effect in the quantitative accuracy of these reported yields. I think it is important that the paper explicitly states how the authors are sure that HD+ is not affecting the yield measurements, or if it is, to what extent this may be the case, as I don't think that using CH3OD is, by itself, enough to be certain of this. If possible, a PIPICO analysis or something similar would be strongly convincing, if this is possible to perform on the data.

Our response:

This is a very important point and we are grateful to the reviewer for making it. While we cannot directly rule out HD^+ contamination in the yield of H_3^+, we know that the likelihood of HD^+ formation is much lower than that of H_3^+. For example, Eland *et al*, in the new Ref. [36] which we have incorporated in the revised manuscript, showed that for CD_3OH^{2+}, the combined branching ratios of pathways leading to HD^+ were 22/1000, compared to D_3^+ that had a branching ratio of 61/1000. A more recent study on CH_3OD [9] reported the ratio of the H_3^+ formation pathway to the HD^+ pathway to be roughly 4.6:1.

To address the above point by Reviewer #2, we have modified the Fig. 2 caption such that the fragment in parentheses that starts with the words "in the case of CH_3OD, we also see …" in the original manuscript is now a separate sentence which begins with the words "For CH_3OD, we also see …" and which also explains that a central HD^+ peak originates from singly ionized methanol. Furthermore, we have also added the following new sentence to the caption of Fig. 2 after the above fragment:

"Based on the previous isotopologue studies involving methanol [9,36], the contribution of HD^+ to the "fwd" and "bwd" peaks for CH_3OD is expected to be minimal, having no significant effect on the reported H_3^+ yields."

Comment by Reviewer #2:

3) I think the ion spectra presented in Figure 1 would be clearer if they were plotted as a series of vertically stacked 2D plots. The 3D perspective makes it harder to directly compare the series of spectra, especially those spectra that have weaker (or non-existent) features. I think it could also be useful to visually indicate the regions from which the H3+ yields were derived.

Our response:

We agree with the reviewer that the original version of Fig. 2 could have made it difficult for the reader to compare the spectra for different compounds. To address this issue, we have modified Fig. 2 by adding an inset with a 2D bar plot of the integrated yields. The redrawn spectra also include shaded regions to indicate the portions of the "fwd" and "bwd" peaks that were integrated to obtain the H_3^+ yields. As a result of the above changes, we have modified the caption to Fig. 2 by adding the following text after the sentence that starts with the words "Each mass spectrum …":

"The shaded portions of the H_3^+ peaks indicate the regions that were integrated and subsequently doubled to calculate the yields of the trihydrogen cation, which are displayed as a bar graph on the right wall of the plot."

To clarify the fact that only the outer portions of the "fwd" and "bwd" peaks were integrated to obtain the yield of H_3^+, we have modified the first sentence in the second paragraph of the Results: Experimental section of the original manuscript by replacing the fragment "the areas of the two peaks in the doublet were integrated and divided by the sum of the peak areas in the mass spectrum that correspond to all ions attributed to dication channels" in it by the following text:

"we first normalized the corresponding mass spectrum to the integral of all ion signals attributed to dication channels. We then fit each of the two peaks in the H_3^+ doublet to a Gaussian, integrated the outer halves of both peaks (the shaded regions in Fig. 2), and doubled the outcome."

Comment by Reviewer #2:

4) CH3Cl seems to have an additional small feature located between the two H3+ peaks, closer to the peak at longer flight times. Is the origin of this spectral feature known? Was it excluded from the yield calculations?

Our response:

We agree with the reviewer that the additional feature located between the two peaks in the CH_3Cl spectrum is noticeable. We collected CH_3Cl data under very similar conditions multiple times and found that this feature is not always present in the spectrum. This additional peak might originate from small C^{4+} contributions or, perhaps, be a result of electronic micro-channel plate detector ringing from the first H_3^+ peak. Regardless of this feature's origin, it was not included in our yield calculations, as already explained in our response to comment 3) by Reviewer #2, where we pointed out that we only considered the "fwd" and "bwd" peaks corresponding to the H_3^+ signals in the mass spectra in determining the H_3^+ yields. To make the above points clear in our manuscript, we have added the following sentence to the second paragraph of the Results: Experimental section:

"We only integrated the outer halves of each doublet to avoid contamination of the measured H_3^+ yields by low kinetic energy features."

To be consistent with the above modification, the beginning of the sentence "We used this procedure to correct …" in the second paragraph of the Results: Experimental section has been replaced by

"We normalized the yields to all ion signals attributed to dication channels to correct …"

and we have made small additional grammatic changes in the sentence that follows.

Comment by Reviewer #2:

5) In Figure 4, according to the calculated fit functions, the probe seems to enhance H3+ product formation in CH3NCS in the limit of long probe delays (Yield ratio ~ 1.2), compared to the other species where a depletion (ratio 0.8 - 0.9) is observed. Based on my understanding of the disruptive probe technique, I would (perhaps naively) expect the trends to be broadly similar for the same final product ion produced by analogous processes under similar experimental conditions, thus can the authors illuminate on why the trend for CH3NCS differs in this respect? Is it simply the lower statistics introducing uncertainty to the fit?

Our response:

We agree with the reviewer that these observations should be discussed in our manuscript. In principle, the ion yield should return to the baseline (ion yield = 1) following the recovery, but other processes can change this. In the case of the CH_3X systems considered in our study, a long pump-probe delay baseline that is larger than expected (>1) indicates that the pump pulse has populated a highly excited state of the CH_3X^+ monocation which has subsequently been ionized by the weak probe to the dication state, resulting in H_3^+ production from an additional channel. A long pump-probe delay baseline that is smaller than expected (<1) indicates fragmentation of the H_3^+ product ion itself while it is still confined within the focal volume. To reflect on these remarks, the following text has been added to the caption of Fig. 4:

"The H_3^+ yields for the CH_3OD^{2+} and CH_3Cl^{2+} transients level off below the baseline (ion yield = 1), indicating fragmentation of the H_3^+ ion while it is still confined within the focal volume. In the case of the CH_3NCS^{2+} transient, the long pump-probe delay asymptote is at a value above the baseline, which suggests that the pump pulse has populated an excited state of the corresponding monocation that has subsequently been ionized by the weak probe to the dication state, resulting in H_3^+ production from an additional channel."

Comment by Reviewer #2:

6) Ref 36. also studied H3 production from methanol as a prototypical system of study as a demonstration of the methodology utilized in this paper. However, there the intensity of the pump was somewhat lower than that used in these experiments (3 vs 5e14 W/cm2) which would yield a sizeable difference in the electron re-collision energy. Can the authors elaborate on how (and why) these specific pump and probe intensities were chosen for these measurements? I gather from Ref 36 that the pump wants to be sufficiently high for efficient ionisation and below the saturation

intensity, but it would be good if the authors and the paper explained briefly how these were set in practice.

Our response:

We agree with the reviewer that the choice of pump intensity should have been commented on in our manuscript. We have addressed this concern by adding the following explanation in the first paragraph of the Methods: Experimental details section, citing Ref. [36] which in the revised manuscript appears as Ref. [38]:

"The pump pulses used in this work are sufficiently intense to doubly ionize the CH_3X molecules, and they are somewhat more intense than those employed in Ref. [38], potentially populating several electronic states of the CH_3X^{2+} dications, but this does not have a significant effect on the outcome of our experiments. The H_3^+ formation dynamics via a roaming mechanism considered in the present study proceeds mainly on the lowest singlet states of the CH_3X^{2+} species [11], which means that any pump pulse providing enough energy to doubly ionize the molecules of interest suffices."

Comment by Reviewer #3:

In this manuscript the authors report a joint theory-experimental work on H3+ formation from a series of doubly ionized methyl halogens and pseudo-halogens. Through a combination of experimental observation and computational simulation, the authors conclude that the different rates of H3+ formation for molecules in the series is dependent on dynamics that ensue following ionization within the manifold of low-lying doubly ionized electronic states. This study concludes that prompt H2 dissociation, and subsequent H3+ formation via a roaming mechanism, occurs on ultrafast (sub-ps) timescales. The computational results presented herein are used rationalize these results via a consideration of the structural relaxation that occurs following strong field ionization, and correlating the amount of internal energy imparted to the system relative to the relevant H2 dissociation barriers to the degree to which H3+ is observed. Ab initio molecular dynamics simulations are also performed and are consistent with the experimental results and static electronic structure computations, with H3+ formation being observed for only a subset of the molecules in the series.

This work employs appropriate and often state-of-the art experimental and theoretical approaches to present a compelling case for the conclusions drawn in this manuscript. The degree to which the various elements of this work present a self-consistent picture of the ionization and nuclear dynamics makes for a coherent and convincing account of H3+ formation in these molecules and will be of interest to a significant cross-section of readers in spectroscopy, dynamics, and interstellar chemistry. This work would be suitable for publication in Nature Communications following minor revision to improve the presentation.

Our response:

We would like to thank the reviewer for a positive assessment of our work and its potential suitability for publication, in an appropriately revised form, in *Nature Communications*.

Comment by Reviewer #3:

1. While it's reasonable to assume the formation of H2 should be energetically favorable in order to proceed on femtosecond timescales, the rate of H2 formation will be determined by the barrier to dissociation, which does not appear to be addressed in this work. Where these structures identified? As this is the more germane for the dynamics, can the barrier to H2 dissociation be estimated for these molecules?

Our response:

We are most grateful to the reviewer for these remarks and questions. In response to this point by Reviewer #3, we computed potential energy profiles for the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ reactions initiated by double ionization of the CH_3X species with X = OH, Cl, and NCS that produce H_3^+ in our experiments. The details of these calculations are described in the new Supplementary Discussion section included in the revised Supplementary Information document. The resulting reaction pathways are shown in Supplementary Fig. 4, which is part of this new section.

In general, there are two key events that must take place for a CH_3X^{2+} dication to form H_3^+: the dissociation of a neutral H_2 molecule from the doubly ionized CH_3X species and the proton abstraction from the remaining CHX^{2+} moiety by the roaming H_2. As shown by Matsubara, who examined the CH_3X^{2+} systems with X = F, Cl, and Br in Ref. [17] (which is cited in the revised Supplementary Information document as Ref. [1]), and as confirmed by our DIP-EOMCC calculations for the CH_3OH^{2+}, CH_3Cl^{2+}, and CH_3NCS^{2+} dications that form H_3^+ in our experiments, the liberation of H_2 from its doubly ionized CH_3X parent is an energetically uphill barrierless process, *i.e.*, there are no intervening transition states between the minima on the lowest singlet potential energy surfaces of the CH_3X^{2+} species and the respective $CHX^{2+} + H_2$ dissociation asymptotes if we treat the release of H_2 as an isolated event. Essentially, upon elongating two of the three C–H bonds, the corresponding hydrogen atoms come close together to form H_2, which starts moving around following the roaming trajectories. While there may exist small barriers along the roaming trajectories, associated with the formation of loosely bound van der Waals complexes between the CHX^{2+} moiety and H_2, no barriers for the $CH_3X^{2+} \rightarrow CHX^{2+} + H_2$ dissociation channels treated in isolation were located in our calculations. There are, however, well-pronounced transition states that connect the equilibrium CH_3X^{2+} structures to the final H_3^+ and CX^+ products associated with the abstraction of a proton from the CHX^{2+} fragment by the roaming H_2, which can be seen in Supplementary Fig. 4 and which are further analyzed in the Supplementary Discussion section included in the revised Supplementary Information document. It is clear from the potential energy profiles describing the $CH_3OH^{2+} \rightarrow COH^+ + H_3^+$, $CH_3Cl^{2+} \rightarrow CCl^+ + H_3^+$, and $CH_3NCS^{2+} \rightarrow CNCS^+ + H_3^+$ reactions shown in Supplementary Fig. 4 that the adiabatic relaxation energies ΔE_{rlx} characterizing the CH_3X^{2+} dications with X = OH, Cl, and NCS are sufficiently large to overcome the barriers associated with the transition states on their respective lowest-energy singlet potentials and liberate neutral H_2 molecules that can subsequently roam their CHX^{2+} companions, abstracting protons from them to form H_3^+ species.

In addition to including the above information in the new Supplementary Discussion section of the revised Supplementary Information document, we have also made the appropriate changes in the revised manuscript that reflect on our reaction profile calculations and the most essential

conclusions that can be drawn from them. Thus, the information about our computations of the potential energy profiles for the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ reactions initiated by double ionization of the CH_3X species with X = OH, Cl, and NCS that produce H_3^+, along with a summary of the key findings of these computations, has been added at the end of the Results: *Ab initio* electronic structure calculations section and, in the form of a new paragraph starting with the words "In addition to the above characteristics …", in Methods: Electronic structure calculations. We have also augmented the original condition (iii) formulated in the Discussion section of the main manuscript with the additional requirement that the adiabatic relaxation energy should also be large enough to overcome the barrier(s) along the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ reaction profiles, including those corresponding to the $CHX^{2+} + H_2 \rightarrow CX^+ + H_3^+$ proton abstraction events by the roaming H_2, adding the complementary text related to this change in the sentence below the statement of condition (iii) that starts with the words "The C–H bond lengths characterizing …". Finally, to emphasize the consistency of our time-independent quantum chemistry calculations of the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ reaction profiles and the time-dependent AIMD simulations reported in our work, which point to the emergence of "edge on" configurations that facilitate the completion of the $CHX^{2+} + H_2 \rightarrow CX^+ + H_3^+$ proton abstraction steps, we have made changes in the sentence that begins with the words "From the trajectories resulting from our AIMD simulations …" in the third paragraph of the Discussion section starting with "As explained in Results and Methods, the mechanism of …".

Comment by Reviewer #3:

2. That there is the possibility for "fwd" and "bwd" Coulomb explosion indicates that the strong ionization process prepares a highly anisotropic axis distribution of dicationic species. For much of the readership of Nature Comms, this may not be immediately obvious and should be explicitly stated and explained.

Our response:

We fully agree with the reviewer that the emergence of forward and backward trajectories of the H_3^+ ions resulting from the Coulomb repulsion of the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ reaction products caused by the preferential double ionization of the CH_3X molecules by the strong laser pulses used in our experiments should be explained in our manuscript. Thus, in response to the reviewer's request, we have incorporated the following fragment into the first paragraph of the Results: Experimental section, after the second sentence that starts with the words "For the CH_3OD, CH_3Cl, and CH_3NCS molecules …":

"This is because out of a set of randomly oriented CH_3X molecules interacting with a laser, those with the dipole moments aligned parallel to the electric field of the laser are preferentially ionized, resulting in H_3^+ ions that move toward or away from the detector. The H_3^+ ions moving directly toward the detector arrive earlier, whereas those moving away arrive with a delay, after being turned around by the static electric field of the mass spectrometer. The forward and backward H_3^+ peaks seen in Fig. 2 are sharp because the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ dissociation processes that produce them are faster than rotations of the CH_3X^{2+} dications (see Results: Timescales of H_3^+ formation for further details). The presence of separate peaks due to the forward and backward trajectories of H_3^+ ions resulting from the Coulomb repulsion of the positively charged CX^+ and

H_3^+ species in our TOF mass spectra for the CH_3OD, CH_3Cl, and CH_3NCS compounds implies that H_3^+ formation in our strong-field ionization experiments originates from the dication states of the parent CH_3X molecules rather than from their singly ionized counterparts."

Comment by Reviewer #3:

3. The authors do not comment on which electronic states are populated during the ionization process, even though they are included in the state electronic structure calculations in Figure 3. In the Methods section, it would appear that the AIMD simulations only involved the dynamics on the singlet dicationic states. In summary, it would seem the experiment will not be particularly sensitive to the multiplicity of the electronic states produced via ionization and this would be difficult to compute from first principles. Furthermore, based on the results in Figure 3 and subsequently rationalization of the results, the structural relaxation in the triplet manifold is perhaps not sufficient to lead to significant H2 dissociation. Firstly, is this the authors' understanding? Secondly, does the ratio of H3+ yield (which is assumed to be formed ultrafast, if formed at all from singlet channels) to all dicationic channels in Table I related to singlet/triplet yields in the ionization process? Whatever the answers to these questions, any discussion of electronic character of the dicationic states following ionization, and the relation to the pertinent observables, is currently absent in the manuscript and should be addressed.

Our response:

We would like to thank the reviewer for raising all these questions. We agree with Reviewer #3, as well as with the closely related remarks by Reviewers #1 and #4, that a clear discussion of which electronic states can be populated during our double ionization experiments and how this affects our reported H_3^+ yields would enhance the clarity of our manuscript. While it is true that the higher excited states of the CH_3X^{2+} dications may be populated following the strong-field double ionization of the neutral CH_3X molecules that result in the production H_3^+ in our experiments, we believe these states do not significantly participate in H_3^+ formation. A detailed explanation of why it is reasonable to assume that the contributions of higher excited singlet states and states belonging to triplet manifolds of the CH_3X^{2+} dications to the yields of H_3^+ are very low has already been included in our responses to the questions raised by the Reviewer #1 on pages 2 and 7 of this document. To reiterate our earlier remarks, which are consistent with the above comments by Reviewer #3, the geometrical distortions characterizing the minima on the triplet and excited singlet potentials of the CH_3X^{2+} dications are not conducive to the release of a neutral H_2 that could subsequently roam and abstract a proton from the CHX^{2+} moiety to form H_3^+. For example, among the minima on the three low-lying potentials of the doubly ionized CH_3Cl species examined in our work, only the CH_3Cl^{2+} geometry in its lowest-energy singlet state satisfies our conditions (i) and (ii). The geometries of the CH_3Cl^{2+} dication in its lowest triplet and second singlet states calculated in our study do not exhibit two substantially elongated C–H bonds and the H–H bond lengths in them are far from the internuclear separation in the isolated hydrogen molecule (see the new Supplementary Table 1 in the revised Supplementary Information document). Similar remarks apply to other H_3^+-producing species. For example, a previous study on the electronic structure and dynamics of the doubly ionized methanol by Livshits *et al.*, reported in Ref. [11], demonstrates that the probability of H_3^+ formation from CH_3OH^{2+} is the highest in its lowest singlet state, rapidly dropping down when higher excited states are examined. Another relevant study by Gope *et al.*,

cited as the new Ref. [22] in the revised manuscript, argues that triplet states of the doubly ionized CH_3OH molecule do not produce H_3^+ due to the enormous amount of energy required to liberate a neutral H_2 molecule, which is a key step for the roaming mechanism considered in the present work (see our response to Reviewer #1 for further comments). All of this discussion indicates that the majority of the H_3^+ ions that we detect in our experiments originate from the lowest singlet states of the CH_3X^{2+} dications that meet our conditions (i)–(iii). This is why our AIMD trajectories were propagated on the lowest singlet electronic potentials of the doubly ionized CH_3X species.

To address the questions raised by Reviewer #3 in point 3 above and the analogous comments made by Reviewers #1, which we discussed on pages 7 and 8 of this document, and Reviewer #4, we have added a few statements explaining why we did not consider higher-lying states of the CH_3X^{2+} dications in our computations to our revised manuscript, citing Refs. [11] and [22]. They appear as the second sentence in section Results: *Ab initio* electronic structure calculations and as the second and third sentences of Results: *Ab initio* molecular dynamics simulations. To re-emphasize the significance of the observation that the low-lying excited states of the CH_3X^{2+} dications that we considered in our work do not undergo the necessary geometrical distortions for liberating H_2, we have added short statements about it in the third paragraph of the Results: *Ab initio* electronic structure calculations section of the revised manuscript that begins with the words "The situation with the CH_3Cl, CH_3CN, and CH_3I molecules …" (see the sentences that begin with "In particular, the C–H bond lengths do not change much …" and "Similarly to the triplet states, they do not undergo …"). These additional statements refer to the new Supplementary Table 1, which is also mentioned in the last sentence of the third paragraph of the Methods: Electronic structure calculations section of the main text. We have also added the following sentence in the last paragraph of the Introduction that begins with the words "In this article, we report …":

"In principle, the returning electron can populate several electronic states of the resulting CH_3X^{2+} dications, but the previous studies on the doubly ionized methanol, reported in Refs. [11] and [22], suggest that the excited manifolds of the CH_3X^{2+} species, including singlet as well as triplet states, do not significantly impact the H_3^+ formation dynamics investigated in this work. The results reported in the present article point to the same conclusion."

In response to the last question posed by Reviewer #3 in point 3, we agree that the relative populations of the singlet and triplet manifolds of the CH_3X^{2+} dications produced in our double ionization experiments may influence the H_3^+ yields. As explained in our manuscript and the discussion above, only the lowest singlet states of the CH_3X^{2+} species contribute significantly to the yields of H_3^+. Thus, larger relative populations of the higher-energy singlet and triplet states of the CH_3X^{2+} species may parasitically decrease the total H_3^+ yields. They could also lead to an increase in the number of other dicationic channels, decreasing the yields of the H_3^+ ions determined relative to these channels. However, in our data processing, we take an additional step and normalize the H_3^+ yields relative to all dication channels to the maximum yield obtained for CH_3OD. In this way, we reduce the impact of the less controllable factors, such as the relative population levels of the singlet and triplet manifolds of the CH_3X^{2+} species produced in our double ionization experiments or the competing fragmentation channels, on the H_3^+ yields reported in Table 1, making them and, most importantly, the trends they follow less sensitive to such factors. To reflect on this analysis, we have added the following sentence in the second paragraph of the

Results: Experimental section that begins with the words "To determine the H_3^+ yield for each of the …":

"Furthermore, by normalizing the H_3^+ yields relative to all dication channels to CH_3OD, we counterbalanced the impact of the less controllable factors, such as the relative population levels of the singlet and triplet manifolds of the CH_3X^{2+} species produced in our double ionization experiments or the competing fragmentation channels, on the H_3^+ yields reported in Table 1, making them and, most importantly, the trends they follow less sensitive to all such factors."

Comment by Reviewer #3:

4. Since the purpose of Figure 6 is to use computed quantities to predict reactive outcomes, the inclusion of CH3F (despite there being no experimental data) would be appropriate, particularly given the amount of discussion in the main body of the manuscript. In particular, the statement "but cannot be so large that other reactive mechanisms, such as the H–H bond breaking in the liberated H2, may become dominant or the H2 molecule escapes" on page 13 would be better motivated via the inclusion of the CH3F results.

Our response:

We agree with the reviewer that our condition (iii) introduced in the Discussion section, which, after revisions necessitated by the comments made by Reviewers #1 and #3 discussed on pages 2–5 and 17–19 of this document, states, in its latter part, that the adiabatic relaxation energy (designated in the revised manuscript, in response to the request from Reviewer #4, as ΔE_{rlx}) cannot be so large that other reactive mechanisms and other ways of decomposing CH_3X^{2+} become dominant, is motivated by our AIMD simulations for CH_3F^{2+}. As shown in the new Supplementary Fig. 3, which is an extended version of Fig. 6 created in response to the request made by Reviewer #3, and which includes the CH_3F^{2+} dication alongside the six CH_3X^{2+} species examined in our experiments, the adiabatic relaxation energy, *i.e.,* the energy released by the geometrical relaxation of CH_3F^{2+} after double ionization of CH_3F, is much higher than in the remaining CH_3X^{2+} species considered in our work and, as a result, redistributed very differently than in the CH_3OH^{2+}, CH_3Cl^{2+}, and CH_3NCS^{2+} dications that form H_3^+. A typical trajectory obtained in our AIMD simulations for CH_3F^{2+} is shown in the new Supplementary Movie 3, where, instead of the roaming mechanism observed, for example, in CH_3Cl^{2+}, the liberated, positively charged, H_2 fragment dissociates and the final products are CH_2F^+ and a proton. In a small number of trajectories for CH_3F^{2+}, the liberated H_2 fragment, having sufficiently large energy available to it, escaped the system, preventing H_3^+ formation as well. While our AIMD simulations, which show that the CH_3F^{2+} dication does not produce H_3^+, are in perfect agreement with the previous experimental [18] and computational [17] studies of the behavior of the doubly ionized methyl fluoride, we did not conduct experiments on CH_3F ourselves and, as a result, we do not have access to the H_3^+ yield information for it. For this reason, we prefer to keep Fig. 6 in the main text unchanged. However, we completely agree with the reviewer that having the adiabatic relaxation and dissociation energies characterizing the CH_3F^{2+} species in Fig. 6 would facilitate comparisons between CH_3F^{2+} and other CH_3X^{2+} dications investigated in our study. Thus, we have incorporated the new Supplementary Fig. 3, which is an extended version of Fig. 6 that includes the CH_3F^{2+} dication alongside the six CH_3X^{2+} species examined in our experiments, into the Supplementary Data

section of the revised Supplementary Information document. We have added information about all of the above and improved our discussion of the behavior of the CH_3F^{2+} system, especially how our conditions (i)–(iii) apply to it, in the second paragraph of the Discussion section that begins with the words "None of the remaining …". Furthermore, information about the new Supplementary Movie 3 has been added at the end of the Results: *Ab initio* molecular dynamics simulations section.

To keep consistency with the calculations for the remaining CH_3X^{2+} species included in Fig. 6 of the main text, especially the smaller ones with X = OH and Cl, we have also improved our description of the neutral and doubly ionized CH_3F species by performing the higher-level DIP-EOMCC(4h-2p)/cc-pVDZ calculations and the CCSD, DIP-EOMCC(3h-1p), and DIP-EOMCC(4h-2p) computations using the larger cc-pVTZ basis set, in addition to the previously considered CCSD/cc-pVDZ and DIP-EOMCC(3h-1p)/cc-pVDZ data, making the appropriate adjustments in Methods: Electronic structure calculations (by deleting the paragraph that begins with the words "To enrich our discussion …" and merging the information about the calculations for CH_3F and CH_3F^{2+} with those for the remaining CH_3X and CH_3X^{2+} species), Methods: *Ab initio* molecular dynamics simulations (in the middle of the paragraph forming this section), and the revised version of the Supplementary Information document. In the latter case, in the Supplementary Data section, we have provided the Cartesian coordinates and electronic energies of the CH_3F and CH_3F^{2+} molecules resulting from the additional CCSD/cc-pVTZ, DIP-EOMCC(3h-1p)/cc-pVTZ, DIP-EOMCC(4h-2p)/cc-pVDZ, and DIP-EOMCC(4h-2p)/cc-pVTZ geometry optimizations, added the new Supplementary Table 1 that shows selected internuclear distances characterizing the geometries of the neutral CH_3F molecule and the lowest singlet and triplet states of the CH_3F^{2+} dication – alongside their CH_3X and CH_3X^{2+} counterparts with X = Cl, CN, and I – obtained in our most accurate CC and DIP-EOMCC calculations, replaced Supplementary Figs. 1 and 2, which contain information needed to calibrate the CASSCF calculations exploited in our AIMD simulations, by their updated versions using the more accurate DIP-EOMCC(4h-2p)/cc-pVDZ data for CH_3F^{2+}, revised the original Supplementary Table 1, which, because of the new Supplementary Table 1, is now called Supplementary Table 2 and which provides the most accurate values of the key bond lengths characterizing the neutral and doubly ionized CH_3F species and the most accurate values of ΔE_{rlx}, and ΔE_{diss} characterizing CH_3F^{2+} obtained in our study, and added the aforementioned Supplementary Fig. 3, which is an extended version of Fig. 6 in the main text that includes the CH_3F^{2+} dication, alongside the six CH_3X^{2+} species examined in our experiments. The addition of the new Supplementary Table 1 also resulted in the appropriate changes in the third paragraph of the Methods: Electronic structure calculations section that begins with the words "The Cartesian coordinates defining all geometries …" and in a couple of places in the Results: *Ab initio* electronic structure calculations section (in the paragraph that begins with "The situation with the CH_3Cl, CH_3CN, and CH_3I molecules …"), where the information included in this table is referenced. For some additional details relevant to the CH_3F^{2+} species, please see our response to Reviewer #1 on pages 4 and 5 of this document.

Comment by Reviewer #3:

5. A few gridlines along the 'mass to charge' axis in Figure 1 would be helpful to aid the reader to show alignment in the H3/H2 peaks between different molecules.

Our response:

We would like to thank the reviewer for this suggestion, which has helped us improve our original Fig. 2 (we are assuming that the reviewer is referring to Fig. 2). Following the reviewer's suggestion, we have added gridlines along both the "Mass to charge ratio [m/z]" and "Ion yield [arb. units]" axes to make Fig. 2 easier to view. We have also made a few additional changes in the original Fig. 2 and the caption to it to address the comments made by Reviewer #2 in points 2, 3, and 4 (see pages 13–15 of this document). In particular, we have included an inset with a 2D bar plot of the integrated yields on the right wall of the revised Fig. 2. To highlight what is being integrated to obtain the yields of H_3^+ from the CH_3X^{2+} dications included in our experiments, we have marked the relevant parts of the mass spectra shown in the revised Fig. 2 by the shaded regions, adding the appropriate explanation to the figure caption. Some of these modifications in Fig. 2 and the caption to it are tied to the additional text incorporated in the second paragraph of the revised Results: Experimental section in response to comments 3 and 4 by Reviewer #2.

Comment by Reviewer #3:

6. On pg. 8, the repeated phrase "two degenerate HOMOS..." is confusing. There is a single HOMO orbital is that doubly-degenerate at C3v configurations.

Our response:

We use the language and follow the tradition adopted in modern many-body theory in which an orbital, including a molecular orbital (MO), is defined as a spatial one-electron function that, after being multiplied by the spin-up and spin-down functions, results in two spin-orbitals capable of accommodating up to two electrons. Thus, in a situation discussed by the reviewer, we have two degenerate HOMOs or one doubly degenerate highest occupied shell consisting of two MOs. This allows us to clearly and precisely distinguish between the degenerate and non-degenerate shells considered in our manuscript and, for example, facilitate the description of the multiconfigurational states mixing, in the zeroth-order description, two closed-shell determinants, in which one of the two degenerate HOMOs remains occupied by two electrons and the other one is empty, as opposed to open-shell singlets where each of the two degenerate HOMOs is singly occupied. Some of the authors involved in the development of new many-body methods of quantum chemistry used similar language in their past publications. We would prefer not to alter this language, so we have not made any changes in the manuscript in response to the above remark. We would greatly appreciate it if the reviewer could accept our explanation.

Comment by Reviewer #4:

Review of manuscript titled H3+ Formation from Methyl Halogens and Pseudohalogens: Experiment Theory and Governing factors. By Stamm and coworkers.

This manuscript describes and explains experiments whereH3+ is observed after CH3X molecules where X= OD, Cl, NSC, CN, SCN, I and F are doubly ionized with an intense non-resonant laser field. Despite the molecules being very similar some form H3+ easily and quickly and other not at all. The authors have done a lovely job in explaining the subtle differences between the systems

that dictate whether the CH3X molecule will produce H3+. It seems that the doubly excited state needs for three things to be simultaneously true; 1) upon excitation two of the H bonds must lengthen and weaken 2) those two Hydrogen atoms must come close together so that their bond length is close to an H2 molecules and 3) the amount of internal energy put into the molecule by the vertical ionization process must exceed the dissociation energy. The authors make a very convincing experimental and theoretical case for this. I think this paper should definitely be published. I do however have a few issues with some of the presentation that I feel the authors should address before publication.

Our response:

We would like to thank the reviewer for a positive assessment of our work and its potential suitability for publication, in an appropriately revised form, in *Nature Communications*.

Comment by Reviewer #4:

On page 10 they talk about the difference in the vertical versus adiabatic ionization energy being important and reference equations 3 and 4 but it is not till page 19 that equations 3 and 4 show up. Not sure why this obvious clumsy organization is here but please move the discussion on page 19 up to page 10 when one talks about those equations. In addition, equation 3 defines DE as the "adiabatic relaxation energy". I think it would be clearer to the audience if it was labeled DEinternal., or something like that, of course in these experiments the available energy for dissociation is this DE plus the internal thermal energy that the molecule has as the experiments are done at room temperature. This is small but considering the small values of DE for CH3CN it may be responsible for the small amount of H3+ that is observed in figure 2.

Our response:

Following the reviewer's request, we have moved Eqs. (3) and (4) to the end of the Results: *Ab initio* electronic structure calculations section of the revised manuscript. They are now labeled as Eqs. (1) and (2), respectively [the original Eqs. (1) and (2) have been relabeled accordingly and appear in the revised manuscript as Eqs. (3) and (4)]. The above migration of Eqs. (3) and (4) has resulted in suitable changes in the text of the last paragraph of the Results: *Ab initio* electronic structure calculations and the fourth paragraph of the Methods: Electronic structure calculations sections.

As suggested by the reviewer, the original symbol ΔE representing the adiabatic relaxation energy has been replaced in the revised manuscript and Supplementary Information document by the more informative ΔE_{rlx} (the subscript "rlx" stands for relaxation).

As far as the last sentence of the above comment by Reviewer #4 is concerned, we would like to point out that the signals in the m/z=3 region of the mass spectra shown in Fig. 2 cannot be entirely attributed to H_3^+. This is because of the possible contributions from the C^{4+} ions at the laser power used in our experiments, as reflected in the last sentence of the caption to Fig. 2: "CH_3CN, CH_3SCN, and CH_3I do not produce appreciable H_3^+ signals that would be distinguishable from the C^{4+} ion, which has the same m/z ratio as H_3^+." In particular, in spite of multiple attempts, we could

not identify any laser power for CH_3CN that would generate a signal at m/z=3 without possible contamination by C^{4+}.

Comment by Reviewer #4:

In Figure 4 why do the signals not come back to the one level, CH3OD asymptotes below one and CH3NCS above one?

Our response:

We thank the reviewer for asking this question, which has already been answered earlier in this document as our response to comment 5 by Reviewer #2 (see page 16 of this document). As explained in our response to point 5 by Reviewer #2, to address the above question, we have added the following text to the caption of Fig. 4:

"The H_3^+ yields for the CH_3OD^{2+} and CH_3Cl^{2+} transients level off below the baseline (ion yield = 1), indicating fragmentation of the H_3^+ ion while it is still confined within the focal volume. In the case of the CH_3NCS^{2+} transient, the long pump-probe delay asymptote is at a value above the baseline, which suggests that the pump pulse has populated an excited state of the corresponding monocation that has subsequently been ionized by the weak probe to the dication state, resulting in H_3^+ production from an additional channel."

Comment by Reviewer #4:

Does the electron that rescatters have plenty of energy to make electronically excited states of the dication. If so is there any indication that excited electronic states play a role or would that just be a parasitic process lowering the quantum yield of H3+?

Our response:

This point has already been thoroughly discussed in our responses to the remarks made by Reviewer #1, which can be seen on pages 7 and 8 of this document, and Reviewer #3, who raised very similar questions in his or her point 3. Our response to point 3 of Reviewer #3 can be seen on pages 20 and 21. In a nutshell, in addition to our own explanations of why it is reasonable to assume that the contributions of higher excited singlet states and states belonging to triplet manifolds of the CH_3X^{2+} dications to the yields of H_3^+ are very low, so that we could safely propagate our AIMD trajectories on the lowest singlet electronic potentials of the doubly ionized CH_3X species, we rely on the results and careful analyses reported in Ref. [11] and the new Ref. [22]. To address the above question raised by Reviewer #4 and the analogous questions and comments by Reviewers #1 and #3, we have added a few statements explaining why we did not consider higher-lying states of the CH_3X^{2+} dications in our computations to our revised manuscript, citing Refs. [11] and [22]. They appear as the second sentence in section Results: *Ab initio* electronic structure calculations and as the second and third sentences of Results: *Ab initio* molecular dynamics simulations. To re-emphasize the significance of the observation that the low-lying excited states of the CH_3X^{2+} dications that we considered in our work do not undergo the necessary geometrical distortions for liberating H_2, we have also added short statements about it

in the third paragraph of the Results: *Ab initio* electronic structure calculations section of the revised manuscript that begins with the words "The situation with the CH_3Cl, CH_3CN, and CH_3I molecules …" (see the sentences that begin with "In particular, the C–H bond lengths do not change much …" and "Similarly to the triplet states, they do not undergo …"). These additional statements refer to the new Supplementary Table 1, which is also mentioned in the last sentence of the third paragraph of the Methods: Electronic structure calculations section of the main text. Last but not least, we have included the following sentence in the last paragraph of the Introduction beginning with the words "In this article, we report …":

"In principle, the returning electron can populate several electronic states of the resulting CH_3X^{2+} dications, but the previous studies on the doubly ionized methanol, reported in Refs. [11] and [22], suggest that the excited manifolds of the CH_3X^{2+} species, including singlet as well as triplet states, do not significantly impact the H_3^+ formation dynamics investigated in this work. The results reported in the present article point to the same conclusion."

Comment by Reviewer #4:

In conclusion this is a very nice manuscript and should be published. I have some small issues with the organization but none with the science.

David Chandler

Our response:

We are most grateful to Reviewer #4 for making this remark. We hope that our responses to the comments, questions, and suggestions by all four reviewers and changes in the main manuscript and Supplementary Information summarized in this document are satisfactory, allowing the Editors of *Nature Communications* to continue processing our submission.

RESPONSES TO COMMENTS BY THE REVIEWERS

Remarks by Reviewer #1:

I commend the authors for their diligent response to my earlier comments. The revisions have certainly enhanced the manuscript. However, I remain concerned about the time-resolved studies, which I consider crucial to this work.

The employed time-resolved experiment, a degenerate 800nm pump/800nm probe setup, while relatively straightforward to implement, particularly with the high sensitivity of charged particle detection, yields data—the multiphoton-induced ion yield—that is notoriously challenging to interpret in terms of the underlying process. As the authors themselves noted in their response, the observed modulations in ion yield are likely due to higher electronic states shifting in and out of resonance with single or multiphoton excitation by the probe pulse. Consequently, these modulations do not directly reflect the dynamics of the dication on the ground state potential energy surface (i.e., the actual formation of H3+), but rather probe energy gaps between the ground state and various excited states of unknown character. How these energy gaps relate to the H3+ generation coordinate remains unclear. Thus, the insights into H3+ generation that can be gleaned from this particular experimental approach are inherently limited.

In light of this, the discrepancy between the timescales observed in the simulation and experiment is unsurprising. The two are fundamentally incommensurate: the simulation tracks product formation, whereas the experiment captures signatures of resonances between the initially populated state and higher-lying states during product formation. It's akin to comparing apples and oranges.

In light of these from my perspective inherent short comings of the study, I do not recommend publication in Nature Communications. The results are certainly interesting but should be published in a more targeted journal.

Our response:

We thank Reviewer #1 for sharing with us the above analysis. We agree with the reviewer that our experimental measurements have certain limitations, and so do the AIMD simulations and the electronic structure computations needed to provide information about the underlying potential energy surfaces. Because of these limitations, which we summarize below, the agreement between our experimental and simulated timescales of H_3^+ formation cannot be made fully quantitative, despite the fact that the experimental and computational techniques employed in our study are state-of-the-art. Having said this, there is a great deal of consistency between our experimental measurements of H_3^+ yields and timescales of H_3^+ formation in several CH_3X systems and the corresponding theoretical analyses and computations, which enables us to provide an in-depth microscopic understanding of the molecular mechanisms and key factors that explain the formation of H_3^+ by some doubly ionized CH_3X species and its absence in the others.

Here are the examples of limitations in our experimental measurements and modeling procedures. Given the mechanism of H_3^+ formation from the doubly ionized CH_3X species examined in our

work, the time-resolved experimental data reported in our study probe the processes where most of the time is spent on H_2 roaming the CHX^{2+} moiety. This roaming occurs on a shallow, multidimensional, potential energy surface which, as evidenced by our AIMD trajectories, makes the resulting dynamics highly sensitive to initial conditions, leading, in turn, to the stochastic character of the H_2 roaming process. If these dynamics were identical for all CH_3X molecules in an ensemble, the time-dependent H_3^+ yield measurements would display the molecule-specific details including oscillations as the H_2 molecule approaches and retreats from the CHX^{2+} species, resulting in transitions in and out of resonance with the probe as the system evolves in time. However, our measurements can only track an ensemble of CH_3X^{2+} molecules that do not behave in exactly the same manner as the H_2 moiety changes orientation and distance from the CHX^{2+} species during the roaming process, averaging out the H_2 roaming dynamics, washing out the molecule-specific details, and providing us only with a measure of the fraction of the ensemble that has yet to form H_3^+ since this fraction is more likely to be in resonance with the probe pulse, even if not all the species are resonant at a given pump-probe delay. As the pump-probe delay becomes larger and the fraction of the roaming ensemble that has undergone the final $CHX^{2+} + H_2 \rightarrow CX^+ + H_3^+$ reaction increases, the yield of H_3^+ begins to grow, eventually leveling off because the H_3^+ ions that have already been formed are not appreciably disturbed by the probe pulse (cf. Fig. 4). Averaging over the ensemble's stochastic roaming dynamics, as summarized above, results in exponential signal dependence proportional to the reaction time, as observed in our study and in other direct measurements of roaming reactions (see Refs. [9,10,39,40] in the current version of the manuscript; please note that Refs. [39] and [40] are new).

As explained in our previous responses to the reviewers, including Reviewer #1, our AIMD simulations have inherent limitations too, such as the relatively small numbers and limited duration of the computed trajectories and the limited quality of the CASSCF potential surfaces on which our AIMD calculations rely (see the Methods: Ab initio molecular dynamics simulations section for further details). It is true that we tailored the active space used in our CASSCF computations to closely reproduce the key molecular characteristics of the species examined in our work resulting from the high-level DIP-EOMCC calculations, which are known to be very accurate, but one has to keep in mind that neither CASSCF nor the DIP-EOMCC approaches used in our study are exact. All of this means that it is hard to expect a fully quantitative agreement with experiment, even though our experimental measurements and computations can be regarded as state-of-the-art. It is simply very difficult to precisely model the stochastic nature of the roaming dynamics probed in our experiments. There is, however, enough agreement between our experimental measurements involving several CH_3X systems and the corresponding AIMD and quantum chemistry computations of the $CH_3X^{2+} \rightarrow CX^+ + H_3^+$ processes to form a consistent picture of the mechanism, yields, and timescales of H_3^+ production and key factors that govern them. In other words, despite the shortcomings of both the experimental techniques and theoretical models employed in our work, they perfectly complement each other, providing a holistic understanding of the roaming dynamics examined in our study.

To reflect on the above remarks in response to the comments made by Reviewer #1 and to address the editorial requests included in the Author Checklist pointing to the same issues, we have made the following changes in the current version of the manuscript:

1. We have replaced the last sentence of the Introduction that previously started with the words "The complementary blend of the state-of-the-art experimental …" by

"While our experimental measurements and theoretical models, despite their state-of-the-art nature, have inherent limitations, their complementary blend provides detailed understanding of the microscopic factors that explain the formation of H_3^+ by some doubly ionized CH_3X species and its absence in the others, alongside the underlying molecular mechanisms, timescales, and yields, which may offer guidelines for examining small organic compounds as alternative sources of the trihydrogen cation in the interstellar medium."

2. We have replaced the three-sentence fragment near the end of the last paragraph of the Results: Timescales of H_3^+ formation section, which previously started with the words "Since the probe accesses this other electronic state …" and ended with "forms in a few hundred femtoseconds", by

"For each CH_3X^{2+} molecule, a resonant single or multiphoton transition induced by the probe has a complicated relationship with the reaction coordinate as the H_2 moiety changes orientation and distance from the CHX^{2+} species during the roaming process. Averaging over the ensemble of CH_3X^{2+} dications excited by the pump pulse washes out these specific details, leaving only a measure of the fraction of the ensemble that has yet to form H_3^+. As the pump-probe delay becomes larger and the fraction of the roaming ensemble that has undergone the $CHX^{2+} + H_2 \rightarrow CX^+ + H_3^+$ reaction increases, the yield of H_3^+ ions begins to grow, eventually leveling off because the H_3^+ ions that have already been formed are not appreciably disturbed by the probe pulse. Averaging over the ensemble's stochastic roaming dynamics results in an exponential signal dependence proportional to the reaction time, as observed here and in other direct measurements of roaming reactions [9, 10, 39, 40]."

As already alluded to above, Refs. [39] and [40] have been added during this revision.

3. We have replaced the second sentence of the third paragraph of the Discussion section that previously started with the words "Our calculated yields and timescales of H_3^+ formation …" by the three-sentence fragment

"AIMD simulations have limitations, which in our case are the relatively small number and limited duration of the computed trajectories and the limited quality of the CASSCF potential surfaces on which we had to rely (see Methods: Ab initio molecular dynamics simulations). It is also very difficult to precisely model the stochastic nature of the roaming dynamics examined in our experiments, discussed in Results: Timescales of H_3^+ formation. Nevertheless, our calculated yields and timescales of H_3^+ formation are in qualitative agreement with the experimental observations."

We hope that our responses to the remarks by Reviewer #1 and the related editorial requests included in the Author Checklist, along with the revisions in our manuscript summarized in the above points 1–3, are satisfactory.

Remarks by Reviewer #2:

The paper is a revision of the previously submitted manuscript NCOMMS-24-10836. The data and conclusions of the paper remain broadly the same as the previous iteration of the manuscript, but the authors have made several important additions and modifications to the manuscript, its figures, and to the supporting material. The authors have addressed the changes and provided rebuttals to the points raised by the four reviewers in an extremely comprehensive rebuttal letter. Cumulatively, I believe that these changes have significantly strengthened the paper and its conclusions.

I provide the following feedback to the rebuttals and changes presented by the authors that were specific to the six points I initially raised (numbered and ordered the same as in the rebuttal letter):

1. The inclusion of the preliminary hydrocarbon data and discussion of these in the broader context of their work strengthens the argument that that their criteria can be more generally applied to other systems and, in my opinion, significantly increases its justification for publication in a broader reach journal. i approve the explanation and additions/changes.

2. I think the changes to the text, which now explicitly explains that the central peak in the TOF data comes from HD+ produced by the monocation, is a welcome addition, but I am a bit less convinced by the following part of the added text. Adding the references that discuss the branching ratios of the two channels is a good step, but I think the sentence "the contribution of HD+ to the "fwd" and "bwd" peaks for CH3OD is expected to be minimal, having no significant effect on the reported H+ 3 yields." would be improved further if they quantified what "minimal" means, since even by their own estimates, a 4.6 ratio derived from their work in Ref 36 would still correspond to more than a 20% contribution, which some readers may not class as "small".

3. I wholeheartedly approve of the changes made to figure 2. The addition of the shaded regions indicating the areas used for yield calculations, the yield integrals on the second axis, and the addition of the "tick lines" suggested by reviewer 3 make for a much improved and comprehensible figure and a fine alternative to the stacked vertical arrangement I suggested. I approve and accept these changes.

4. I accept this explanation, and the addition of explicitly showing the integration regions in the figure removes any ambiguity as to what was treated as "signal". I approve and accept these changes.

5. I approve of the explanation, and its inclusion in the text.

6. I welcome and approve of the inclusion of this additional information.

Addressing the manuscript as a whole: the additions/changes made to figure 1 and the surrounding discussion of the laser/field free dynamics is a welcome improvement, and better justifies the applicability of these results to more general scenarios/environments where double ionsation processes may arise (the interstellar environment in particular). Reviewer 3 also raised an important point (#2) regarding the origin of the fwd and bwd peaks in the time-of-flight data not being immediately obvious to someone outside of the field of ion time of flight spectroscopy, and

the changes made by the authors do well to make the results more accessible to a broader audience. Overall, I also think that the authors have done well in addressing the other points raised by the three reviewers other than myself, and the substantial additions to the main text have provided a wealth of additional context and discussion that only serves to strengthen the paper.

In summary, if the minor change I suggested (see point 2 above) is addressed, I would have no hesitation in recommending the manuscript (or a lightly edited form of it) being published in Nature Communications.

Our response:

We would like to thank Reviewer #2 for a positive assessment of our work and its potential suitability for publication, in a slightly revised form addressing point 2 above, in *Nature Communications*. Regarding point 2 by Reviewer #2, we fully agree that further quantification of the magnitude of the contribution of HD^+ to the forward and backward H_3^+ peaks observed in the mass spectrum of CH_3OD shown in Fig. 2 would greatly improve the quality of our manuscript. In response to this request by Reviewer #2, we performed additional mass spectrometry measurements for the CD_3OH form of methanol, using the same experimental conditions as those used for all other molecules examined in our study. In contrast to CH_3OD, where the forward and backward peaks of the H_3^+ doublet in the $m/z = 3$ region, associated with the $CH_3OD^{2+} \rightarrow COD^+ + H_3^+$ process of interest in our work, overlap with the HD^+ signals resulting from the $CH_3OD^{2+} \rightarrow CH_2O^+ + HD^+$ dissociation, the roaming mechanism in the doubly ionized CD_3OH produces the D_3^+ cation, which appears as distinct peaks at $m/z = 6$ that are clearly separated from the HD^+ signals. This clean separation of the D_3^+ and HD^+ peaks in our additional experiments involving CD_3OH allowed us to directly determine the HD^+ yield from CD_3OH^{2+} normalized to all dication channels in CD_3OH and compare it with the H_3^+ yield normalized to all dication channels in CH_3OD. By forming a ratio of the HD^+ yield normalized to all dication channels in CD_3OH to the H_3^+ yield normalized to all dication channels in CH_3OD, we demonstrated that the contribution of HD^+ to the forward and backward peaks of the H_3^+ doublet obtained for CH_3OD, shown in Fig. 2, is about 9%.

To reflect on the above information and the additional measurements performed in response to point 2 by Reviewer #2, while addressing the analogous editorial request included in the Author Checklist, we have added the following text at the end of the first paragraph of the Results: Experimental section:

"As shown in Refs. [9,36], the contribution of HD^+ to the forward and backward peaks for CH_3OD is expected to be small. We confirmed this by performing separate measurements on CD_3OH which demonstrated that the contribution of HD^+ to the forward and backward peaks, determined by forming a ratio of the HD^+ yield normalized to all dication channels in CD_3OH to the H_3^+ yield normalized to all dication channels in CH_3OD, is ~9%."

In light of the above discussion and change in the main text, we have also appropriately updated the sentence in the caption to Fig. 2 beginning with the words "Based on the previous isotopologue studies involving methanol …", while replacing the word "minimal" in it by "small".

Remarks by Reviewer #3:

The authors have satisfactorily addressed the comments raised in my previous report.

Our response:

We thank Reviewer #3 for accepting our revisions made in response to the comments raised by this reviewer in their previous report on our manuscript.

Remarks by Reviewer #4:

I believe the authors have addressed all of the issues I have raised and the manuscript is now suitable for publication. The issues of time scale and the nature of the potential energy surfaces involved are very hard to be definitive about.

Our response:

We are grateful to Reviewer #4 for accepting our previous changes and recommending the publication of our manuscript in *Nature Communications*. We agree with the reviewer that the challenging issues of timescales and potential energy surfaces involved in our experiments and computations (and the analogous studies by others) are difficult to be completely definitive about. This is one of the main reasons why, in an effort to improve our understanding of H_3^+ formation following double ionization of organic compounds and the underlying roaming dynamics, we have decided to study several molecular systems using a combination of state-of-the-art experimental and computational techniques that complement each other.