

Factors governing H_3^+ formation from methyl halogens and pseudohalogens

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The formation of H_3^+ following the double ionization of small organic compounds via a roaming mechanism, which involves the generation of H_2 and subsequent proton abstraction, has recently garnered significant attention. Nonetheless, a cohesive model explaining trends in the yield of H_3^+ characterizing these unimolecular reactions is yet to be established. We report yield and femtosecond time-resolved measurements following the strong-field double ionization of CH_3X molecules, where $\text{X} = \text{OD}, \text{Cl}, \text{NCS}, \text{CN}, \text{SCN}, \text{and I}$. These measurements, combined with double-ionization-potential equation-of-motion coupled-cluster ab initio calculations used to determine the geometries and energetics of CH_3X^{2+} dications, are employed to identify the key factors governing the formation of H_3^+ in certain doubly ionized CH_3X species and its absence in others. We also carry out ab initio molecular dynamics simulations to obtain detailed microscopic insights into the mechanism, yields, and timescales of H_3^+ production. We find that the excess relaxation energy released after double ionization of CH_3X molecules combined with substantial geometrical distortion that favors H_2 formation prior to proton abstraction boost the generation of H_3^+ . Our study provides useful guidelines for examining alternative sources of H_3^+ in the universe.

The role of the trihydrogen cation (H_3^+) as a catalytic protonator of atoms and molecules, along with its capacity for radiative cooling, renders it one of the most important species in interstellar chemistry^{1–3}. The formation of H_3^+ ions within the interstellar medium proceeds via the Hogness and Lunn mechanism⁴, $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$, where H_2^+ is generated through the ionization of molecular hydrogen by cosmic rays. The resulting H_3^+ species are highly acidic and exhibit enhanced reactivity by acting as universal proton donors to other species (M) through the proton-hop reaction $\text{M} + \text{H}_3^+ \rightarrow \text{H}_2 + \text{MH}^+$ ¹. Furthermore, reactions involving H_3^+ display very high rate constants² that can be attributed to its ability to polarize and attract neutral molecules, even at large distances⁵. The abundance of H_3^+ in the interstellar medium and its key role as the initiator of ion-molecule

reactions highlight the importance of understanding the mechanisms, timescales, and yields of H_3^+ production.

In recent years, various small molecules, including CH_3X , where X is a halogen or pseudohalogen, have been identified as potential sources of H_3^+ in interstellar and star-forming environments⁶. Upon double ionization, the three C–H bonds in CH_3X may be cleaved and three new bonds between the detached H atoms may form, leading to the formation of H_3^+ . Given that equal numbers of bonds are broken and formed, this unimolecular reaction was initially thought to proceed via a concerted pathway in which the three H atoms in CH_3X^{2+} coalesce and H_3^+ is ejected by Coulombic repulsion^{7,8}. However, it was observed that in methanol, the mechanism of H_3^+ formation involves a three-step process, where the double ionization of CH_3OH generates a

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neutral H_2 which then roams the CHOH^{2+} dication before abstracting a proton from it⁹. In this case, femtosecond time-resolved strong-field ionization and photoion-photoion coincidence measurements on CH_3OH and its isotopologues, accompanied by ab initio molecular dynamics (AIMD) simulations, revealed two distinct routes for the production of H_3^+ depending on which proton is abstracted from CHOH^{2+} by H_2 , including a faster ~ 100 fs process, in which the H atom attached to carbon is attacked, and a slower ~ 250 fs one, when the abstracted proton originates from the hydroxyl group⁹ (for the follow-up studies of H_3^+ formation from CH_3OH and other alcohols, see refs. 10–12). It was also demonstrated that the faster pathway, corresponding to the deprotonation of carbon by the roaming H_2 , as shown in the lower half of Fig. 1, is the dominant process in CH_3OH . In this study, we argue that a similar process applies to the H_3^+ -producing doubly ionized CH_3X molecules in which X lacks hydrogen atoms. It should also be noted that this way of generating H_3^+ from CH_3X molecules closely resembles the Hogness and Lunn mechanism, as both involve the abstraction of a proton by a neutral H_2 molecule. In support of this observation, a recent experiment applying a two-color femtosecond laser field to D_2 – D_2 dimers confirmed a 139 fs timescale for D_3^+ production¹³, which matches the timeframe of H_3^+ formation from the doubly ionized methanol via the pathway shown in Fig. 1, suggesting the possibility of a similar roaming mechanism in the interstellar space.

Another CH_3X species that has been identified as a source of H_3^+ in the interstellar clouds is methyl chloride¹⁴. Previous experiments on the strong-field ionization of CH_3Cl ^{7,15} have focused on the kinetic energy release and anisotropy of various fragmentation channels of the $\text{CH}_3\text{Cl}^{2+}$ dication, but insights into the timescale and mechanism of H_3^+ formation from methyl chloride remain largely unexplored. Computational studies have predicted a variety of pathways for producing the trihydrogen cation from CH_3Cl , including the mechanism in which H_3^+ emerges from ionization of the Rydberg state of CH_3Cl^+ based on the lower appearance energy of the $\text{CCl}^+/\text{H}_3^+$ pair compared to the double ionization of methyl chloride¹⁶ or the concerted process without involving the roaming of H_2 ⁸, but the most recent calculations combining high-level quantum chemistry and molecular dynamics¹⁷ suggest the roaming mechanism similar to Fig. 1. Thus, there is a growing need to understand the intimate details of the molecular picture behind H_3^+ formation following the double ionization of CH_3Cl and other methyl halides and pseudohalides. A number of other observations are worth

exploring as well. For example, complementary cross-section measurements at 70 eV electron ionization of the CH_3X molecules with $\text{X} = \text{F}$, Br , and I have shown that similarly to CH_3Cl , H_3^+ forms readily from CH_3Br , but only trace amounts of the trihydrogen cation have been found in the case of the doubly ionized CH_3F and CH_3I species¹⁸. This pattern, which remains consistent across different experimental studies, including two-color laser field ionization¹⁹, suggests that one has to look for factors other than electronegativities of the halogen atoms to explain H_3^+ formation from methyl halogens. The behavior of methyl pseudohalides upon double ionization is not well understood either. For instance, as shown in the early photoionization and electron impact mass spectrometry measurements involving several small organic molecules²⁰, the doubly ionized methyl cyanide produces negligible amounts of H_3^+ despite the high electronegativity of the CN group. A comprehensive explanation of the varied yields of H_3^+ from methyl halogens and pseudohalogens remains elusive to this date.

In this article, we report femtosecond time-resolved measurements following the strong-field double ionization of several CH_3X molecules, where X is a halogen (Cl and I) or a pseudohalogen (OH, represented by OD, NCS, CN, and SCN). In the ultrafast experiments carried out in this work, the double ionization is triggered by electron rescattering²¹, as opposed to being induced by radiation or collision with high-energy light nuclei and electrons, which are the dominant processes in the interstellar medium. In electron rescattering, a departing electron, after tunnel-ionization of the molecule by the electric field of the laser, accelerates back toward the molecule when the field reverses its direction. The returning electron can gain tens of eV of kinetic energy, sufficient to remove the second electron from the molecule within the optical cycle of the laser pulse (~ 2.66 fs). 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, 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. 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

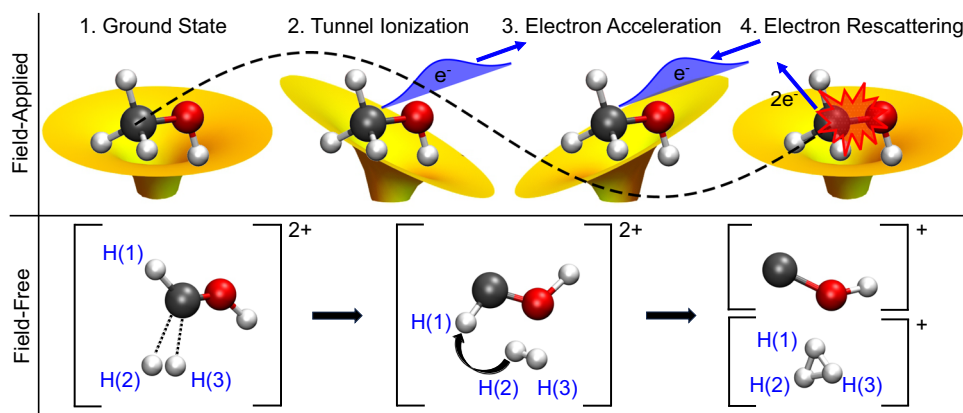


Fig. 1 | The roaming model for the production of H_3^+ following the strong-field double ionization of methanol. The upper half of the figure illustrates the process of generating a molecular dication by doubly ionizing methanol via electron rescattering. The electric field of the ultrafast laser pulse (represented by the dashed line) bends methanol's potential (shown in yellow), resulting in tunnel ionization which creates a high-energy electron that accelerates back toward the molecule when the field reverses its direction. The returning electron has sufficiently high kinetic energy to remove the second electron from the molecule within

the same optical cycle, producing the $\text{CH}_3\text{OH}^{2+}$ dication. Given the short pulse duration (~ 35 fs), the dynamics of the $\text{CH}_3\text{OH}^{2+}$ species, shown in the lower half of the figure, are not influenced by the electric field of the laser. The dication in its lowest singlet state ejects a neutral H_2 fragment consisting of the hydrogen atoms labeled as H(2) and H(3), which then roams the remaining CHOH^{2+} moiety until it abstracts the proton corresponding to the hydrogen atom H(1) bound to the carbon, leading to the formation of H_3^+ .

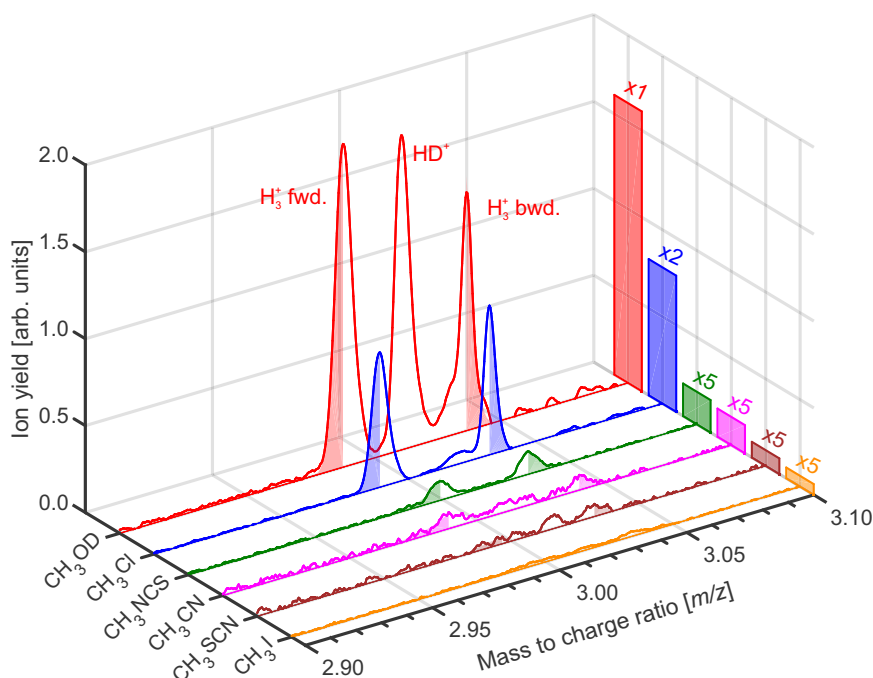


Fig. 2 | The $m/z = 3$ regions of the mass spectra obtained in this work. The provided spectra correspond to CH_3OD (red), CH_3Cl (blue), CH_3NCS (green), CH_3CN (magenta), CH_3SCN (brown), and CH_3I (orange). In the case of the CH_3OD , CH_3Cl , and CH_3NCS species, which produce the trihydrogen cation, the signal from H_3^+ appears as a doublet labeled as fwd and bwd peaks, which are associated with the forward and backward trajectories of the H_3^+ ion resulting from the Coulomb repulsion of the $\text{CH}_3\text{X}^{2+} \rightarrow \text{CX}^+ + \text{H}_3^+$ reaction products. For CH_3OD , we also see a central HD^+ peak from singly ionized methanol between the fwd and bwd peaks of the H_3^+ doublet since H_3^+ and HD^+ have the same m/z ratio. Based on the previous isotopologue studies involving methanol^{9,36} and our additional measurements on CD_3OH discussed in Results: Experimental, the contribution of HD^+ to the fwd and bwd peaks for CH_3OD is expected to be small, having no significant

effect on the reported H_3^+ yields. For each studied compound, the single pulse intensity used for ionization was $5 \times 10^{14} \text{ W/cm}^2$. Each mass spectrum has been normalized by dividing the signal by the area of all peaks attributed to dication channels. 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. In addition, to improve the visibility of the less intense signals, all mass spectra other than CH_3OD have been scaled up by the numerical factors shown at the edges of the respective traces. CH_3CN , CH_3SCN , and CH_3I do not produce appreciable H_3^+ signals that would be distinguishable from the C^{2+} ion, which has the same m/z ratio as H_3^+ . All data are included in the Source Data folder.

is formed. This also means that they do not depend on the specific method by which the CH_3X^{2+} dications are created. To gain further insights into the yields and timescales of H_3^+ formation from the various methyl halides and pseudohalides under investigation and to obtain information about the low-lying electronic states of the CH_3X^{2+} dications involved, we augment the ultrafast time-resolved measurements reported in this study with the high-level double-ionization-potential (DIP) equation-of-motion (EOM) coupled-cluster (CC) ab initio computations with up to 3-hole-1-particle (3h-1p)^{23–29} and 4-hole-2-particle (4h-2p)^{28,29} correlations on top of the CC treatment^{30–32} with singles and doubles (CCSD)^{33,34} of the parent CH_3X species, abbreviated as DIP-EOMCC(3h-1p) and DIP-EOMCC(4h-2p), respectively, and the AIMD simulations employing the complete-active-space self-consistent-field (CASSCF) approach³⁵ calibrated to the DIP-EOMCC data. While our experimental measurements and theoretical models, despite their state-of-the-art nature, have inherent limitations, their complementary blend provides a 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.

Results

Experimental

The H_3^+ regions of the time-of-flight (TOF) mass spectra of all CH_3X compounds with $\text{X} = \text{OD}$, Cl , NCS , CN , SCN , and I are shown in Fig. 2.

For the CH_3OD , CH_3Cl , and CH_3NCS molecules, which after double ionization produce the trihydrogen cation, the H_3^+ signal in the mass spectrum appears as a doublet due to the forward and backward trajectories of the H_3^+ ion resulting from the Coulomb repulsion of the $\text{CH}_3\text{X}^{2+} \rightarrow \text{CX}^+ + \text{H}_3^+$ reaction products. 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 $\text{CH}_3\text{X}^{2+} \rightarrow \text{CX}^+ + \text{H}_3^+$ 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. We used the deuterated form of methanol, CH_3OD , where the ^1H atom in the OH group is replaced by its ^2H isotope, to ensure that the trihydrogen cation produced in our double ionization experiments originated from the three hydrogens of the methyl group. This gives rise to the HD^+ signal from singly ionized methanol, which appears at $m/z = 3$ in Fig. 2 between the H_3^+ forward and backward peaks. As

Table 1 | Normalized H_3^+ yields from the CH_3X compounds with $X = OD, Cl,$ and NCS , which after double ionization produce the trihydrogen cation

CH_3X Compound	H_3^+ Yield/Dication Channels	H_3^+ Yield/All Ions
CH_3OD	1.00	0.77
CH_3Cl	0.24	1.00
CH_3NCS	0.02	0.24

Each number in the second column represents the H_3^+ yield relative to all ions attributed to dication channels, normalized to the maximum yield obtained for CH_3OD , which we set to 1.0. The analogous H_3^+ yields normalized to all positive ion channels, again relative to the maximum yield, which in this case is obtained for CH_3Cl , are shown in the third column. The remaining CH_3X compounds examined in the present study, which do not generate appreciable H_3^+ signals that would be clearly distinguishable from the C^{2+} species having the same m/z ratio as the trihydrogen cation, are not included.

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 $\sim 9\%$.

To determine the H_3^+ yield for each of the three CH_3X compounds that produce it, shown in Table 1, 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. We only integrated the outer halves of each doublet to avoid contamination of the measured H_3^+ yields by low kinetic energy features. We normalized the yields to all ion signals attributed to dication channels to correct for slight changes in pressure and/or intensity that may occur when going from one molecule to another, although these variables were carefully controlled in our experiments. In presenting the H_3^+ yields resulting from the above procedure, we normalized them to the maximum one obtained for CH_3OD , which was set to 1.0. This provided us with the relative H_3^+ yields used in our later theoretical analysis. 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. To illustrate the effect of the number of ion channels on yield determination, we also show in Table 1 the relative yields of H_3^+ normalized to all positive ion channels. We only included cations in normalizing the H_3^+ yields since our TOF system is configured for the detection of positively charged species. Our relative H_3^+ yields match the results of the previous measurements using 70 eV electron impact ionization¹⁸.

Ab initio electronic structure calculations

To provide insights into the molecular mechanisms leading to the observed trends in H_3^+ yields and the geometrical and energetic factors that affect them, we performed high-level ab initio quantum chemistry calculations for the low-lying electronic states of the neutral and doubly ionized CH_3X species examined in this work, details of which are provided in Methods: Electronic structure calculations. We did not consider higher-lying states since, as shown in ref. 11 using methanol as an example, the probability of H_3^+ formation is the highest when a given dicationic species is in its lowest singlet state. The selected bond lengths, which are crucial for our analysis, characterizing the equilibrium geometries of the CH_3X molecules with $X = OH, Cl, NCS, CN,$

$SCN,$ and I in their ground electronic states and the minima on the lowest singlet potential energy surfaces of the corresponding CH_3X^{2+} dications resulting from our most accurate CC and DIP-EOMCC computations, are shown in Table 2. The complete information about the geometries of the CH_3X molecules included in our experiments and the CH_3F species, which was only considered in computations, and the low-lying states of the corresponding CH_3X^{2+} dications obtained in all of our CC and DIP-EOMCC calculations, along with the associated electronic energies, can be found in Supplementary Information (see Supplementary Data). For the three H atoms bonded to the carbon in the CH_3X and CH_3X^{2+} species, H(2) and H(3) designate hydrogens that may coalesce in the CH_3X^{2+} dication and subsequently approach the remaining H atom on carbon, labeled as H(1), to form H_3^+ (see Fig. 1). The vertical and adiabatic double ionization energies associated with the low-lying states of the CH_3X^{2+} dications relevant to our discussion, obtained in our most accurate DIP-EOMCC calculations, are provided in Fig. 3. Our CC and DIP-EOMCC geometries of the $CH_3Cl, CH_3Cl^{2+}, CH_3F,$ and CH_3F^{2+} species and double ionization energies corresponding to the lowest singlet states of CH_3Cl^{2+} and CH_3F^{2+} are in very good agreement with the CASSCF-based second-order multireference perturbation theory calculations reported in ref. 17.

As shown in Fig. 3, the neutral $CH_3OH, CH_3NCS,$ and CH_3SCN molecules in their ground electronic states are characterized by the $C_s,$ $C_1,$ and C_s symmetries, respectively, while the remaining $CH_3Cl, CH_3CN,$ and CH_3I species are all C_{3v} -symmetric. Our computations demonstrate that the doubly ionized $CH_3OH, CH_3NCS,$ and CH_3SCN molecules in their lowest-energy singlet states relax to the respective adiabatic minima, adopting a C_s symmetry. As can be seen in Table 2, in the case of CH_3OH^{2+} and CH_3NCS^{2+} , the resulting geometrical reorganization elongates the C–H(2) and C–H(3) bonds while bringing the H(2) and H(3) atoms close together, so that the distances between them are almost as small as in the isolated H_2 molecule ($0.741 \text{ \AA}^{37}$). This should be contrasted with the behavior of CH_3SCN , where the H(2)–H(3), C–H(2), and C–H(3) distances do not change much when the geometries of the ground-state CH_3SCN molecule and the CH_3SCN^{2+} dication in its lowest singlet state are compared with each other.

The situation with the $CH_3Cl, CH_3CN,$ and CH_3I molecules is more complex. These three species, in their neutral forms, possess C_{3v} -symmetric ground electronic states in which all C–H bonds have the same length. Following vertical double ionization, prior to any geometric relaxation, the three lowest electronic states of each of the resulting dications include a spatially nondegenerate triplet of the $A_2(C_{3v})$ symmetry and a doubly degenerate singlet that belongs to the E irreducible representation of C_{3v} (see Fig. 3). The two components of the doubly degenerate singlet consist of a multi-configurational state mixing two closed-shell determinants, in which one of the two highest-occupied molecular orbitals (HOMOs) of the neutral species remains occupied by two electrons and the other one is empty, and the open-shell singlet state where each of the two degenerate HOMOs of the neutral system is singly occupied. The two degenerate HOMOs are also singly occupied in the lowest triplet state. Upon the geometric relaxation after double ionization, the lowest-energy triplet states of $CH_3Cl^{2+}, CH_3CN^{2+},$ and CH_3I^{2+} remain C_{3v} -symmetric, having structures similar to their neutral counterparts. In particular, the C–H bond lengths do not change much and the hydrogen atoms remain separated by rather large distances (see Supplementary Data, especially Supplementary Table 1). However, the lowest doubly degenerate singlets of these dications undergo Jahn–Teller (JT) distortion that removes the degeneracy and lowers their symmetry to C_s , splitting the $^1E(C_{3v})$ singlets into the $^1A'(C_s)$ and $^1A''(C_s)$ states. While the geometrical distortions and the JT splitting in CH_3I^{2+} are minimal, so that the $^1A'(C_s)$ and $^1A''(C_s)$ states, having three practically equidistant C–H bonds and large H–H separations, remain nearly degenerate and the $A_2(C_{3v})$ -symmetric triplet remains the ground state, the analogous

Table 2 | Comparison of the key internuclear distances, in Å, characterizing the doubly ionized CH_3X molecules with $\text{X} = \text{OH}, \text{Cl}, \text{NCS}, \text{CN}, \text{SCN},$ and I in their lowest singlet states, which influence H_3^+ formation, with their counterparts in the neutral CH_3X species obtained in the most accurate CC and DIP-EOMCC computations carried out in this study (see Methods: Electronic structure calculations for the details)

X = OH			X = Cl			X = NCS		
Bond	Neutral	Dication	Bond	Neutral	Dication	Bond	Neutral	Dication
C–H(1)	1.087	1.110	C–H(1)	1.084	1.104	C–H(1)	1.087	1.088
C–H(2)	1.093	1.442	C–H(2)	1.084	1.357	C–H(2)	1.088	1.263
C–H(3)	1.093	1.442	C–H(3)	1.084	1.357	C–H(3)	1.089	1.263
H(2)–H(3)	1.777	0.861	H(2)–H(3)	1.780	0.890	H(2)–H(3)	1.776	0.923
X = CN			X = SCN			X = I		
Bond	Neutral	Dication	Bond	Neutral	Dication	Bond	Neutral	Dication
C–H(1)	1.088	1.099	C–H(1)	1.088	1.087	C–H(1)	1.083	1.106
C–H(2)	1.088	1.284	C–H(2)	1.085	1.136	C–H(2)	1.083	1.107
C–H(3)	1.088	1.284	C–H(3)	1.085	1.136	C–H(3)	1.083	1.107
H(2)–H(3)	1.772	0.949	H(2)–H(3)	1.788	1.664	H(2)–H(3)	1.785	1.844

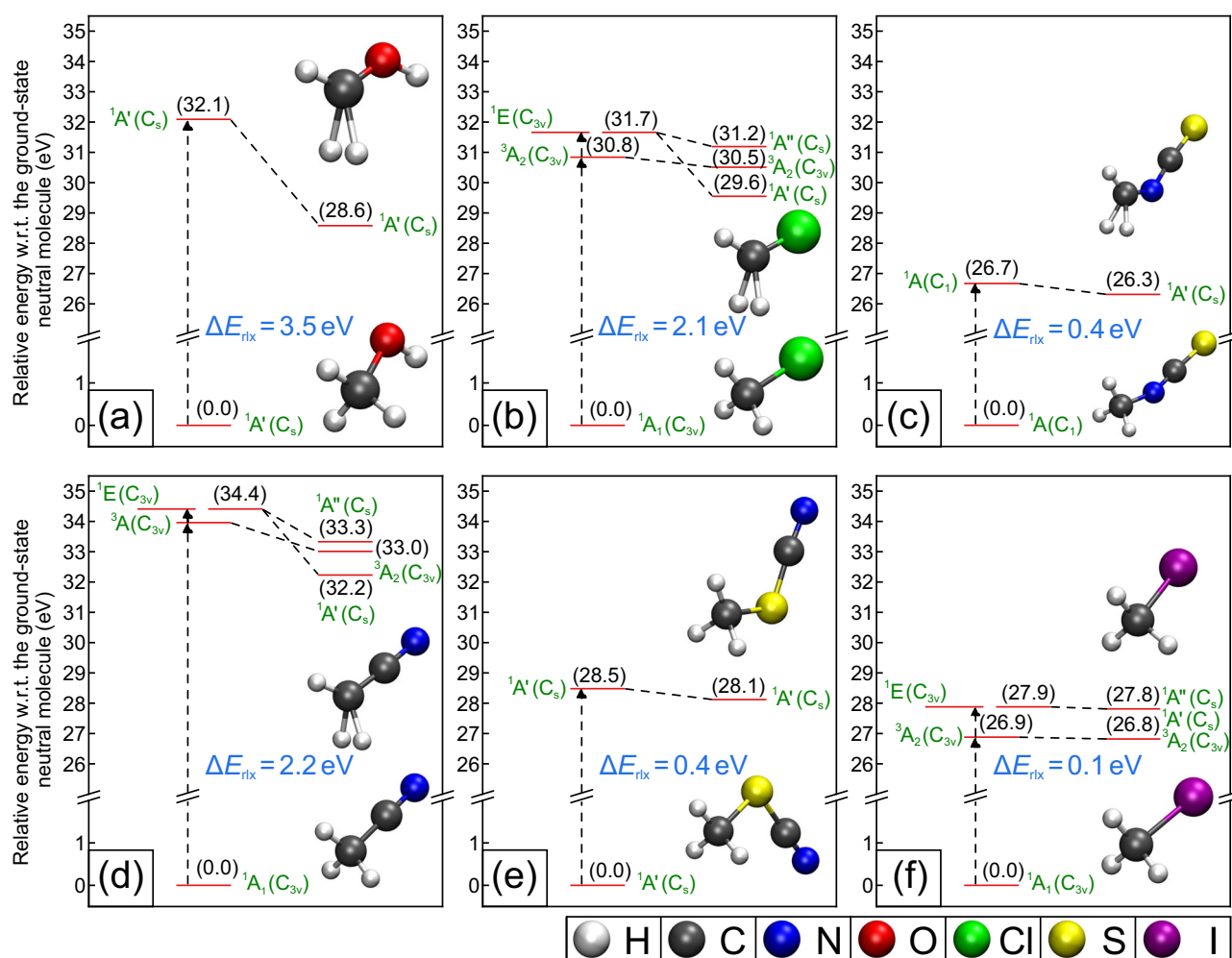


Fig. 3 | Energy level diagrams and molecular geometries associated with the double ionization of CH_3X species. The vertical and adiabatic double ionization energies, in eV, of (a) CH_3OH , (b) CH_3Cl , (c) CH_3NCS , (d) CH_3CN , (e) CH_3SCN , and (f) CH_3I molecules associated with the lowest singlet (all systems) and triplet (CH_3Cl , CH_3CN , and CH_3I) states of the respective dications resulting from the most accurate DIP-EOMCC computations performed in the present study (see Methods: Electronic structure calculations for the details) are shown. In each panel, the

multiplicities, irreducible representations, and point group symmetries of the states of interest are highlighted in green and the adiabatic relaxation energies ΔE_{rlx} , obtained by subtracting the adiabatic double ionization energies from their vertical counterparts corresponding to the lowest singlet states of the CH_3X^{2+} dications, Eq. (1), are emphasized using blue font. All data used to create the figure are included within it.

changes in the $\text{CH}_3\text{Cl}^{2+}$ and $\text{CH}_3\text{CN}^{2+}$ species are massive. Indeed, as shown in Fig. 3, the $^1\text{A}'(\text{C}_s)$ states of the $\text{CH}_3\text{Cl}^{2+}$ and $\text{CH}_3\text{CN}^{2+}$ dications lower their energies so much, compared to the multi-configurational closed-shell components of the respective $\text{E}(\text{C}_{3v})$ -symmetric singlets from which they originate, that they become the nondegenerate, predominantly single-reference, ground states. The $^1\text{A}'(\text{C}_s)$ states resulting from the JT splitting of the $\text{E}(\text{C}_{3v})$ -symmetric singlets of $\text{CH}_3\text{Cl}^{2+}$ and $\text{CH}_3\text{CN}^{2+}$, which retain the open-shell singlet character upon geometrical relaxation, lower their energies too, but not enough to go below the $\text{A}_2(\text{C}_{3v})$ -symmetric triplet states. Similarly to the triplet states, they do not undergo significant structural changes compared to the neutral CH_3Cl and CH_3CN molecules either (see Supplementary Data and Supplementary Table 1). As a result, the ordering of the adiabatic minima on the lowest potential energy surfaces of the $\text{CH}_3\text{Cl}^{2+}$ and $\text{CH}_3\text{CN}^{2+}$ dications becomes $^1\text{A}'(\text{C}_s) < ^3\text{A}_2(\text{C}_{3v}) < ^1\text{A}''(\text{C}_s)$. The stabilization of the C_s -symmetric structures of $\text{CH}_3\text{Cl}^{2+}$ and $\text{CH}_3\text{CN}^{2+}$ in their ground electronic states and the distortion in nuclear geometries compared to their neutral parents are so significant that the main features of the ground-state geometries of these two dications relevant to H_3^+ production are similar to those characterizing the lowest singlet states of $\text{CH}_3\text{OH}^{2+}$ and $\text{CH}_3\text{NCS}^{2+}$. Indeed, as shown in Table 2, and in analogy to the lowest singlet states of $\text{CH}_3\text{OH}^{2+}$ and $\text{CH}_3\text{NCS}^{2+}$, the $\text{H}(2)$ – $\text{H}(3)$ distances in the ground-state $\text{CH}_3\text{Cl}^{2+}$ and $\text{CH}_3\text{CN}^{2+}$ structures are close to that in the isolated H_2 molecule and the C – $\text{H}(2)$ and C – $\text{H}(3)$ bonds are considerably elongated compared to the neutral CH_3Cl and CH_3CN species. This should be contrasted with CH_3F^{2+} , where the H – H distances in the lowest singlet and triplet states are similar to those in neutral CH_3I , preventing two of the three hydrogen atoms from coalescing and disabling the roaming mechanism of H_3^+ production examined in this study.

One might think that the CH_3X systems that undergo significant structural changes upon double ionization, which bring the $\text{H}(2)$ and $\text{H}(3)$ atoms bonded to the carbon close together while elongating the C – $\text{H}(2)$ and C – $\text{H}(3)$ bonds, favor H_3^+ generation via the roaming mechanism shown in Fig. 1, but these structural changes are not the only factors influencing the yield of H_3^+ . For example, as shown in Table 2, the $\text{H}(2)$ – $\text{H}(3)$ distance in the lowest singlet state of $\text{CH}_3\text{CN}^{2+}$ is quite close to that in the isolated H_2 (and much shorter than in neutral CH_3CN) and the C – $\text{H}(2)$ and C – $\text{H}(3)$ bonds substantially elongate upon the double ionization of CH_3CN , and yet we do not see an appreciable H_3^+ signal in our experiments involving CH_3CN (cf. Fig. 2 and Table 1). As noted in the Introduction, only trace amounts of the trihydrogen cation were found in the double ionization experiments involving CH_3F^{18} despite the fact that CH_3F^{2+} has a lot in common with its $\text{CH}_3\text{Cl}^{2+}$ analog, which readily forms H_3^+ (as pointed out in Discussion, our AIMD simulations show no evidence for H_3^+ production from the CH_3F^{2+} species either). Indeed, the effects of JT distortion in the CH_3F^{2+} and $\text{CH}_3\text{Cl}^{2+}$ species are similar, resulting in the $^1\text{A}'(\text{C}_s)$ -symmetric ground states and short, nearly identical, $\text{H}(2)$ – $\text{H}(3)$ distances (see the geometry of the CH_3F^{2+} dication in its lowest-energy $^1\text{A}'(\text{C}_s)$ state and the electronic state ordering in CH_3F^{2+} in Supplementary Data, especially Supplementary Fig. 1 and Supplementary Tables 1 and 2), but unlike in $\text{CH}_3\text{Cl}^{2+}$, no H_3^+ is produced from CH_3F^{2+} . For all these reasons, in addition to examining the relationship between the geometrical changes in the CH_3X systems upon double ionization and the observed yield of H_3^+ , we also considered other factors that might affect the production of trihydrogen cation from the CH_3X^{2+} species. Thus, as further elaborated on in Methods: Electronic structure calculations, we computed the adiabatic relaxation energies

$$\Delta E_{\text{rlx}} = \Delta E_{\text{vert}} - \Delta E_{\text{adiab}}, \quad (1)$$

where ΔE_{vert} and ΔE_{adiab} are the vertical and adiabatic double ionization energies corresponding to the lowest singlet states of the CH_3X^{2+} dications, and the dissociation energies associated with the H_2

formation from the doubly ionized CH_3X molecules, defined as

$$\Delta E_{\text{diss}} = E(\text{CHX}^{2+}) + E(\text{H}_2) - E(\text{CH}_3\text{X}^{2+}), \quad (2)$$

where $E(\text{CHX}^{2+})$ and $E(\text{CH}_3\text{X}^{2+})$ are the energies of the CHX^{2+} and CH_3X^{2+} species in their lowest singlet states, respectively, and $E(\text{H}_2)$ is the ground-state energy of a neutral H_2 . ΔE_{rlx} provides a measure of the excess energy available to the CH_3X^{2+} dications at their adiabatic minima, which may drive the separation of a neutral H_2 from the CHX^{2+} moiety and facilitate H_3^+ generation via a roaming mechanism shown in Fig. 1. ΔE_{diss} estimates the energy required to liberate H_2 from the parent CH_3X^{2+} ion. We also computed potential energy profiles for the $\text{CH}_3\text{X}^{2+} \rightarrow \text{CX}^+ + \text{H}_3^+$ reactions initiated by double ionization of the CH_3X species with $\text{X} = \text{OH}$, Cl , and NCS that produce H_3^+ in our experiments, finding out that the adiabatic relaxation energies ΔE_{rlx} characterizing the $\text{CH}_3\text{OH}^{2+}$, $\text{CH}_3\text{Cl}^{2+}$, and $\text{CH}_3\text{NCS}^{2+}$ dications are sufficiently large to overcome the barriers associated with the transition states on their lowest singlet potentials and release neutral H_2 molecules that can subsequently roam their CHX^{2+} companions, abstracting protons from them to form H_3^+ (see Supplementary Discussion and Supplementary Fig. 4). As shown in Discussion, the $\text{H}(2)$ – $\text{H}(3)$ distances combined with the ΔE_{rlx} and ΔE_{diss} values characterizing the doubly ionized CH_3X species and information about the $\text{CH}_3\text{X}^{2+} \rightarrow \text{CX}^+ + \text{H}_3^+$ reaction profiles, including barrier heights associated with the final $\text{CHX}^{2+} + \text{H}_2 \rightarrow \text{CX}^+ + \text{H}_3^+$ proton abstraction steps, can be used to explain why some CH_3X species form H_3^+ while others do not and rationalize the observed H_3^+ ion yields.

Timescales of H_3^+ formation

For each compound, we also studied the H_3^+ formation time using a technique called disruptive probing, as outlined in Methods: Experimental details³⁸. In short, we split the laser pulse into a strong pump (5×10^{14} W/cm²) and a weak probe (9.5×10^{13} W/cm²). By changing the delay between these two pulses with a variable delay stage, the weak probe can disrupt the formation of some ions in the mass spectra, leading to an exponential decay and recovery in the ion yields as a function of pump-probe delay. The timescale of formation of each ion seen in the mass spectrum, including H_3^+ , can be determined by fitting the corresponding pump-probe delay-dependent ion yield to the function

$$P(t, \tau_1, \tau_2) = Ae^{-t^2/s^2} + P_1(t, \tau_1) + P_2(t, \tau_2), \quad (3)$$

where

$$P_i(t, \tau_i) = A_i e^{-t/\tau_i} \left[1 + \text{erf} \left(\frac{t}{s} - \frac{s}{2\tau_i} \right) \right], \quad i = 1, 2, \quad (4)$$

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 $\tau_{\text{FWHM}} = 2s\sqrt{\ln 2}$.

To obtain information about the time-resolved dynamics of H_3^+ formation for each of the three CH_3X compounds that produce the trihydrogen cation in measurable amounts, i.e., CH_3OD , CH_3Cl , and CH_3NCS , the peak area of the doublet assigned to H_3^+ in the

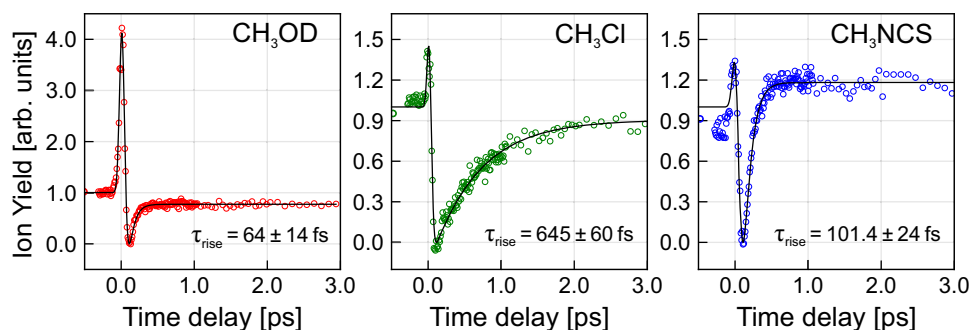


Fig. 4 | Pump-probe delay dependent H_3^+ yields. The H_3^+ yields are shown for CH_3OD (red), CH_3Cl (green), and CH_3NCS (blue). Black lines indicate fits of the experimental data to Eq. (3). The resulting values of parameter τ_{rise} , displayed in the panels, indicate the times of formation of H_3^+ from the three molecules. 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. All data are included in the Source Data folder.

corresponding mass spectrum was integrated as a function of pump-probe delay. The resulting time-resolved yields of H_3^+ from CH_3OD , CH_3Cl , and CH_3NCS , shown in Fig. 4, were normalized such that the ion yield at negative pump-probe delays is 1.0 and the minimum is 0.0. We could not perform the analogous analysis for the remaining CH_3X species examined in this study since they do not generate enough H_3^+ to obtain time-resolved data with sufficient signal-to-noise ratio (cf. Fig. 2 and Table 1).

From the time-resolved H_3^+ yields in Fig. 4, we see a large spike at the pump-probe delay $t=0$. The presence of this spike is a consequence of the intensities of the pump and probe pulses combining to give an increased ionization efficiency within the focal volume. Shortly after the double ionization of the CH_3X compounds by the pump pulse, the resulting CH_3X^{2+} dications are far from equilibrium and can easily be disrupted by the probe pulse. 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. 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}. Interestingly, the doubly ionized CH_3OD generates the most H_3^+ (Table 1), while having the shortest time for H_3^+ formation when compared to CH_3Cl and CH_3NCS (Fig. 4).

Ab initio molecular dynamics simulations

To further investigate the timescale and mechanism of H_3^+ formation, AIMD simulations were conducted for a few representative CH_3X^{2+} species in their lowest singlet states using the CASSCF approach to generate electronic energies and energy gradients (see Methods: Ab

initio molecular dynamics simulations for the details). Exploring single-state dynamics on the lowest-energy singlet potentials of the CH_3X^{2+} species is sufficient to provide useful insights that help us understand the outcomes of our experiments since, as already alluded to above (cf. the beginning of Results: Ab initio electronic structure calculations), the probability of H_3^+ formation from the doubly ionized methanol is the highest in its lowest singlet state, rapidly dropping down when higher excited states are considered¹¹. At the same time, states belonging to triplet manifolds 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^+ ²². Of all the molecules that we examined with AIMD, H_3^+ only forms from the doubly ionized CH_3OH and CH_3Cl , and, to a much lesser extent, CH_3CN . Consistent with the experiment, from the trajectories obtained in our AIMD calculations, the doubly ionized CH_3OH produced the most H_3^+ (9% of the trajectories, counting only those where all three hydrogens in H_3^+ originate from the methyl group), followed by CH_3Cl (6% of the trajectories). In the case of CH_3CN^{2+} , the calculated H_3^+ yield was much smaller than those obtained for CH_3OH^{2+} and CH_3Cl^{2+} (only 1% of the trajectories). This matches our experimental findings too, as the doubly ionized CH_3CN molecule does not produce an appreciable H_3^+ signal in the mass spectrum under the conditions of our ionization experiments (cf. Fig. 2). Furthermore, formation of the H_2 precursor, which in the roaming mechanism explored in this work leads to H_3^+ , rarely occurred in CH_3CN^{2+} trajectories. In agreement with our experiments, none of the trajectories obtained for CH_3SCN^{2+} produced H_3^+ . Consistent with the earlier experimental¹⁸ and computational¹⁷ studies, no trajectories obtained for the doubly ionized CH_3F molecule resulted in the formation of H_3^+ either.

To understand the different timescales of H_3^+ formation, trajectories that resulted in H_3^+ were further analyzed. On average, H_3^+ formed faster from CH_3OH^{2+} (~ 208 fs) than from CH_3Cl^{2+} (~ 343 fs), which agrees with previous AIMD simulations^{9,11,17} and our experimental observations. Interestingly, in a majority of the trajectories that led to H_3^+ , the neutral H_2 fragment formed very fast (in ~ 30 fs) and then roamed the CHX^{2+} moiety for most of the remaining time prior to proton abstraction. Snapshots of one of the AIMD trajectories resulting in the formation of H_3^+ from the doubly ionized CH_3Cl are shown in Fig. 5. Supplementary Movies 1 and 2 show representative trajectories leading to H_3^+ formation from CH_3Cl^{2+} and CH_3OH^{2+} . Supplementary Movie 3 shows an example of a trajectory obtained for CH_3F^{2+} , where the liberated H_2 fragment becomes positively charged and subsequently dissociates, so that the final products are the CH_2F^+ moiety and a proton.

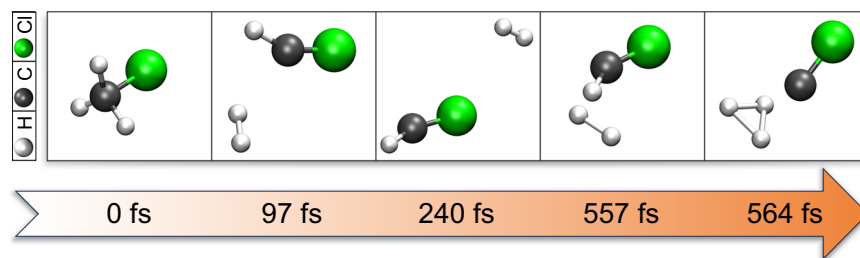


Fig. 5 | Snapshots of an AIMD trajectory of the doubly ionized CH_3Cl resulting in H_3^+ formation. The trajectory from which these snapshots originate is shown in Supplementary Movie 1. The Cartesian coordinates of the molecular geometries

shown in the figure, along with the corresponding AIMD trajectory, are included in the Source Data folder.

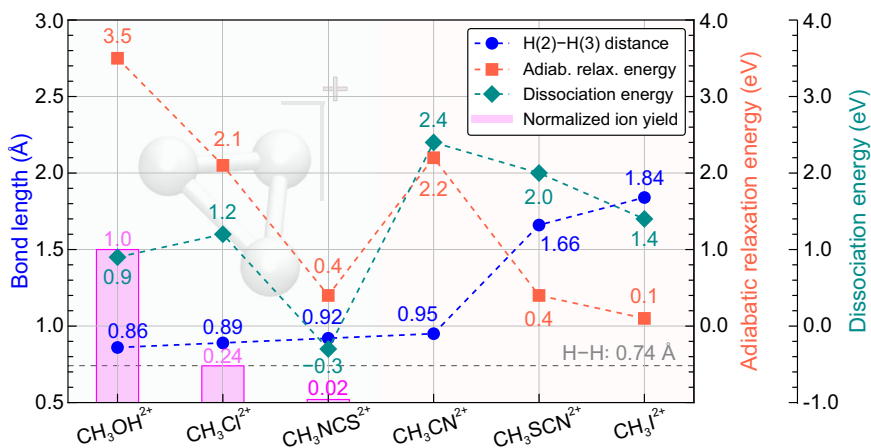


Fig. 6 | Comparison of the parameters that are most relevant to explaining the trends in H_3^+ yields. The H(2)–H(3) distances, in Å, in the CH_3X^{2+} dications, where X = OH, Cl, NCS, CN, SCN, and I (blue numbers, circles, and line), the adiabatic relaxation energies ΔE_{rlx} , Eq. (1), in eV, corresponding to the lowest singlet states of the doubly ionized CH_3X molecules (red numbers, squares, and line), and the dissociation energies ΔE_{diss} , Eq. (2), also in eV, associated with the fragmentation of the CH_3X^{2+} species into H_2 and CHX^{2+} (green numbers, diamonds, and line) resulting

from the most accurate DIP-EOMCC computations carried out in the present study described in Methods: Electronic structure calculations are shown alongside the normalized yields of H_3^+ relative to all dication channels taken from Table 1 for X = OD, Cl, and NCS (magenta numbers and bars) and assumed to be zero for the remaining species that do not generate appreciable H_3^+ amounts. The H–H bond length of an isolated H_2 molecule is highlighted in gray. All data used to create the figure are included within it.

Discussion

In our ultrafast time-resolved double ionization experiments on a series of methyl halides and pseudohalides, we observed a progressive decrease in the yield of H_3^+ from CH_3OD to CH_3Cl to CH_3NCS , while no appreciable amount of this ion was detected in CH_3CN , CH_3SCN , and CH_3I (see Table 1 and Fig. 2). Moreover, as shown in Fig. 4, the process of forming H_3^+ from the doubly ionized CH_3X species was the fastest for CH_3OD , followed by CH_3NCS and CH_3Cl , with the time of H_3^+ formation from CH_3Cl being the longest. Based on our experiments and computations, 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^+ via a roaming mechanism illustrated in Figs. 1 and 5:

- Geometrical distortion following double ionization should result in two substantially elongated C–H bonds compared to the neutral CH_3X molecule.
- The H(2)–H(3) internuclear distance characterizing the equilibrium geometry of a given CH_3X^{2+} dication in its lowest singlet electronic state should be close to the H–H bond length in an isolated H_2 molecule.
- The adiabatic relaxation energy ΔE_{rlx} characterizing the CH_3X^{2+} dication, as defined by Eq. (1), should exceed the dissociation energy ΔE_{diss} , Eq. (2), associated with the fragmentation of the doubly ionized CH_3X species into CHX^{2+} and H_2 , and be large enough to overcome the barrier(s) along the $\text{CH}_3\text{X}^{2+} \rightarrow$

$\text{CX}^+ + \text{H}_3^+$ potential energy profile, including that corresponding to the $\text{CHX}^{2+} + \text{H}_2 \rightarrow \text{CX}^+ + \text{H}_3^+$ proton abstraction by the roaming H_2 , but it cannot be so large that other reactive mechanisms and other ways of decomposing CH_3X^{2+} become dominant.

The C–H bond lengths characterizing the neutral and doubly ionized CH_3X molecules in their lowest singlet states, summarized in Table 2, and the H(2)–H(3) distances and the ΔE_{rlx} and ΔE_{diss} values characterizing the CH_3X^{2+} dications, reported in Fig. 6, along with the $\text{CH}_3\text{X}^{2+} \rightarrow \text{CX}^+ + \text{H}_3^+$ (X = OH, Cl, and NCS) reaction profiles shown in Supplementary Fig. 4, demonstrate that of all CH_3X compounds considered in our experiments, only CH_3OH , CH_3Cl , and CH_3NCS satisfy all three conditions listed above in their entirety. This is in perfect agreement with our observations, where CH_3OD , CH_3Cl , and CH_3NCS are the only three molecules of the six CH_3X species considered in our double ionization experiments that produce H_3^+ (the experimental H_3^+ yields normalized to $\text{CH}_3\text{OH}^{2+}$, taken from Table 1, are included in Fig. 6 as well). In fact, as shown in Fig. 6, the sequence of the experimental H_3^+ yields $\text{CH}_3\text{OH} > \text{CH}_3\text{Cl} > \text{CH}_3\text{NCS}$ closely mirrors the difference between the adiabatic relaxation and dissociation energies, ΔE_{rlx} and ΔE_{diss} , respectively. This difference is the largest for CH_3OH , which produces the highest amount of H_3^+ , smaller for CH_3Cl , resulting in a correspondingly lower yield, and the smallest for CH_3NCS , characterized by the least production of H_3^+ .

None of the remaining CH_3X compounds included in our experiments satisfy all three conditions (i)–(iii), which means that they should not generate H_3^+ upon double ionization, and, as shown in Fig. 2, they do not. The CH_3SCN and CH_3I systems violate each of the three conditions. CH_3CN , which meets conditions (i) and (ii), violates condition (iii), which states that ΔE_{rlx} must be greater than ΔE_{diss} . Clearly, the energy released by the geometrical relaxation of the CH_3X^{2+} dication, measured by the difference of the vertical and adiabatic double ionization energies defining ΔE_{rlx} , must be large enough to liberate a neutral H_2 , without which the roaming and proton abstraction mechanism of H_3^+ production shown in Figs. 1 and 5 cannot be initiated, and $\text{CH}_3\text{CN}^{2+}$ does not satisfy this requirement. This demonstrates that the elongation of two of the three C–H bonds and two of the three hydrogens bonded to the carbon in CH_3X^{2+} coming close, while important, do not suffice; one also has to meet the condition $\Delta E_{\text{rlx}} > \Delta E_{\text{diss}}$. Interestingly, despite satisfying conditions (i) and (ii) and the $\Delta E_{\text{rlx}} > \Delta E_{\text{diss}}$ requirement, which is part of condition (iii) (see Supplementary Tables 1 and 2 for the C–H and H(2)–H(3) distances characterizing the neutral and doubly ionized CH_3F molecule and the ΔE_{rlx} and ΔE_{diss} values obtained in our best DIP-EOMCC calculations for CH_3F^{2+}), the CH_3F species that we studied only computationally does not form H_3^+ upon double ionization. As mentioned in Results: Ab initio molecular dynamics simulations, and in agreement with the older experimental¹⁸ and more recent computational¹⁷ studies, none of the trajectories obtained in our AIMD simulations for CH_3F^{2+} produced H_3^+ . In this case, as shown in Supplementary Fig. 3, the adiabatic relaxation energy ΔE_{rlx} , 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 included in our experiments and, as a result, redistributed very differently than in the $\text{CH}_3\text{OH}^{2+}$, $\text{CH}_3\text{Cl}^{2+}$, and $\text{CH}_3\text{NCS}^{2+}$ dications that form H_3^+ . This is illustrated by Supplementary Movie 3, which shows a typical trajectory obtained in our AIMD simulations for CH_3F^{2+} , where the liberated, positively charged, H_2 fragment dissociates and the final products are CH_2F^+ and a proton. It may be worth noticing that the adiabatic relaxation energy ΔE_{rlx} resulting from our most accurate DIP-EOMCC computations for the CH_3F^{2+} dication, reported in Supplementary Table 2 and Supplementary Fig. 3, is large enough to dissociate both H_2 and H_2^+ , and we plan to study the significance of this finding further in the future work, but we can already observe that CH_3F^{2+} is the only CH_3X^{2+} species considered in the present study which has this property. In a small number of trajectories, the liberated H_2 fragment, having sufficiently large energy available to it, escaped the system, preventing H_3^+ formation as well. Once again, this is consistent with condition (iii), which allows such a scenario if the adiabatic relaxation energy ΔE_{rlx} is high enough, which is the case when CH_3F^{2+} is examined.

As explained in Results and Methods, the mechanism of H_3^+ formation from the doubly ionized CH_3X species that emerges from the above conditions (i)–(iii), in which the neutral H_2 fragment resulting from a geometrical distortion of the CH_3X^{2+} dication roams CHX^{2+} , abstracting a proton from it, was confirmed and further examined using AIMD simulations. 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. The analysis of the AIMD trajectories shows that the timescale of H_3^+ formation is related to the ability of the roaming H_2 to appropriately align itself relative to the CHX^{2+} fragment. From the trajectories resulting from our AIMD simulations, such as that shown in Fig. 5 or those visualized by Supplementary Movies 1 and 2, for a substantial portion of time prior to

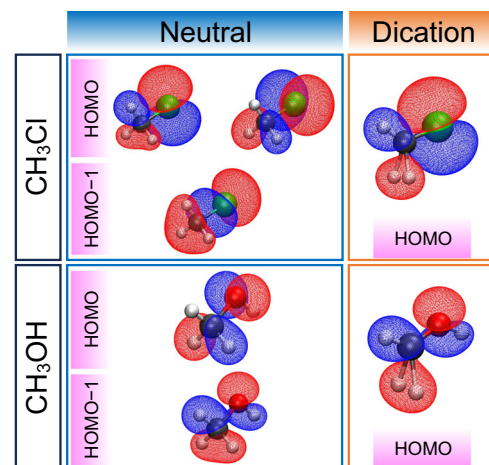


Fig. 7 | Highest-energy occupied orbitals of methyl chloride, methanol, and their dications. The RHF/cc-pVTZ orbitals describe the HOMO – 1 and HOMO(s) of the neutral CH_3OH and CH_3Cl molecules and the HOMOs of the corresponding dications at their respective equilibrium geometries. The GAMESS input and output files and information about the software used to plot the orbitals are provided in the Source Data folder.

the formation of H_3^+ , a neutral H_2 roams the CHX^{2+} moiety before orienting itself in a suitable edge-on configuration facing the hydrogen of CHX^{2+} , which facilitates the completion of the $\text{CHX}^{2+} + \text{H}_2 \rightarrow \text{CX}^+ + \text{H}_3^+$ proton abstraction step (molecular structures corresponding to these edge-on configurations can also be seen in the $\text{CH}_3\text{X}^{2+} \rightarrow \text{CX}^+ + \text{H}_3^+$ reaction profiles shown in Supplementary Fig. 4). The easier it is for the H_2 and CHX^{2+} fragments to find this configuration, the faster the timescale of H_3^+ formation becomes. This is reflected in our AIMD computations which demonstrate that the neutral H_2 roaming the CHCl^{2+} fragment in the doubly ionized CH_3Cl species explores a much larger portion of the phase space, when searching for a suitable alignment with CHCl^{2+} , than the H_2 roaming CHOH^{2+} in $\text{CH}_3\text{OH}^{2+}$. As a result, the average timescale of H_3^+ formation from the doubly ionized CH_3Cl species seen in our experiments and AIMD simulations is longer than in the CH_3OH case (see Fig. 4, Results: Ab initio molecular dynamics simulations, and Supplementary Movies 1 and 2). Based on the above observation that the H_2 and CHX^{2+} fragments have to align in a very specific configuration to enable H_3^+ formation, one might speculate that larger adiabatic relaxation energy of a given doubly ionized CH_3X molecule should lead to a faster exploration of the phase space and, thus, a shorter time needed to produce H_3^+ , but the results in Figs. 4 and 6 show that there is no direct correlation between the ΔE_{rlx} values characterizing the CH_3X^{2+} dications and the timescales of H_3^+ formation from these ions. This agrees with the recent computational study of the CH_3X systems with $\text{X} = \text{F}, \text{Cl},$ and Br^{17} .

Finally, an interesting pattern emerges when we compare the molecular orbitals obtained in the restricted Hartree–Fock (RHF) calculations for the CH_3X molecules and the corresponding CH_3X^{2+} dications that produce H_3^+ . This is illustrated in Fig. 7 using the neutral CH_3OH and CH_3Cl species and the corresponding dications at the respective equilibrium geometries as examples. In the neutral CH_3Cl molecule, the two degenerate HOMOs exhibit bonding and antibonding characteristics with respect to the H(2) and H(3) atoms involved in H_2 formation. The same is true when the nondegenerate HOMO – 1 and HOMO of the neutral CH_3OH are examined. According to our DIP-EOMCC computations, the dominant process defining the double ionization of the CH_3OH and CH_3Cl species is the removal of two electrons from the highest-energy occupied orbital that has the antibonding H_2 character. This makes the orbital that binds the two hydrogens of H_2 the HOMO of the respective dication, bringing the

H(2) and H(3) atoms close together, almost as in the isolated H₂ molecule, facilitating its liberation and initiating the roaming mechanism shown in Figs. 1 and 5.

In conclusion, we reported highly accurate yield and femtosecond time-resolved measurements following the strong-field double ionization of the CH₃X molecules with X = OD, Cl, NCS, CN, SCN, and I, along with the ab initio quantum chemistry and AIMD computations. The goal was to obtain a detailed understanding of the microscopic factors that govern the production of H₃⁺ via a roaming mechanism in which a neutral H₂ liberated from the CH₃X²⁺ dication abstracts a proton from the CHX²⁺ moiety. By combining state-of-the-art experiments and computations, we provided deep insights into the molecular mechanism of H₃⁺ formation from the doubly ionized CH₃X species, which allowed us to explain the observed yields and time-scales and determine geometric and energetic conditions that must be met in order for H₃⁺ to form. The results reported in this work may be used to predict the behavior of methyl halides and pseudohalides upon strong-field double ionization and help future studies of alternative sources of H₃⁺ in the universe. 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^{41–44} and longer-chain alcohols^{10,45}, which may produce H₃⁺ 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 CH₃X systems, which are analyzed in greater detail in the Supplementary Discussion section of Supplementary Information, and our earlier studies of ethanol^{10,45} suggest that our conditions (i)–(iii) may apply to organic compounds outside the CH₃X 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 H₃⁺ formation from the doubly ionized methyl halides and pseudohalides apply to other organic compounds in future work.

Methods

Experimental details

We employed the disruptive probing technique for the synchronous monitoring of the ultrafast time-resolved product yields induced by strong-field ionization³⁸. Our experimental setup features a regeneratively amplified Ti:sapphire laser system as the ionization source, which produces 35 fs pulses at a central wavelength of ~800 nm and operates at a repetition rate of 1 kHz. The pulses were compressed using a Multiphoton Intrapulse Interference Phase Scan (MIIPS)⁴⁶, which measures all orders of spectral phase distortions and compensates them using a pulse shaper (MIIPS-HD) with a spatial light modulator (640 × 800, Hamamatsu). Following compression, the pulses were split into a strong pump and a weak probe, with intensities of 5 × 10¹⁴ W/cm² and 9.5 × 10¹³ W/cm², respectively, using a beam splitter. The pump pulses used in this work are sufficiently intense to doubly ionize the CH₃X molecules, and they are somewhat more intense than those employed in ref. 38, potentially populating several electronic states of the CH₃X²⁺ dications, but this does not have a significant effect on the outcome of our experiments. The H₃⁺ formation dynamics via a roaming mechanism considered in the present study proceeds mainly on the lowest singlet states of the CH₃X²⁺ species¹¹, which means that any pump pulse providing enough energy to doubly ionize the molecules of interest suffices. For yield measurements, the probe pulse was blocked, allowing only the pump pulse to interact with the sample. The time delay between the pump and probe pulses was controlled using an optical delay line equipped with a programmable translation stage capable of nanometer-level precision control. The laser pulses were focused inside a Wiley-McLaren TOF mass spectrometer by a gold-coated concave focusing mirror with *f* = 300 mm. At

the focus, the pump and probe pulses reached their peak intensities, which were calibrated by measuring the Ar²⁺/Ar⁺ ion yield ratios⁴⁷.

The ionization potentials of the compounds under investigation span a range of approximately 9–12 eV, which corresponds to an average Keldysh parameter γ of 0.4 under our laser conditions⁴⁸. It is well-known that $\gamma < 1$ suggests tunnel ionization as the dominant process, where the timescale of classical ionization is faster than the optical cycle. On the other hand, $\gamma > 1$ signifies that the ionization spans multiple optical cycles, indicative of multiphoton ionization. The average γ value of 0.4 in our experiments points to the tunneling regime, implying that the electric field is strong enough to ionize the molecules within a single optical cycle.

The CH₃OD, CH₃Cl, CH₃NCS, CH₃CN, CH₃SCN, and CH₃I samples, used without further purification, were degassed and loaded into the TOF chamber as a room-temperature effusive beam through a needle valve. The static pressure inside the vacuum chamber was maintained below 1 × 10^{−5} Torr during data acquisition. Upon closing the needle valve, the vacuum pressure quickly dropped to the baseline pressure of 5 × 10^{−8} Torr, which ensures fast sample refresh. The positively charged ions formed in the interaction volume were sent to a Chevron dual microchannel plate detector (RM Jordan) by a +2168 V repeller plate and a +1080 V extractor plate separated by 10 mm. Ion signals generated at the microchannel plate detector were digitized using an oscilloscope (LeCroy WaveRunner 610Zi, 1 GHz) and transferred to a computer for further processing and analysis.

Electronic structure calculations

To enhance our understanding of the experimental findings, we performed a series of high-level ab initio quantum chemistry calculations which shed light on the geometrical, energetic, and other factors that influence the mechanisms and yields of H₃⁺ formation following the strong-field double ionization of the methyl halides and pseudohalides examined in this work. As is normally done, all of our electronic structure calculations, including those for methanol, which in our experiments was represented by its deuterated CH₃OD form, were performed using masses of atomic nuclei that correspond to the most abundant isotopes since isotopic substitution has no effect on electronic properties. We started by optimizing the ground-state equilibrium geometries of the closed-shell neutral CH₃X (X = OH, Cl, NCS, CN, SCN, I, and F) molecules using the CCSD approach^{33,34}. Then, in order to obtain the desired information about the electronic states of the CH₃X²⁺ dications involved in our strong-field double ionization experiments and, to enrich our discussion of the behavior of the CH₃X systems upon double ionization, of CH₃F²⁺, we computed vertical double ionization energies of all studied CH₃X species at their respective CCSD-optimized geometries using high-level methods belonging to the DIP-EOMCC hierarchy^{23–29}. For the CH₃X systems with the smaller X = OH, Cl, and F groups, we used both the state-of-the-art DIP-EOMCC(4h-2p) approach^{28,29} and its more economical DIP-EOMCC(3h-1p) counterpart^{23–26,28,29}. In the case of the remaining CH₃X molecules with the larger X = NCS, CN, SCN, and I fragments, we utilized DIP-EOMCC(3h-1p). The same DIP-EOMCC methods were applied to determine the minima on the ground and low-lying excited-state potential energy surfaces of the CH₃X²⁺ species, which allowed us to obtain information about the adiabatic double ionization energies associated with the respective dicationic states and, more importantly, the energies released upon geometrical relaxation of the doubly ionized CH₃X molecules to their respective equilibrium structures. We chose the particle-nonconserving DIP-EOMCC methodology in our computations since it is particularly well suited for an accurate description of the many-electron systems that are formally obtained by removing two electrons from their closed-shell parents (which themselves were treated by a highly correlated CCSD level) while relaxing the remaining electrons after double ionization. Furthermore,

the DIP-EOMCC methods, including the DIP-EOMCC(3h-1p) and DIP-EOMCC(4h-2p) approaches used in our calculations, offer several advantages over the conventional particle-conserving CC^{30–32} and EOMCC^{49–52} treatments of open-shell species employing unrestricted or restricted open-shell reference determinants, such as rigorous spin and symmetry adaptation of the calculated electronic states and the ability to describe singlet and triplet manifolds of the doubly ionized species in a well-balanced manner.

The DIP-EOMCC computations for the CH_3X^{2+} , CHX^{2+} , and CX^+ ions and the preceding CCSD calculations for their closed-shell CH_3X , CHX , and CX^- parents, needed to set up the respective DIP-EOMCC eigenvalue problems, in addition to the aforementioned geometry optimizations for the CH_3X molecules, were performed using the routines described in refs. 28,29,53, 54, which are part of the GAMESS software package^{55–57}. In constructing the relevant wave functions, all CCSD and DIP-EOMCC computations relied on the RHF molecular orbitals of the CH_3X , CHX , and CX^- species and the correlation-consistent basis sets, including the cc-pVDZ and cc-pVTZ bases for H, C, N, F, O, S, and Cl atoms^{58,59}, as implemented in GAMESS, with the additional tight d functions for S and Cl taken from ref. 60, and cc-pVTZ-PP^{61,62}, taken from the EMSL Basis Set Exchange⁶³, for iodine. In all post-RHF calculations, the core orbitals correlating with the 1s shells of the C, N, F, and O atoms and the 1s, 2s, and 2p shells of the S and Cl atoms were kept frozen. For the heavier I atom, the 28 inner-shell electrons ($[\text{Ar}]3d^{10}$) were replaced by the relativistic effective core potential of Peterson et al.^{61,62} and the remaining 25 valence electrons were described by the cc-pVTZ-PP basis set. All of our geometry optimizations were initially carried out without imposing any symmetry constraints, but, once the minima on the relevant potential energy surfaces were found and a given species had symmetry higher than C_1 , which was the case for all systems examined in this work other than CH_3NCS , we reoptimized the resulting structures using the appropriately chosen symmetrized Cartesian coordinates adapted to the point group symmetries of the molecules of interest. To confirm that all of our optimized geometries are minima on the respective potential energy surfaces, we determined the corresponding harmonic vibrational frequencies, which were real in each studied case.

The Cartesian coordinates defining all geometries of the CH_3X and CH_3X^{2+} species optimized in our CCSD (all CH_3X molecules), DIP-EOMCC(3h-1p) (all CH_3X^{2+} dications), and DIP-EOMCC(4h-2p) ($\text{CH}_3\text{OH}^{2+}$, $\text{CH}_3\text{Cl}^{2+}$, and CH_3F^{2+}) calculations, along with the corresponding total electronic energies, can be found in Supplementary Data. In presenting the selected bond lengths in Table 2, which are important for the material included in Results and the follow-up analysis in Discussion, characterizing the optimized geometries of the CH_3X molecules with $\text{X} = \text{OH}$, Cl , NCS , CN , SCN , and I in their ground electronic states and the minima on the lowest singlet potential energy surfaces of the corresponding CH_3X^{2+} dications, we use the data obtained in the most accurate CCSD (neutral CH_3X molecules), DIP-EOMCC(4h-2p) ($\text{CH}_3\text{OH}^{2+}$ and $\text{CH}_3\text{Cl}^{2+}$), and DIP-EOMCC(3h-1p) ($\text{CH}_3\text{NCS}^{2+}$, $\text{CH}_3\text{CN}^{2+}$, $\text{CH}_3\text{SCN}^{2+}$, and CH_3I^{2+}) calculations performed in this work in which we utilized the cc-pVTZ basis set for H, C, N, O, S, and Cl (with additional tight d functions on S and Cl) and the cc-pVTZ-PP basis for iodine. The same applies to the vertical and adiabatic double ionization energies of the CH_3OH , CH_3Cl , CH_3NCS , CH_3CN , CH_3SCN , and CH_3I molecules reported in Fig. 3 and the geometries of the lowest singlet and triplet states of the CH_3X^{2+} species with $\text{X} = \text{F}$, Cl , CN , and I and their ground-state CH_3X parents shown in Supplementary Table 1 (the computational methodologies applied to CH_3F and CH_3F^{2+} were exactly the same as those used for the neutral and doubly ionized CH_3OH and CH_3Cl molecules).

Among the quantities that are useful in our theoretical analyses (other than the geometries and energies of the neutral and doubly ionized CH_3X molecules) are the adiabatic relaxation energies ΔE_{rlx} characterizing the CH_3X^{2+} dications, shown in Figs. 3 and 6,

Supplementary Figs. 1–4, and (for $\text{X} = \text{F}$ only) Supplementary Table 2 and defined by Eq. (1), and the dissociation energies ΔE_{diss} associated with the fragmentation of the doubly ionized CH_3X species into CHX^{2+} and H_2 prior to H_3^+ formation, Eq. (2), reported in Fig. 6, Supplementary Fig. 3, and Supplementary Table 2. In our most accurate calculations presented in Figs. 3 and 6, Supplementary Fig. 3, and Supplementary Table 2, the vertical and adiabatic double ionization energies entering the definition of ΔE_{rlx} were calculated at the DIP-EOMCC(4h-2p)/cc-pVTZ level of theory for $\text{X} = \text{OH}$, Cl , and F and the DIP-EOMCC(3h-1p)/cc-pVTZ approach (using cc-pVTZ-PP for I atom) for the remaining CH_3X^{2+} dications. The energies of the CHX^{2+} and CH_3X^{2+} species in their lowest singlet states entering the definition of ΔE_{diss} were determined using the DIP-EOMCC(3h-1p)/cc-pVDZ theory level for all CH_3X^{2+} and CHX^{2+} dications except CH_3I^{2+} and CHI^{2+} , which were treated with DIP-EOMCC(3h-1p)/cc-pVTZ (cc-pVTZ-PP for I atom). To be consistent in our calculations of the energies that appear on the right-hand side of Eq. (2), the energy of the H_2 molecule entering the definition of ΔE_{diss} was computed using the CCSD/cc-pVDZ approach when the $\text{X} = \text{OH}$, Cl , NCS , CN , SCN , and F systems were considered and CCSD/cc-pVTZ in the $\text{X} = \text{I}$ case (determining the equilibrium H–H distance in H_2 at the respective CCSD/cc-pVDZ or CCSD/cc-pVTZ level using GAMESS). We note that the CCSD calculation for H_2 , which has only two electrons, is equivalent to an exact, full configuration interaction, computation.

In addition to the above characteristics of the CH_3X^{2+} ions, we calculated potential energy profiles for the $\text{CH}_3\text{X}^{2+} \rightarrow \text{CX}^+ + \text{H}_3^+$ reactions following double ionization of the CH_3X molecules with $\text{X} = \text{OH}$, Cl , and NCS , along with the corresponding $\text{CH}_3\text{X}^{2+} \rightarrow \text{CHX}^{2+} + \text{H}_2$ dissociation asymptotes relevant to the roaming mechanism examined in the present study (see Supplementary Fig. 4). In the case of the CH_3X^{2+} , CHX^{2+} , and CX^+ ions, we used the DIP-EOMCC(3h-1p)/cc-pVDZ approach, whereas the CH_3X , H_2 , and H_3^+ molecules were handled with CCSD/cc-pVDZ (again using additional tight d functions for S and Cl atoms). These calculations allowed us to demonstrate that the doubly ionized CH_3OH , CH_3Cl , and CH_3NCS species have enough energy to liberate molecular hydrogen, which is a key step in the roaming mechanism considered in this work, and to overcome the barriers for H_3^+ formation.

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.

Ab initio molecular dynamics simulations

To gain further insights into the yields and timescales of H_3^+ formation, we performed AIMD simulations for the CH_3X^{2+} ions with $\text{X} = \text{OH}$, Cl , CN , SCN , and F by utilizing the GPU-accelerated CASSCF code implemented in the TeraChem software^{64–67}. For each CH_3X^{2+} species, the potential energy surface corresponding to its lowest singlet electronic state and its gradients were computed on-the-fly by using the CASSCF method with 4 electrons in 4 orbitals as an active space, abbreviated as CAS(4,4)SCF, in conjunction with the cc-pVDZ basis set. The orbital active spaces were carefully tailored to closely reproduce the adiabatic relaxation energies ΔE_{rlx} , Eq. (1), and the geometries of the CH_3X^{2+} dications in their lowest singlet states obtained using the DIP-EOMCC(4h-2p)/cc-pVDZ approach for $\text{CH}_3\text{OH}^{2+}$, $\text{CH}_3\text{Cl}^{2+}$ and CH_3F^{2+} and DIP-EOMCC(3h-1p)/cc-pVDZ for the remaining species (see Supplementary Fig. 2). To provide a reasonable representation of the molecular dynamics following double ionization, a total of 200 trajectories were computed for each CH_3X^{2+} system. All trajectories were initiated and subsequently propagated on the lowest singlet states of the CH_3X^{2+} dication species reached after vertical double ionization of their CH_3X parents. The initial conditions (positions and momenta of atomic nuclei) were sampled from the Wigner distributions obtained for the neutral CH_3X molecules using the B3LYP/cc-pVDZ

approach^{68,69}. All trajectories were integrated for 700 fs with a time step of 0.5 fs by using the velocity Verlet algorithm. Of the six CH₃X systems included in our experiments, three, namely, CH₃OH, CH₃Cl, and CH₃NCS, produce H₃⁺ after double ionization, so we wanted to perform AIMD simulations for CH₃NCS²⁺ as well. However, the low yield of H₃⁺ resulting from the double ionization of CH₃NCS would necessitate the determination of a much larger number of trajectories than in the CH₃OH²⁺ and CH₃Cl²⁺ cases to obtain sufficiently good statistics for describing the dynamics of the CH₃NCS²⁺ → CNCS⁺ + H₃⁺ process, which turned out to be prohibitively expensive for us.

Data availability

All data needed to evaluate the conclusions of this study are included in the article and Supplementary Information. Source data are provided in the Source Data folder. Any additional information related to this study may be requested from the authors.

Code availability

All ab initio DIP-EOMCC computations for the CH₃X²⁺, CHX²⁺, and CX⁺ cations and the preceding CCSD calculations for the CH₃X, CHX, and CX⁺ parent molecules, as well as the additional computations for the neutral and doubly ionized ethane and ethene, were performed using the routines described in refs. 28, 29, 53, 54, which are part of the GAMESS software package^{55–57} that can be obtained from <https://www.msg.chem.iastate.edu/gamess/download.html>. The AIMD simulations for the selected CH₃X²⁺ species, using CASSCF information calibrated to the DIP-EOMCC data, were carried out using the development version of TeraChem software^{64–67} provided by B.G.L.

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Author contributions

M.D. conceived the project and oversaw the execution of all experiments. J. Stamm, S.K., and C.W. carried out the experiments under M.D.'s supervision, and J. Sandhu helped with the analysis of experimental data. P.P. and B.G.L. conceived the computational parts of the project. A.C., S.S.P., and J. Shen performed all ab initio electronic structure calculations using the CC and DIP-EOMCC methodologies under P.P.'s supervision. S.S. performed all AIMD simulations, consulting A.M., B.G.L., and P.P. All authors contributed to the interpretation of the results and J. Stamm, S.S.P., S.S., A.C., P.P., and M.D. led the manuscript writing, with the remaining authors offering comments and helping with respective tables and/or figures.

Competing interests

The authors declare no competing interests.

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