

Time-resolved three-body fragmentation of methane in strong laser fields

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Distinct strong-field fragmentation pathways can converge to identical final products in polyatomic molecules, making the underlying reaction dynamics difficult to identify. In methane, Jahn-Teller symmetry breaking after ionization creates distinct intermediate geometries that lead to different three-body routes within the same final fragments. Using delay-dependent, coincidence-resolved momentum correlations in pump-probe Coulomb-explosion imaging, we discriminate fragmentation pathways within the $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$ channel. We discover a delay-dependent sequential pathway with a transient H_2 fragment, characterized by symmetric proton-proton correlations, and separate it from an asymmetric sequential route and concerted fragmentation. Our results establish that delay-resolved coincidence mapping can disentangle intermediate-mediated fragmentation pathways even within an identical three-body final state, and show that in methane such pathways are seeded by Jahn-Teller-driven symmetry breaking.

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Ultrafast fragmentation provides a sensitive probe of how molecular geometry evolves under strong external fields. In polyatomic molecules, strong-field ionization can launch coupled electronic and nuclear motion on femtosecond timescales, opening multiple fragmentation pathways through transient intermediate structures [1]. In molecules like methanol, channel-specific measurements can distinguish between direct dissociation, hydrogen migration, and roaming dynamics [2].

A greater challenge arises when distinct fragmentation pathways evolve on similar timescales yet converge to the same set of fragment ions. In such cases, channel-resolved yields alone cannot reveal the underlying reaction dynamics. Delay-dependent coincidence momentum correlations within a fixed final state provide a way to recover this hidden information, because they retain sensitivity to the evolving molecular geometry throughout fragmentation.

A central mechanism behind such geometric changes is the Jahn-Teller (JT) effect [3], which destabilizes high-symmetry configurations after ionization, lifts electronic degeneracies, and remodels the coupled potential-energy surfaces. JT-driven dynamics are widespread under strong-field conditions and

have been observed in many molecules [4]. It remains unresolved how these initial symmetry-breaking motions determine branching among multibody breakup pathways leading to the same charge fragments [5].

Methane (CH_4), the simplest polyatomic hydrocarbon, is a prototypical system for studying JT-driven structural dynamics. Upon photoionization, in the ground (X , $^2T_2$) state, JT coupling lifts the tetrahedral (T_d) symmetry and drives the cation through a sequence of lower-symmetry geometries—including a C_{3v} configuration with an elongated C-H bond, a D_{2d} distortion, and a C_{2v} structure with a transient H_2 intermediate [6–19]. Ultrafast studies show that this symmetry breaking occurs on few-femtosecond timescales [18–20]. Here, we do not attempt to resolve this onset directly. Instead, we treat it as pump-prepared JT-distorted molecular geometries and probe them at later times through channel-resolved three-body coincidence observables. This allows us to investigate how the early distortions seed distinct intermediates and whether their signatures persist in the final fragmentation.

For two-body breakup in methane, correlations between geometry and channel are well established: Loss of a hydrogen atom reflects a C_{3v} -type stretch, while transient formation of H_2 signals a C_{2v} -type pairing [21]. However, the consequences of JT-prepared geometries for more complex three-body breakup within a single channel, such as $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$, are not yet resolved. Previous single-pulse and collision experiments have observed correlated proton emission in this channel [22–24], but these studies have not tracked its time evolution or determined whether the C_{2v} -associated H_2 intermediate mediates sequential three-body breakup.

In this work, we use few-cycle near-infrared pump-probe coincidence Coulomb-explosion imaging in a reaction microscope [25] to establish coincidence-resolved pathway

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discrimination within an identical three-body final state. By selecting the $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$ channel, we identify a distinct delay-dependent sequential pathway most consistently explained by a transient H_2 intermediate. In this pathway, the probe ionizes the transient H_2 , generating the $\text{H}^+ + \text{H}^+$ pair with a symmetric proton-proton correlation pattern. We also resolve an asymmetric sequential route and concerted fragmentation cases. Together, these provide internal contrasts that allow distinct pathways to be separated even though the final charge fragments are identical. Simulations support these findings and establish a channel-specific link between JT-driven symmetry breaking and three-body pathway selection in methane. More broadly, our results show how delay-resolved coincidence maps can uncover intermediate-mediated dynamics that remain hidden in channel yields, KER traces, and delay-integrated correlation maps, thereby providing a general strategy for disentangling hidden fragmentation pathways in polyatomic strong-field dynamics.

A Ti:sapphire laser delivers 25 fs pulses at 785 nm, which are spectrally broadened in a hollow-core fiber and compressed to 10 fs using a spatial light modulator (SLM) for dispersion compensation [26]. The SLM also splits each pulse into two identical replicas with a variable time delay that serve as pump and probe. These few-cycle pulses, each at a peak intensity of $3 \times 10^{14} \text{ W cm}^{-2}$, are focused into a reaction microscope [25] with parallel linear polarization aligned along the spectrometer z axis. The pump ionizes methane and drives JT-induced rearrangements of the cation, while the delayed probe induces Coulomb explosion of the evolving system. Charged fragments in the three-body final state $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$ are detected in coincidence, providing three-dimensional momentum vectors for all fragments as a function of pump-probe delay.

Within the fixed three-body final state $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$, the coincidence data separate into distinct momentum-correlation classes with different delay dependences, showing that identical final products can encode multiple hidden fragmentation pathways. Figure 1 summarizes the key observations. Under our conditions, it is the dominant three-body breakup pathway. The competing channel $\text{CH}^+ + \text{H}_2^+ + \text{H}^+$ contributes only $\sim 7\%$ of the $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$ yield.

Panel (a) shows the proton-proton kinetic-energy correlation, which is sensitive to the molecular geometry at breakup. Four regions, labeled 1–4, can be identified. Regions 1 and 3 lie close to the diagonal and correspond to nearly equal proton energies, giving rise to symmetric signatures. This symmetry suggests that the two proton-emitting bonds evolve in a similar way before breakup and is consistent with intermediate H_2 formation. In contrast, regions 2 and 4 occupy off-diagonal sectors and exhibit strongly asymmetric energy sharing, consistent with sequential emission from an asymmetric stretch in which one proton departs first and the second follows later. The delay-coded representation therefore defines the four regions and, at the same time, gives their qualitative delay dependence: Regions 3 and 4 are concentrated near temporal overlap, whereas regions 1 and 2 appear mainly at positive delays.

To test these intermediate-geometry assignments, we performed semiclassical surface-hopping simulations of CH_4^+ as a representative case, launching a Wigner-sampled ensemble

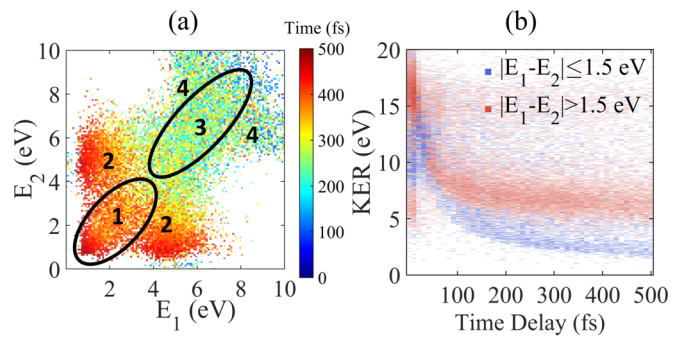


FIG. 1. (a) Proton-proton kinetic-energy map for the channel $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$. Regions 1–4 mark distinct classes of events. The colormap is delay coded rather than count coded, with cold colors corresponding to short pump-probe delays and warm colors to longer delays. (b) Total KER as a function of pump-probe delay; positive delay denotes the probe arriving after the pump. Colors correspond to the energy-sharing condition in panel (a): blue denotes near-diagonal events with $|E_1 - E_2| \leq 1.5$ eV, and red marks off-diagonal events with $|E_1 - E_2| > 1.5$ eV. The 1.5 eV threshold is used to separate the two classes.

of trajectories on the second excited electronic state. Representative geometries from these trajectories were then used in classical Coulomb-explosion simulations of the final $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$ channel. Two mechanistic classes emerge. Trajectories that reorganize toward C_{2v} yield transient H_2 formation and provide representative geometries for the symmetric regions 1/3. Trajectories evolving toward C_{3v} produce rapid hydrogen loss and provide representative geometries for the asymmetric regions 2/4. The close correspondence between the resulting classical Coulomb-explosion Newton plots and the measured momentum-correlation patterns supports the pathway assignments.

Panel (b) shows the total kinetic-energy release as a function of pump-probe delay. Two distinct behaviors appear. Delay-independent bands at 15.0 ± 0.5 eV, corresponding to regions 3 and 4 in panel (a), are assigned to prompt, concerted fragmentation of CH_4^+ based on single-pulse benchmarks [22]. In contrast, pronounced delay-dependent ridges in regions 1 and 2 indicate sequential breakup following pump-induced nuclear rearrangement. For the symmetric branch, region 1 ridge starts from approximately the same KER range as the prompt, delay-independent region 3 band near temporal overlap and separates into a clearly delay-dependent feature over the first ~ 50 fs. Region 1 appears exclusively in pump-probe measurements and is absent in the single-pulse reference [22]. For the asymmetric branch, the ridge in region 2 evolves into the higher-energy band of region 4, consistent with ongoing bond-selective elongation.

Together, the proton-proton correlations, their delay evolution, and the simulations support two mechanistic classes within the identical final state: (1) a symmetric pathway, represented by regions 1 and 3 and linked to transient H_2 formation at C_{2v} , and (2) an asymmetric pathway, represented by regions 2 and 4 and associated with bond-selective elongation at C_{3v} .

Before analyzing these delay-dependent pathways in detail, we first constrain the intermediate charge state populated

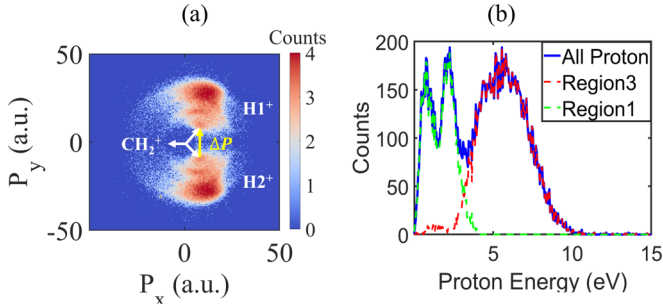
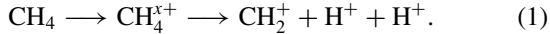


FIG. 2. (a) Newton plot (center-of-mass frame) for the three-body final state $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$, with regions 1 and 3 selected. The x axis is aligned with CH_2^+ momentum; proton momenta are shown in the fragmentation plane. The two inner rings correspond to region 1, while the outer ring corresponds to region 3. (b) Proton energy reconstructed from panel (a) via Eq. (5); region 1 (green) and region 3 (red), as assigned in Fig. 1(a), are overlaid with the total contribution (blue).

by the pump pulse, since the overall reaction proceeds as

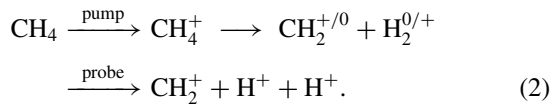


A key question is whether regions 1 and 2 originate from CH_4^+ or involve higher charge states. To address this, we compare the pump-probe data with single-pulse measurements and with two-body reference channels, thereby excluding routes via CH_4^{2+} based on characteristic KER ranges and fragment correlations. The corresponding comparison plots and selection criteria are provided in Appendix A.

We focus first on the symmetric branch, region 1, because it provides the clearest evidence for a hidden intermediate within the identical final state.

I. SYMMETRIC PATHWAY

We assign the symmetric fragmentation channel to sequential dissociation, in which the pump pulse prepares CH_4^+ and, via Jahn-Teller distortion toward a C_{2v} geometry, two protons form an H_2 intermediate. The probe pulse then induces a Coulomb explosion, fragmenting this intermediate into CH_2^+ and two protons:



If the probe acts on a transient H_2 , the final ionization step is formally analogous to the strong-field dissociation of free H_2 , which has been extensively studied [27–29]. This analogy provides a useful benchmark for interpreting the symmetric pathway. To test whether the intermediate indeed exhibits H_2 -like behavior, we analyze the Newton plot of the three-body breakup in Fig. 2, following Ref. [30]. Here, the two proton momenta lie in the fragmentation plane (labels H1^+ and H2^+ serve only to distinguish identical particles), and the H_2 center-of-mass (CM) recoil and internal relative momentum are given by

$$\mathbf{p}_{\text{pair}} = \mathbf{p}_{\text{H1}} + \mathbf{p}_{\text{H2}} \quad (\text{H}_2 \text{ CM recoil}), \quad (3)$$

$$\Delta \mathbf{p} = \mathbf{p}_{\text{H1}} - \mathbf{p}_{\text{H2}} \quad (\text{relative}). \quad (4)$$

TABLE I. Momentum, energy, and $\text{H}^+ - \text{H}^+$ distance corresponding to the three peaks in Fig. 2.

	Peak 1	Peak 2	Peak 3
Momentum $\Delta \mathbf{p}/2$ (a.u.)	9.0	16.8	28.4
Energy (eV, one proton)	0.60	2.09	5.90
$\text{H1}^+ - \text{H2}^+$ distance R (a.u.)	22.7	6.51	2.27

Transforming to the H_2 CM frame, the energy per proton obtained is

$$\text{Energy}_{\text{H}^+} = \frac{\|\Delta \mathbf{p}/2\|^2}{2m_p}. \quad (5)$$

Here, m_p is the proton mass and $\Delta \mathbf{p}$ is the relative momentum between the two protons, as illustrated in Fig. 2(a). Within the sudden Coulomb-explosion approximation [31], the proton-proton kinetic energy reflects the H-H internuclear separation R at the moment of probe-induced explosion. The resulting $E_p - R$ relation, obtained from the proton-proton energy distribution in Fig. 2(b), is summarized in Table I.

The three ringlike structures marked in Fig. 2(a) correspond to the three proton-energy peaks in Fig. 2(b) and Table I. As shown in Fig. 2(b), the proton-proton energy spectrum exhibits three peaks. The highest-energy peak (peak 3 in Table I), at $E_p = 5.9$ eV, corresponds to the shortest separation, $R = 2.27$ a.u., close to the equilibrium bond length of H_2^+ . This component is therefore consistent with probe-induced Coulomb explosion of a transient intermediate H_2 fragment. The green dotted curve marks the region 1 contribution, corresponding to the two inner rings in panel (a), while the red curve marks the region 3 contribution, corresponding to the outer ring.

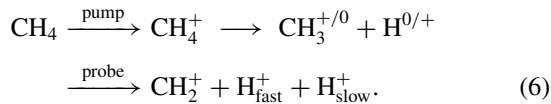
More importantly, however, the proton-energy distribution contains information beyond this minimum-distance Coulomb explosion. It reflects not only the shortest accessible H-H separation, but also the strong-field ionization and dissociation dynamics of the transient H_2 fragment under the probe field. We therefore compare the extracted $E_p - R$ distribution with established signatures of strong-field H_2 ionization. In particular, charge-resonance-enhanced ionization (CREI) [32–34] leads to enhanced ionization probability for $R \sim 5$ to 12 a.u., owing to strong coupling between charge-resonant states. The middle peak in our distribution falls within this CREI range, showing that the region 1 spectrum is characterized not only by a short-distance Coulomb explosion, but also by a proton-energy distribution consistent with the known strong-field response of H_2 . This provides even stronger evidence for a transient H_2 intermediate than the bond-length inference alone. We note, however, that the transient H_2 in our experiment may populate excited states not spectroscopically resolved here. Further support comes from polarization control: The region 1 signature is prominent for parallel pump-probe polarizations but strongly suppressed for orthogonal polarizations (see Appendix B). This behavior is consistent with probe-induced ionization of a transient H_2 fragment and with the known polarization sensitivity of CREI to the H-H axis.

Taken together, the symmetric Newton-plot structure, the E_p -to- R mapping of the Coulomb explosion, the proton-energy distribution with its CREI-consistent intermediate-energy peak, the polarization dependence, and the exclusion of dicationic alternatives support the assignment of region 1 to a sequential pathway involving a transient H_2 intermediate. Region 1 evolves continuously toward the delay-independent region 3 in the KER map, which is consistent with concerted breakup. We now turn to the asymmetric branch, represented by regions 2 and 4.

II. ASYMMETRIC PATHWAY

We now consider the asymmetric pathway, where the two protons show distinct delay-dependent behavior (Fig. 3). Panel (a) displays the Newton plot, separating a fast and a slow H^+ . The fast, high-energy proton evolves as shown in panel (b), whereas the slow, low-energy proton follows a different delay dependence in panel (c). This fast/slow partition indicates a two-step sequential emission process.

The data are most consistent with a mechanism in which one hydrogen atom (neutral or ionized) dissociates during the pump step, followed by probe-induced Coulomb explosion of the remaining CH_3^+ , which emits the second, faster proton. The reaction sequence is



This sequence is consistent with Jahn-Teller relaxation of CH_4^+ toward a C_{3v} -like geometry, which selectively weakens a

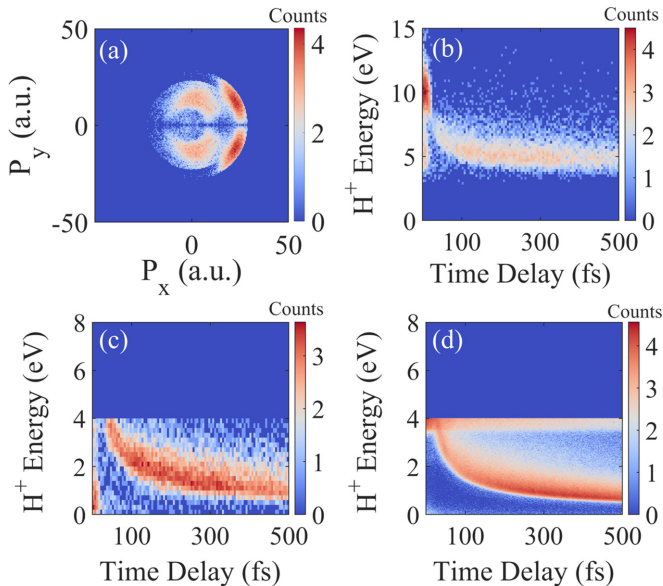


FIG. 3. Asymmetric sequential pathway (region 2). (a) Newton plot of region 2. The x axis is aligned with CH_2^+ momentum; proton momenta are shown in the fragmentation plane. (b)–(d) Proton kinetic energy versus pump-probe delay for the asymmetric sequential pathway. (b) Fast H^+ component selected from region 2. (c) Slow H^+ component selected from region 2. (d) H^+ from the two-body $CH_3^+ + H^+$ channel. Positive delay denotes probe after pump.

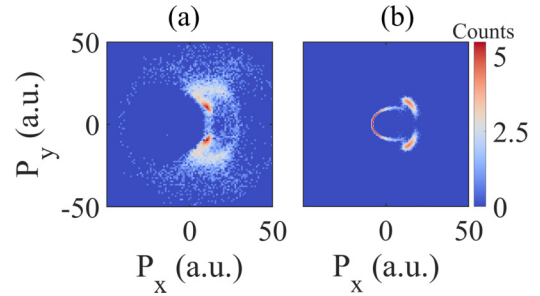


FIG. 4. Simulated Newton plots. (a) Region 1 (symmetric pathway; two-ring structure; the inner high-density features and the diffuse outer arc indicate the two-ring structure). (b) Region 2 (asymmetric pathway; off-diagonal lobes). The x axis is aligned with the CH_2^+ recoil, and proton momenta are projected onto the fragmentation plane.

single C-H bond, enabling the first hydrogen atom to escape. The remaining $CH_3^{+/0}$ is then Coulomb exploded by the probe pulse, producing the second proton.

Further support comes from comparing the slow proton in region 2 [panel (c)] to the proton in the two-body channel $CH_3^+ + H^+$ [panel (d)]. Both show similar delay dependence and energy distributions (0.3–4 eV), consistent with a shared origin: C-H bond dissociation in the pump step. The fast proton in panel (b), in contrast, reflects probe-induced explosion of the residual CH_3^+ fragment.

Taken together, these observations support the assignment of region 2 to a sequential asymmetric pathway: pump-driven dissociation of one hydrogen atom from CH_4^+ , followed by probe-driven Coulomb explosion of CH_3^+ . The delay-independent region 4 is consistent with the same pathway, but from a higher charge state, with both protons emitted promptly within a single pulse.

III. SIMULATION

Semiclassical surface-hopping simulations are consistent with distinct JT-driven precursor geometries, while the classical Coulomb-explosion simulations test how these geometry classes map onto the measured Newton plots. To test whether the experimentally observed symmetric and asymmetric branches can be traced to distinct JT-distorted precursor geometries, we performed classical Coulomb-explosion simulations of the three-body breakup $CH_2^+ + H^+ + H^+$, following the approach of Ref. [35]. The simulations are intended as qualitative tests of the geometry assignment rather than quantitative *ab initio* calculations. At each pump-probe delay τ , the probe is modeled as an instantaneous charge switch to $[CH_2^+, H^+, H^+]$, after which the nuclei evolve under Coulomb forces in the center-of-mass frame.

The simulations explore a range of initial nuclear geometries representative of JT-distorted configurations prepared by the pump pulse. Specifically, we set C-H bond lengths and H-C-H angles to reflect two key symmetry-broken structures: C_{2v} (symmetric, transient H_2 formation) and C_{3v} (asymmetric, bond-selective stretch), with initial velocities chosen to reproduce the observed momentum and KER widths. The simulated Newton plots for these geometries are shown in Fig. 4. For

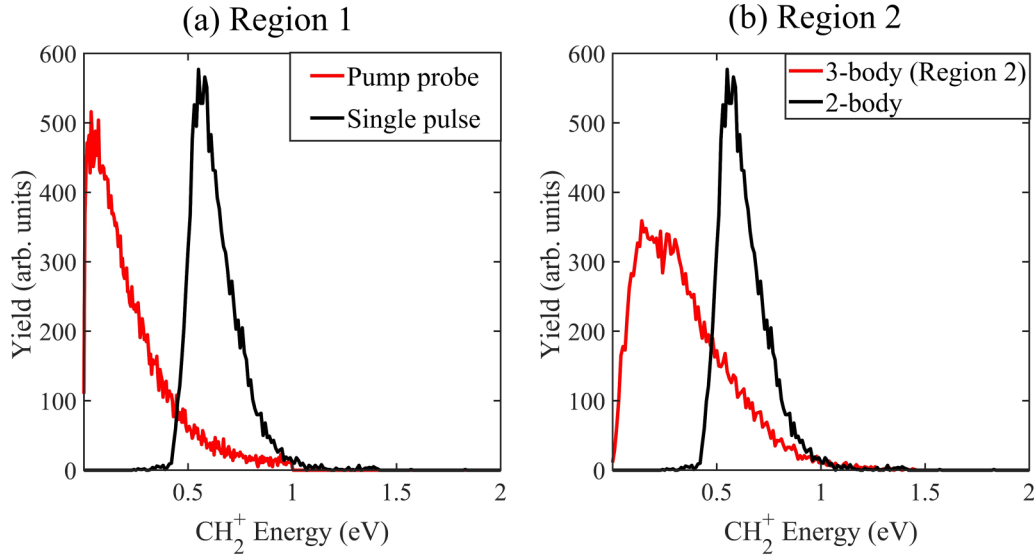


FIG. 5. CH_2^+ kinetic-energy distributions for (a) region 1 (red) and the two-body reference channel $\text{CH}_2^+ + \text{H}_2^+$ from single-pulse data (black), and (b) region 2 (red) and the same two-body reference (black). In both cases, the region 1/2 distributions are clearly shifted to lower energies compared with the dicationic reference.

C_{2v} starting conditions, the Newton plot displays a symmetric two-ring structure (region 1), which closely matches the experimental data in Fig. 2(a). For C_{3v} initial geometries, the plot features off-diagonal asymmetric lobes (region 2), which reflect the presence of one fast and one slow proton, as seen in Fig. 3(a).

Notably, simulations initialized at alternative geometries such as T_d and D_{2d} do not reproduce these branch topologies. The simulations therefore support the assignment of the two experimental branches to distinct JT-prepared geometry classes.

To summarize, we show that distinct strong-field fragmentation mechanisms can be disentangled even when they converge to the same three-body final state, $\text{CH}_2^+ + \text{H}^+ + \text{H}^+$. Within this channel, we identify a delay-dependent sequential pathway involving a transient H_2 intermediate and distinguish it from an asymmetric sequential route and prompt concerted fragmentation. Although hidden in conventional yield measurements, the H_2 -mediated pathway is revealed by its symmetric proton-proton correlation signature in delay-resolved coincidence momentum maps. Semiclassical and classical simulations support this interpretation by linking Jahn-Teller-distorted precursor geometries to the observed branch structure.

More generally, our results establish delay-dependent, coincidence-resolved momentum correlations as a practical way to uncover intermediate-mediated pathways that remain hidden when different mechanisms converge to identical final products in polyatomic strong-field fragmentation.

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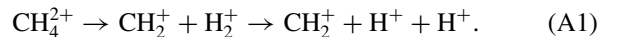
DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: CHARGE-STATE CONSTRAINTS ON REGIONS 1 AND 2

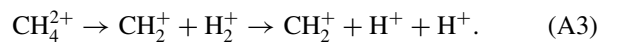
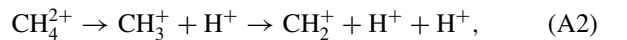
Because pump and probe have comparable intensities, one might suspect that the pump creates CH_4^{2+} and that regions 1 and 2 originate from dicationic breakup followed by probe ionization. We test this using CH_2^+ recoil energies and delay dependence and find that CH_4^{2+} is not the dominant precursor.

For region 1, a representative dicationic pathway would be



If this sequence dominated, the CH_2^+ recoil-energy distribution $P(E_{\text{CH}_2^+})$ in region 1 should match the two-body reference channel $\text{CH}_2^+ + \text{H}_2^+$ measured in single-pulse data. Figure 5(a) instead shows a clear mismatch: Region 1 peaks near 0.03 eV, whereas the reference peaks near 0.55 eV. This excludes CH_4^{2+} as the main precursor of region 1.

For region 2, possible dicationic pump-step channels include



If prompt dicationic breakup dominated region 2, then $P(E_{\text{CH}_2^+})$ would again match the single-pulse $\text{CH}_2^+ + \text{H}_2^+$ reference. Figure 5(b) shows that region 2 peaks near 0.2 eV, in clear disagreement with the reference peak at 0.55 eV. In addition, prompt dicationic breakup would be expected to

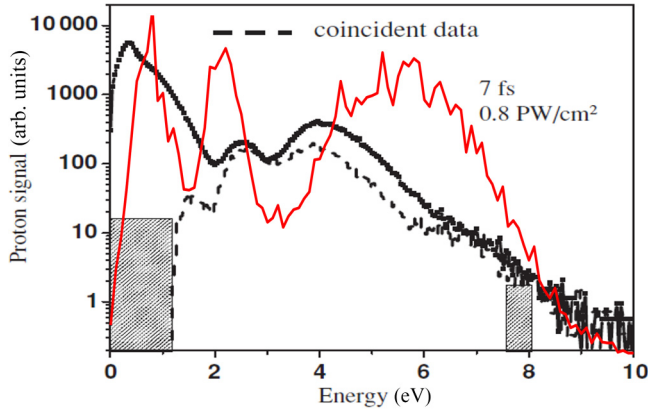


FIG. 6. Comparison of proton-energy spectra. Benchmark dissociative ionization spectrum of H_2 from Rudenko *et al.* [27] (black curves) overlaid with the proton-energy distribution extracted from methane region 1 (red curve, logarithmic scale). The similarity supports the interpretation of region 1 as a probe-induced Coulomb explosion of an H_2 -like fragment prepared during the pump step.

yield a delay-independent high-energy proton feature, which is not observed. Instead, proton energies evolve systematically with pump-probe delay (see Fig. 3), consistent with sequential dynamics in which the probe acts as a geometry-sensitive readout.

Together, the CH_2^+ energy mismatches in regions 1 and 2 and the absence of a prompt, delay-independent high-energy proton component in region 2 exclude CH_4^{2+} as the dominant precursor. The delay-dependent features instead point to sequential dynamics on CH_4^+ , with the probe providing a geometry-sensitive readout.

APPENDIX B: BENCHMARK AND POLARIZATION CONTROL FOR THE H_2 -LIKE INTERMEDIATE IN REGION 1

Figure 6 compares the proton-energy distribution extracted from region 1 with the dissociative ionization spectrum of H_2 in a single-pulse strong-field measurement reported by Rudenko *et al.* [27]. In our experiment, the pump prepares an H_2 -like fragment and the probe acts as a single near-infrared pulse that ionizes and Coulomb explodes this fragment. From the perspective of the intermediate H_2 , the probe step is therefore directly comparable to the single-pulse H_2 experiment. In both cases, the dissociative ionization produces a broad proton-energy distribution extending from very low energies up to several electron volts, with a pronounced intermediate-energy peak associated with CREI. The close similarity in peak positions and overall spectral structure shows that the region 1 protons are consistent with such a probe step on an H_2 -like intermediate.

A complementary test comes from polarization control, which probes another characteristic signature of CREI: its strong dependence on the angle between the laser polarization and the molecular axis. In the main experiment, pump and probe were linearly polarized in parallel. To test the role of an aligned H_2 -like fragment, we repeated the measurement with orthogonal pump-probe polarizations under otherwise identi-

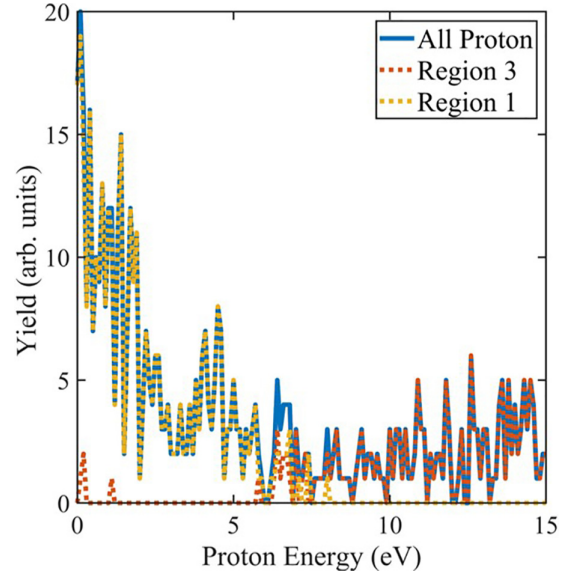


FIG. 7. Polarization control for region 1. The pump and probe are orthogonally polarized. The analysis is compared with Fig. 2(b), where pump and probe are parallel. The CREI-associated Newton-plot/proton-energy feature is prominent for parallel polarizations but strongly suppressed for orthogonal polarizations, consistent with ionization of an aligned transient H_2 intermediate.

cal conditions. Because strong-field H_2 ionization and CREI are highly sensitive to the angle between the laser polarization and the H-H axis, the orthogonal configuration is expected to suppress the region 1 signature (middle peak) strongly.

Figure 7 shows that the characteristic region 1 feature is pronounced for parallel pump-probe polarizations but strongly suppressed for orthogonal polarizations. This polarization sensitivity is consistent with CREI-type strong-field ionization of an aligned transient H_2 -like intermediate and reinforces the interpretation based on the spectral benchmark in Fig. 6.

APPENDIX C: SUPPLEMENTARY SIMULATION DETAILS: CLASSICAL COULOMB EXPLOSION

Model. To simulate the probe event at delay τ , we instantaneously switch to the final charge configuration [CH_2^+ , H_1^+ , H_2^+] and propagate the nuclei under classical pairwise Coulomb forces,

$$m_i \ddot{\mathbf{r}}_i = \sum_{j \neq i} \frac{q_i q_j (\mathbf{r}_i - \mathbf{r}_j)}{\|\mathbf{r}_i - \mathbf{r}_j\|^3}, \quad (C1)$$

in the center-of-mass frame until the momenta reach their asymptotic values. Newton plots and KER distributions are computed from these asymptotic momenta. The methodology is described and adapted from Ref. [35].

Initial geometries and binding potentials. Preprobe structures represent the JT-distorted classes inferred from the experiment. For region 1 (symmetric pathway), coordinates are sampled around a C_{2v} configuration with an H-H paired fragment (H_2 -like). For region 2 (asymmetric pathway), coordinates are sampled around a C_{3v} bond-selective elongation (one elongated C-H bond, three shorter bonds). For prompt

breakup (regions 3 and 4), initial coordinates correspond to a tetrahedral T_d geometry. In all cases, bond lengths and angles are drawn from Gaussian distributions around the ideal structures, with widths chosen to reproduce the observed Newton-plot topology and KER bandwidth.

To prevent unphysical divergence of neutral fragments before the probe, short-range binding is included up to time τ and switched off at the charge switch. For region 1, the H-H pair is bound by a Morse potential (H_2 -like). For region 2,

the CH_2 -H interaction is modeled by a Lennard-Jones potential. For regions 3 and 4, no prepulse binding is included. Initial velocities are sampled from Gaussian distributions constrained by single-pulse reference measurements.

In this model, when we start region 1 with C_{2v} -type H_2 and region 2 with C_{3v} -type bond-selective elongation, the simulated Newton plots show the same main features as the experiment. If we do not include these geometry constraints, the simulations fail to reproduce the observed patterns.

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