

Imaging photoinduced isomerization in triply ionized acetonitrile

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Isomerization is a fundamental process usually initiated in molecules via photoionization. Using intense femtosecond IR laser pulses, in combination with coincident Coulomb explosion imaging, we are able to reconstruct the structure of the acetonitrile tri-cation after it undergoes isomerization and prior to fragmentation. Using momentum imaging, the Newton diagrams in tandem with native frame analysis reveal the signature of a triangular geometry. This indicates that upon photoionization to a triply ionized state, acetonitrile undergoes a clear structural change from its linear canonical form along with hydrogen migration. We further corroborate this with the aid of quantum chemistry calculations, which allow us to fully resolve this unique isomerization process. Understanding the underlying mechanisms behind such complex processes is relevant to biology and industrial applications.

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I. INTRODUCTION

Photoinduced molecular isomerization is the transformation of a molecule following photon absorption into a structural isomer that retains the same molecular formula but differs in atomic connectivity, frequently yielding altered chemical properties. Thus, photoinduced isomerization plays a crucial role in numerous chemical reactions [1–6] and facilitates structural rearrangements that precede or compete with fragmentation, ionization, and new bond formation. Upon photoionization, breakage of the chemical bonds yields a strong repulsive interaction of the positively charged molecular fragments, causing a Coulombic explosion of the molecule. These Coulomb explosions do not always occur directly, and atomic reorganization can occur prior to molecular dissociation. These rearrangement processes enable important biological functions, such as vision [1,7–9] or vitamin D formation [2,3], or in the case of the movement of hydrogen atoms within the molecule, determining protein structure [10].

Among small organic molecules, acetonitrile is a particularly interesting system. Acetonitrile is the simplest organic

nitrile molecule, containing a cyano group ($-\text{C} \equiv \text{N}$) bonded to a methyl group ($-\text{CH}_3$). It exhibits a range of photodissociation pathways, from isomerization processes [11] to roaming of neutral species where the molecule follows flat regions of the potential energy surface rather than the minimum energy pathway to form new products [12]. The present study is motivated by prior joint experimental and theoretical works on singly and doubly ionized acetonitrile (CH_3CN^+ and $\text{CH}_3\text{CN}^{2+}$) that focused on hydrogen migration [11] and more complex isomerization processes [13]. In those works, dominant isomerization pathways through which the acetonitrile ion fragments, leading to much higher yields compared to direct breakup through the C–C bond, were observed. Theoretical calculations revealed single and double H-migration pathways, a surprising linear structure in which the N and C atoms swap positions, as well as transient cyclic structures.

In this work, we directly image the structural dynamics of triply ionized deuterated acetonitrile ($\text{CD}_3\text{CN}^{3+}$) to provide evidence of isomerization processes that transform the linear molecule to one with a triangular signature.

The transformation from the canonical geometry (CH_3CN) to a cyclic, an angular, or even a linear structure involving a change in the relative position of the C and N atoms (CH_2NCH) is driven by the coexistence of several isomeric minima with comparable stability and by the low-energy barriers on the potential energy surface that connect them. A schematic of this process is shown in Fig. 1. These isomerization processes have already been explored theoretically in the context of doubly charged acetonitrile ($\text{H}_3\text{C}-\text{C} \equiv \text{N}^{2+}$) and supported experimentally using pump-probe spectroscopy [13]. In this present complementary work, we instead focus on time-independent data where the molecule is triply

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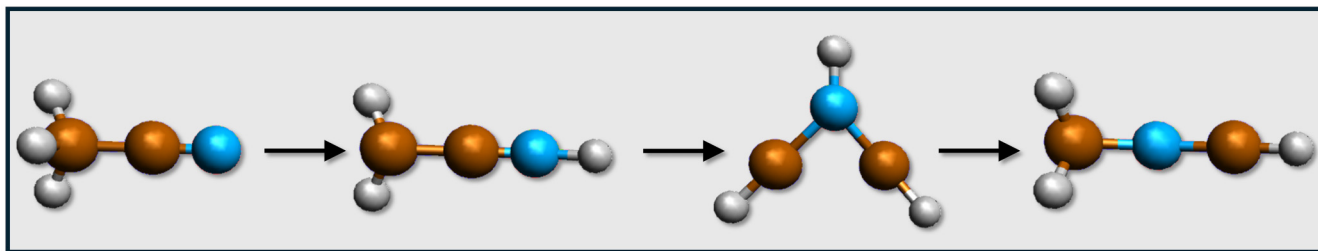


FIG. 1. Schematic representation of the isomerization process in triply ionized acetonitrile studied in this work. Starting from the canonical structure $\text{CD}_3\text{-C}\equiv\text{N}$, hydrogen/deuterium migration $\text{CD}_2\text{-C}\equiv\text{ND}$, cyclization $\text{CD}\equiv\text{ND-CD}$, and finally formation of the isonitrile form $\text{CD}_2\text{-N}\equiv\text{CD}$ are considered.

ionized by a single laser pulse alone without a secondary probe pulse interaction. The data generated from a single-step ionization process ensure that the molecular structure at the point of ionization is preserved for Coulomb explosion imaging, allowing us to directly resolve the triangular molecular geometry of transient isomers in triply charged acetonitrile ($\text{H}_3\text{C-C}\equiv\text{N}^{3+}$) through three-ion coincidence detection. Our experimental findings are supported with new calculations for $\text{H}_3\text{C-C}\equiv\text{N}^{3+}$.

Our experimental approach combines coincident momentum spectroscopy with Coulomb explosion imaging (CEI) for a comprehensive understanding of photoinduced changes in molecular geometry. Coulomb explosion imaging involves the rapid removal of electrons from the molecule, thereby triggering an explosion of the ions due to Coulomb repulsion. Subsequent reconstruction of the momentum information of the ion fragments enables an accurate mapping of the instantaneous molecular structure. This method has been effectively used to image complex femtochemistry dynamics within a single molecule [14–22]. The momenta of the ionic fragments formed as a result of laser-molecule interaction are measured in coincidence using the cold-target recoil-ion momentum spectrometer (COLTRIMS) technique [23–25]. By selecting ion fragments detected in coincidence that collectively account for all atoms in the parent molecule, we obtain kinematically complete information for each fragmentation process. This technique is powerful to allow for the observation of weak processes like in the case of H_2 neutral roaming [12]. Our findings are complemented with new quantum chemistry calculations that explore the potential energy surface of the triply ionized acetonitrile, identifying isomers and pathways connecting them. We utilize Newton diagrams and native frame analysis to uncover the experimental signature of nonlinear acetonitrile structures.

II. METHOD

A. Experimental details

The experimental setup has been previously described elsewhere [11–13,26–28]. We used a 5-kHz Ti:sapphire laser producing 35-fs pulses with a central wavelength of 790 nm. The laser beam was split into two independent arms which were time-delayed with respect to one another. For this experiment, the intensities were in the range of 10^{14} W/cm² for both the pump and probe arms. The intensity of the single-pulse measurements were matched to the pump arm. The two beams

were directed into the interaction region where they were overlapped and back focused to a spot size of about 10 μm . Both beams were linearly polarized in the direction of the time-of-flight axis of the spectrometer. Approximately 10 ml of liquid deuterated acetonitrile sample was put in a stainless-steel gas bubbler. A cold, molecular gas jet of this sample was produced by expansion through a 30- μm nozzle seeded with 1 bar of helium gas and propagated into the spectrometer perpendicular to the laser pulses. Deuterated acetonitrile was ionized and resulting charged fragments were detected by a COLTRIMS [23–25]. Using a fully deuterated sample allows better separation between channels in the photoion-photoion-photoion coincidence (PIPIPICO) maps. Using a homogeneous electric field in the range of 60 V/cm, the ions were directed towards a position-sensitive detector, which is capable of measuring the three-dimensional momentum distributions of the charged particles. For CEI, we are focused on measuring the fragmented ions, and for the present experimental conditions, we have an ion momentum resolution of 0.1 a.u. By applying the coincidence technique, we can isolate specific ion coincidence channels of acetonitrile and gain the most relevant information about the fragmentation dynamics.

B. Computational details

Quantum chemistry calculations were carried out using the GAUSSIAN 16 package [29] and in the framework of density-functional theory. We use the B3LYP [30–33] functional in combination with the 6-31++G(d,p) basis set [34–36], a split-valence double-zeta basis set that includes diffuse and polarization functions centered on heavy atoms (C and N) and hydrogen. We performed an exhaustive exploration of the potential energy surface of the triply ionized molecule with doublet spin multiplicity. The relevant points located on the potential energy surface, i.e., minima and transition states, were characterized by computing the harmonic vibrational frequencies. The number of imaginary frequencies indicates the nature of the point: For minima, all frequencies are real, while transition states exhibit one imaginary frequency, indicating a first-order saddle point on the potential energy surface. This imaginary frequency represents the motion along the reaction coordinate, where atomic rearrangements involving bond cleavage or formation occur. We checked the validity of the computed transition states by an intrinsic reaction coordinate (IRC) calculation. An IRC traces the minimum energy path from the transition state, thus

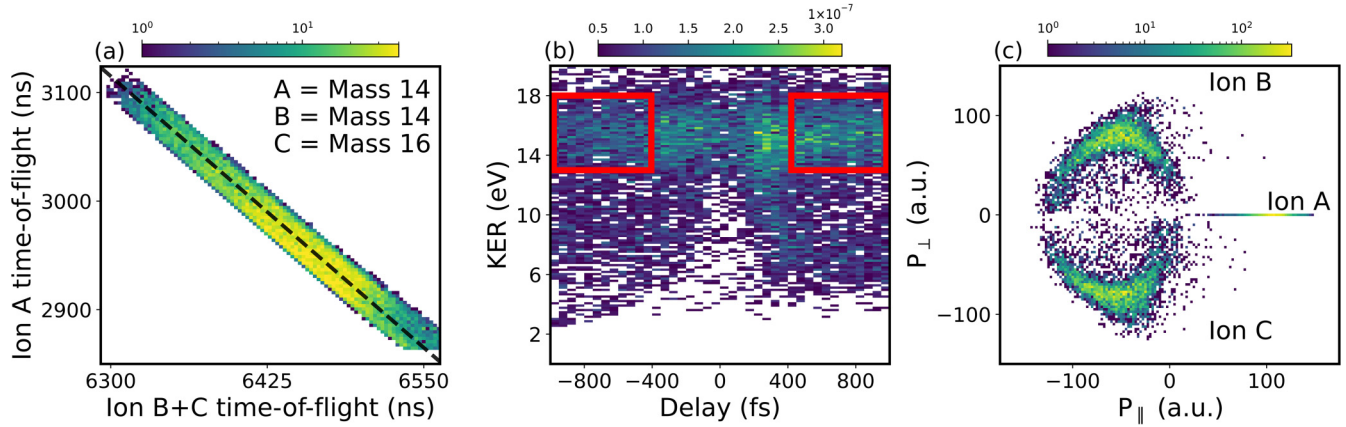


FIG. 2. (a) Photoion-photoion-photoion coincidence channel for the dissociation of triply ionized deuterated acetonitrile taken using a pump-probe spectroscopy laser arrangement. The channel of ion fragments with mass-to-charge ratios m/q of 14, 14, and 16 is shown. Two sets of mass fragments satisfy the coincident m/q criteria: (i) $\text{CD}^+ + \text{CD}^+ + \text{ND}^+$ and (ii) $\text{CD}^+ + \text{N}^+ + \text{CD}_2^+$. For clarity, the first mass 14 is labeled as ion A, the second mass 14 as ion B, and mass 16 as ion C. The channel is isolated by applying momentum conservation conditions on the mass fragments. A black dashed line of slope -1 is overlaid on the PIPICO channel to show agreement with the expected slope of a kinematically complete channel. (b) Kinetic energy release versus pump-probe delay for the channel of interest. Only the fragmentation events with KER between 13 and 17 eV and delay outside the region between -400 and 400 fs (red boxes) were considered for analysis. (c) Newton diagram for the channel of mass fragments 14 (ion A), 14 (ion B), and 16 (ion C) for kinetic energy release between 13 and 17 eV, as indicated by the highlighted region in (b). The momentum vector of ion A is plotted on the x axis, while those of ion B and ion C are plotted on the top and bottom halves, respectively. The semicircular structure indicates sequential dissociation, while concentrated intensity indicates concerted dissociation.

confirming that it connects to the correct reactants and products on the potential energy surface.

III. RESULTS AND DISCUSSION

In order to investigate the structural change in deuterated acetonitrile (CD_3CN) upon laser ionization, we investigate the triple-ion coincidence maps and isolate a complete three-body coincidence channel with mass-to-charge ratios m/q of $14 + 14 + 16$, as highlighted in Fig. 2(a). There are two possible combinations of mass fragments that satisfy the coincident m/q criteria: (i) $\text{CD}^+ + \text{CD}^+ + \text{ND}^+$ and (ii) $\text{CD}^+ + \text{N}^+ + \text{CD}_2^+$. The time-of-flight of the first detected mass fragment is plotted on the y axis, whereas the sum of the second and third fragments is plotted on the x axis. The ion coincidence line is a result of momentum conservation among the three ions [37]. With our experimental technique, it is not possible to uniquely identify between these two channels because they have identical m/q ratios. To distinguish between the different masses, the first mass 14 is labeled as ion A, the second mass 14 as ion B, and mass 16 as ion C. Using a COLTRIMS, we can reconstruct the initial three-dimensional momentum vector of each ion. The recoil momenta of the ionic fragments describe the molecular geometry at the time of ionization, as they arise from Coulombic repulsion between charges localized near the atomic positions. Using these momentum vectors, we can calculate the total kinetic energy release (KER) as a function of pump-probe delay for this fragmentation channel, as shown in Fig. 2(b). The KER map has two sets of features: a flat static band that has a constant KER for all delays and dynamic bands that decrease in energy for increasing delay. In this work, we isolate the static band by selecting events with KER between 13 and 17 eV in order to

focus on the three-body breakup events that are solely initiated through direct triple ionization by a single pulse. Within this KER range, we exclude the delay region between -400 and 400 fs to remove any contributions from overlapping static and dynamic features, as indicated by the red boxes in Fig. 2(b). The time-dependent features of this KER map, which reflect the dynamics of the doubly charged isonitrile ions, have been examined previously [13]. Additionally, multiple momentum conservation conditions were explored to best isolate this coincidence channel. This does result in small reductions of the background signal, particularly in the dynamic bands, but yields only minor changes to the selected regions of the KER map.

Newton diagrams offer an intuitive means of visualizing the momentum correlations among multibody ion fragments [14,15,20,22,38]. They are useful tools that provide direct structural information about a fragmentation process and can also help distinguish between concerted and sequential fragmentation processes. In general, concerted fragmentation processes appear as a localized distribution in a Newton diagram [14,39], reflecting the rapid breakup of chemical bonds, and the molecular geometry at the moment of fragmentation is largely preserved. However, sequential fragmentation results in a semicircular ringlike distribution due to the rotation of the intermediate fragment relative to the initial ion dissociation [14,22,40]. Figure 2(c) shows the Newton plot for our channel of interest after applying the restrictions based on the KER map in Fig. 2(b). The momentum vector of the first detected mass 14 is fixed on the x axis, whereas those of the second mass 14 and mass 16 are plotted relative to the x axis on the top and bottom halves, respectively.

The Newton diagram of a three-body dissociation is forced to lie in the two-dimensional plane due to conservation of

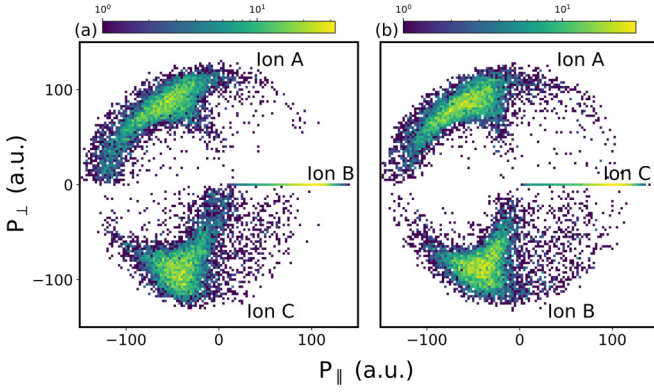


FIG. 3. Newton diagrams of additional orientations from Fig. 2(c). (a) Momentum vector of ion *B* fixed on the horizontal axis with ions *A* and *C* on the top and bottom, respectively. (b) Ion *C* fixed on the horizontal axis with ions *A* and *B* on the top and bottom, respectively. The Newton diagram orientation in Fig. 2(c) was chosen for further analysis as ion *A* dissociates first, which leads to an easier distinction between sequential and concerted events.

momentum among the three fragments. All orientations for the Newton diagram are shown in Fig. 3.

While Newton diagrams can in principle allow for the identification of sequential and concerted fragmentation processes, for an unambiguous analysis of the dynamics, it is crucial to properly separate the signals arising from these two types of processes. In order to do this, we implement the native frame analysis technique [15,41–44]. In this approach, each fragmentation step in a sequential breakup process is analyzed in its respective center-of-mass reference frame using the conjugate momenta calculated from the Jacobi coordinates associated with each step [45–49]. Specifically, for a three-body sequential breakup, we observe a uniform angular distribution between two conjugate momenta due to the rotation of the intermediate molecule in the fragmentation plane with a lifetime longer than its rotation period. This approach has been successfully applied in previous works to distinguish between concerted and sequential fragmentation processes [15,41–44].

The native frame analysis for the channel of interest is shown in Fig. 4(a). The angle between the conjugate momenta for ion *A* and intermediate ion *BC*, $\theta_{BC,A}$, is plotted against the kinetic energy of the intermediate, KER_{BC} . This angle is further defined in the schematic of conjugate momenta vectors in Fig. 4(b). In order to image the molecular structure, we remove sequential contributions by applying boundaries of 60° – 150° to $\theta_{BC,A}$ and 4–15 eV on KER_{BC} . Using this condition, we plot the Newton diagram as shown in Fig. 4(c). The angular distributions between the momentum vectors of each ion fragment are plotted in Fig. 4(d). The intensity-weighted average of these distributions are used to identify the vertices for the overlaid triangle on the Newton diagram in Fig. 4(c). The restricted Newton diagram exhibits a triangular distribution and a significant reduction in its semicircular structure. This indicates that upon photoionization, the linear C–C–N acetonitrile skeleton undergoes isomerization involving not only hydrogen migration, but also a bending or reordering of the C–C–N backbone. Some broadening remains, however,

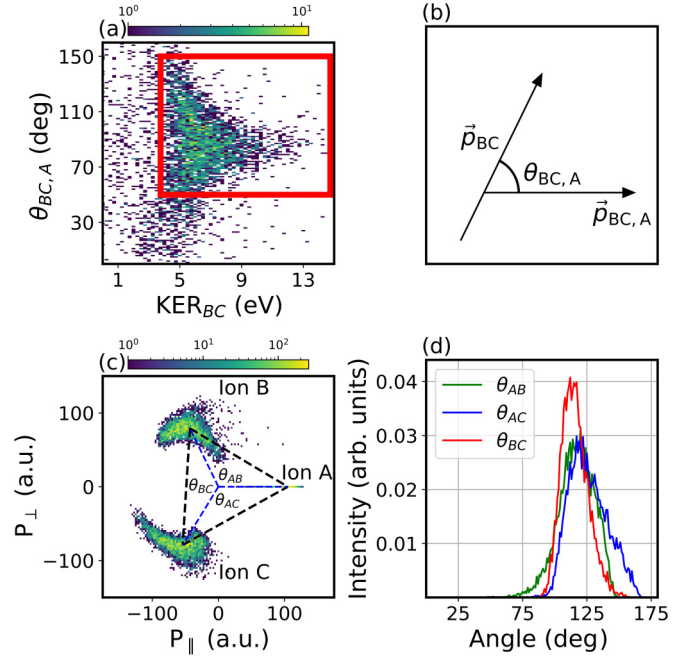


FIG. 4. (a) Native frame diagram used to differentiate concerted and sequential fragmentation. The angle between ion *A* and the intermediate ion *BC* is plotted against the kinetic energy carried by the intermediate. The ranges 60° – 150° for this angle and 4–15 eV on the intermediate energy KER_{BC} are applied to remove sequential ionization contributions in order to directly image the molecular structure. Here 15 eV is used as an upper bound as there are no counts beyond this range. (b) Schematic of the relationship between conjugate momentum vectors used to determine $\theta_{BC,A}$ and KER_{BC} . (c) Replot of the Newton diagram shown in Fig. 2(c) after gating on the chosen native frame range. (d) The angular distribution between the different ion fragments plotted and the intensity-weighted average of the distributions is used to identify vertices of the triangular structure in (c).

due to residual sequential contributions at low KER_{BC} , where sequential and concerted fragmentation pathways overlap. Additional analysis of this native frame isolating the sequential process is shown in Fig. 5.

We observe that the dissociation angles for ions *A-B*, *A-C*, and *B-C* are very similar, with distributions peaking near 110° – 120° and widths of approximately 20° – 30° . The very low formation probability of this channel made dynamical calculations computationally unfeasible since an impractically large number of trajectories would be required to observe this dissociation channel in the triply charged species and due to the high cost of these simulations. In the absence of such calculations, we can only speculate on the origins of this angular behavior. Given the variety of molecular geometries capable of producing a triangular Newton signature (see the potential energy surface discussed below), some broadening in both the Newton diagrams and the corresponding angular distributions is expected. Note that the two fragmentation pathways contributing to the $14 + 14 + 16$ mass channel differ only in the bonding of the deuterium atoms ($CD^+ + CD^+ + ND^+$ and $CD^+ + N^+ + CD_2^+$), while involving the same distribution of heavy atoms (C, C, and N), such that their combined contribu-

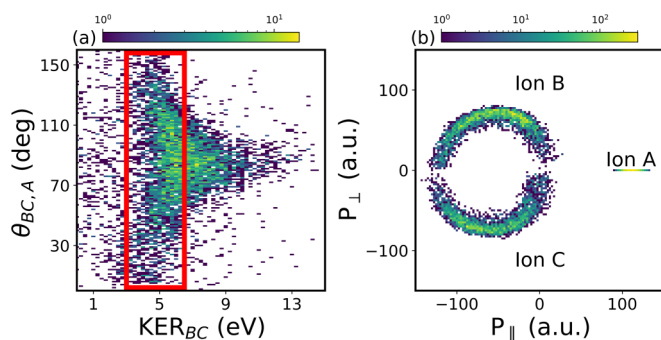


FIG. 5. Isolating sequential events using native frame analysis. (a) Native frame of the pump-probe measurements shown in Fig. 4(a) with the KER_{BC} range of 3–6 eV for all angles highlighted. This range is applied to the Newton diagram in Fig. 2(c) and replotted in (b) to elucidate the semicircular structure resulting from sequential ionization.

tion does not alter the structural interpretation of the Newton diagram.

While the analysis presented focuses on data taken using a pump-probe laser arrangement, the same PIPICO map and channel can be observed using a single-laser-pulse arrangement by matching the pulse intensity to the pump pulse. This was performed to confirm that a single pulse was sufficient to form $DACN^{3+}$. The results of this analysis are summarized in Figs. 6 and 7. While some differences are observed relative to the data taken with a pump-probe setup, namely, the kinetic energy of the intermediate ion BC , the similar triangular dissociation distributions are revealed after applying native frame filtering. The pump-probe data were utilized for this study due to significantly higher statistics relative to the single-pulse data.

We have performed quantum chemistry calculations to infer the mechanisms behind the formation of nonlinear structures. We carried out a thorough exploration of the potential

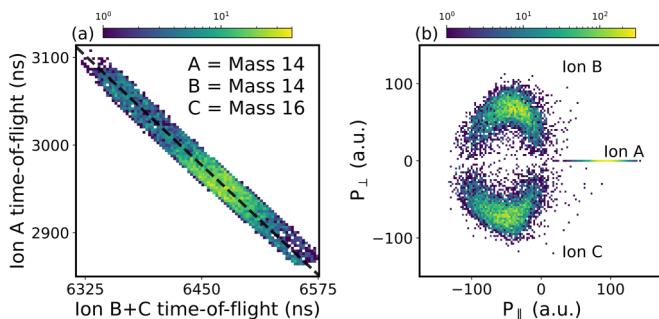


FIG. 6. (a) PIPICO channel for the dissociation of triply ionized deuterated acetonitrile taken using a single laser pulse arrangement whose intensity is matched to the pump pulse of the pump-probe data. The channel of ion fragments with mass-to-charge ratios m/q of 14, 14, and 16 is shown. (b) Newton diagram for the channel of interest. The momentum vector of ion A is plotted on the x axis, while those of ion B and ion C are plotted on the top and bottom halves, respectively. The semicircular structure indicates sequential dissociation, while concentrated intensity indicates concerted dissociation.

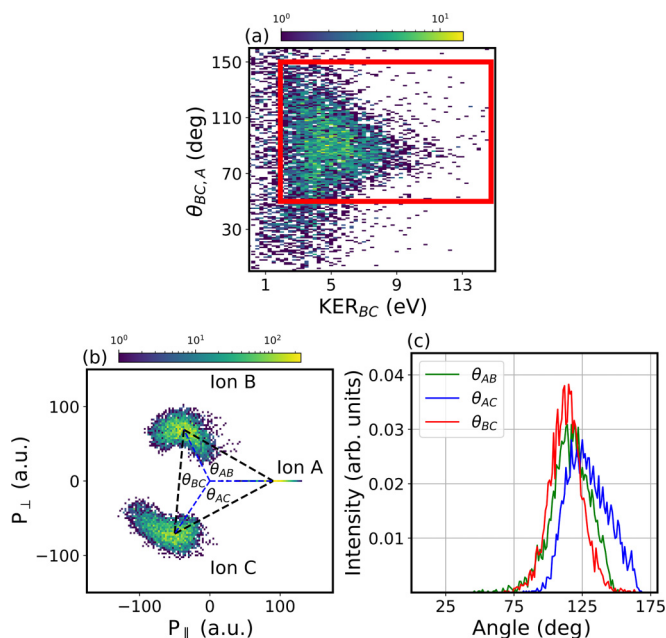


FIG. 7. (a) Native frame diagram used to differentiate concerted and sequential fragmentation. The angle between ion A and the intermediate ion BC is plotted against the kinetic energy carried by the intermediate. The ranges 60° – 150° for $\theta_{BC,A}$ and 2–15 eV on KER_{BC} are applied to isolate concerted fragmentation events. (b) Replot of the Newton diagram shown in Fig. 6(b) after gating on the chosen native frame ranges. (c) Angular distribution between the different ion fragments. The intensity-weighted average of the distributions is used to identify vertices of the triangular structure in (b).

energy surface as shown in Fig. 8. The entrance channel is the triply ionized acetonitrile molecule (ACN^{3+}). We assume that ionization occurs in the Franck-Condon region, i.e., keeping the geometry of the neutral molecule in its ground state. From this structure, relaxation through hydrogen migration appears as a first step, stabilizing the system in approximately 5 eV and giving rise to structure A1. Further isomerization processes occur and several stable structures, i.e., minima in the potential energy surface, are found. L1 and L2 are linear structures, and C1 is a cyclic structure. All three structures are similar to those observed in the doubly ionized case [13]. A1, A2, A3, A4 and A5 are angular structures, showing a relatively open angle formed by the three heavy atoms, $C-C-N$ or $C-N-C$; A5 presents a geometry rather similar to that of C2 in the doubly ionized isonitrile [13].

Interestingly, it is a very flat potential energy surface, where all minima are accessible through very small energy barriers and mainly about 8 eV below the entrance channel. Note that hydrogen migration, the dominant isomerization process, is very rapid, as observed in previous works [12,26,27,50–52], typically occurring in less than approximately 10 fs. The barrier connecting A2 with C1 is responsible for the structural flipping of CCN to CNC, the so-called nitrile-isonitrile isomerization, changing the position of the N atom to the center of the molecular skeleton. This process shows a very low-energy barrier. Thus, reaching the cyclic

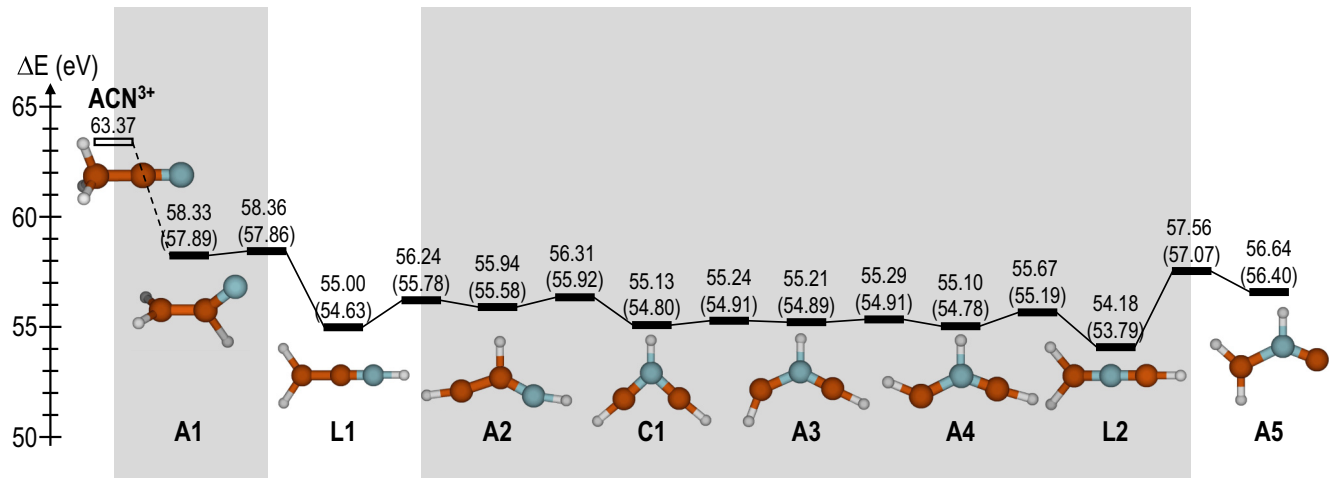


FIG. 8. Exploration of the potential energy surface of triply ionized acetonitrile with doublet spin multiplicity computed at the B3LYP/6-31 + +G(*d*, *p*) level of theory. The open box corresponds to the triple ionization from the acetonitrile neutral molecule in its ground state. Filled boxes are critical points in the potential energy surface: Minima and transition states connecting them are shown. The geometry of each minimum is given with the following color code: H atoms in white, C atoms in brown, and N atoms in blue. The numbers at each point of the potential energy surface correspond to the relative energy ΔE (in eV), referring to neutral acetonitrile (ACN); in parentheses, ΔE has been corrected with the zero-point energy, and without parentheses, ΔE has been computed directly using the electronic energy. The shaded region corresponds to those structures where direct C–C and C–N bond cleavage leads to the triple coincidences of the channel of interest $[\text{CH}^+/\text{CH}^+/\text{NH}^+]$ or $[\text{N}^+/\text{CH}_2^+/\text{CH}^+]$. Structure C1 is labeled cyclic for consistency with the nomenclature in Ref. [13], despite the absence of a fully bonded ring.

structure C1 implies several structural modifications, but it is energetically accessible. Furthermore, cyclization in ionized acetonitrile is a very rapid process, occurring in approximately 30 fs, as we have recently demonstrated for the doubly charged species [13].

The shaded area in the figure corresponds to those structures where direct C–C or C–N cleavage leads to the triple coincidence of the channel of interest $[\text{CH}^+/\text{CH}^+/\text{NH}^+]$ or $[\text{N}^+/\text{CH}_2^+/\text{CH}^+]$. In these isomers, the angle between the heavy atoms, $\widehat{\text{C}-\text{C}-\text{N}}$ and $\widehat{\text{C}-\text{N}-\text{C}}$, varies between approximately 90° (structure C1) and 180° (structure L2); in structure A1, the angle is approximately 140° and in A2 approximately 132° . With this variety of angles and having shown that the potential energy surface is quite flat, one can deduce that after ionization all the minima are accessible, and when it explodes Coulombically, the trend to separate the three charges will lead to a triangular distribution.

Within the assumptions of direct bond-cleavage fragmentation and in the absence of hydrogen migration, structures A1, A2, A3, A4, and C1 are identified as the most likely candidates to explain the experimental measurements discussed above.

This is possible because the potential energy surface is quite flat, with isomerization barriers barely reaching 1 eV in most cases, and the system has at least 8 eV available, so that all structures associated with the minima can be easily reached. Such a molecular rearrangement is necessary to accommodate the three positive charges, which favors the formation of nonlinear structures.

Therefore, the distribution of the experimentally observed fragments is most consistently explained by triangular or quasitriangular structures, such as A1, A2, A3, A4, or C1, thus supporting the occurrence of ultrafast isomerization follow-

ing triple ionization of acetonitrile. Given the proximity in energy of several isomeric minima on the potential energy surface, the measured angular distributions are most naturally explained by contributions from an ensemble of bent structures, rather than by a unique static structure. Furthermore, simple classical calculations of the Coulomb explosion of the A1, A2, A3, A4, and C1 structures starting from the geometry associated with their corresponding local minima (see Fig. 8), in which each heavy atom has an initial charge of +1, show the appearance of perfectly distinguishable triangular patterns in the Newton plots.

IV. CONCLUSION

We have successfully imaged directly the photoinduced isomerization of triply ionized acetonitrile from a linear to a triangular structure. We took measurements exploiting and pushing the limits of ion-ion-ion coincidence spectroscopy. The results were examined using a combination of Newton diagrams in conjunction with native frame analysis, which enabled us to isolate and study the concerted fragmentation of the molecule. This approach revealed evidence for a triangular geometry suggestive of several isomers in acetonitrile which had previously been proposed but never directly observed. We complemented our experimental findings with quantum chemistry calculations, allowing us to simulate the original structure and differentiate between genuine isomerization involving bond formation and the mere bending of the linear geometry. A wide variety of isomers were found, all of them energetically accessible through hydrogen migration and cyclization processes and connected by very low potential energy barriers. Our comprehensive approach has provided insights into this transformative process, shedding light on

the intricate dynamics of acetonitrile isomerization. It is our hope that this work will stimulate further studies aimed at resolving the intermediate structures that facilitate molecular isomerization.

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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.

- [1] R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, and C. V. Shank, The first step in vision: Femtosecond isomerization of rhodopsin, *Science* **254**, 412 (1991).
- [2] T. J. A. Wolf, D. M. Sanchez, J. Yang, R. M. Parrish, J. P. F. Nunes, M. Centurion, R. Coffee, J. P. Cryan, M. Gühr, K. Hegazy, A. Kirrander, R. K. Li, J. Ruddock, X. Shen, T. Vechionne, S. P. Weathersby, P. M. Weber, K. Wilkin, H. Yong, Q. Zheng, *et al.*, The photochemical ring-opening of 1,3-cyclohexadiene imaged by ultrafast electron diffraction, *Nat. Chem.* **11**, 504 (2019).
- [3] S. Deb and P. M. Weber, The ultrafast pathway of photon-induced electrocyclic ring-opening reactions: The case of 1,3-cyclohexadiene, *Annu. Rev. Phys. Chem.* **62**, 19 (2011).
- [4] M. Ni, D. Y. Leung, and M. K. Leung, A review on reforming bio-ethanol for hydrogen production, *Int. J. Hydrogen Energy* **32**, 3238 (2007).
- [5] A. R. Ledvina, G. C. McAlister, M. W. Gardener, S. I. Smith, J. A. Madsen, J. C. Schwartz, G. C. Stafford, Jr., J. E. Syka, J. S. Brodbelt, and J. J. Coon, Infrared photo-activation reduces peptide folding and hydrogen atom migration following ETD tandem mass spectrometry, *Angew. Chem. Int. Ed. Engl.* **48**, 8526 (2009).
- [6] S. Sharma, S. Raman, and W. H. Green, Intramolecular hydrogen migration in alkylperoxy and hydroperoxyalkylperoxy radicals: Accurate treatment of hindered rotors, *J. Phys. Chem. A* **114**, 5689 (2010).
- [7] G. Hayward, W. Carlsen, A. Siegman, and L. Stryer, Retinal chromophore of rhodopsin photoisomerizes within picoseconds, *Science* **211**, 942 (1981).
- [8] G. Wald, Molecular basis of visual excitation, *Science* **162**, 230 (1968).
- [9] M. Kono, P. W. Goletz, and R. K. Crouch, 11-*cis*- and all-*trans*-retinols can activate rod opsin: Rational design of the visual cycle, *Biochemistry* **47**, 7567 (2008).
- [10] S. W. Englander and M. M. Krishna, Hydrogen exchange, *Nat. Struct. Biol.* **8**, 741 (2001).
- [11] M. McDonnell, A. C. LaForge, J. Reino-González, M. Disla, N. G. Kling, D. Mishra, R. Obaid, M. Sundberg, V. Svoboda, S. Díaz-Tendero, *et al.*, Ultrafast laser-induced isomerization dynamics in acetonitrile, *J. Phys. Chem. Lett.* **11**, 6724 (2020).
- [12] D. Mishra, A. C. LaForge, L. M. Gorman, S. Díaz-Tendero, F. Martín, and N. Berrah, Direct tracking of H₂ roaming reaction in real time, *Nat. Commun.* **15**, 6656 (2024).
- [13] S. Díaz-Tendero, N. Frese, D. Mishra, A. C. LaForge, N. Berrah, and F. Martín, Ultrafast transient cyclization of doubly charged acetonitrile, *Phys. Rev. Lett.* **136**, 048002 (2026).
- [14] S. Bhattacharyya, K. Borne, F. Ziaee, S. Pathak, E. Wang, A. S. Venkatachalam, X. Li, N. Marshall, K. D. Carnes, C. W. Fehrenbach, *et al.*, Strong-field-induced Coulomb explosion imaging of tribromomethane, *J. Phys. Chem. Lett.* **13**, 5845 (2022).
- [15] S. Pathak, R. Obaid, S. Bhattacharyya, J. Bürger, X. Li, J. Tross, T. Severt, B. Davis, R. C. Bilodeau, C. A. Trallero-Herrero, A. Rudenko, N. Berrah, and D. Rolles, Differentiating and quantifying gas-phase conformational isomers using Coulomb explosion imaging, *J. Phys. Chem. Lett.* **11**, 10205 (2020).
- [16] X. Li, X. Yu, P. Ma, X. Zhao, C. Wang, S. Luo, and D. Ding, Ultrafast Coulomb explosion imaging of molecules and molecular clusters, *Chin. Phys. B* **31**, 103304 (2022).
- [17] X. Li, A. Rudenko, M. S. Schöffler, N. Anders, T. M. Baumann, S. Eckart, B. Erk, A. De Fanis, K. Fehre, R. Dörner, *et al.*, Coulomb explosion imaging of small polyatomic molecules with ultrashort x-ray pulses, *Phys. Rev. Res.* **4**, 013029 (2022).
- [18] M. Pitzer, G. Kastirke, M. Kunitski, T. Jahnke, T. Bauer, C. Goihl, F. Trinter, C. Schober, K. Henrichs, J. Becht, *et al.*, Absolute configuration from different multifragmentation pathways in light-induced Coulomb explosion imaging, *ChemPhysChem* **17**, 2465 (2016).
- [19] H. Hasegawa, A. Hishikawa, and K. Yamanouchi, Coincidence imaging of Coulomb explosion of Cs₂ in intense laser fields, *Chem. Phys. Lett.* **349**, 57 (2001).
- [20] T. Jahnke, S. Mai, S. Bhattacharyya, K. Chen, R. Boll, M. E. Castellani, S. Dold, U. Frühling, A. E. Green, M. Ilchen, *et al.*, Direct observation of ultrafast symmetry reduction during internal conversion of 2-thiouracil using Coulomb explosion imaging, *Nat. Commun.* **16**, 2074 (2025).
- [21] S. Chelkowski, P. B. Corkum, and A. D. Bandrauk, Femtosecond Coulomb explosion imaging of vibrational wave functions, *Phys. Rev. Lett.* **82**, 3416 (1999).
- [22] N. Neumann, D. Hant, L. P. H. Schmidt, J. Titze, T. Jahnke, A. Czasch, M. S. Schöffler, K. Kreidi, O. Jagutzki, H. Schmidt-Böcking, and R. Dörner, Fragmentation dynamics of Co₂³⁺

- investigated by multiple electron capture in collisions with slow highly charged ions, *Phys. Rev. Lett.* **104**, 103201 (2010).
- [23] J. Ullrich, R. Moshhammer, R. Dörner, O. Jagutzki, V. Mergel, H. Schmidt-Böcking, and L. Spielberger, Recoil-ion momentum spectroscopy, *J. Phys. B* **30**, 2917 (1997).
- [24] J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. P. H. Schmidt, and H. Schmidt-Böcking, Recoil-ion and electron momentum spectroscopy: Reaction-microscopes, *Rep. Prog. Phys.* **66**, 1463 (2003).
- [25] R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, J. Ullrich, R. Moshhammer, and H. Schmidt-Böcking, Cold target recoil ion momentum spectroscopy: A ‘momentum microscope’ to view atomic collision dynamics, *Phys. Rep.* **330**, 95 (2000).
- [26] N. G. Kling, S. Díaz-Tendero, R. Obaid, M. Disla, H. Xiong, M. Sundberg, S. Khosravi, M. Davino, P. Drach, A. Carroll, *et al.*, Time-resolved molecular dynamics of single and double hydrogen migration in ethanol, *Nat. Commun.* **10**, 2813 (2019).
- [27] D. Mishra, J. Reino-González, R. Obaid, A. C. LaForge, S. Díaz-Tendero, F. Martín, and N. Berrah, Ultrafast molecular dynamics in ionized 1- and 2-propanol: From simple fragmentation to complex isomerization and roaming mechanisms, *Phys. Chem. Chem. Phys.* **24**, 433 (2021).
- [28] N. Frese, D. Mishra, C. Bray, C. Brady, A. C. LaForge, A. R. Rossi, J. A. Gascón, and N. Berrah, Photodissociation pathways of methanol: Dissociation, roaming, and migration, *J. Phys. Chem. Lett.* **16**, 11324 (2025).
- [29] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, *et al.*, GAUSSIAN 16, Gaussian, Inc., Wallingford, 2016, revision C.01.
- [30] S. H. Vosko, L. Wilk, and M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis, *Can. J. Phys.* **58**, 1200 (1980).
- [31] C. Lee, W. Yang, and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* **37**, 785 (1988).
- [32] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* **98**, 5648 (1993).
- [33] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *Ab initio* calculation of vibrational absorption and circular dichroism spectra using density functional force fields, *J. Phys. Chem.* **98**, 11623 (1994).
- [34] W. J. Hehre, R. Ditchfield, and J. A. Pople, Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules, *J. Chem. Phys.* **56**, 2257 (1972).
- [35] P. C. Hariharan and J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chim. Acta* **28**, 213 (1973).
- [36] T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. V. R. Schleyer, Efficient diffuse function-augmented basis sets for anion calculations. III. the 3-21+G basis set for first-row elements, Li–F, *J. Comput. Chem.* **4**, 294 (1983).
- [37] J. Eland, Dynamics of fragmentation reactions from peak shapes in multiparticle coincidence experiments, *Laser Chem.* **11**, 259 (1991).
- [38] R. Boll, J. M. Schäfer, B. Richard, K. Fehre, G. Kastirke, Z. Jurek, M. S. Schöffler, M. M. Abdullah, N. Anders, T. M. Baumann, *et al.*, X-ray multiphoton-induced Coulomb explosion images complex single molecules, *Nat. Phys.* **18**, 423 (2022).
- [39] X. Xie, C. Wu, Y. Yuan, X.-Z. Li, C. Wu, P. Wang, Y. Deng, Y. Liu, and Q. Gong, Structural determination of argon trimer, *AIP Adv.* **5**, 097213 (2015).
- [40] X. Ding, M. Haertelt, S. Schlauderer, M. S. Schuurman, A. Y. Naumov, D. M. Villeneuve, A. R. W. McKellar, P. B. Corkum, and A. Staudte, Ultrafast dissociation of metastable Co_2^+ in a dimer, *Phys. Rev. Lett.* **118**, 153001 (2017).
- [41] J. Rajput, T. Severt, B. Berry, B. Jochim, P. Feizollah, B. Kaderiya, M. Zohrabi, U. Ablikim, F. Ziaee, K. Raju P., *et al.*, Native frames: Disentangling sequential from concerted three-body fragmentation, *Phys. Rev. Lett.* **120**, 103001 (2018).
- [42] T. Severt, Z. L. Streeter, W. Iskandar, K. A. Larsen, A. Gatton, D. Trabert, B. Jochim, B. Griffin, E. G. Champenois, M. M. Brister, *et al.*, Step-by-step state-selective tracking of fragmentation dynamics of water dications by momentum imaging, *Nat. Commun.* **13**, 5146 (2022).
- [43] J. Rajput, H. Kumar, P. Bhatt, and C. Safvan, A new technique for measurement of subrotational lifetime of molecular ions, *Sci. Rep.* **10**, 20301 (2020).
- [44] H. Kumar, P. Bhatt, C. Safvan, and J. Rajput, Three-body dissociation of OCS^{3+} : Separating sequential and concerted pathways, *J. Chem. Phys.* **148**, 064302 (2018).
- [45] C. D. Lin, Hyperspherical coordinate approach to atomic and other Coulombic three-body systems, *Phys. Rep.* **257**, 1 (1995).
- [46] J. Z. H. Zhang, *Theory and Application of Quantum Molecular Dynamics* (World Scientific, Singapore, 1998).
- [47] P. Cornille, *Advanced Electromagnetism and Vacuum Physics* (World Scientific, Singapore, 2003), Vol. 21.
- [48] D. J. Tannor, *Introduction to Quantum Mechanics: A time-Dependent Perspective* (University Science Books, Melville, 2007).
- [49] Y. Wang, *Universal Efimov Physics in Three- and Four-Body Collisions* (Kansas State University, Lawrence, 2010).
- [50] S. Maclot, D. G. Piekarski, A. Domaracka, A. Méry, V. Vizcaino, L. Adoui, F. Martín, M. Alcamí, B. A. Huber, P. Rousseau, *et al.*, Dynamics of glycine dications in the gas phase: Ultrafast intramolecular hydrogen migration versus Coulomb repulsion, *J. Phys. Chem. Lett.* **4**, 3903 (2013).
- [51] D. G. Piekarski, R. Delaunay, S. Maclot, L. Adoui, F. Martín, M. Alcamí, B. A. Huber, P. Rousseau, A. Domaracka, and S. Díaz-Tendero, Unusual hydroxyl migration in the fragmentation of β -alanine dication in the gas phase, *Phys. Chem. Chem. Phys.* **17**, 16767 (2015).
- [52] P. Rousseau, D. G. Piekarski, M. Capron, A. Domaracka, L. Adoui, F. Martin, M. Alcamí, S. Díaz-Tendero, and B. A. Huber, Polypeptide formation in clusters of β -alanine amino acids by single ion impact, *Nat. Commun.* **11**, 3818 (2020).