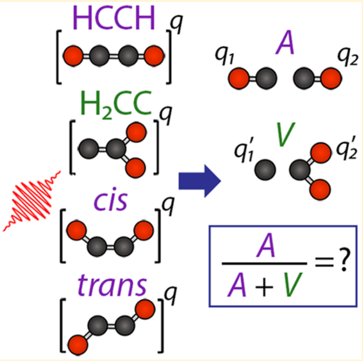
THE JOURNAL OF PHYSICAL CHEMISTRY Letters
Letter
Cite This: J. Phys. Chem. Lett. 2019, 10, 2320−2327
pubs.acs.org/JPCL

Dependence on the Initial Configuration of Strong Field-Driven Isomerization of C_2H_2 Cations and Anions

Bethany Jochim,*[†] Ben Berry,[†] T. Severt,[†] Peyman Feizollah,[†] M. Zohrabi,[†] Kanaka Raju P.,[†] E. Wells,[‡] K. D. Carnes,[†] and I. Ben-Itzhak*[†]

[†]J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, United States
[‡]Department of Physics, Augustana University, Sioux Falls, South Dakota 57197, United States

ABSTRACT: We have investigated the femtosecond laser-induced fragmentation of $C_2H_2^q$ ion beam targets in various initial configurations, including acetylene (linear HCCH), vinylidene (H_2CC), and *cis*/*trans*. The initial configuration is shown to have a tremendous impact on the branching ratio of acetylene-like (CH^{q_1} + CH^{q_2}) and vinylidene-like ($C^{q_1'}$ + $CH_2^{q_2'}$) dissociation of a specific $C_2H_2^q$ molecular ion. In particular, whereas $C_2H_2^+$ generated from C_2H_2, a linear HCCH target, exhibits comparable levels of acetylene-like and vinylidene-like fragmentation, vinylidene or *cis*/*trans* configuration ion beams preferably undergo vinylidene-like fragmentation, with an acetylene branching ratio ranging from 13.9% to zero.



Photochemistry studies often involve probing molecular dynamics starting from stable configurations. The initial configuration, however, can have a great influence on the dynamics. Examining various geometries beyond those commonly studied can therefore offer a different perspective. One well-studied topic that may benefit from such an alternative approach is isomerization.

Widespread in nature[1−4] and key to many industrial applications,[5−7] isomerization reactions have been extensively studied in chemistry and physics, both experimentally and theoretically.[8,9] The C_2H_2 molecule in particular has proven to be a useful testing ground for examining isomerization. Conversion between its acetylene (HCCH) and vinylidene (H_2CC) isomers, an example of 1,2 hydrogen migration,[10] is one of the simplest bond rearrangement isomerization reactions.

A wide array of experimental techniques have been applied to examine isomerization of C_2H_2 molecules. Photodetachment spectroscopy measurements on $C_2H_2^-$ ions have collectively provided a fuller picture of the energetics and $H_2CC \rightarrow HCCH$ isomerization dynamics of the resulting transient neutral vinylidene.[11−16] With an alternative approach, stimulated emission spectroscopy (SEP)[17−19] and dispersed fluorescence (DF)[17,19−21] measurements have examined the reverse reaction, preparing acetylene (HCCH) in highly excited vibrational states close to the isomerization threshold and looking for signatures of $HCCH \rightarrow H_2CC$ transitions.

In addition to being heavily studied in traditional linear spectroscopy,[13−19,21] C_2H_2 isomerization has also garnered significant interest in the photofragmentation community. Here, a far less "gentle" approach is taken, breaking the molecule and extracting information from the measured fragments. The signatures of isomerization are thus fundamentally different from those in the aforementioned types of spectroscopy. For example, common signatures in fragmentation studies are measurement of C^{q_1} + $CH_2^{q_2}$ final products for acetylene → vinylidene isomerization and $CH^{q_1'}$ + $CH^{q_2'}$ for vinylidene → acetylene isomerization.

These photofragmentation studies have involved an assortment of excitation sources. Extreme ultraviolet (XUV) and X-ray sources have been fruitfully employed to study C_2H_2 isomerization through dissociative ionization.[22−34] Following early suggestions and demonstrations of the potential utility of intense, ultrafast laser pulses in probing C_2H_2 isomerization dynamics, particularly the relevant time scale(s), a plethora of studies have used these sources.[35−47]

Despite the abundance of studies of C_2H_2 isomerization, it is nevertheless an intriguing and important topic to explore further, as much remains unknown. For instance, in addition to the ongoing debate about topics like the lifetime of the neutral vinylidene,[12,13,48−51] open questions about the ions of C_2H_2 are even greater in number.[52]

In this Letter, we utilize our unique capability to prepare $C_2H_2^q$ ion beams in a variety of initial configurations to investigate the role these configurations play in ultrafast laser-induced isomerization and dissociation. To do so, we examine target configurations ranging from vinylidene to acetylene, including *cis*/*trans* configurations. These would not be easily accessible as neutral gas phase targets.

Received: February 22, 2019
Accepted: April 19, 2019
Published: April 19, 2019

DOI: 10.1021/acs.jpclett.9b00520

In our experiment, $C_2H_2^q$ ions are produced via fast electron impact in an ion source. Specifically, an electron cyclotron resonance (ECR) ion source is used to create the $C_2H_2^+$ beams, while the $C_2H_2^-$ beam is generated in a duoplasmatron source. The ions are accelerated to an energy of ~8 keV, and the ion beam of interest is selected with a magnet according to its momentum-to-charge ratio. At the laser interaction region, the ion beam has a cross section of ~0.9 mm × ~0.9 mm. The typical current varies widely depending on the specific ion beam over the range of 25 pA to 1 nA.

The Ti:sapphire laser used in this study[53] produces 790 nm central wavelength, 2 mJ, linearly polarized pulses with a duration of ~23 fs fwhm (full width at half-maximum in intensity) at a rate of 10 kHz. The pulse duration is measured with second-harmonic generation frequency-resolved optical gating (SHG FROG).[54] The laser beam is focused onto the ion beam target by an $f = 203$ mm, 90° off-axis parabolic mirror. Typical intensities utilized in our experiment fall in the range of $10^{13}-10^{15}$ W/cm^2. The peak intensity is determined from the measured power, pulse duration, and focal profile image.[55] The intensity is controlled by translating the position of the laser focus relative to the ion beam center as well as by attenuating the laser power.[55,56]

Our setup is schematically illustrated in Figure 1. Signals from a microchannel plate delay-line detector provide arrival time and position information and hence enable calculation of the velocity for each fragment on an event-by-event basis. Each fragmentation channel appears as a diagonal stripe in the coincidence time-of-flight (CTOF) spectrum due to momentum conservation, like those shown in Figure 2a. The typical event rate depends strongly upon the particular ion beam, with event rates for our measurements being at most on the order of 0.1 Hz (for $C_2H_2^+$ from C_2H_2) to 0.001 Hz (for $C_2H_2^+$ from $C_2H_2F_2$). Further details regarding our experimental technique can be found in our previous publications.[57,58]

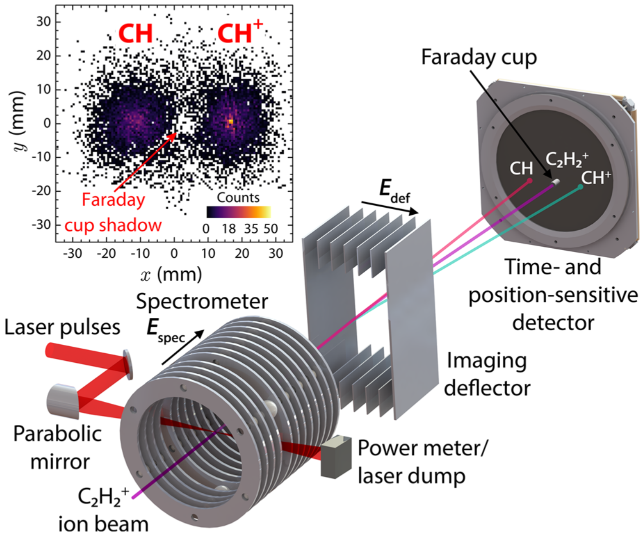


Figure 1. Schematic of our coincidence three-dimensional momentum imaging setup showing the $C_2H_2^+ \rightarrow CH^+ + CH$ breakup channel. Intense, femtosecond laser pulses interact with the ion beam inside a spectrometer that provides a longitudinal field, E_{spec}, to separate fragments in time. An imaging deflector supplies a transverse field, E_{def}, which separates the fragments in position. The inset shows a sample position spectrum.

Momentum conservation allows the discernment of true events from background signals and random coincidences. Random coincidences originate from the interaction of a single laser pulse with multiple molecules, whereby a fragment from one molecule is accidentally paired with another from a different molecule.[57,59−62] To eliminate these events, we pair fragments from different laser shots to generate a spectrum mimicking the random coincidences, scale this generated spectrum to a purely random feature like those marked in Figure 2a, and then subtract it from the measured data.

Recall that in fragmentation studies, a commonly used signature of molecules being in the acetylene configuration is measurement of the $CH^{q_1} + CH^{q_2}$ channel, which we denote as A. Similarly, a signature of molecules in the vinylidene configuration is measurement of the $C^{q_1'} + CH_2^{q_2'}$ channel, which we denote as V. We adopt this notation from this point forward.

For the case of $C_2H_2^+$ ions being produced from C_2H_2, these ions predominantly exist in the same configuration as the parent C_2H_2, HCCH. This assertion is based on electron impact ionization studies.[63−66] The results for this target are similar to those of the aforementioned photofragmentation studies starting from a neutral C_2H_2 target.[22−47] Like those studies, we observe both acetylene-like and vinylidene-like two-body breakup channels, visible in the CTOF spectrum in Figure 2a.

Given our ability to measure neutral fragments directly, we focus on the two-body dissociation channels, $CH^+ + CH$ (A), $C^+ + CH_2$ (V_1), and $C + CH_2^+$ (V_2), i.e., those with no ionization of the target, and compute their branching ratios after imposing momentum conservation. Note that the presence of two V channels is merely a consequence of the fact that either the C or the CH_2 fragment is positively charged. The CTOF spectrum for these channels after analysis is shown in Figure 2c. The branching ratios are summarized in Table 1, where the sum of the vinylidene-like channel yields, $V_1 + V_2$, is denoted as V. These results suggest a substantial amount of isomerization of the initially acetylene (linear HCCH configuration) target, as the $V/(A + V)$ branching ratio is ~60%.

While the $C_2H_2^+$ target produced from C_2H_2 likely has a linear HCCH geometry, the $C_2H_2^-$ target possesses the other isomeric configuration of C_2H_2, vinylidene. This beam is produced by electron attachment in a duoplasmatron ion source loaded with a mixture of 10% ethylene and 90% argon. $C_2H_2^-$ is known to be long-lived in its electronic ground state, $\tilde{X}\ ^2B_2$. It remains in the vinylidene configuration for >100 s,[12,67,68] decaying by adiabatic electron loss and subsequent isomerization of the resulting neutral vinylidene to acetylene.[69] The linear $HCCH^-$ isomer, on the other hand, has a large negative electron affinity (EA) of −2.6 eV, and it autodetaches within a few femtoseconds.[69−71] Because the ion beam travel time from the ion source to the laser interaction region in our setup is approximately 20 μs, the $C_2H_2^-$ target survives purely in the vinylidene configuration.

In stark contrast to the $C_2H_2^+$ results, we find that the laser-induced fragmentation of $C_2H_2^-$ is conspicuously reminiscent of the initial target configuration. Predominantly vinylidene-like breakup is observed for all $C_2H_2^{q+}$ daughter ions, as evident from the CTOF spectrum in Figure 2b. Figure 2d contains the CTOF spectrum of events fulfilling momentum conservation for two-body dissociation of the $C_2H_2^+$ daughter

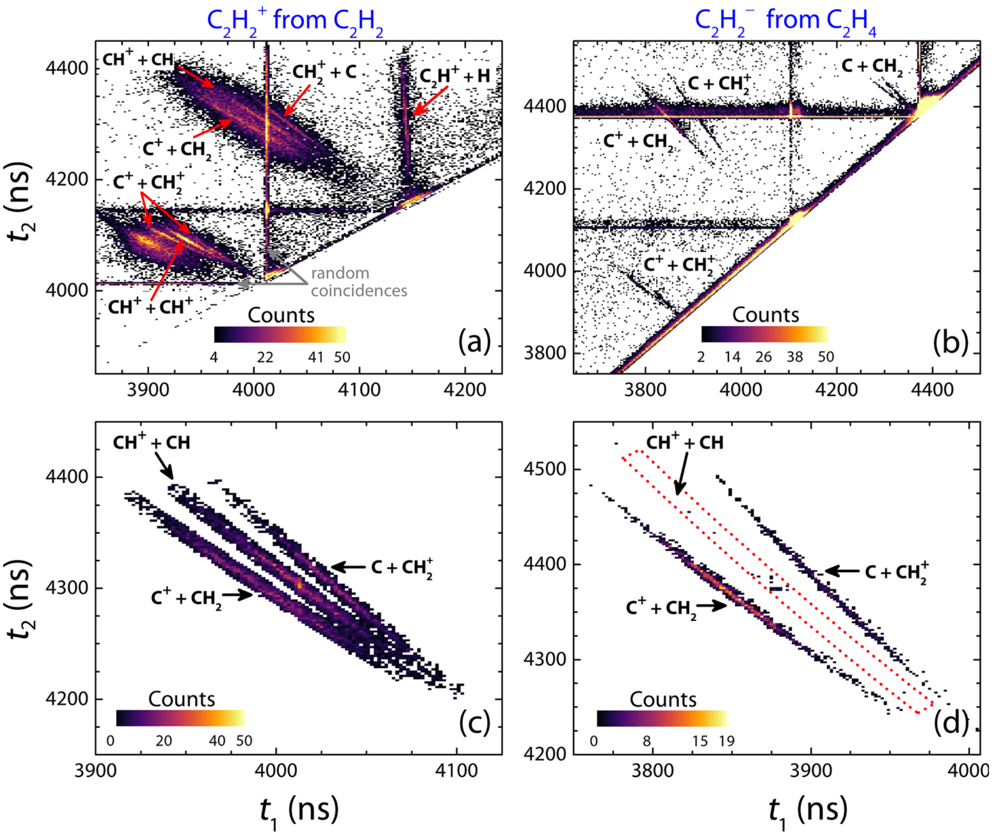


Figure 2. Coincidence time-of-flight (CTOF) spectra for fragmentation of $C_2H_2^+$ generated from C_2H_2 (left) and $C_2H_2^-$ (right). (a and b) Raw data. (c and d) Fragmentation channels of $C_2H_2^+$ after momentum conservation. The dashed red box in panel d indicates the expected position of the $CH^+ + CH$ channel, i.e., the channel associated with the HCCH final configuration. Gray arrows in panel a mark examples of random coincidence features (see the text). Note that there are other channels not discussed here that will be covered in a future publication(s). For instance, the rate of $CH^+ + CH^+$ in panel a is ~0.2 Hz.

Table 1. Branching Ratios for Different Initial $C_2H_2^q$ Configurations ($q = -1$, 0, or 1) Exposed to Laser Pulses with an Intensity of ~3×10^{15} W/cm^2 [a]

target	source gas	current (nA)	initial configuration	A	$A/(A + V)$ (%)
$C_2H_2^+$	C_2H_2	1.0	HCCH	$CH^+ + CH$	37.6 ± 3.8
$C_2H_2^+$	$C_2H_2F_2$	0.025	H_2CC	$CH^+ + CH$	13.9 ± 2.4
$C_2H_2^+$	$C_2H_2Br_2$	0.1	*cis/trans*	$CH^+ + CH$	1.7 ± 0.3
$C_2H_2^-$	C_2H_4	0.2	H_2CC	$CH^+ + CH$	0.1 ± 0.5
$C_2H_2^-$	C_2H_4	0.2	H_2CC	$CH + CH$	3.9 ± 2.5
C_2H_2 [b]	C_2H_4	0.2	H_2CC	$CH^+ + CH$	0.1 ± 0.1
C_2H_2 [b]	C_2H_4	0.2	H_2CC	$CH + CH$	3.6 ± 1.2

[a] The labels A and V refer to the $CH^{q_1} + CH^{q_2}$ and $C^{q_1'} + CH_2^{q_2'}$ channels, respectively (note $q_1 + q_2 = q_1' + q_2'$ for each case). Also, in some cases, V includes two channels, as either the C or the CH_2 fragment can be positively charged. [b] The neutral target is produced from the $C_2H_2^-$ beam by a pump pulse 300 fs before interaction with the probe pulse (see the text).

of $C_2H_2^-$, specifically the $CH^+ + CH$ (A), $C^+ + CH_2$ (V_1), and $C + CH_2^+$ (V_2) channels. The acetylene branching ratio for this process, displayed in Table 1, is consistent with zero. Moreover, this trend of negligible acetylene-like breakup persists for the range of peak laser intensities studied (5×10^{14} to 3×10^{15} W/cm^2).

The contrast between the $C_2H_2^+$ and $C_2H_2^-$ outcomes discussed so far is surprising. These observations suggest that while $C_2H_2^+$ generated from C_2H_2, an HCCH target, isomerizes efficiently, the reverse process does not occur for $C_2H_2^-$, a target of the H_2CC initial configuration. More precisely, isomerization of the vinylidene target leading to dissociation is not observed. One should note that this does not preclude the possibility of isomerization of molecules that remain bound. Also, while it is likely that the contrasting $C_2H_2^+$ and $C_2H_2^-$ results are due to very different excitation pathways, it is not easy to resolve the participating electronic states in the present strong field study, as many electronic states could be populated. For isolating dissociation pathways, further work employing single-photon excitation of these systems[32,72,73] could be informative.

Some theoretical studies have suggested that neutral vinylidene that results from $C_2H_2^- \rightarrow C_2H_2 + e^-$ photodetachment not only isomerizes to acetylene but then undergoes multiple acetylene ↔ vinylidene recrossings.[50,74] This process happens due to the fact that acetylene is highly excited after crossing the vinylidene → acetylene barrier. The period of these recrossings is calculated to be on the order of

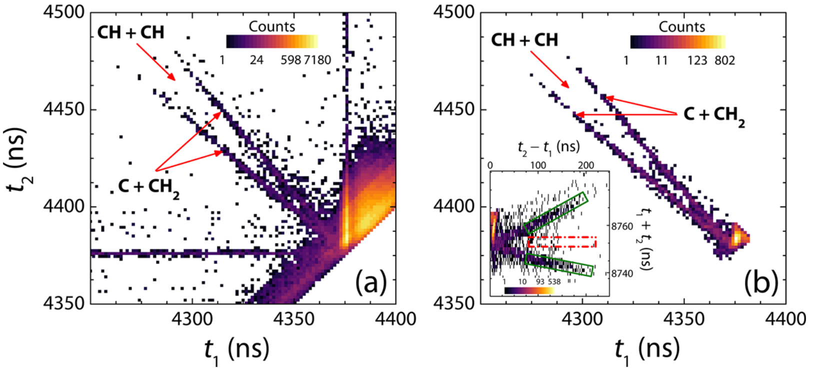


Figure 3. CTOF spectra for fragmentation of $C_2H_2^-$ by a two-pulse scheme zoomed in on the neutral−neutral fragmentation channels. (a) Raw data. (b) After imposing momentum conservation. The inset shows a rotated spectrum. The dashed red and solid green boxes indicate where yields of CH + CH and C + CH_2 were evaluated, respectively.

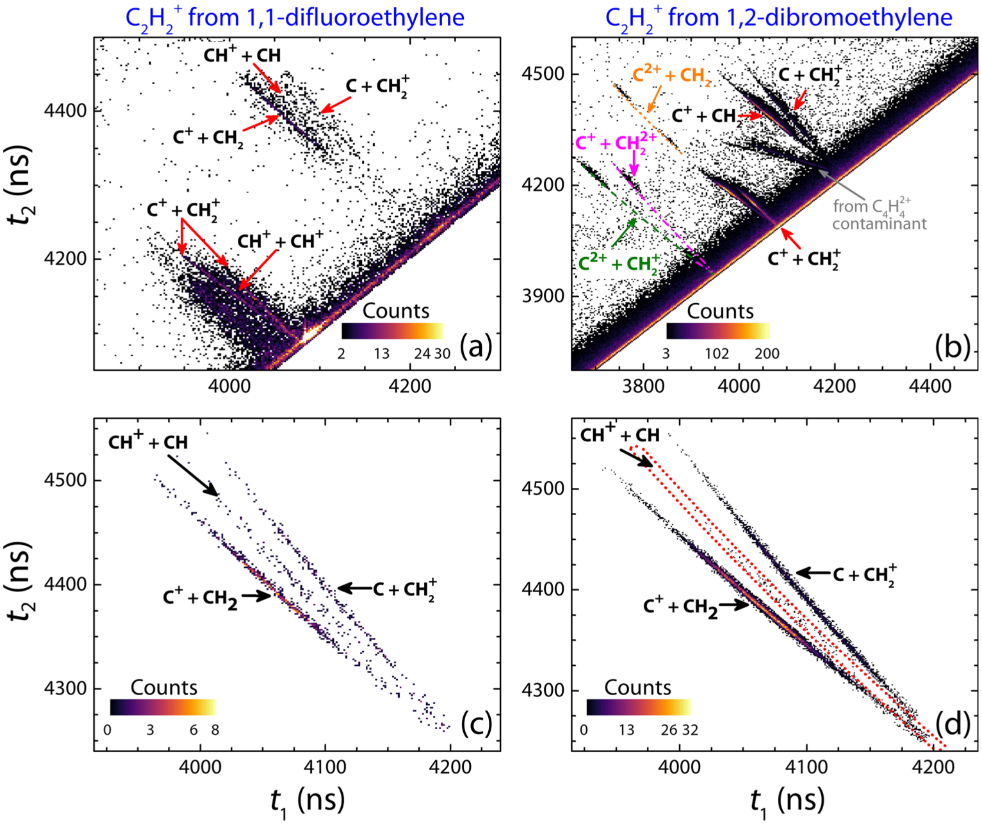


Figure 4. CTOF spectra for laser-induced fragmentation of $C_2H_2^+$ generated from 1,1-difluoroethylene (left) and 1,2-dibromoethylene (right). (a and b) Raw data. (c and d) The three fragmentation channels of $C_2H_2^+$ after momentum conservation. The dashed red box in panel d highlights the expected position of the CH$^+$ + CH channel.

100 fs, but the exact period depends heavily upon the initial conditions.[50]

In light of this idea, we performed a two-pulse measurement, where the first pulse causes photodetachment and possibly initiates isomerization and the second pulse probes any ensuing recrossing dynamics. The pump pulse that removes the weakly bound electron of $C_2H_2^-$ (EA = 0.49 eV[12]) has a peak intensity of 2×10^{14} W/cm^2 and efficiently neutralizes the $C_2H_2^-$ molecules within the laser focus, according to our estimates. To arrive at this conclusion, we use our estimated ion beam density, ∼6×10^3 molecules/cm^3 (i.e., ∼0.03 molecule/pulse), and the measured rate of neutral C_2H_2 molecules (∼285 Hz) for a single 5×10^{14} W/cm^2 pulse, which results in negligible fragmentation. The probe pulse is delayed by 300 fs with respect to the pump pulse, close to the typical recrossing period, and has a much higher peak intensity of 2×10^{15} W/cm^2.

Here too, the vinylidene-like breakup channel, C + CH_2, heavily dominates, as clearly shown in Figure 3. In contrast, the acetylene-like fragmentation channel, CH + CH, is hardly visible. Careful analysis including momentum conservation and random coincidence subtraction sets an upper bound for the acetylene branching ratio at 3.6 ± 1.2%. This result is consistent with that of a single pulse similar to the probe pulse, for which the acetylene branching ratio is 3.9 ± 2.5%. Moreover, in the pump−probe measurement, the branching

DOI: 10.1021/acs.jpclett.9b00520
J. Phys. Chem. Lett. 2019, 10, 2320−2327

ratio of the acetylene-like fragmentation channel for which two electrons are removed, $CH^+ + CH$, is 0.1 ± 0.1% (see Table 1), also in accord with the single-pulse results. Theory more closely replicating the initial conditions would aid in guiding future two-pulse experiments sampling recrossing dynamics.

To further explore this strong dependence of isomerization on the initial configuration, we look at another vinylidene-like target, $C_2H_2^+$ generated from 1,1-difluoroethylene. Charge inversion mass spectrometry measurements indicate that a beam of $C_2H_2^+$ produced from 1,1-dichloroethylene is long-lived in the vinylidene configuration, with a lifetime of >8.5 μs.[75,76] Given the chemical similarity between 1,1-dichloroethylene and 1,1-difluoroethylene, it is most likely that a $C_2H_2^+$ beam generated from the latter is also of the vinylidene configuration. Panels a and c of Figure 4 contain the measured CTOF spectra for this target. One can see that both vinylidene-like and acetylene-like breakup occurs, with a vast majority of vinylidene-like breakup.

While a beam of $C_2H_2^+$ generated from 1,1-difluoroethylene has the vinylidene configuration like $C_2H_2^-$, there also are compelling reasons to examine the former target. Here, we observe dissociation and thus can avoid any complication ionization might add. In contrast, in the $C_2H_2^-$ case, it is possible that fragmentation of $C_2H_2^+$ daughter ions involves sequential ionization. For example, the weakly bound electron could be removed early in the laser pulse, followed by propagation on the C_2H_2 surface(s) and eventual removal of the second electron. This process is clearly different from dissociation of a $C_2H_2^+$ target initially in the vinylidene configuration, such as that produced from 1,1-difluoroethylene.

As a final example, we generate a *cis*/*trans* $C_2H_2^+$ beam from 1,2-dibromoethylene. The dibromoethylene sample is composed of a mixture of the *cis* and *trans* isomers with a *cis*:*trans* ratio of approximately 1:3. This sample and information regarding its *trans*:*cis* isomer ratio were obtained from Sigma-Aldrich. Intuitively, removal of the bromine atoms will result in $C_2H_2^+$ far from equilibrium, with excitation likely in the symmetric (*trans*) and antisymmetric (*cis*) C−C−H bending vibrational modes.[77] What impact will this excitation have on the branching ratio between acetylene-like and vinylidene-like channels?

The CTOF spectra in panels b and d of Figure 4 and the branching ratio in Table 1 show that, similar to the $C_2H_2^-$ results, the predominant breakup is vinylidene-like. This behavior continues over the range of intensities explored (5×10^{13} to 3×10^{15} W/cm^2). For this *cis*/*trans* target, it should be noted that it is unclear if the initial bending excitation of the ion beam facilitates unimolecular HCCH → H_2CC isomerization in flight to the laser interaction or if the isomerization is laser-induced. While in assessing the geometry of this target we have assumed a logic similar to that applied for the H_2CC^+ beam produced from 1,1-difluoroethylene,[75,76] a future study of the lifetimes of *cis*/*trans* beams would shed further light on this issue. The key point, however, is that isomerization to vinylidene is much more likely in the *cis*/*trans* case than in the case of $C_2H_2^+$ produced from C_2H_2. Furthermore, the branching ratios measured with the *cis*/*trans* target are significantly different from those measured with the other targets.

The *cis*/*trans* $C_2H_2^+$ measurement suggests that the initial bending excitation of the ions enhances isomerization toward the vinylidene configuration. This observation is in agreement with previous work highlighting the influence of bending motion on the isomerization process, both for acetylene becoming vinylidene and vice versa. The previously mentioned DF and SEP spectroscopy measurements[17−21] exploit a high degree of vibrational excitation to examine the coupling of acetylene and vinylidene states resulting in isomerization of HCCH. In these spectroscopic measurements, the minimum energy path for hydrogen migration falls along the C−C−H bending coordinate. Several theoretical studies have also emphasized that bending excitation in acetylene molecules has a decisive impact on the isomerization dynamics.[50,78−81] Moreover, photoelectron spectroscopy experiments on the vinylidene anion $C_2H_2^-$ by the Neumark group and collaborators have shown that excitation of the in-plane rocking mode of vinylidene readily leads to isomerization, as this state connects to the C−C−H bending vibrational states of acetylene.[16]

In summary, our measurements of the laser-induced fragmentation of $C_2H_2^q$ ion beams with assorted unique configurations demonstrate the strong effect of the initial configuration on the isomerization dynamics. While $C_2H_2^+$ generated from C_2H_2, a linear HCCH molecule, exhibits acetylene-like and vinylidene-like fragmentation at similar levels, the vinylidene and *cis*/*trans* configuration $C_2H_2^+$ molecules that we examined mainly fragment in a vinylidene-like manner, a markedly different and surprising outcome. These intriguing results, which raise the question of the reversibility of the isomerization process, call for future theoretical endeavors to explain them. Measurements of *cis*/*trans* targets appear to be congruent with experimental and theoretical work pinpointing the pivotal influence of bending excitation in isomerization, but similarly, further work is needed for a detailed understanding and to disentangle the possible unimolecular and laser-driven dynamics.

Finally, we anticipate that our approach for studying $C_2H_2^q$ ($q = -1$, 0, or 1) isomerization is not limited to this particular problem. Rather, ion beam targets offer an avenue for examining photoinduced dynamics in a variety of chemical systems in initial configurations that are not easily accessible, a unique vantage point that is complementary to mainstream approaches for studying molecular dynamics.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: bjochim@phys.ksu.edu.
*E-mail: ibi@phys.ksu.edu.

ORCID

Bethany Jochim: 0000-0003-2040-1453
E. Wells: 0000-0002-1044-4479

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Daniel M. Neumark for stimulating and fruitful discussions and Jyoti Rajput for her involvement in the preliminary stages of this project. The authors also acknowledge C. W. Fehrenbach for assistance with the laser and ion beams. This work is supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, under Grant DE-FG02-86ER13491. E.W. acknowledges the same funding source for partial sabbatical leave support as well as continued support from National Science Foundation Grant PHY-1723002.

REFERENCES

(1) Wald, G. Molecular Basis of Visual Excitation. *Science* **1968**, *162*, 230−239.

(2) Gai, F.; Hasson, K. C.; McDonald, J. C.; Anfinrud, P. A. Chemical Dynamics in Proteins: The Photoisomerization of Retinal in Bacteriorhodopsin. *Science* **1998**, *279*, 1886−1891.

(3) Polli, D.; Altoè, P.; Weingart, O.; Spillane, K. M.; Manzoni, C.; Brida, D.; Tomasello, G.; Orlandi, G.; Kukura, P.; Mathies, R. A.; et al. Conical intersection dynamics of the primary photoisomerization event in vision. *Nature* **2010**, *467*, 440.

(4) Allmann, S.; Baldwin, I. T. Insects Betray Themselves in Nature to Predators by Rapid Isomerization of Green Leaf Volatiles. *Science* **2010**, *329*, 1075−1078.

(5) Perry, S. F. Isomerization. *Ind. Eng. Chem.* **1952**, *44*, 2037−2039.

(6) Durán, R. P.; Amorebieta, V. T.; Colussi, A. J. Pyrolysis of acetylene: a thermal source of vinylidene. *J. Am. Chem. Soc.* **1987**, *109*, 3154−3155.

(7) Valavarasu, G.; Sairam, B. Light Naphtha Isomerization Process: A Review. *Pet. Sci. Technol.* **2013**, *31*, 580−595.

(8) Dugave, C.; Demange, L. Cis-trans isomerization of organic molecules and biomolecules: implications and applications. *Chem. Rev.* **2003**, *103*, 2475−2532.

(9) Levine, B. G.; Martínez, T. J. Isomerization through conical intersections. *Annu. Rev. Phys. Chem.* **2007**, *58*, 613−634.

(10) Schaefer, H. F. The 1,2 hydrogen shift: a common vehicle for the disappearance of evanescent molecular species. *Acc. Chem. Res.* **1979**, *12*, 288−296.

(11) Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. Observation of $X\ ^1A_1$ vinylidene by photoelectron spectroscopy of the $C_2H_2^-$ ion. *Chem. Phys. Lett.* **1983**, *100*, 124−128.

(12) Ervin, K. M.; Ho, J.; Lineberger, W. C. A study of the singlet and triplet states of vinylidene by photoelectron spectroscopy of $H_2C = C^-$, $D_2C = C^-$, and $HDC = C^-$. vinylidene−acetylene isomerization. *J. Chem. Phys.* **1989**, *91*, 5974−5992.

(13) Levin, J.; Feldman, H.; Baer, A.; Ben-Hamu, D.; Heber, O.; Zajfman, D.; Vager, Z. Study of unimolecular reactions by Coulomb explosion imaging: the nondecaying vinylidene. *Phys. Rev. Lett.* **1998**, *81*, 3347−3350.

(14) Gerardi, H. K.; Breen, K. J.; Guasco, T. L.; Weddle, G. H.; Gardenier, G. H.; Laaser, J. E.; Johnson, M. A. Survey of Ar-tagged predissociation and vibrationally mediated photodetachment spectroscopies of the vinylidene anion, $C_2H_2^-$. *J. Phys. Chem. A* **2010**, *114*, 1592−1601.

(15) DeVine, J. A.; Weichman, M. L.; Zhou, X.; Ma, J.; Jiang, B.; Guo, H.; Neumark, D. M. Non-adiabatic effects on excited states of vinylidene observed with slow photoelectron velocity-map imaging. *J. Am. Chem. Soc.* **2016**, *138*, 16417−16425.

(16) DeVine, J. A.; Weichman, M. L.; Laws, B.; Chang, J.; Babin, M. C.; Balerdi, G.; Xie, C.; Malbon, C. L.; Lineberger, W. C.; Yarkony, D. R.; et al. Encoding of vinylidene isomerization in its anion photoelectron spectrum. *Science* **2017**, *358*, 336−339.

(17) Abramson, E.; Field, R. W.; Imre, D.; Innes, K. K.; Kinsey, J. L. Fluorescence and stimulated emission $S_1 \rightarrow S_0$ spectra of acetylene: regular and ergodic regions. *J. Chem. Phys.* **1985**, *83*, 453−465.

(18) Chen, Y.; Jonas, D. M.; Kinsey, J. L.; Field, R. W. High resolution spectroscopic detection of acetylene−vinylidene isomerization by spectral cross correlation. *J. Chem. Phys.* **1989**, *91*, 3976−3987.

(19) Yamanouchi, K.; Ikeda, N.; Tsuchiya, S.; Jonas, D. M.; Lundberg, J. K.; Adamson, G. W.; Field, R. W. Vibrationally highly excited acetylene as studied by dispersed fluorescence and stimulated emission pumping spectroscopy: vibrational assignment of the feature states. *J. Chem. Phys.* **1991**, *95*, 6330−6342.

(20) Jacobson, M. P.; Silbey, R. J.; Field, R. W. Local mode behavior in the acetylene bending system. *J. Chem. Phys.* **1999**, *110*, 845−859.

(21) Jacobson, M. P.; Field, R. W. Acetylene at the threshold of isomerization. *J. Phys. Chem. A* **2000**, *104*, 3073−3086.

(22) Eland, J. H. D.; Wort, F. S.; Lablanquie, P.; Nenner, I. Mass spectrometric and coincidence studies of double photoionization of small molecules. *Z. Phys. D: At., Mol. Clusters* **1986**, *4*, 31−42.

(23) Eland, J. H. D.; Price, S. D.; Cheney, J. C.; Lablanquie, P.; Nenner, I.; Fournier, P. G. Towards a spectroscopy of doubly charged ions. *Philos. Trans. R. Soc., A* **1988**, *324*, 247−255.

(24) Cooper, G.; Ibuki, T.; Iida, Y.; Brion, C. Absolute dipole oscillator strengths for photoabsorption and the molecular and dissociative photoionization of acetylene. *Chem. Phys.* **1988**, *125*, 307−320.

(25) Thissen, R.; Delwiche, J.; Robbe, J. M.; Duflot, D.; Flament, J. P.; Eland, J. H. D. Dissociations of the ethyne dication $C_2H_2^{2+}$. *J. Chem. Phys.* **1993**, *99*, 6590−6599.

(26) Osipov, T.; Cocke, C. L.; Prior, M. H.; Landers, A.; Weber, T.; Jagutzki, O.; Schmidt, L.; Schmidt-Böcking, H.; Dörner, R. Photoelectron-photoion momentum spectroscopy as a clock for chemical rearrangements: isomerization of the di-cation of acetylene to the vinylidene configuration. *Phys. Rev. Lett.* **2003**, *90*, 233002.

(27) Flammini, R.; Fainelli, E.; Maracci, F.; Avaldi, L. Vinylidene dissociation following the Auger-electron decay of inner-shell ionized acetylene. *Phys. Rev. A: At., Mol., Opt. Phys.* **2008**, *77*, 044701.

(28) Osipov, T.; Rescigno, T. N.; Weber, T.; Miyabe, S.; Jahnke, T.; Alnaser, A. S.; Hertlein, M. P.; Jagutzki, O.; Schmidt, L. P. H.; Schöffler, M.; et al. Fragmentation pathways for selected electronic states of the acetylene dication. *J. Phys. B: At., Mol. Opt. Phys.* **2008**, *41*, 091001.

(29) Jiang, Y. H.; Rudenko, A.; Herrwerth, O.; Foucar, L.; Kurka, M.; Kühnel, K. U.; Lezius, M.; Kling, M. F.; van Tilborg, J.; Belkacem, A.; et al. Ultrafast extreme ultraviolet induced isomerization of acetylene cations. *Phys. Rev. Lett.* **2010**, *105*, 263002.

(30) Alagia, M.; Callegari, C.; Candori, P.; Falcinelli, S.; Pirani, F.; Richter, R.; Stranges, S.; Vecchiocattivi, F. Angular and energy distribution of fragment ions in dissociative double photoionization of acetylene molecules at 39 eV. *J. Chem. Phys.* **2012**, *136*, 204302.

(31) Jiang, Y. H.; Senftleben, A.; Kurka, M.; Rudenko, A.; Foucar, L.; Herrwerth, O.; Kling, M. F.; Lezius, M.; Tilborg, J. V.; Belkacem, A.; et al. Ultrafast dynamics in acetylene clocked in a femtosecond XUV stopwatch. *J. Phys. B: At., Mol. Opt. Phys.* **2013**, *46*, 164027.

(32) Gaire, B.; Lee, S. Y.; Haxton, D. J.; Pelz, P. M.; Bocharova, I.; Sturm, F. P.; Gehrken, N.; Honig, M.; Pitzer, M.; Metz, D.; et al. Photo-double-ionization of ethylene and acetylene near threshold. *Phys. Rev. A: At., Mol., Opt. Phys.* **2014**, *89*, 013403.

(33) Liekhus-Schmaltz, C. E.; Tenney, I.; Osipov, T.; Sanchez-Gonzalez, A.; Berrah, N.; Boll, R.; Bomme, C.; Bostedt, C.; Bozek, J. D.; Carron, S.; et al. Ultrafast isomerization initiated by X-ray core ionization. *Nat. Commun.* **2015**, *6*, 8199.

(34) Li, Z.; Inhester, L.; Liekhus-Schmaltz, C.; Curchod, B. F. E.; Snyder, J. W.; Medvedev, N.; Cryan, J.; Osipov, T.; Pabst, S.; Vendrell, O.; Bucksbaum, P.; Martinez, T. J. Ultrafast isomerization in acetylene dication after carbon K-shell ionization. *Nat. Commun.* **2017**, *8*, 453.

(35) Hishikawa, A.; Matsuda, A.; Fushitani, M.; Takahashi, E. J. Visualizing recurrently migrating hydrogen in acetylene dication by intense ultrashort laser pulses. *Phys. Rev. Lett.* **2007**, *99*, 258302.

(36) Hishikawa, A.; Matsuda, A.; Takahashi, E. J.; Fushitani, M. Acetylene-vinylidene isomerization in ultrashort intense laser fields studied by triple ion-coincidence momentum imaging. *J. Chem. Phys.* **2008**, *128*, 084302.

(37) Matsuda, A.; Fushitani, M.; Takahashi, E. J.; Hishikawa, A. Visualizing hydrogen atoms migrating in acetylene dication by time-resolved three-body and four-body Coulomb explosion imaging. *Phys. Chem. Chem. Phys.* **2011**, *13*, 8697−8704.

(38) Xie, X.; Doblhoff-Dier, K.; Roither, S.; Schöffler, M. S.; Kartashov, D.; Xu, H.; Rathje, T.; Paulus, G. G.; Baltuška, A.; Gräfe, S.; et al. Attosecond-recollision-controlled selective fragmentation of polyatomic molecules. *Phys. Rev. Lett.* **2012**, *109*, 243001.

(39) Wells, E.; Rallis, C.; Zohrabi, M.; Siemering, R.; Jochim, B.; Andrews, P.; Ablikim, U.; Gaire, B.; De, S.; Carnes, K.; et al. Adaptive strong-field control of chemical dynamics guided by three-dimensional momentum imaging. *Nat. Commun.* **2013**, *4*, 2895.

(40) Ibrahim, H.; Wales, B.; Beaulieu, S.; Schmidt, B. E.; Thiré, N.; Fowe, E. P.; Bisson, E.; Hebeisen, C. T.; Wanie, V.; Giguére, M.; et al. Tabletop imaging of structural evolutions in chemical reactions demonstrated for the acetylene cation. *Nat. Commun.* **2014**, *5*, 4422.

(41) Gong, X.; Song, Q.; Ji, Q.; Pan, H.; Ding, J.; Wu, J.; Zeng, H. Strong-field dissociative double ionization of acetylene. *Phys. Rev. Lett.* **2014**, *112*, 243001.

(42) Xie, X.; Doblhoff-Dier, K.; Xu, H.; Roither, S.; Schöffler, M. S.; Kartashov, D.; Erattupuzha, S.; Rathje, T.; Paulus, G. G.; Yamanouchi, K.; et al. Selective control over fragmentation reactions in polyatomic molecules using impulsive laser alignment. *Phys. Rev. Lett.* **2014**, *112*, 163003.

(43) Gong, X.; Song, Q.; Ji, Q.; Lin, K.; Pan, H.; Ding, J.; Zeng, H.; Wu, J. Channel-Resolved Above-Threshold Double Ionization of Acetylene. *Phys. Rev. Lett.* **2015**, *114*, 163001.

(44) Kübel, M.; Siemering, R.; Burger, C.; Kling, N. G.; Li, H.; Alnaser, A. S.; Bergues, B.; Zherebtsov, S.; Azzeer, A. M.; Ben-Itzhak, I.; et al. Steering Proton Migration in Hydrocarbons Using Intense Few-Cycle Laser Fields. *Phys. Rev. Lett.* **2016**, *116*, 193001.

(45) Burger, C.; Kling, N. G.; Siemering, R.; Alnaser, A. S.; Bergues, B.; Azzeer, A. M.; Moshammer, R.; de Vivie-Riedle, R.; Kübel, M.; Kling, M. F. Visualization of bond rearrangements in acetylene using near single-cycle laser pulses. *Faraday Discuss.* **2016**, *194*, 495−508.

(46) Kübel, M.; Burger, C.; Siemering, R.; Kling, N. G.; Bergues, B.; Alnaser, A. S.; Ben-Itzhak, I.; Moshammer, R.; de Vivie-Riedle, R.; Kling, M. F. Phase- and intensity-dependence of ultrafast dynamics in hydrocarbon molecules in few-cycle laser fields. *Mol. Phys.* **2017**, *115*, 1835−1845.

(47) Burger, C.; Atia-Tul-Noor, A.; Schnappinger, T.; Xu, H.; Rosenberger, P.; Haram, N.; Beaulieu, S.; Légaré, F.; Alnaser, A. S.; Moshammer, R.; et al. Time-resolved nuclear dynamics in bound and dissociating acetylene. *Struct. Dyn.* **2018**, *5*, 044302.

(48) Carrington, T.; Hubbard, L. M.; Schaefer, H. F.; Miller, W. H. Vinylidene: Potential energy surface and unimolecular reaction dynamics. *J. Chem. Phys.* **1984**, *80*, 4347−4354.

(49) Germann, T. C.; Miller, W. H. Quantum mechanical calculation of resonance tunneling in acetylene isomerization via the vinylidene intermediate. *J. Chem. Phys.* **1998**, *109*, 94−101.

(50) Hayes, R. L.; Fattal, E.; Govind, N.; Carter, E. A. Long live vinylidene! a new view of the H_2=CC:→HC⋮CH rearrangement from ab initio molecular dynamics. *J. Am. Chem. Soc.* **2001**, *123*, 641−657.

(51) Guo, L.; Han, H.; Ma, J.; Guo, H. Quantum dynamics of vinylidene photodetachment on an accurate global acetylene-vinylidene potential energy surface. *J. Phys. Chem. A* **2015**, *119*, 8488−8496.

(52) Boyé-Péronne, S.; Gauyacq, D.; Liévin, J. Vinylidene-acetylene cation isomerization investigated by large scale ab initio calculations. *J. Chem. Phys.* **2006**, *124*, 214305.

(53) Ren, X.; Summers, A. M.; P., Kanaka Raju; Vajdi, A.; Makhija, V.; Fehrenbach, C. W.; Kling, N. G.; Betsch, K. J.; Wang, Z.; Kling, M. F.; Carnes, K. D.; Ben-Itzhak, I.; Trallero-Herrero, C.; Kumarappan, V. Single-shot carrier-envelope-phase tagging using an f−2f interferometer and a phase meter: a comparison. *J. Opt.* **2017**, *19*, 124017.

(54) Trebino, R.; DeLong, K. W.; Fittinghoff, D. N.; Sweetser, J. N.; Krumbügel, M. A.; Richman, B. A.; Kane, D. J. Measuring ultrashort laser pulses in the time-frequency domain using frequency-resolved optical gating. *Rev. Sci. Instrum.* **1997**, *68*, 3277−3295.

(55) Sayler, A. M.; Wang, P. Q.; Carnes, K. D.; Ben-Itzhak, I. Determining intensity dependence of ultrashort laser processes through focus z-scanning intensity-difference spectra: application to laser-induced dissociation of H_2^+. *J. Phys. B: At., Mol. Opt. Phys.* **2007**, *40*, 4367.

(56) Wang, P.; Sayler, A. M.; Carnes, K. D.; Esry, B. D.; Ben-Itzhak, I. Disentangling the volume effect through intensity-difference spectra: application to laser-induced dissociation of H_2^+. *Opt. Lett.* **2005**, *30*, 664−666.

(57) Ben-Itzhak, I.; Sayler, A. M.; Leonard, M.; Maseberg, J.; Hathiramani, D.; Wells, E.; Smith, M.; Xia, J.; Wang, P.; Carnes, K.; et al. Bond rearrangement caused by sudden single and multiple ionization of water molecules. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2005**, *233*, 284−292.

(58) Wang, P. Q.; Sayler, A. M.; Carnes, K. D.; Xia, J. F.; Smith, M. A.; Esry, B. D.; Ben-Itzhak, I. Dissociation of H_2^+ in intense femtosecond laser fields studied by coincidence three-dimensional momentum imaging. *Phys. Rev. A: At., Mol., Opt. Phys.* **2006**, *74*, 043411.

(59) Bay, Z.; Slawsky, M. M. General Relation between Genuine and Chance Coincidences and Its Application to Measurement of High Activity Sources. *Phys. Rev.* **1950**, *77*, 414−415.

(60) Eland, J. H. D. Photoelectron-photoion coincidence spectroscopy: I. Basic principles and theory. *Int. J. Mass Spectrom. Ion Phys.* **1972**, *8*, 143−151.

(61) Knoll, G. F. *Radiation Detection and Measurement*, 3rd ed.; John Wiley & Sons, 2000.

(62) Henrichs, K.; Waitz, M.; Trinter, F.; Kim, H.; Menssen, A.; Gassert, H.; Sann, H.; Jahnke, T.; Wu, J.; Pitzer, M.; et al. Observation of electron energy discretization in strong field double ionization. *Phys. Rev. Lett.* **2013**, *111*, 113003.

(63) Zheng, S.-H.; Srivastava, S. K. Electron-impact ionization and dissociative ionization of acetylene. *J. Phys. B: At., Mol. Opt. Phys.* **1996**, *29*, 3235.

(64) Josifov, G.; Lukic, D.; Djuric, N.; Kurepa, M. Total, direct and dissociative electron impact ionization cross sections of the acetylene molecule. *J. Serb. Chem. Soc.* **2000**, *65*, 517−527.

(65) Feil, S.; Głuch, K.; Bacher, A.; Matt-Leubner, S.; Böhme, D. K.; Scheier, P.; Märk, T. D. Cross sections and ion kinetic energy analysis for the electron impact ionization of acetylene. *J. Chem. Phys.* **2006**, *124*, 214307.

(66) Feil, S.; Sulzer, P.; Mauracher, A.; Beikircher, M.; Wendt, N.; Aleem, A.; Denifl, S.; Zappa, F.; Matt-Leubner, S.; Bacher, A.; et al. Electron Impact Ionization/Dissociation of Molecules: Production of Energetic Radical Ions and Anions. *Journal of Physics: Conference Series* **2007**, *86*, 012003.

(67) Jensen, M. J.; Pedersen, U. V.; Andersen, L. H. Stability of the ground state vinylidene anion H_2CC^-. *Phys. Rev. Lett.* **2000**, *84*, 1128−1131.

(68) Goode, G. C.; Jennings, K. R. Reactions of O^- Ions with Some Unsaturated Hydrocarbons. *Adv. Mass Spectrom.* **1974**, *6*, n/a.

(69) Chandrasekhar, J.; Kahn, R. A.; von Ragué Schleyer, P. The preferred structure of $C_2H_2^-$. *Chem. Phys. Lett.* **1982**, *85*, 493−495.

(70) Frenking, G. The neutral and ionic vinylidene−acetylene rearrangement. *Chem. Phys. Lett.* **1983**, *100*, 484−487.

(71) Falcetta, M. F.; DiFalco, L. A.; Ackerman, D. S.; Barlow, J. C.; Jordan, K. D. Assessment of various electronic structure methods for characterizing temporary anion states: application to the ground state anions of N_2, C_2H_2, C_2H_4, and C_6H_6. *J. Phys. Chem. A* **2014**, *118*, 7489−7497.

(72) Cosby, P. C.; Möller, R.; Helm, H. Photofragment spectroscopy of N_2^{2+}. *Phys. Rev. A: At., Mol., Opt. Phys.* **1983**, *28*, 766−772.

(73) Pedersen, H. B.; Altevogt, S.; Jordon-Thaden, B.; Heber, O.; Rappaport, M. L.; Schwalm, D.; Ullrich, J.; Zajfman, D.; Treusch, R.; Guerassimova, N.; et al. Crossed Beam Photodissociation Imaging of $HeH^+$with Vacuum Ultraviolet Free-Electron Laser Pulses. *Phys. Rev. Lett.* **2007**, *98*, 223202.

(74) Schork, R.; Köppel, H. Barrier recrossing in the vinylidene−acetylene isomerization reaction: A five-dimensional ab initio quantum dynamical investigation. *J. Chem. Phys.* **2001**, *115*, 7907−7923.

(75) Hayakawa, S.; Takahashi, M.; Arakawa, K.; Morishita, N. Definitive evidence for the existence of a long-lived vinylidene radical cation, $H_2C = C^+$. *J. Chem. Phys.* **1999**, *110*, 2745−2748.

(76) Hayakawa, S. Charge inversion mass spectrometry: dissociation of resonantly neutralized molecules. *J. Mass Spectrom.* **2004**, *39*, 111−135.

(77) Steinfeld, J. I. *Molecules and Radiation: An Introduction to Modern Molecular Spectroscopy*; Dover Publications, 2005.

(78) McCoy, A. B.; Sibert, E. L. The bending dynamics of acetylene. *J. Chem. Phys.* **1996**, *105*, 459−468.

(79) Sibert, E. L.; McCoy, A. B. Quantum, semiclassical and classical dynamics of the bending modes of acetylene. *J. Chem. Phys.* **1996**, *105*, 469−478.

(80) Ma, J.; Xu, D.; Guo, H.; Tyng, V.; Kellman, M. E. Isotope effect in normal-to-local transition of acetylene bending modes. *J. Chem. Phys.* **2012**, *136*, 014304.

(81) Han, H.; Li, A.; Guo, H. Toward spectroscopically accurate global ab initio potential energy surface for the acetylene-vinylidene isomerization. *J. Chem. Phys.* **2014**, *141*, 244312.