

Butterfly structure: Signature of vibrational flopping in dissociative acetylene

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We report experimental evidence for molecular deformation due to a vibrationally active transition state of multiply charged acetylene molecules under the impact of low energy Ar^{8+} projectiles. “Butterflylike” structures are observed in the experimental coincidence spectra between hydrogen and carbon ionic fragments. Such structures can be generated by numerical simulations and are found to originate from the bending motion of the dissociating molecule. Angular distributions for dissociation products from triply charged C_2H_2 ion are reported. © 2007 American Institute of Physics. [DOI: 10.1063/1.2769633]

Determination of the structures and bond arrangements of multiply charged molecules lead to a wealth of knowledge about the nature of interatomic interactions within molecules. Experimental information on the stability of multiply charged molecules, and the energetics involved in their formation and fragmentation, play an important role in verifying and validating contemporary quantum chemical techniques for computing transition states on the potential energy surfaces. A highly charged ion (HCI), 1.2 MeV Ar^{8+} in our case, traverses the molecular dimension of a few angstroms in attosecond time scales, whereas, the typical rotational and vibrational time periods for molecules are in the range of picoseconds and/or femtoseconds, respectively. Therefore HCI-molecule interaction is a unique probe to study molecular dynamics on time scales in which all internal degrees of freedom remain essentially “frozen.” Our aim is to investigate the motional dynamics of the nuclear structure of multiply charged polyatomic species under the instantaneous perturbation generated by a swiftly passing HCI and discuss the effect of bending motion of structure on dissociation pathways.

We report here results of experiments that provide evidence for molecular deformation due to a vibrationally active transition state involving multiply charged acetylene molecules after interaction with low energy highly charged Ar^{8+} projectiles. In a recent theoretical study, Palaudoux and Hochlaf¹ have reported a “dibridged” structure in doubly charged C_2H_2 molecule and predicted that it is a new way in which acetylene dication can decompose. We present here an

experimental verification of that theoretical prediction. We have observed “crosslike” images in the experimental spectrum which resemble the predicted patterns from numerical Monte Carlo simulations as later explained in this paper. The images are a manifestation of a new mechanism of dissociation dynamics in which the field generated from HCI excites the system to active bending structure before it undergoes fragmentation due to charge separation. Such crosslike images were also observed for higher charge states of the dissociative molecular ion which signify that even multiply charged $\text{C}_2\text{H}_2^{q+}$ ($q > 2$) might possess similar bent structures in their transition state of potential energy surface, yet to be explored.

In the experiment, at the center of the collision chamber, Ar^{8+} ($E/q=150$ kV) projectiles collided with the acetylene molecules effusing from a needle at right angles to the ion beam. The dissociated fragments were extracted from the interaction zone into the linear, two-field time-of-flight mass spectrometer (TOFMS) by applying a uniform electric field and were detected by a microchannel plate detector. Ejected electrons were extracted opposite to the TOFMS and detected by a Channeltron which gives the trigger for data acquisition (DAQ). The TOF spectrum was acquired in the multihit mode by a time-to-digital converter where several fragment ions were recorded in coincidence to obtain the information on correlated dissociation products. Details on the setup and DAQ have been described elsewhere.²

The TOF spectrum of acetylene molecules shows undissociated molecular ions such as C_2H_2^+ and $\text{C}_2\text{H}_2^{2+}$, fragments losing H atoms due to breakage of C–H bonds (C_2H^+ and C_2^+) and complete rupture of C–C and C–H skeleton producing H^+ and C^{q+} where q varies from 1 to 3. A detailed analy-

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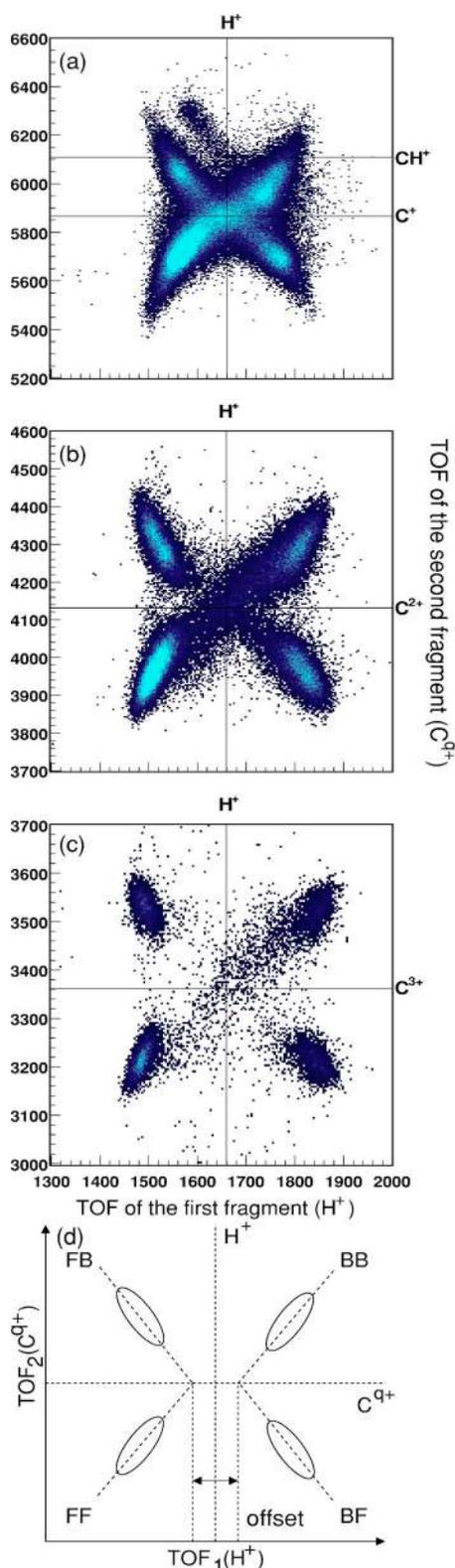


FIG. 1. (Color online) Coincidence map of $H^+ - C^{q+}$ ($q=1,2,3$) formation pathways and its graphical representation. Here the first alphabet corresponds to the hydrogen fragment and the second to the carbon ion.

sis of the total fragmentation pathways will be published elsewhere. From the offline analysis of the acquired multihit data, we have generated a coincidence map which is a 2-dimensional spectrum between TOF of the first fragment ion versus that of the second. This technique has been used

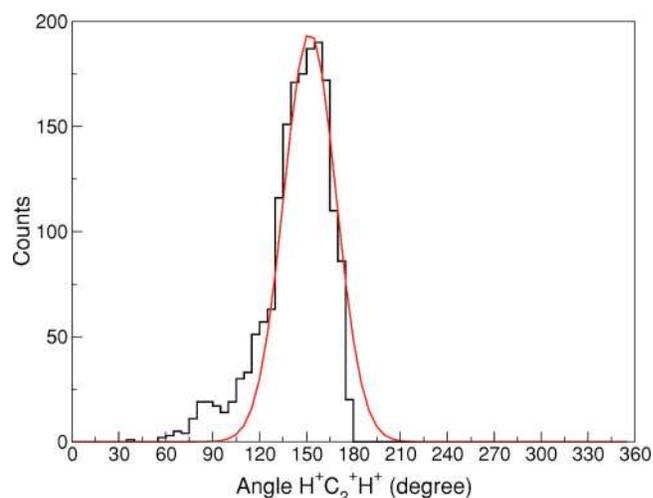


FIG. 2. (Color online) Distribution of $H^+ - C_2^+ - H^+$ angle fitted with a Gaussian.

quite extensively in molecular dissociation studies (see Refs. 3 and 4 and references therein).

Figure 1 shows the H^+ formation pathways in coincidence with (a) C^+ , (b) C^{2+} , and (c) C^{3+} fragments, respectively, along with its (d) graphical representation. The important feature in all these plots is the crosslike structure. We can define the four blocks or ellipses of the coincidence image between H^+ and C^{q+} according to the four breakup possibilities assuming a complete dissociation of the molecule. If both H^+ and C^{q+} fragments move in the same direction along the TOF extraction field, a correlated image will be formed at minimum channel numbers for both the ions. We denote these events as forward-forward (FF). On the other hand, if both fragments move together in the opposite direction of the TOF extraction field, they are eventually “turned around” and populate the backward-backward (BB) block. In addition to these, there can be correlated events where anyone among the H^+ and C^{q+} fragments can move towards or against the extraction field after dissociation. These correlated pairs will form the FB or BF images. For FF and BB cases, the fragments break away from the CH bond of the same end of the C_2H_2 molecule whereas for the FB and BF cases, a hydrogen ion of one CH bond is detected in coincidence with the carbon ion of the other CH bond after complete rupture of the molecule. In Fig. 1(a), we find a small island just above the $H^+ - C^+$ crosslike structure. This is formed due to the correlation between H^+ and CH^+ fragments where we shall only get a FB-BF slope because the two fragments emerge from two opposite ends of the dissociating molecule.

On careful inspection of the correlated images in Fig. 1, we found that the end wings of the images move away from the line joining them at the center giving them a somewhat “rotated” shape. This rotation is in perfect symmetry with each other for all the four blocks which gives the complete structure a distinct “butterflylike” look. On drawing straight lines manually along the major axis of these nearly elliptical images as shown in Fig. 1(d), we observe that the straight lines do not meet each other at the center of $H^+ - C^{q+}$ crossing. Rather the slopes form an “offset” with respect to the

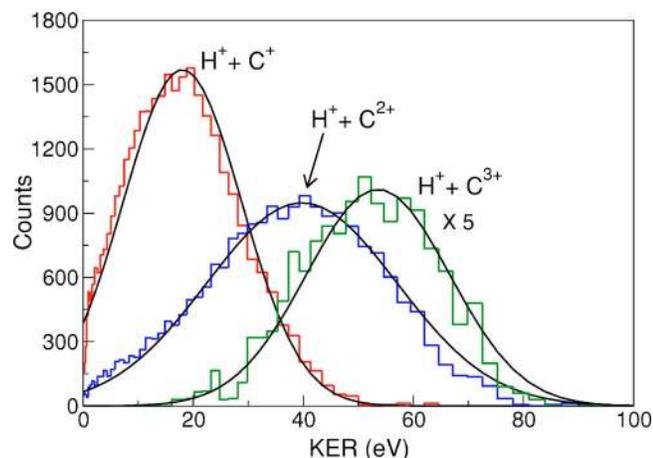


FIG. 3. (Color online) Gaussian fit to the KER distributions of H^+ derived from the H^+-C^{q+} ($q=1,2,3$) dissociation channels.

$m/q=1$ time axis which increases with the increase in the C^{q+} charge state. This offset is a manifestation of rotation of the coincidence image due to change in orientation of the molecule as we show later.

Figure 2 shows the distribution of angle between $H^+-C_2^+-H^+$ determined from triple-ion coincidence data. We would expect a linear molecule to have this angular distribution peaked at 180° . But after fitting a Gaussian to the distribution in Fig. 2, we found the mean value peaked at 152° with a full width at half maximum of 39° . This value has close resemblance with the measured H-H correlation angle distribution in triply charged acetylene reported in Ref. 5.

In the photofragmentation study of acetylene in the UV region using photoelectron-photoion-photoion coincidence method, Thissen *et al.*⁶ had reported multiple dissociation channels and proposed that the H^++C^+ channel arises from the dissociation of C_2H^+ to C^+ . In another study, Cornaggia *et al.*⁷ tried to investigate the dynamics of the structure of acetylene just before Coulomb explosion in a strong laser field through H^+-C^{q+} ($q=1,2,3$) correlation peak shapes. According to their study, the molecular ion structure cannot be frozen and one must consider the stretching and bending motions during the laser-molecule interaction. They found

TABLE I. Average bending angle of the C_2H_2 molecule deduced from Monte Carlo calculations corresponding to H^+-C^{q+} breakup channels.

Coincidence channels	Bending angle (Monte Carlo)
H^+-C^+	20°
H^+-C^{2+}	25°
H^+-C^{3+}	30°

that during the laser-induced alignment and subsequent stabilization of the molecular frame around the laser polarization direction, the C-C axis undergoes small damped oscillations and deviates from the initial linear structure. The interaction time for the photon pulses (130 fs) used in their experiment are typically of the order of intrinsic molecular vibrational and rotational time scales (10 fs–10 ps), so the photon field remains intertwined with the dissociation process. As a result, several physical mechanisms such as laser-field induced orientation, bond softening, or laser-induced dressed states can modify the molecular ion's nuclear structure. On the other hand, in our case the ion-induced interaction time is around 100 as (1.2 MeV Ar^{8+} collision), which allows us access to the virgin molecular ion in its vibrationally active structure devoid of any interference from the ion electric field.

Figure 3 shows the kinetic energy release (KER) distributions of H^+ ions derived from H^+-C^{q+} ($q=1,2,3$) dissociation channels. Similarly, we have derived KER distributions for carbon ions for the H^+-C^{q+} dissociation channels and fitted a Gaussian to find out the most probable KER along with its width. The measured KERs were used for simulating the dissociation process in a Monte Carlo simulation to generate the coincidence spectra. Randomly oriented molecules with respect to the TOF axis with a distribution of angles between C-C and C-H bonds were considered.

Figure 4 represents the simulated coincidence map of H^+ and C^{2+} correlated pairs for FF and BB configurations. In the simulation, the mean KER values (μ) for H^+ and C^{2+} ions were taken as 39.7 and 14.0 eV, respectively, which were the experimentally observed “most probable” values of the KER.

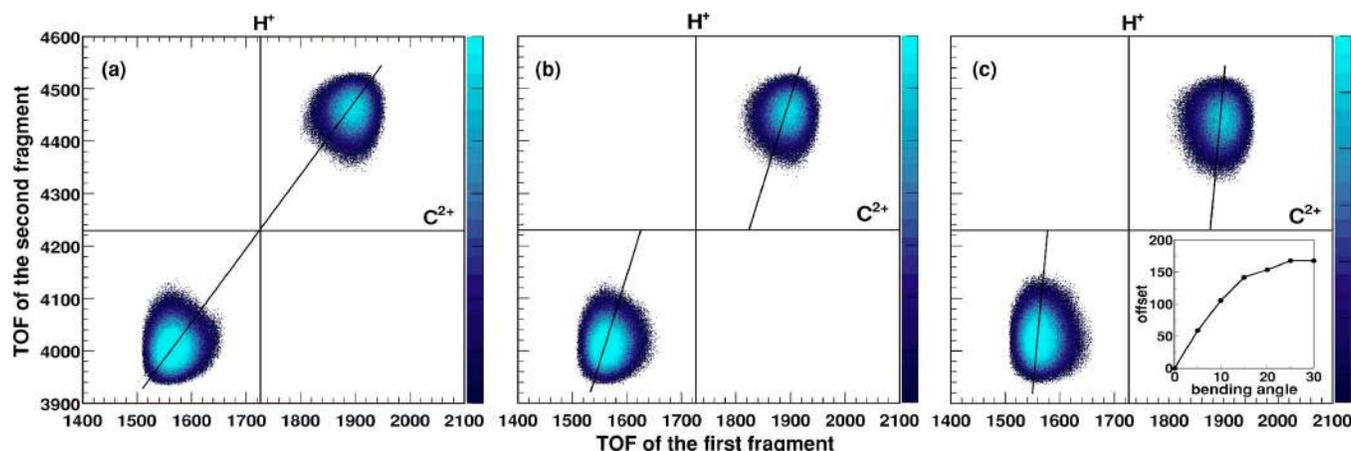


FIG. 4. (Color online) Simulated coincidence map of H^+-C^{2+} correlated pairs where the bending angle ($\angle CCH$) is a Gaussian distribution peaked at (a) 0° , (b) 10° , and (c) 20° . Inset shows the bending angle vs offset plot.

The standard deviation (σ) was taken from the observed width of KER spectra (17.2 and 9.0 eV, respectively for H^+ and C^{2+} fragments) and the energy was varied between $\mu \pm 2\sigma$. Distinct change in slopes of the coincidence pattern due to different orientations of the molecular frame during dissociation can be seen in Fig. 4. When we consider a linear structure of the C_2H_2 molecule, the simulation gives a uniform image of twin blobs passing through the central crossing of the $m/q=1$ (H^+) and $m/q=6$ (C^{2+}) lines [Fig. 4(a)]. On introduction of a Gaussian angular distribution between the C–C axis and C–H bond ($\angle CCH$), forming a bent structure of the multiply charged molecule, the dissociation partners, H^+ and C^{2+} , produce two symmetric nearly elliptical blobs in the correlation image which deviate from the earlier shape and give rise to rotations and “offsets” similar to what we have observed in the experimental spectrum. The spectrometer parameters (dimensions and voltages) chosen here correspond to the actual experimental conditions and no effort was made to fit and normalize the results. A general agreement between the calculated and the observed spectrum confirms that the offsets in the correlation islands are due to different geometries of the dissociating molecule. An inset plot in Fig. 4(c) shows the bending angle versus offset effect for $H^+ - C^{2+}$ correlated pairs. Similar plots have been drawn for all other coincidence partners ($H^+ - C^{q+}$) and the average bending angle deduced from the comparison of Monte Carlo calculation with experiment is listed in Table I. Since linear configuration calculations do not reproduce the observed correlation map fully, the observed elliptical shapes of the correlation islands result from the bent structure. Thus, the “bent” structure of the multiply charged acetylene ions when dissociating gives rise to the crosslike structures in the coincidence maps with the rotations and offsets an indication of the amount of nonlinearity at the moment of dissociation. In order to negate any possibility of artifact due to the effect of inhomogeneous extraction field of TOFMS, we have performed the experiment at higher (two times) extraction field and observed similar structures in the coincidence map for all dissociation channels.

We have also considered the possibility of sequential dissociation of C_2H_2 molecule where one of the bonds might break earlier in time with respect to the other. We incorporated an additional energy factor in the calculations to take care of the primary breakup and added the extra velocity term vectorially to get the resultant velocity of the final fragment ions. In doing so, we found that the energy gets distrib-

uted asymmetrically between the FF-BB and FB-BF blocks in the coincidence map. This leads to a “rhombus” shape in the image instead of a symmetric crosslike square structure when instantaneous breakup of the whole molecule is considered.

In summary, we have experimentally verified the theoretical prediction of the formation of a vibrationally active transition state of a doubly charged acetylene.¹ We have measured experimentally the $H^+ - C_2^+ - H^+$ angle to be around 152° . This arises from the triply charged acetylene parent ion. We have generated the salient crosslike features observed in the experimental coincidence spectra between hydrogen and carbon ionic partners by numerical calculations and found that they originate from the bent structures of the dissociating molecule. The bent structure of acetylene ions therefore gives rise to the measured offsets and rotations in the coincidence spectrum. Since the same features are observed for different carbon charge states, we conclude that “transition states” reported in Ref. 1 may also exist for highly charged C_2H_2 molecular ions. The angular distribution between $H^+ - C_2^+ - H^+$ gives a direct experimental evidence of bent structure for a triply charged acetylene molecule. The molecule is not rigid but flopping around the mean bending angle as observed from the spread in the distribution.

The molecular deformation caused by the nuclear motion is of particular interest because it plays an important role in the decay processes of core excited states, and may even open up new dynamical channels that are not reachable in the initial geometry of the neutral molecule. This study might be the first step towards using ion-induced Coulomb explosion as a tool for stereostructure studies of small polyatomic ions.

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