PHYSICAL REVIEW A **83**, 014501 (2011)

Effect of the charge localization in the C^+-H^+ fragmentation pathway of the ethyne dication

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(Received 27 September 2010; published 7 January 2011)

The C^+-H^+ channel in the fragmentation of the ethyne dication following inner-shell ionization has been studied by Auger electron-ion-ion coincidence spectroscopy. The ion-ion coincidence map shows a peculiar feature which corresponds to the emission of both the H^+ and C^+ ions in the same direction. The analysis of the data, complemented by *ab initio* calculations, suggests an interpretation in terms of a two-step, asynchronous concerted reaction, in which the charge of the ethynyl intermediate ion localizes on the terminal carbon atom.

DOI: 10.1103/PhysRevA.83.014501 PACS number(s): 34.80.Gs, 34.80.Ht

The detailed investigation of the dissociation of molecular dications has been boosted by the introduction of experimental techniques which exploit the correlation between the flight times of the ions generated during the process [1,2]. These techniques, which represent the data via the correlation map of the times needed for two ions to fly from the interaction zone to the detector, uniquely identify paired fragments coming from the *same* dissociation process. When a dication is produced, the positive charges in the valence shell localize as far away as possible from each other due to the Coulomb repulsion. Therefore if the system undergoes a dissociation, the two charged fragments fly away back-to-back and they are correlated in the time domain because they have been generated in the same dissociation process. Thus in the correlation map a charged fragment emitted in the direction of the detector (F, forward) is paired with the other one emitted in the opposite direction (B, backward) and vice versa. This kind of correlation (FB-BF) causes the coincidence pattern to have a negative slope [1]. Here, we face a peculiar case in which the time correlation between the two fragments leads to a crosslike feature with most of the intensity in the arm with *positive* slope (Fig. 1). This is unusual because this means that the ions depart toward the same direction (FF-BB) and the charges must localize on the same side of the molecule, regardlessof the Coulomb repulsion.

Electron and heavy-ion beams, synchrotron, and laser radiation have been used [3–8] to produce double ionization either directly via the ejection of two valence electrons or indirectly via inner-shell ionization followed by the Auger decay [9,10]. In the present work, we report on the fragmentation of the ethyne dication via the C^+-H^+ fragmentation channel formed following inner-shell ionization by electron impact, studied by Auger electron-ion-ion coincidence spectroscopy.

Although the first complete studies on the fragmentation of the ethyne dication date back to the eighties [11,12], the positive slope in the ion-ion maps was observed for the first time by Thissen *et al.* [13] in 1993, using the photoelectron photoion photoion coincidence (PEPIPICO) technique. However, this anomalous slope was not explained by the authors. In addition, King and Price [14], in agreement with Thissen, reported data for the C^+-H^+ ion pair with positive slope, in the case of low-energy electron ionization (20–300 eV). Sorensen in [15] studied the production of the C^+-H^+ ion pair at the C $1s \rightarrow \pi^*$ and $3\sigma^*$ resonances and reported the observation of a cross structure with equal intensity for both arms in the time correlation map. The positive arm has been ascribed to the fragmentation of the triply ionized molecule. In agreement with this result, De *et al.* [8] observed a cross-shaped feature in an experiment where heavy charged ions (Ar^{8+}) are used to fragment C_2H_2. They observed a larger intensity in the arm with a positive slope. These results have been interpreted in terms of a concerted reaction in which the multiply charged molecule explodes in one step due to the very short interaction time with the energetic ion beam (∼100 *as*). The structure and fragmentation of the ethyne dication has also attracted considerable theoretical effort [16–19]. Despite several fragmentation paths having been considered in these works, the C^+-H^+ channel has attracted less interest.

In our experiment the C $1s$ atomic orbital is ionized by a 4-KeV electron beam. The molecule then relaxes via the emission of an Auger electron. The ions produced in the fragmentation of the dication are detected in coincidence with the Auger electrons using a time-of-flight spectrometer and a cylindrical mirror analyzer, respectively. The setup allows the Auger electron-ion and Auger electron-ion-ion coincidence spectra to be measured simultaneously. The details of the experimental setup and the procedures for the data analysis, have been recently described in [20] and will not be repeated here.

The measurement of the energy of the Auger electron along with the known value of the C $1s$ ionization potential (291.14 eV; [21]) allows the final dication state to be determined as shown in our previous studies of the acetylene to vinylidene isomerization [22]. At the energy of the Auger electrons chosen in this experiment (256 eV) due to the energy resolution of our apparatus ($\Delta E/E = 1.1\%$), the three lowest electronic states of the dications, namely $^3\Sigma_g^-$, $^1\Sigma_g^+$, and $^1\Delta_g$ states are populated. According to calculations [23], the adiabatic threshold for these three states are 31.35, 32.47, and 32.24 eV [double ionization potential (DIP)]). When these states are populated the configuration of the molecule is known to be linear [16,17].

In Fig. 1 the ion-ion coincidence map relative to the C^+-H^+ ion pair, measured at an Auger electron energy of 256 eV, is shown. On the two axes the time of flight of each fragment ion is displayed. The feature, characterized by the positive slope, is definitely better defined than in the case of Thissen

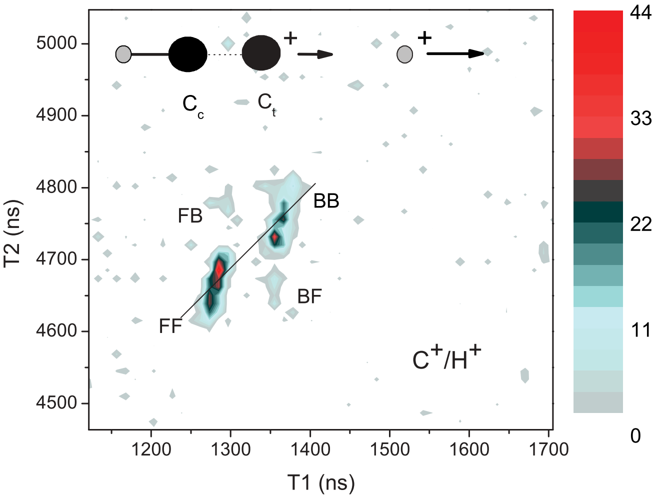

FIG. 1. (Color online) Auger electron-ion-ion coincidence map relative to the C^+-H^+ fragmentation channel. The F and B labels stand for forward and backward, respectively.

et al. [13], and can only be ascribed to the fragmentation of the dication, in contrast to those reported in Refs. [8,15]. In the figure, while the arm with negative slope (FB-BF) can be easily rationalized in terms of momentum conservation in an energetically allowed fragmentation channel, the arm with a positive slope asks for deeper thought. With this aim in mind, we will consider all the one-step and two-step fragmentations of $C_2H_2^{2+}$ in a linear configuration, with the constraint of a FF-BB time correlation.

Two one-step reactions (synchronous processes) can be taken into consideration: $HCCH^{2+} \rightarrow H^+ + C^+ + CH$ and $HCCH^{2+} \rightarrow H + C^+ + C + H^+$. From the point of view of the dynamics of the reaction the two charged particles can fly toward the same semispace, only if the dication is in a bent configuration, because the momentum of the CH (or C + H) fragment should equal that of the sum of the momenta of the two charged particles. Moreover, the appearance thresholds associated with these reactions have been found to lie at a value larger than 39.0 eV DIP [16]. This energy is above the energy of the dication states sampled in our experiment and the hypothesis of a one-step fragmentation is discarded.

Among the two-step reactions, the symmetric reaction $HCCH^{2+} \rightarrow CH^+ + CH^+$ might be considered: Nonetheless it can be ruled out due to the initial Coulomb explosion in which the two CH^+ fly away in opposite directions. For the same reason the vinylidene reaction $HCCH^{2+} \rightarrow C^+ + CH_2^+$ cannot be taken into consideration, although energetically allowed [22,24]. Indeed, in the second step two more constraints exist for the CH_2^+ fragment: The charge should be localized on one of the H atoms and the proton should be released in the same direction as the C^+ ion (i.e., a rotation of about 180° should take place). Both the conditions are very unlikely to be satisfied: The charge localizes always on the carbon atom in the lower excited states of the CH_2^+ and a free rotation up to 180° would have implied equal intensities for both the arms of the "butterfly" pattern, contrary to the experimental results.

The other possibility is an asymmetric reaction: In the first step the deprotonation reaction takes place, then the CH fragment is released in the second step [13,14], $C_2H_2^{2+} \rightarrow H^+ + C_2H^+$ then $C_2H^+ \rightarrow C^+ + CH$. Our calculations of the deprotonation reaction (first fragmentation step) show that at the Auger electron energy of 256 eV, the system can have energy enough to exceed the barrier of 3.0 eV. Indeed, the energy left in the target at this Auger electron energy is 35.14 ± 2.81 eV, that is, enough for the deprotonation process to occur (taking into account the overall experimental uncertainty). The kinetic energies associated with the C^+ and H^+ amount to 8.5 ± 3.4 eV and 0.96 ± 0.41 eV, respectively. These values, in agreement with the literature, seem to suggest a short interaction with the incident beam, followed by a fast fragmentation process [8,13]. However, the asymmetric process implies two fundamental requirements: The second step of the fragmentation should occur shortly after the first one because the rotation of the ethynyl ion is not allowed; the departing terminal carbon ion must face the proton ejected in the first step. Therefore, an *asynchronous concerted* reaction [25] should take place. The second requirement forces the global charge of the ethynyl ion to localize on the terminal carbon atom (C_t) during the second step of the fragmentation ($C_tC_cH^+ \rightarrow C_t^+ + C_cH$). Failing this (i.e., localization of the charge on C_c), besides the ulterior fragmentation ($C_c^+ + H$), the constraint of the positive slope would imply a rotation of the ethynyl ion of 180° and an equal intensity of the two arms (as for the CH_2^+ ion in the vinylidene reaction process discussed earlier).

To understand whether the charge may be preferentially localized on the terminal atom, the potential energy surfaces (PES) of the ethynyl ion have been calculated. The computational methodology used to obtain the energetic (ground and excited states) and geometrical results is based on the time-dependent density functional theory (TDDFT) [26] with the Tamm-Dancoff approximation [27]. In particular, the Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional has been adopted. The unrestricted wave functions have been expanded on the correlation consistent basis sets aug-cc-pvtz of Dunning [28]. The DFT calculations have been performed with Casida-Salahub '00 asymptotic correction with a real value of shift of 0.1 atomic units [29]. The three-dimensional PES for the ground state of C_2H^+ has been calculated at a higher level of theory with a more accurate correlation included. In particular, the MCSCF have been used with eight electrons in nine active orbitals. The estimate of the atomic charges has been performed with the Mulliken population analysis on the total density. All the calculations have been carried on with the NWCHEM *ab initio* code [30] and the cc-pvtz basis set. The PES for the lowest electronic energy state of the linear ethynyl ion is shown in Fig. 2. Beside the ellipsoidal bound region, located around $R_{CH} = 1.11$ Å and $R_{CC} = 1.34$ Å, the PES shows that the C–C and C–H fragmentations occur after passing a shallow valley (along the horizontal axis) or along a deeper valley (along the vertical axis), respectively. This latter channel shows a strictly localized conical intersection region with a higher electronic state. During the second step of the fragmentation leading to the C^+ ion, the system evolves along the horizontal axis. As is clearly seen in Fig. 2, if lower excited vibrational states

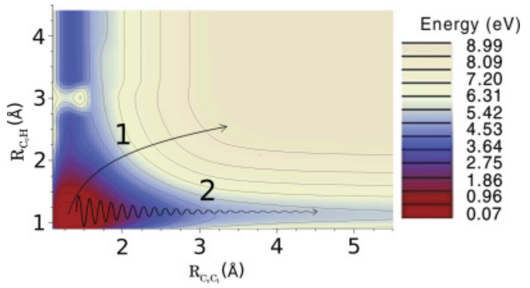

FIG. 2. (Color online) Potential energy surface (PES) for the lowest electronic energy state of the ethynyl ion. The red zone refers to the bound region. The number 1 and 2 refer to the two possible dynamics leading to the fragmentation of the CC bond; see text.

are populated, the dynamics of the system remains within the valley centered around $R_{CH} = 1.2$ Å (path number 2). In contrast, if the first dissociation step leads to a highly vibrational excited state of the $HC_cC_t^+$ the evolution from the bound region can follow trajectories corresponding to the elongation of both the CC and CH bonds at the same time (path number 1), that is, the systems move directly toward the plateau without passing in the valleys.

In order to understand which of the two dynamics supports the experimental results, we have studied the distribution of the partial charge on the three atoms of the ethynyl ion relative to the electronic ground-state potential energy surface shown earlier. In Fig. 3, the distribution of the charge of the terminal carbon atom as a function of the C–C and C–H distances, is shown. If the system is prepared in a highly vibrational excited state, and the dynamics implies the elongation of both the two bonds, the terminal carbon atom remains neutral except for a narrow region localized at $R_{CH} = 2$ Å and $R_{CC} \leqslant 2.5$ Å. In this region, the charge distribution is the result of a complex interplay between the two lowest diabatic electronic surfaces. The zero charge region of C_t around $R_{HC} \simeq 3$ Å and $R_{CC} \simeq 1.4$ Å corresponds to the conical intersection mentioned earlier with an electronic excited state in which the positive charge is localized on the H atom. In contrast, when the vibrational energy content is lower and the system evolves around the minimum energy path (path number 2 in the PES), the terminal carbon atom is released as an ion (white zone in the bottom of the figure). This suggests that the terminal carbon atom takes the charge if the CH bond remains intact. In other words the charge sits on the terminal carbon atom, due to the presence of the hydrogen atom.

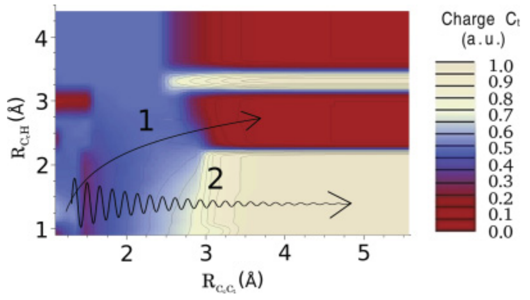

FIG. 3. (Color online) Partial charge localized on the C_t terminal carbon atom in the ethynyl ion; see text.

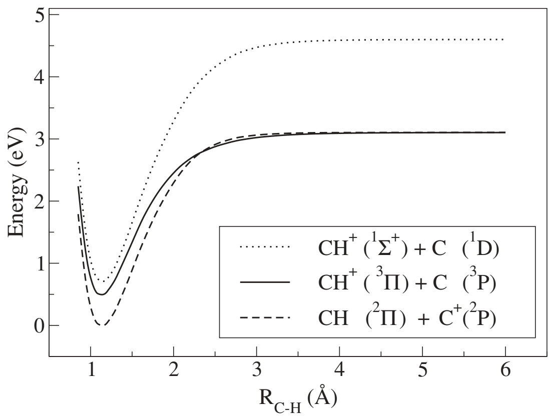

FIG. 4. Potential energy curves related to the R_{CH} coordinate, where the C_t atom is at infinite distance. In the label, the different electronic states of the fragments corresponding to the different localization of the positive charge.

For the sake of completeness, we have calculated also the asymptotic behavior of the potential energy curves as a function of C_cH distance for the lower energy electronic states of $(C_cH + C_t^+)$, where the separation between C_cH and C_t is infinite (see Fig. 4). In the CH bound region the electronic ground state is characterized by the positive charge localized on the terminal carbon atom being in its doublet P state, whereas the CH is in its Π doublet state. This curve at $R_{CH} = 2.8$ Å crosses another electronic state, in which the positive charge is on the triplet Π state of the C_cH molecule, and the C_t neutral atom is in a triplet P state. At higher energy, the electronic curve of the two singlet states of the neutral carbon atom and cation C_cH can be found. Hence, if the system is prepared in the lower vibrational states, the fragmentation of the CC bond leads always to the localization of the positive charge on the terminal carbon. These results prove that in the proposed asynchronous concerted reaction, the charge can be localized on the terminal carbon atom, following the dissociation of the ethynyl ion. This explains the experimental observation. On the other hand the highest intensity of the positive arm in the experimental map indicates $C_2H_2^{2+} \to H^+ + C_tC_cH^+ \to H^+ + C_t^+ + CH$ reaction is more likely, at least at the studied energy, than other reactions leading to the C^+-H^+ ion pair.

In conclusion, the Auger electron-ion-ion coincidence technique has been employed to study the fragmentation of the doubly ionized ethyne molecule. The C^+-H^+ fragmentation channel has been analyzed and discussed because of the observed peculiar ion-ion time correlation map. Indeed, the experimental findings suggest that the two charged atomic fragments fly in the same direction, despite the Coulomb repulsion. The analysis of the data, complemented by *ab initio* calculations, suggests that the results can be interpreted in terms of a two-step, asynchronous concerted reaction, in which the charge of the ethynyl intermediate ion localizes on the terminal carbon atom.

This work was partially supported by the MIUR-FIRB Program “Probing the microscopic dynamics of chemical reactivity” and by the MIUR-FIRB “SPARX.”

[1] J. H. D. Eland, Mol. Phys. **61**, 725 (1987).
[2] L. J. Frasinsky, K. Codling, and P. Hatherly, Science **246**, 1029 (1989).
[3] C. Cornaggia, M. Schmidt, and D. Normand, Phys. Rev. A **51**, 1431 (1995).
[4] N. Saito *et al.*, Chem. Phys. Lett. **393**, 295 (2004).
[5] A. S. Alnaser *et al.*, J. Phys. B **39**, S485 (2006).
[6] J. Adachi *et al.*, J. Phys. B **40**, F285 (2007).
[7] A. Hishikawa *et al.*, J. Chem. Phys. **128**, 084302 (2008).
[8] S. De *et al.*, J. Chem. Phys. **127**, 051101 (2007).
[9] G. Alberti *et al.*, Rev. Sci. Instrum. **76**, 073101 (2005).
[10] E. Kukk *et al.*, J. Phys. B **40**, 3677 (2007).
[11] J. H. D. Eland *et al.*, Z. Phys. D **4**, 31 (1986).
[12] J. H. D. Eland *et al.*, Philos. Trans. R. Soc. London A **324**, 247 (1988).
[13] R. Thissen *et al.*, J. Chem. Phys. **99**, 6590 (1993).
[14] S. J. King and S. J. Price, J. Chem. Phys. **127**, 174307 (2007).
[15] S. Sorensen, Eur. Phys. J. Special Topics **169**, 79 (2009).
[16] D. Duflot, J. M. Robbe, and J. P. Flament, J. Chem. Phys. **102**, 355 (1995).
[17] T. S. Zyubina *et al.*, J. Chem. Phys. **123**, 134320 (2005).
[18] J. Palaudoux and M. Hochlaf, J. Chem. Phys. **126**, 044302 (2007).
[19] V. Kimberg, N. Kosugi, and F. Gel'mukhanov, J. Chem. Phys. **130**, 114302 (2009).
[20] R. Flammini *et al.*, New J. Phys. **11**, 083006 (2009).
[21] D. W. Davis and D. A. Shirley, J. Electron Spectrosc. Relat. Phenom. **3**, 137 (1974).
[22] R. Flammini, E. Fainelli, F. Maracci, and L. Avaldi, Phys. Rev. A **77**, 044701 (2008).
[23] E. M.-L. Ohrendorf, F. Tarantelli, and L. S. Cederbaum, J. Chem. Phys. **92**, 2984 (1990).
[24] T. Osipov *et al.*, J. Phys. B **41**, 091001 (2008).
[25] C. Maul and K. H. Gericke, Int. Rev. Phys. Chem. **16**, 1 (1997).
[26] C. Jamorski, M. E. Casida, and D. R. Salahub, J. Chem. Phys. **104**, 5134 (1996); R. Bauernschmitt and R. Ahlrichs, *ibid.* **256**, 454 (1996); R. Bauernschmitt *et al.*, *ibid.* **264**, 573 (1997).
[27] S. Hirata and M. Head-Gordon, Chem. Phys. Lett. **314**, 291 (1999).
[28] T. H. Dunning Jr., J. Chem. Phys. **90**, 1007 (1989).
[29] M. E. Casida *et al.*, J. Chem. Phys. **108**, 4439 (1998).
[30] M. Valiev *et al.*, Comput. Phys. Commun. **181**, 1477 (2010).