

Vinylidene dissociation following the Auger-electron decay of inner-shell ionized acetylene

R. Flammini,* E. Fainelli, F. Maracci, and L. Avaldi

IMIP-CNR Istituto di Metodologie Inorganiche e dei Plasmi, CP10, Area della Ricerca di Roma 1,
00016 Monterotondo Scalo (RM), Italy

(Received 29 November 2007; published 17 April 2008)

The acetylene-vinylidene isomerization and the dissociation of the $C_2H_2^{2+}$ dication formed in the inner-shell ionization by electron impact have been studied via Auger-electron-ion and Auger-electron-ion-ion coincidence experiments. The occurrence of the isomerization is proved by measuring the production of the CH_2^+ fragment ion as well as by detecting the $C^+-CH_2^+$ ion pair in coincidence. The state selectivity of the technique shows that isomerization mainly takes place in the three $1\pi_u^{-2}$ lower states of the acetylene dication.

DOI: 10.1103/PhysRevA.77.044701

PACS number(s): 34.80.Gs, 34.80.Ht

Acetylene-vinylidene isomerization is an example of hydrogen migration, a process that occurs in several chemical reactions. As such it has attracted a lot of theoretical and experimental interest. In the last decade vinylidene has been studied in the anion [1–3], cation [4–7], dication [8,9], and radical [10] forms. Studies of the reaction barrier [2,11] and the possible stable energetic configurations leading to vinylidene [9,12,13] have been also performed. On the experimental side Thissen *et al.* [14] investigated the decay paths of $C_2H_2^{2+}$ and provided information on the $C^+-CH_2^+$ dissociation channel. Levin *et al.* [15] and Hayakawa *et al.* [16] confirmed the long-lived existence of vinylidene using the Coulomb explosion imaging technique and charge inversion mass spectra, respectively. More recently, Osipov *et al.* [17] investigated the rearrangement from acetylene to vinylidene following inner-shell photoionization. By measuring the photoelectron angular distribution in coincidence with the CH_2^+ ion these authors estimated a time scale of a few tens of fs for the hydrogen migration in $C_2H_2^{2+}$ formed in the Auger-electron decay of the inner-shell ionized molecules. The theoretical analysis by Duflot *et al.* [9] showed that from the low-lying states of acetylene $C_2H_2^{2+}$, it is possible to populate the low-lying state of vinylidene H_2CC^{2+} , which in turn decays into the $C^+-CH_2^+$ ion pair. Two paths have been foreseen: one through a planar transition state and the other through a nonplanar one. The recent theoretical work by Zyubina *et al.* [12], which takes into account both the ground and excited states of the dication, reported that the isomerization is favored in the excited states due to the lower potential barrier and in these states the process can occur on the time scale estimated by Osipov *et al.* [17].

In this work we have studied the acetylene-vinylidene isomerization via Auger-electron-ion and Auger-electron-ion-ion coincidence experiments. These techniques via the selection of the proper ion fragment (CH_2^+) or ion pair ($C^+-CH_2^+$) can prove the occurrence of the isomerization and the coincidence with the Auger electron enables the identification of the dication state involved. Thus the present study completes the experimental information of the photoionization experiment by Osipov *et al.* [17] and can be directly compared with the theoretical predictions.

The setup for these experiments and the procedures for

the data collection have been recently described [18]. Here only the details relevant to the present work are reported. The setup consists of a vacuum chamber (base pressure $\leq 10^{-7}$ mbar) equipped with an electron gun operated at 4 keV and two spectrometers. A dc extraction field of 120 V/cm was applied to the interaction region to extract the ions. These are detected by a Wiley-McLaren time-of-flight mass spectrometer (TOFMS) [19], while the electrons are detected by a cylindrical mirror analyzer (CMA) placed in front of the TOFMS. The angular acceptance of the CMA is $\Delta\phi = \pm 7^\circ$ around the angle $\phi = 42.7^\circ$ and results in an accepted geometrical solid angle of $\Delta\Omega = 1.53$ sr. The electron energy resolution $\Delta E/E$ is about 1.1%. The presence of the dc field in the interaction region systematically worsens the electron energy resolution (0.6 eV with a field of 120 V/cm). However, at Auger-electron energies of a few hundred eV this is $\leq 30\%$ of the overall ΔE and does not affect the resolution of the spectral features (see Fig. 1). The Auger-electron-ion coincidence electronics is based on a CAMAC time-to-digital converter operated in a multihit configuration with a common start. The triple coincidence spectra are built via a proper software *a posteriori* [18]. The current of the electron beam (≈ 1 nA) and the density of the gas (10^{-4} mbar in the interaction region) are chosen in order to

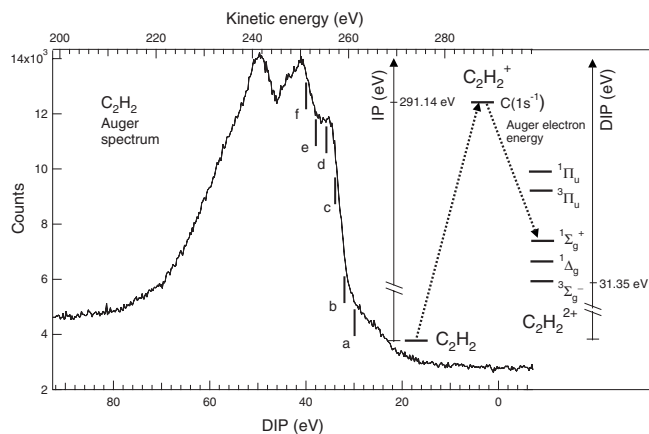


FIG. 1. C 1s Auger-electron spectrum of C_2H_2 measured in our experiment at 4 keV electron energy. The bars labeled *a...f* indicate the energies of the Auger-electron-ion measurements reported in Fig. 3. A schematic of the process leading to the acetylene dication is shown in the inset.

*roberto.flammini@imip.cnr.it

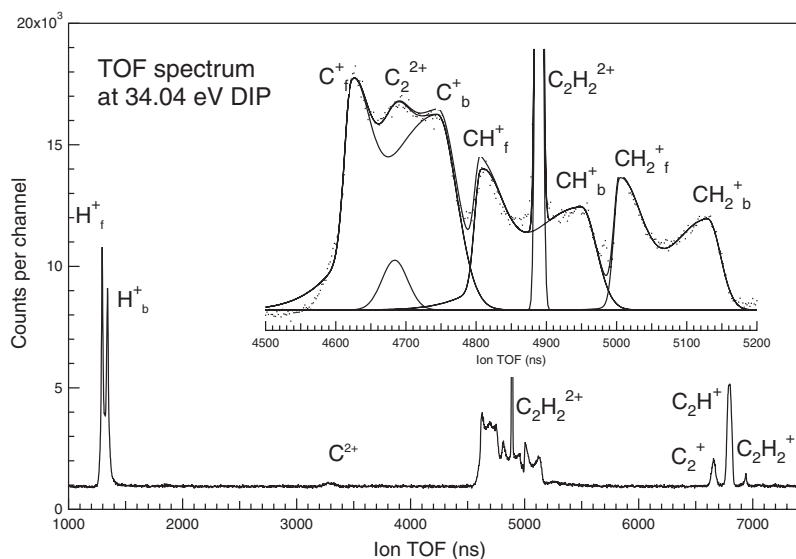
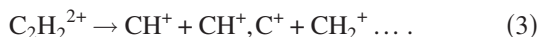
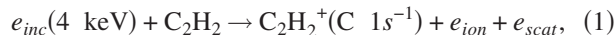


FIG. 2. Auger-electron-ion coincidence spectrum measured at a DIP of 34.04 eV. In the inset, the central feature of the spectrum (dots), where the peaks due to the CH_2^+ ion are located and the best fit (solid lines) to the different features obtained by the simulation of the ion trajectories are shown.

have ion and electron count rates of about 120 kHz and 20 Hz, respectively. These values ensure an almost constant contribution of random coincidences over the full time spectrum (8 μs) investigated. In such a condition an accumulation time of about 100 h, for each Auger-electron-ion-ion triple coincidence map is needed.

The process studied can be written as



A fast electron ionizes the C $1s$ orbital in C_2H_2 . The cation with an inner-shell hole relaxes via an Auger process leading to the formation of the dication, which then may suffer fragmentation into several ion pairs. For the sake of simplicity only two among the several final channels are indicated in step (3) of the scheme. The formation and fragmentation of the dication has been studied via the detection of Auger electrons, Auger electrons in coincidence either with an ion or an ion pair. The results of these three kinds of measurements are separately described in the following.

The measured C $1s$ Auger-electron spectrum of C_2H_2 is shown in Fig. 1. The energy calibration has been done using the previously published spectrum by Kivimaki *et al.* [20]. In an electron impact experiment both inner-shell ionization and excitation may occur. While the former produces the Auger-electron spectrum in the decay of the inner hole, the rearrangement following the core excitation results in the resonant Auger-electron spectrum that partially overlaps with the normal Auger-electron spectrum [20]. Previous studies on diatomic molecules [21,22] showed that at keV incident energies the contribution of the resonant Auger-electron spectrum to the $1s$ overall Auger-electron spectrum is negligible. Thus in our experimental conditions we neglected such a contribution in both the spectrum reported in Fig. 1 and in the Auger-electron-ion spectra of Figs. 2 and 3, as will be discussed later. Of course the resonant Auger-electron spec-

trum cannot contribute to the Auger-electron-ion-ion spectrum of Fig. 4.

The energy scale of the double ionization potentials, DIP, is defined as the difference between the C $1s$ ionization potential (291.14 eV [23]) and the measured kinetic energy of

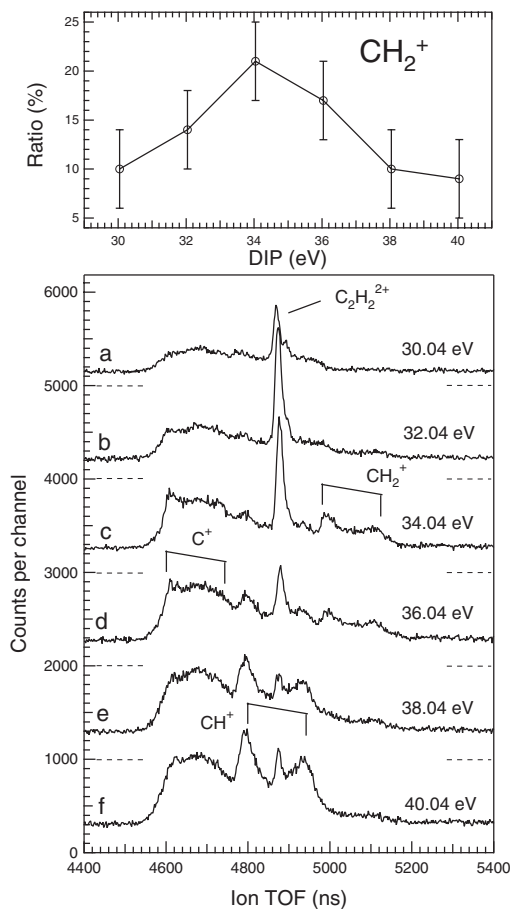


FIG. 3. Auger-electron-ion coincidence spectrum measured at several DIP values. In the top panel the relative intensity (see the text) of the CH_2^+ ion is also shown.

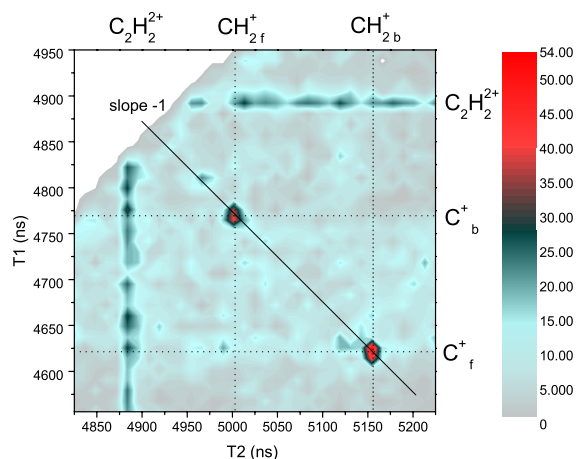


FIG. 4. (Color online) Auger-electron-ion-ion coincidence map measured at a DIP of 34.04 eV. The horizontal and vertical lines at about 4890 ns are due to the random coincidence of the undissociated $C_2H_2^{2+}$ with an uncorrelated ion. They have been left in the figure to provide to the reader a reference for comparison with Fig. 2. The two features aligned along the line with slope -1 corresponds to the $C^+-CH_2^+$ ion pair.

the Auger electrons. In this work we will focus our interest in the DIP range 30–40 eV, where we observed the fingerprints of the isomerization process, i.e., the production of the CH_2^+ ion and of the $C^+-CH_2^+$ ion pair. The peak at about 256 eV kinetic energy in the Auger-electron spectrum of Fig. 1 is attributed to the $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$ configurations, which correspond to states with two holes in the $1\pi_u$ valence outer orbital. According to calculations, the adiabatic threshold of these states has been found to lie at 31.35, 32.47, and 32.24 eV (DIP) [24], respectively. The $^1\Delta_g$ state is predicted to give the largest contribution to this peak, thus following Kivimaki *et al.* [20] we assigned the centroid of the peak in the spectrum to this state. The second feature at about 250 eV is assigned to the $3\sigma_g^{-1}1\sigma_g^{-1}(^1\Pi_g)$ and $2\sigma_u^{-1}1\pi_u^{-1}(^1\Pi_g)$ configurations. Toward lower kinetic energies the structure at 242 eV and the following tail cannot be assigned to single $2h$ configurations as they contain several $2h$, $3h1p$ states and higher excited configurations [24].

Auger-electron-ion spectra have been measured at several Auger-electron energies (labeled *a...f* in Fig. 1). In Fig. 2 an Auger-electron-ion coincidence spectrum measured at a DIP of 34.04 ± 2.81 eV is shown, while in Fig. 3 a series of TOF spectra in the region of interest is reported. The latter have been acquired simultaneously with less statistics as can be seen by a comparison of Figs. 3(c) and 2 taken at the same DIP. A procedure based on the calculation of the ion trajectories from the interaction zone to the detector [18,25] enabled us to assign the features in the TOF spectrum to the different ionic species and to analyze the shape of each feature according to the kinetic energy release (KER) of each ion. The feature at about 1300 ns with a double peak is assigned to H^+ ions. The extraction field allows the collection of light and fast ions only over a finite solid angle [18]. Hence, the two peaks correspond to the H^+ ions directed toward the detector (labeled “*f*”, forward), and to those directed in the opposite direction (labeled “*b*”, backward). The

asymmetry in the forward or backward intensity is due to the different solid angle accepted by the TOF [18]. Trajectory simulations show that it depends on the kinetic energy of the ions and on the distortion of the extraction field induced by the position, the applied voltage, and the finite dimension of the gas needle.

After a small feature attributed to C^{2+} (at 3300 ns), a series of peaks is observed in the range 4500–5200 ns. This region is enlarged in the inset where the best fit to the experimental data obtained via the simulation of $C_2H_2^{2+}$ fragmentation with the same procedure of Refs. [18,25] is also shown. The highest peak is assigned to the long-lived undissociated $C_2H_2^{2+}$ ion. To both sides of this peak the well resolved peaks attributed to CH^+ ions are observed. In symmetric positions with respect to the dication peak the features assigned to C^+ and the CH_2^+ ions have been observed as well. The tiny feature at about 4700 ns between the forward and backward C^+ peaks is assigned to the C_2^{2+} ion, which is likely to be produced via the release of the two H atoms or a H_2 molecule by the $C_2H_2^{2+}$ ion. At TOFs of about 6700 ns, two peaks are observed. They are attributed to C_2^+ and C_2H^+ . They do not display any splitting, because, due to their masses, they are produced with small kinetic energy. The tiny peak at 6950 ns is attributed to the $C_2H_2^+$ ion. It results either from a coincidence with secondary electrons produced in the direct ionization of acetylene or from a coincidence with a resonant Auger electron. $C_2H_2^+$ is the most abundant species in the mass spectrum produced by electron ionization [26], thus its low intensity in our coincidence spectrum indicates that the contribution of the background and of the resonant Auger electrons is vanishing. Our main interest here is the formation of the CH_2^+ ions, because this fragment is the fingerprint of acetylene-vinylidene isomerization. A complete study of the different fragmentation channels of the $C_2H_2^{2+}$ at several DIPs and the analysis of the KER of the different fragments will be reported elsewhere [27]. To better define the isomerization we performed six measurements at a step of 2 eV in the DIP range where the three lowest dication states are mainly populated. The results are summarized in Fig. 3. Each spectrum has been analyzed following the same procedure [18,25] of Fig. 2. From the analysis we extracted the relative percentage of CH_2^+ production as the ratio of the area of the feature assigned to CH_2^+ and the total area of the TOF spectrum in the range 4.400–5.400 ns. The variation of the ratio versus the DIP is shown in the top panel of Fig. 3. The figure shows that CH_2^+ is formed in a narrow energy window, roughly ranging from 32 to 38 eV DIP. To provide a direct evidence of the isomerization an experiment where the $C^+-CH_2^+$ ion pair is detected in coincidence with the Auger electron has been also done at a DIP of 34.04 eV. The results are shown in the 3D map of Fig. 4. In this figure the contour lines provide the yield of the triple coincidence. The two main features in the map correspond to the $CH_{2b}^+-C_b^+$ and $CH_{2f}^+-C_f^+$ ion pairs. In the figure also the traces of the random coincidences between the undissociated acetylene dication with an uncorrelated ion are shown to guide the reader in the comparison of the 3D map and the Auger-electron-ion spectra of Fig. 2. Beside the direct proof of the occurred isomerization, from the features of the 3D map we

learn that the two fragments are produced in a Coulomb explosion of the dication. Indeed, the two peaks are aligned along a line with slope -1 , as expected by momentum conservation [28,29]. The width of the two features is only due to the thermal motion of the molecules at room temperature before ionization and the experimental resolution of the setup. The total KER amounts to 5.9 ± 2.7 eV, shared by the C^+ and CH_2^+ ions as 3.2 ± 1.4 eV and 2.7 ± 1.2 eV, respectively. This KER is consistent with the formation of the two fragments in their ground states $CH_2^+(^2A_1)+C^+(^2P)$ at about ~ 29.8 eV by Dufflot *et al.* [9] and at 30.35 eV by Zyubina *et al.* [12].

Our results clearly show that the decay of the inner-shell ionized C_2H_2 can result in a doubly charged ion in the vinylidene form and that the channel leading to isomerization of the $C_2H_2^{2+}$ dication before the fragmentation is not a negligible channel. This confirms the results of Osipov [17]. Indeed, the investigated process can be interpreted as follows. Calculations [30] indicate that in the $C\ 1s$ singly ionized molecule both the internuclear equilibrium distances R_{C-C} and R_{C-H} are shorter than those of the doubly ionized molecules [14,12]. Thus in the subsequent decay, the population of the lowest dication states ($^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$), occurs on the repulsive part of the potential surface and leads to dications with a certain internal energy. Previous works indicate that a total energy of 34.55 eV [12] or 34.0 eV [14] is needed, to overcome the proton migration barrier as well as the dissociation barrier toward $CH_2^++C^+$. Taking into account the energy resolution of our experiment, this is consistent with our observation of a noticeable production of CH_2^+ at about 34.04 eV (Fig. 3, spectrum *c*). By decreasing the energy of the Auger electron the population of the lowest dication states becomes less probable, and the excited ($^1\Pi_u$, $^3\Pi_u$) states are more likely to be populated. At these DIPs (38–40 eV) the CH_2^+ production is strongly reduced. The observation of the CH_2^+ ion in a narrow DIP energy range

might appear in disagreement with the results of Thissen *et al.* [14]. They observed the increase of the CH_2^+ formation from 34 eV, the appearance potential, up to 40 eV and then a plateau. The difference between the present observations and their results can be rationalized considering that in our work the formation of the dication proceeds via the inner-shell ionization and the detection of the Auger electron selects the final dication state. Thissen *et al.* did not detect the photoelectrons produced in the double photoionization process. Therefore it is likely that, above the threshold, the observed CH_2^+ ions were always produced by double photoionization of the ground or one of the lowest dication states. Zyubina predicted that the isomerization of acetylene occurs more likely in the excited states of the dication, due to the lowering of the proton migration barrier. In fact, the $^3\Pi_u$ state lies above the proton migration threshold. Moreover, once the vinylidene isomerization has occurred there is almost no barrier (~ 0.15 eV) for the $CH_2^++C^+$ dissociation. Our results do not support this prediction, although the isomerization cannot be excluded in the excited states. It might occur, but if the C-C dissociation barrier amounts to few eV [14], the dication formed would not have enough internal energy to overcome it. Another possibility is that isomerization takes place but $CH_2^++C^+$ is a minor dissociation channel with respect, for example, to the CH^++H+C^+ one.

In conclusion it has been shown that acetylene can undergo the isomerization to a vinylidene dication in the decay after inner-shell ionization. This confirms the previous measurements of the $C\ 1s$ photoelectron angular distribution [17], but due to the energy selection of the Auger electron, here it is shown that the isomerization process preferentially occurs in the ground state and in the low-lying excited states of the dication.

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

- [1] S. Zou and J. M. Bowman, *J. Chem. Phys.* **116**, 6667 (2002).
 [2] J. Stanton and J. Gauss, *J. Chem. Phys.* **110**, 6079 (1999).
 [3] M. J. Jensen, U. V. Pedersen, and L. H. Andersen, *Phys. Rev. Lett.* **84**, 1128 (2000).
 [4] P. Rosmus, P. Botschwina, and J. P. Mayer, *Chem. Phys. Lett.* **84**, 71 (1981).
 [5] G. Frenking, *Chem. Phys. Lett.* **100**, 484 (1983).
 [6] J. Baker, *Chem. Phys. Lett.* **159**, 447 (1989).
 [7] T. P. Hamilton and H. F. Schaefer III, *J. Phys. Chem.* **93**, 7560 (1989).
 [8] J. Palaudoux and M. Hochlaf, *J. Chem. Phys.* **126**, 044302 (2007).
 [9] D. Dufflot, J. M. Robbe, and J. P. Flament, *J. Chem. Phys.* **102**, 355 (1995).
 [10] M. Ahmed, D. S. Peterka, and A. G. Suits, *J. Chem. Phys.* **110**, 4248 (1999).
 [11] N. Chang, M. Shen, and C. Yu, *J. Chem. Phys.* **106**, 3237 (1997).
 [12] T. S. Zyubina *et al.*, *J. Chem. Phys.* **123**, 134320 (2005).
 [13] K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **106**, 4119 (1997).
 [14] R. Thissen *et al.*, *J. Chem. Phys.* **99**, 6590 (1993).
 [15] J. Levin *et al.*, *Phys. Rev. Lett.* **81**, 3347 (1998).
 [16] S. Hayakawa *et al.*, *J. Chem. Phys.* **110**, 2745 (1999).
 [17] T. Osipov *et al.*, *Phys. Rev. Lett.* **90**, 233002 (2003).
 [18] G. Alberti *et al.*, *Rev. Sci. Instrum.* **76**, 073101 (2005).
 [19] W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.* **26**, 1150 (1955).
 [20] A. Kivimaki *et al.*, *J. Phys. B* **29**, 2701 (1996).
 [21] W. E. Moddeman *et al.*, *J. Chem. Phys.* **55**, 2317 (1971).
 [22] V. Feyer *et al.*, *J. Chem. Phys.* **123**, 224306 (2005).
 [23] D. W. Davis and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.* **3**, 137 (1974).
 [24] E. M.-L. Ohrendorf, F. Tarantelli, and L. S. Cederbaum, *J. Chem. Phys.* **92**, 2984 (1990).
 [25] E. Fainelli *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **161**, 51 (2007).
 [26] <http://webbook.nist.gov/chemistry>, and references therein.
 [27] R. Flammini *et al.* (unpublished).
 [28] J. H. D. Eland, *Laser Chem.* **11**, 259 (1991).
 [29] J. H. D. Eland, *Mol. Phys.* **61**, 725 (1987).
 [30] K. J. Børve *et al.*, *Phys. Rev. A* **63**, 012506 (2000).