Fragmentation Dynamics of Astrochemical Molecules Induced by UV and EUV Photons

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Abstract. The present paper reports on an experimental and computational study aimed at characterizing the microscopic fragmentation dynamics of molecules in space that are subject to double photoionization phenomena by UV and EUV (Extreme Ultraviolet) photons. This kind of processes happening in planetary ionospheres and interstellar medium are simulated at the GASPHASE and CIRCULAR POLARIZATION beamlines of the ELETTRA Synchrotron Facility of Basovizza, Trieste (Italy) using the ARPES (Angle Resolved PhotoEmission Spectroscopy) end station: a molecular beam apparatus coupled with the PEPIPICO (Photoelectron-Photoion-Photoion Coincidence) technique and the TOF (Time-of-Flight) mass spectrometry. The used synchrotron radiation is in the 25.0–45.0 eV photon energy range. Preliminary data are presented for the case of the double photoionization of allene molecules whose photoinduced decomposition highlights 8 different open two-body fragmentation channels and 3 three-body dissociations. For each investigated dissociation channels threshold energies, relative cross sections and the appearing energy for the allene $(C_3H_4)^{2+}$ dication as a function of the photon energy have been measured. Based on a Monte Carlo trajectory simulation, the computational analysis of the PEPIPICO spectra experimentally collected which is still in progress allows the possible extraction of the kinetic energy released (KER) and the angular distributions for the final fragment ions. These observables are very important to rationalize the physical chemistry of the elementary processes induced by the interaction between molecules and ionizing radiations in space.

Keywords: allene · synchrotron radiation · double photoionization · photoelectron-photoion-photoion coincidence · mass spectrometry · astrochemistry

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1 Introduction

Ionic species can be formed in space in various ways, depending on the specific conditions of the environment [1–5], manly by the interaction of neutral precursors with cosmic rays, UV photons and X-rays. In particular, the absorption of UV and EUV (Extreme Ultraviolet) photons as well as cosmic rays can induce multiple ionization phenomena with formation of doubly charged atomic or molecular species, also named as atomic/molecular dications. They were predicted to exist in the ionospheres of Mars, Venus and Titan and, then, considerable amounts have been detected in such environments highlighting their relevant role, as for example, in the ion escape process from the atmosphere of Mars and Titan [6–10]. Moreover, molecular dications were found in the comet tails, as in the case of the Hyakutake comet. The physico-chemical role of molecular dications in space can be simulated in laboratory using the molecular beam technique coupled with a tunable and intense source of UV and EUV photons as it is the synchrotron radiation. Our research group, since early 2000 is able to produce and characterize molecular dications of atmospheric and astrochemistry interest at the ELETTRA Synchrotron Facility of Basovizza (Trieste, Italy) performing double photoionization experiments. Many molecular species have been studied in the last two decades, as for example N_2O [11, 12], CO_2 [13, 14], C_6H_6 [15, 16], C_2H_2 [17, 18], propylene oxide (CH_2CHCH_2O) [19, 20], ClNO [21, 22], and very recently allene (CH_2CCH_2) molecules.

Allene (C_3H_4) is the first member of the cumulene series C_nH_4. It is well known that allene and the other odd cumulenes belong to the D_{2d} symmetry group, and exhibit stereoisomerism (axial chirality) [23]. The ground state electronic structure is of special interest since the HOMO level is doubly degenerate, having two helical shape MOs of opposite chirality [24]. Although this molecule has no electric dipole moment, and hence could not be directly identified in the interstellar media (ISM), it is thought to be present in space at least as intermediate species [19, 25]. Despite the importance of such a molecule, information on high energy processes involving multiply charged ions of allene is poor. Our research group decided to contribute in order to fill this gap, exploiting our experience in the preparation and generation of effusive molecular beams of simple organic molecules and their employment in a molecular beam apparatus (the ARPES - Angular Resolved PhotoEmission Spectroscopy - end station of the GAS-PHASE). This technique allows photoionization studies to be performed using a tunable and high photon flux of a third-generation synchrotron source. Such experimental studies were mainly based on the use of a PEPIPICO (PhotoElectron–PhotoIon–PhotoIon Coincidence) detector coupled with TOF (Time-of-Flight) mass spectrometer specially designed and built to measure the spatial momentum components of product fragments ions in the double photoionization experiments as we have done in the past [19, 26].

In the case of allene, the investigated process can be schematized by Eq. (1) below:

$$C_3H_4 + h\nu \rightarrow (C_3H_4)^{2+} + 2e^- \rightarrow \text{fragment ions} \quad (1)$$

where, $(C_3H_4)^{2+}$ is the intermediate molecular dication of allene. This a doubly charged molecular ion can be a stable, unstable or metastable species according to the relative

position of the intermolecular potentials describing the fragment ion-ion and neutral-doubly charged ion interactions characterizing the system [26]. Such a variability can be rationalized by the use of the scheme reported in Fig. 1.

Electron excitation and single photoionization processes of allene have been experimentally and theoretically investigated by several research groups. Information on high energy processes involving multiply charged ions of allene is relatively much poorer. Very recently, a detailed experimental and theoretical investigation of double and triple ionization of allene, by single photon absorption, has been carried out [27], providing the energy pattern of dication electronic states, as well as some details on their nuclear dissociation dynamics. The present study is aimed to show preliminary results obtained

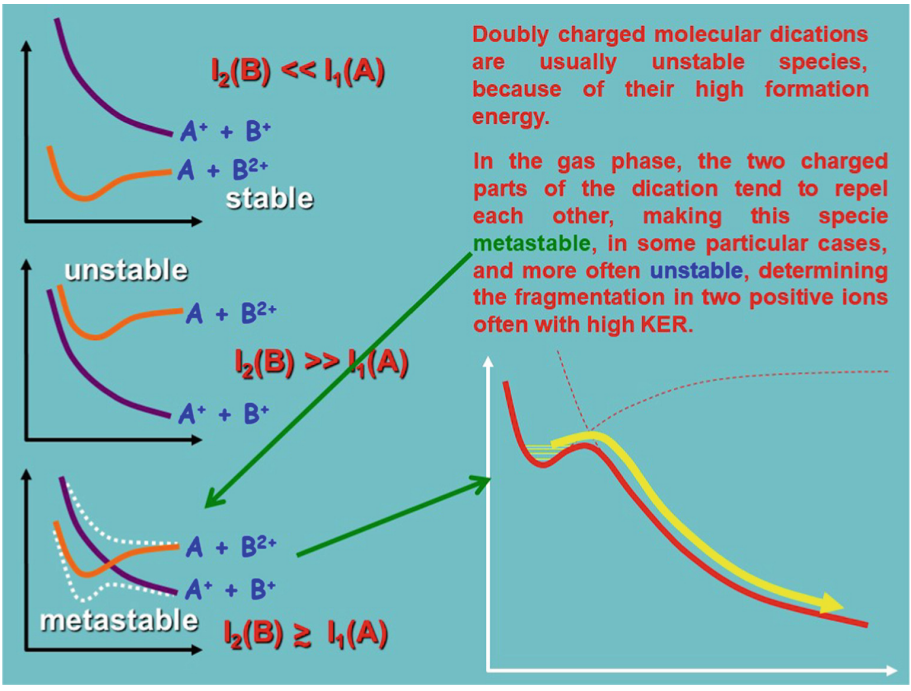

Fig. 1. The scheme of the of the potential energy curves for the simple case of AB^{2+} diatomic molecular dications. *Left upper panel* shows the case of the thermodynamically stable dications; *Center left panel*: the case of unstable species that cannot be detected in gas phase; *Lower left panel*: molecular dications in a metastable state which are the result of an avoided crossing of the potential energy curves involved. In this latter case, the resulting potential energy curve schematized in the *right lower panel*, shows the generation of the two A^+ and B^+ fragment ions having in general a high relative kinetic energy release. This process is named Coulomb explosion of the metastable dication and produces monocations with a translational energy content that can range between 1–10 eV. In the Figure: i) I_2 stands for the second ionization potential of the bounded atom having the lower electronegativity (in this case B); ii) I_1 represents the first ionization potential of the other atom (A); iii) the interatomic distance between A and B is shown in the x axis while the energy is shown in the y axis.

in a recent experiment performed at the GASPHASE beamline of the ELETTRA Synchrotron Facility of Basovizza (Trieste, Italy). In this investigation a synchrotron radiation in the 25.0 – 45.0 eV photon energy range has been used in order to conduct a detailed study of the nuclear dissociation dynamics of allene dications $(C_3H_4)^{2+}$ by single photon valence electron double ionization by means of the 3D-ion imaging spectroscopy. This different multi-coincidence technique allows higher mass resolution and much higher sensitivity than before [27], and to shed light into metastable dissociation channels where ions differ by a single unit of mass. Ion-ion coincidence yields, and the associated relative intensities, were measured from below to several tens of eV above the first double ionization threshold. High statistics ion-ion t_1-t_2 [where t_1 and t_2 are the arrival times into the ion-position-sensitive detector (see Fig. 2) of the two fragments ions generated by the Coulomb explosion of the intermediate $(C_3H_4)^{2+}$ molecular dication and detected in coincidence with the electrons ejected by double photoionization of the neutral precursor allene molecule] contour plots are recorded at selected photon energies, just above the lowest lying groups of dication states, which have been assigned to the observed photoelectron-photoelectron bands in the previous study [27], to probe with high sensitivity the topology of potential hypersurfaces [28] of dication electronic states.

2 Experimental

For the study here discussed we used the ARPES end station of the GASPHASE beamline at ELETTRA Synchrotron Radiation Facility, equipped with the same ion-imaging technique device that we have successfully applied before to HX (where X = Cl, Br and I) double photoionization experiments [29, 30, 32]. In particular, this device consists of a 3D-time of flight (TOF) ion coincidence spectrometer equipped with a multi-anode detector. It has been specially designed to properly measure vector momenta of all ion products [29]. The monochromatic synchrotron light beam operating above 22 eV will cross at right angles an effusive molecular beam of the allene molecule, and the ion products are then detected in coincidence with photoelectrons. The allene is used as a commercial sample as done in previous experiments [27].

It is important to note that the analysis of the experimental data, collected with our ion position sensitive detector, is based on the recorded ion imaging coincidence plots, and should allow us to evaluate both the kinetic energy distributions of the final product ions, and their angular distributions with respect to the polarization vector direction (see next section). It is well known [29] that such angular distributions can provide valuable information about the dissociation dynamics of intermediate molecular dications as we have done in previous works [16, 29]. Since allene is a species characterized by a low first ionization energy (9.69 eV, respectively), a conservative estimate of the photon energy range, in which the fixed energy spectra need to be recorded, should approximately be from 22 to 45 eV. Parent $(C_3H_4)^{2+}$ dications and ion-ion coincidence efficiency curves are obtained with a small energy step from the fixed energy spectra in order to measure with good accuracy the appearing potential for the molecular dication, the appearing thresholds for the ion-ion dissociation channels and their branching ratios. At the selected photon energies long acquisition times (6–8 h) were required to achieve sufficiently high

statistics in the ion-ion coincidence plots, especially in the case of dication metastable decay processes.

For the present experiments we used 24 shifts (192 h) of beamtime. The employed PEPIPICO experimental device is mounted in the molecular beam ARPES-end apparatus which is schematized in Fig. 2 [29, 30–34], where a typical coincidence plot that can be obtained in this kind of experiments is also shown.

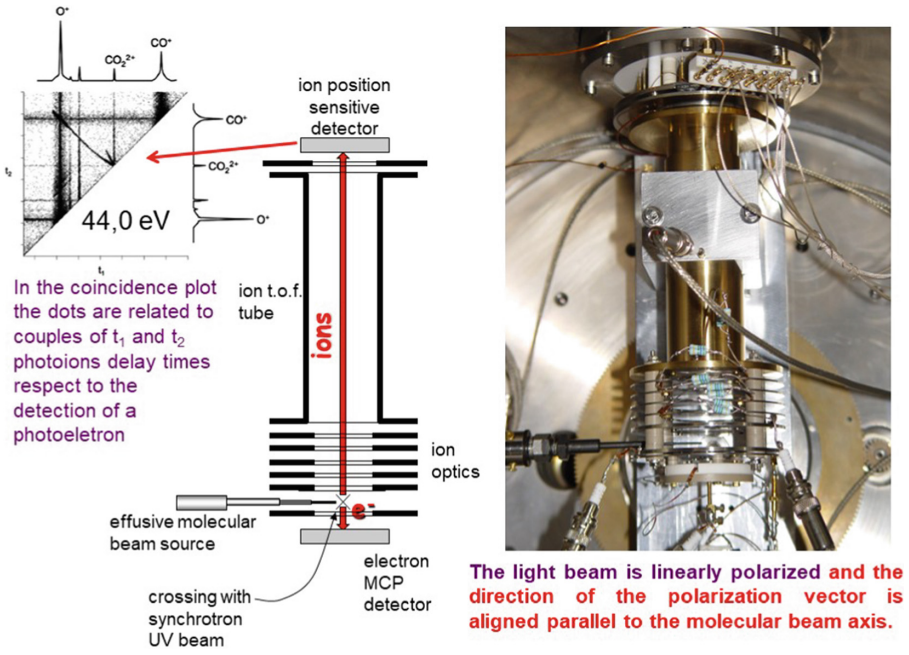

Fig. 2. The scheme of the prototype PEPIPICO (PhotoElectron-PhotoIon-PhotoIon Coincidence) device used in our 3D-ion-imaging TOF (Time-of-Flight) mass spectrometric determinations. On the *right side* is reported a picture of the device mounted inside the molecular beam ARPES (Angle Resolved PhotoEmission Spectroscopy) end station operating at the GASPHASE and CIRCULAR POLARIZATION beamlines of the ELETTRA Synchrotron Facility of Basovizza (Trieste, Italy). In the *center panel* the scheme of our coincidence ion-position-sensitive detector working coupled with a TOF tube mass spectrometer is highlighted. In the *left upper panel*, is shown a typical coincidence plot that can be recorded as a function of the investigated photon energy range using this kind of detector: in the Figure, as an example, are reported the coincidence dots distribution related to couples of t_1 and t_2 delay arrival times of fragments photo-ions respect to the photo-electons ejected in the double photoionization of carbon dioxide investigated at a photon energy of 44 eV.

3 Computational Methods

In Fig. 2 the reader can have an idea of a typical coincidence spectrum that can be recorded in our PEPIPICO experiments: as an example, this kind of observable can be appreciated as it has been collected in the case of the double photoionization of carbon dioxide performed at a synchrotron radiation photon energy of 44.0 eV. On the upper left side panel of the same figure are also visible the mass spectra associated to the ions produced either by single and double photoionization events. Such a coincidence spectrum is characteristic of all double photoionization experiments: i) the two time-of-flight values, indicated as t_1 and t_2 in the figure and text, are shown for a pair of ions (in this case CO^+ and O^+ fragments) and define a point in the diagram since they are produced by the same photoionization event (i.e. the points in the coincidence spectrum represent the coincidence events as a function of the arrival time of the first ion, t_1, and of the second ion, t_2 to the detector - see Refs. [35–37]); ii) the diagonal weak traces correspond to "false" and spurious coincidences that are neglected in the analysis performed by the Monte Carlo computational model adopted (see below).

From the mass spectra, all peaks of the generated ions are well evident as well as the recorded background signal. In the coincidence spectrum of Fig. 2 is also quite evident the "V-shaped" typical trace due to the formation of the metastable CO_2^{2+} dication that evolves by Coulomb explosion towards CO^+ and O^+ with a life time of $\tau = 3.1 \pm 0.9\ \mu s$, experimentally recorded in previous studies [13, 14].

The careful analysis of the coincidence distribution maps (as the one reported in Fig. 2) as a function of the investigated photon energy, permits the determination of the KER (kinetic energy released) of the two ionic product fragments. This can be obtained by analysing the ion intensity maps based on the method proposed by Lundqvist et al. [37] and widely used in double photoionization experiments. In particular, this target can be reached by examining the peak dimensions and shapes recorded for each ion pair product in the coincidence diagrams.

As mentioned above, a crucial experimental observable is the coincidence dots density distribution in the diagram's area of the clearly visible "tail" and the "V-shaped" traces in the coincidence plots of Fig. 2.

By using a powerful computational method introduced by Field and Eland [35], an accurate analysis of this kind of distributions as a function of the arrival time differences (t_2-t_1) of the fragment ions to our MCP (multi-channel plate) ion-position-sensitive detector (see Fig. 2), can be performed to extract the lifetime of the intermediate molecular dication which is formed in a metastable electronic state (as is the case of CO_2^{2+} [13, 14]). As a confirmation test, a second data analysis is generally carried out determining the lifetime of the metastable dications, with an alternative procedure using a Monte Carlo trajectory simulation performed in our laboratory (see for instance Ref. [13, 14]). For such a purpose, we developed a proper computer routine able to determine the t_1 and t_2 distribution delay times once the kinetic energy released (KER) by the two ionic fragments and the dissociation lifetime, τ, of the metastable dication have been fixed. The experimental distribution of the coincidence dots density $I(t_2\text{-}t_1)$ is simulated adjusting KER and τ. Then, we evaluate the standard deviation as a reliability level of the simulation with 10^6 trajectories. The $I(t_2\text{-}t_1)$ behavior is analized in order to obtain the lifetime of the metastable dication during the dication dissociation. This can achieve

by plotting the number of coincidence points along the track of the tail as a function of the $(t_2 - t_1)$ difference. After that we perform a data fitting by a Monte Carlo simulation of the trajectories of fragment ions inside the TOF mass spectrometer [38, 39].

The reader interested in a detailed description of such a computational routine can find details in Refs. [40–43].

By this procedure, we are able to determine also:

i) the KER distributions of the fragment ions as previously done in recent papers [20–22];
ii) the angular distribution of final ions with respect to the polarization vector direction of the used synchrotron radiation [11,12]: as specified in Fig. 2, in our experiments performed at the CIRCULAR POLARIZATION beamline of ELETTRA, the synchrotron light beam is linearly polarized, and the direction of the polarization vector is aligned parallel to the molecular beam axis.

It has been well demonstrated [44, 45] that the angular distributions of fragment ions so recorded, give crucial information about the dissociation microscopic dynamics of the Coulomb explosion of intermediate molecular dications. Such distributions are in general represented by $I(\theta)\sin\theta$, according to Eq. (2) below:

$$I(\theta)sin\theta = \frac{\sigma_{tot}}{4\pi}\left[1 + \frac{\beta}{2}\left(3cos^2\vartheta - 1\right)\right] \tag{2}$$

where $I(\theta)$ and σ_{tot} are the differential and total cross sections of the dissociation process, respectively; θ represents the angle between the velocity vector of the fragment ion and the polarization vector of the synchrotron light; β is the so called "anisotropy parameter" and, in general, ranges from $\beta = -1$, in the case that product ions are emitted along a direction perpendicular to the polarization vector, up to the value of $\beta = 2$ for a parallel direction. Angular distributions of fragment ions characterized by an isotropic behavior are associated to a value of $\beta = 0$ or almost zero.

4 Results

New information provided by the present study is the energetics and dissociation dynamics of allene dications by direct double photoionization of the precursor molecule, thus avoiding the core hole formation involved in previous measurements [27]. The direct approach is the most effective type of investigation of $(C_3H_4)^{2+}$ dication energetics and topology of their potential energy surfaces (PESs) [28]. The observables aimed to be recorded are: i) the threshold energies for the formation of different ionic products; ii) the related branching ratios; iii) the angular and kinetic energy distribution of fragment ions at different photon energies. These important experimental data are mandatory information for further investigations of the topology of PESs of the relevant electronic states characterizing the dissociation dynamics of $(C_3H_4)^{2+}$ dications.

The study described here is a first attempt to investigate the role of excited electronic states on the reactivity of allene dication which is a relevant species in astrochemistry.

In Fig. 3 is shown the coincidence plot (analogous to the one of the left upper panel of Fig. 2 and discussed in detail in Sects. 2 and 3) recorded in the double photoionization

of allene molecule at a synchrotron photon energy of 40.8 eV. In this type of plot, which is typical of double photoionization experiments, the two time of flight values of a couple of ions, t_1 and t_2 (both reported in the x and y axis in ns), produced in the same photoionization event define a point. In the Figure are also shown the mass spectra related to the recorded double coincidences (red color).

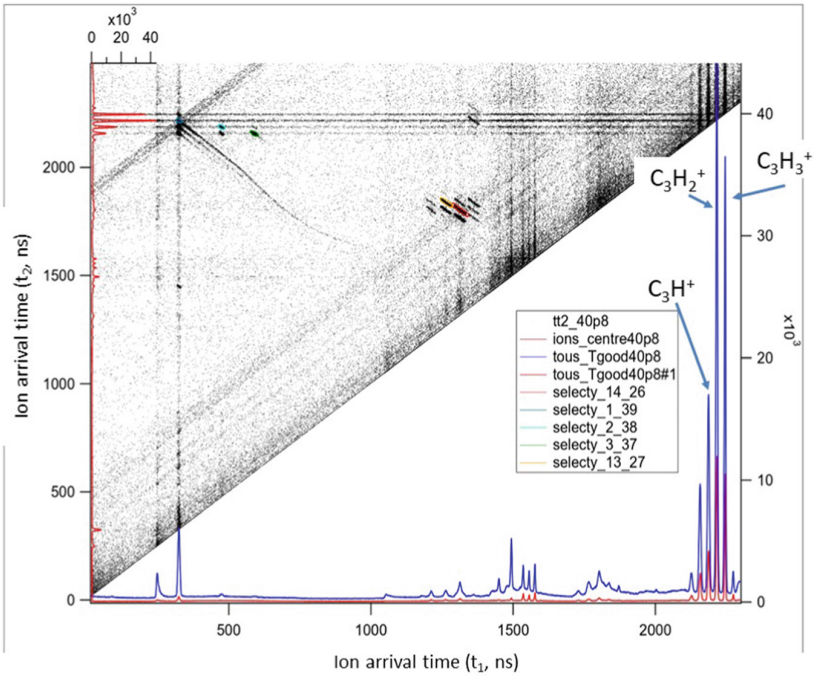

Fig. 3. The coincidence plot recorded in the double photoionization of allene molecule at a photon energy of 40.8 eV. In the figure, the mass spectra related to the double coincidences are shown in red color, while in blue color (on the x axis) the mass spectrum of the single ionization can be appreciated.

Preliminary results are here presented for the double photoionization experiment on allene (C_3H_4) molecules performed at the ELETTRA Synchrotron Radiation Facility (GASPHASE Beamline), recording data from 25.0 up to 45.0 eV photon energy. During the assigned beam time it was possible to explore the energetics of formation and the fragmentation microscopic dynamics of the intermediate $(C_3H_4)^{2+}$ dication.

First of all, it was possible to extract the energy thresholds for several fragmentation channels produced by double photoionization of C_3H_4 recording the relative cross sections for the formation of the different open dissociation channels. They are listed below with the relative threshold energy in eV:

$$C_3H_4 + hv \rightarrow H^+ + C_3H^+ + H_2 + 2e- \quad hv \geq 30.0\,eV \tag{3}$$

$$\rightarrow H_2^+ + C_3H^+ + H + 2e- \quad hv \geq 30.0\,eV \tag{4}$$

$$\rightarrow H_3^+ + C_3H^+ + 2e- \quad h\nu \geq 30.0\ eV \tag{5}$$

$$\rightarrow H^+ + C_3H_2^+ + H + 2e- \quad h\nu \geq 35.0\ eV \tag{6}$$

$$\rightarrow H_2^+ + C_3H_2^+ + 2e- \quad h\nu \geq 34.0\ eV \tag{7}$$

$$\rightarrow H^+ + C_3H_3^+ + 2e- \quad h\nu \geq 28.0\ eV \tag{8}$$

$$\rightarrow CH^+ + C_2H_2^+ + 2e- \quad h\nu \geq 37.5\ eV \tag{9}$$

$$\rightarrow CH^+ + C_2H_3^+ + 2e- \quad h\nu \geq 33.0\ eV \tag{10}$$

$$\rightarrow CH_2^+ + C_2H^+ + 2e- \quad h\nu \geq 38.0\ eV \tag{11}$$

$$\rightarrow CH_2^+ + C_2H_2^+ + 2e- \quad h\nu \geq 32.5\ eV \tag{12}$$

$$\rightarrow CH_3^+ + C_2H^+ + 2e- \quad h\nu \geq 33.5\ eV \tag{13}$$

The measured threshold energies reported above were obtained by accumulating 6–8 h at each investigated photon energy with a 200 meV photon energy step.

Furthermore, by recording the coincidence plots along 4–8 h accumulation period (see, for example, the Fig. 3 where is reported the coincidence plot recorded at 40.8 eV) as well as the mass spectra by using the PEPIPICO device mounted in the ARPES end station and described in Sect. 2, we could be able to extract:

i) the threshold energy for the formation of the allene dication $(C_3H_4)^{2+}$, whose preliminary value of 27.8 ± 0.1 eV is determined on the basis of the analysis of the recorded mass spectra as a function of the photon energy which is shown in Fig. 4;
ii) for each fragment ion produced, the respective kinetic energy released (KER);
iii) the angular distributions of the final product ions at various investigated photon energies in the range of 25.0–45.0 eV.

Such data are still in analysis in order to get the beta anisotropy parameter for the collected angular distributions (accordingly to Eq. (2)) in order to fully characterize the microscopic dynamics of recorded fragmentation reaction channel (3)–(13) listed above. In this respect, further theoretical efforts will be done with the aim of calculating the potential energy surfaces of interest, investigating the location of the lowest stationary points at the B3LYP level of theory, in conjunction with the 6–311 + G(d) basis set as we have done in various previously studied systems [26, 46–49].

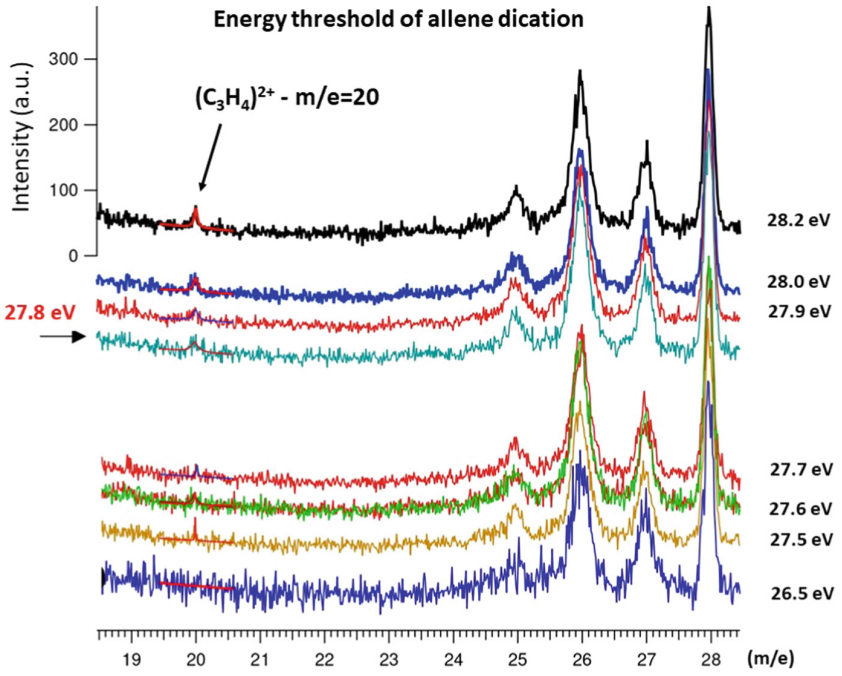

Fig. 4. The evaluation of the threshold energy for the formation of $(C_3H_4)^{2+}$ allene dication collecting mass spectra of ions produced by the double photoionization of allene in the 25.0–45.0 eV photon energy range. On the left side of the figure, the appearance energy value of 27.8 ± 0.1 eV for the allene dication is highlighted in red color next to the mass spectrum to which it refers.

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