Production and Characterization of Cyanoacetylene Dications by Synchrotron Radiation

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Abstract. In this work, the production of the cyanoacetylene dication and the characterization of its fragmentation dynamics followed by Coulomb explosion are presented, as well as its possible role in astrochemistry. The molecular dication $(HC_3N)^{2+}$ was formed by double photoionization of the neutral precursor molecule HC_3N after its in-situ synthesis. The dissociation dynamics has been studied using the photoelectron-photoion-photoion coincidence (PEPIPICO) technique coupled with time-of-flight (TOF) mass spectrometry and synchrotron radiation in the photon energy range of 30.0–50.0 eV. Preliminary results, analyzed by a Monte Carlo computational approach, are presented regarding the threshold energy for the formation of the molecular dication $(HC_3N)^{2+}$ and of all the open fragmentation channels resulting from its Coulomb explosion. Furthermore, a more in-depth analysis of the experimental data is outlined that can determine: i) the relative cross sections of the observed fragmentation channels as a function of photon energy; ii) the kinetic energy released for the formation of each fragment ion. This work is in progress in our laboratory and highlights its relevance for fully characterizing the energetics and microscopic dynamics of a process important for both environmental chemistry and astrochemistry.

Keywords: Astrochemistry · double photoionization · synchrotron radiation · molecular dications · cyanoacetylene

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1 Introduction

Despite the importance of the cyanoacetylene molecule, mainly due to its great astrochemical interest and its fundamental nature as a relatively small and reactive species, experimental data regarding the energetics and dynamics of fragmentation are still scarce.

Indeed, cyanoacetylene (HC_3N), see Fig. 1, is an important nitrogen-containing product that can be formed by the action of an electrical discharge on a mixture of methane and nitrogen. It reacts with simple inorganic substances in aqueous solution to give products including aspartic acid, asparagine, and cytosine. Furthermore, cytosine can be formed by the reaction between cyanoacetylene and cyanate, which in prebiotic chemistry is considered a potential route to the production of RNA bases on early Earth [1]. The first precursor for this reaction, an abundant interstellar molecule, is produced by an electrical discharge in a CH_4/N_2 mixture [1, 2]. However, this molecule is not commercially available and for this reason its experimental characterization, mainly from a spectroscopic point of view, is challenging.

On the other hand, the importance of ions in space has been highlighted in several papers [3–6] where the role of multiply charged ions is well emphasized. In this context, particular attention must be paid to molecular doubly positive charged ions, commonly called molecular dications: they are detected in many natural plasmas as comet tails, interstellar clouds and planetary ionospheres [7, 8]. This is the case, for example, of N_2^{2+}, O_2^{2+}, CO_2^{2+} which can be formed by double ionization induced by cosmic rays and UV-EUV photons in the upper atmospheres of Venus, Mars and Titan, Saturn's largest moon [9, 10]. Once formed, these molecular dications are in a metastable electronic state and, through a Coulomb explosion process, dissociate producing fragment monocations with a kinetic energy of several eV which allows some of them to overcome the gravitational attraction with the planet and disperse into space. [11, 12]. Several recent studies have demonstrated that these processes are responsible for the slow erosion that some planetary atmospheres, such as that of Mars, undergo due to ion escape. The latter can be generated, as mentioned above, by the Coulomb explosion of the metastable dication when it forms due to double ionization phenomena affecting the neutral precursor molecule in the ionosphere of these planets [13–15].

It is therefore important to carefully consider that the role of metastable molecular dications in the production of fast fragment ions capable of escaping into space is still underestimated in the kinetic modeling of the physical chemistry of planetary ionospheres. The goal of this type of study is also to stimulate research in the field of chemical and physical characterization of planetary atmospheres, in order to fully and more carefully consider the possible formation of molecular dications for more accurate modeling of what happens in such environments.

2 Experimental

The experiment was performed during a recent beamtime approved and performed at the GasPhase beamline of the ELETTRA Synchrotron Facility of Basovizza, Trieste, Italy (Proposal-Nr. 20235063). We were able to successfully perform the synthesis of cyanoacetylene through a procedure already well tested by our group following the one

proposed by Miller and Lemmon [16] where cyanoacetylene can be obtained at 225 °C by dehydrating C_3H_3NO (propiolamide), which has been purchased from Merck, using P_2O_5, as follows:

$$C_3H_3NO + P_2O_5 \rightarrow C_3HN + P_2O_5 - H_2O \rightarrow HC_3N + H_3PO_4 \quad (1)$$

The reaction (1) was carried out using a Pyrex system schematized in Fig. 1: round-bottom flasks with three necks are connected to a vacuum pump and a Pyrex glass container immersed in liquid nitrogen.

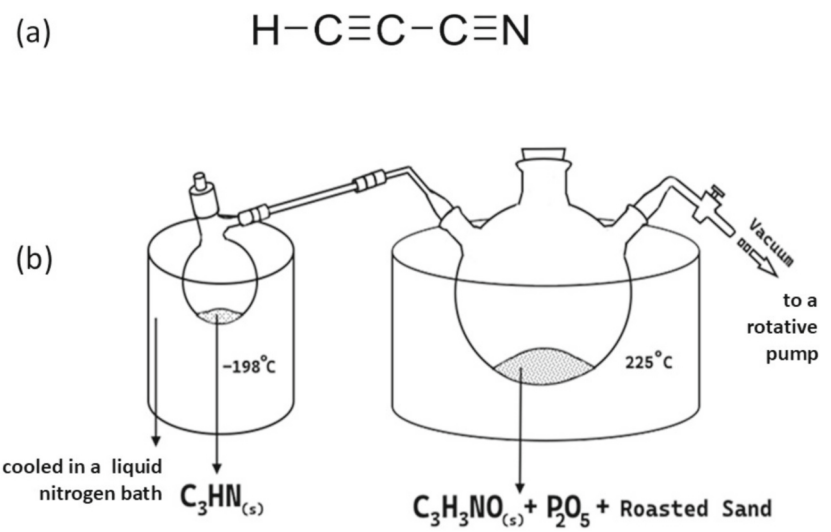

Fig. 1. (a) The Lewis structure of the cyanoacetylene molecule. (b) The scheme of the Pyrex glass setup used for the synthesis of cyanoacetylene.

The entire set-up was previously evacuated in order to remove any humidity present through the use of a rotary vacuum pump capable of obtaining a residual pressure of 10^{-2}–10^{-3} mbar. Further details of this synthesis procedure are reported in a recent article, to which we refer interested readers [17].

Then, a high-grade purity sample of cyanoacetylene has been used to produce an effusive beam exploiting its typical partial pressure of 100 mbar at room temperature. This allowed to accurately measure the threshold energy for the formation of the cyanoacetylene $(HC_3N)^{2+}$ molecular dication and for the various fragmentation channels produced by double photoionization of HC_3N in the photon energy range between 30.0 and 50.0 eV with a 100 meV energy step at the GasPhase beamline of Elettra Synchrotron Facility (Trieste, Italy).

Furthermore, by analyzing the coincidence plots recorded at each studied photon energy using the photoelectron-photoion-photoion coincidence (PEPIPICO) device mounted in the Angle-Resolved PhotoEmission Spectroscopy (ARPES) end station [18] with the use of time-of-flight (TOF) mass spectrometry, we were able to extract the threshold energy for all accessible dissociation channels. Furthermore, through careful

data analysis work that is still in progress, we will also be able to obtain the kinetic energy released (KER) distributions for the formation of each fragment ion. The ARPES station of the GasPhase beamline, whose picture is reported in Fig. 2, is a molecular beam apparatus operating in a typical vacuum regime between 10^{-7} and 10^{-8} mbar, which allow photoionization studies to be performed using a tunable and high photon flux of a third-generation synchrotron source as it is the Elettra Synchrotron Facility of Trieste, Italy [17, 18].

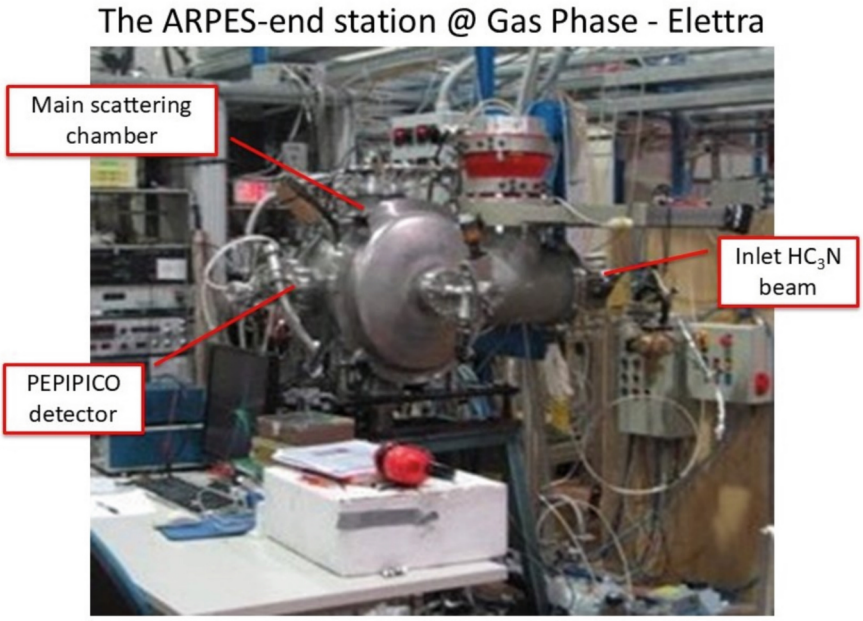

Fig. 2. The Angle-Resolved PhotoEmission Spectroscopy (ARPES) experimental station which is available at the GasPhase beamline of the Elettra synchrotron facility (Trieste, Italy) in order to perform double photoionization studies on precursor molecules of environmental and astrochemical interest.

These experimental studies have relied primarily on the use of our PEPIPICO detector coupled to a TOF mass spectrometer. This experimental setup is an ion extraction and detection system that uses a position-sensitive detector. It consists of a stack of three microchannel plates with a multi-anode array arranged in 32 rows and 32 columns. This array was specifically designed to measure the spatial momentum components of fragment ions produced in double photoionization experiments, as our research group has done in the past, starting with the in-depth and comprehensive characterization of simple halogen-bonded molecules [19–21].

In Fig. 3 are reported: (a) the scheme of the GasPhase beamline, where is operating a Monochromator 400 lines/mm spherical grating in first order diffraction with entrance and exit slits adjusted in order to give a photon energy resolution of 1.5 meV; (b) a picture

of the PEPIPICO device used in our experimental determinations whose characteristics are fully described elsewhere [22].

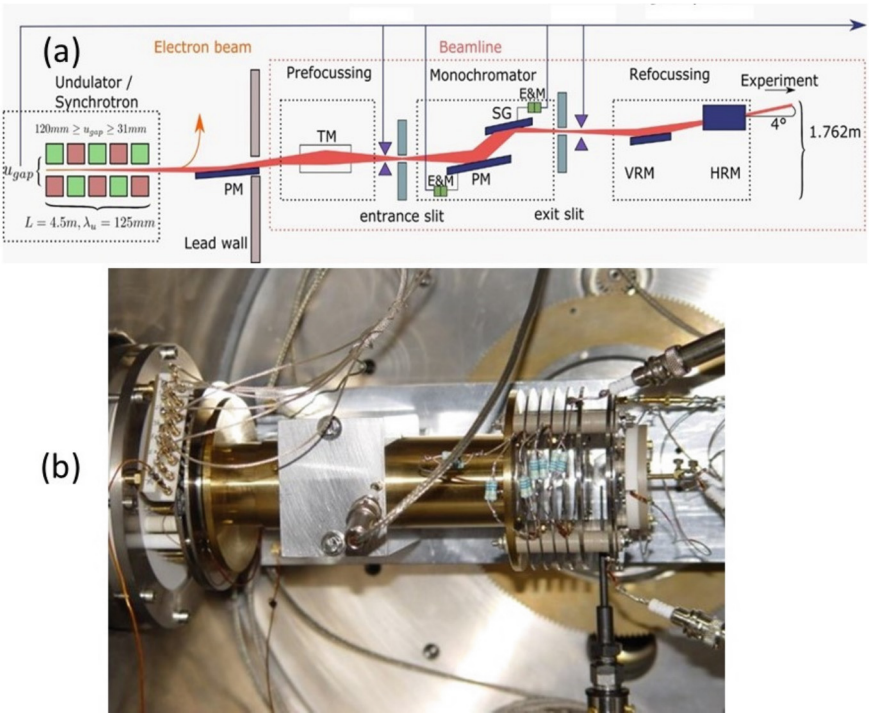

Fig. 3. (a) The scheme of the GasPhase beamline, reproduced courtesy of the Elettra Synchrotron Facility (Italy). (b) A photo of the photoelectron-photoion-photoion coincidence (PEPIPICO) device used in our experiments.

For the GasPhase beamline experiment it was necessary to use 6 shifts (48 h) of beam time in which the cyanoacetylene sample, after being produced using the above-mentioned synthesis procedure and schematized in Fig. 1, was easily employed to produce an effusive molecular beam, being safely stored at −20 °C at the Elettra chemistry laboratory.

3 Computational

The Fig. 4 shows the coincidence spectrum obtained in the double photoionization of cyanoacetylene by PEPIPICO, recorded at a photon energy of 45.0 eV. The figure, in red, also reports the mass spectra of the ions formed in both the single and double photoionization events. This kind of spectrum is typical of any coincidence plot recorded in double photoionization experiments with the PEPIPICO technique. In particular, t_1 and t_2 are the two time-of-flight values for any pair of fragment ions produced by Coulomb explosion of the short-lived HC_3N^{2+} molecular dication: they are related to

the blue dots in the diagram because they are generated by the same photoionization event. Indeed, all dots in the plot of coincidence of Fig. 4 are related to the coincidence events as a function of the arrival times, t_1 and t_2, of the two fragments ions to the detector of our TOF mass spectrometer. It has to be noted that the diagonal traces in the diagram are generated from "false" and spurious coincidences that must be neglected in the data analysis which is conducted using the Monte Carlo computational model specially developed in our laboratory (see below).

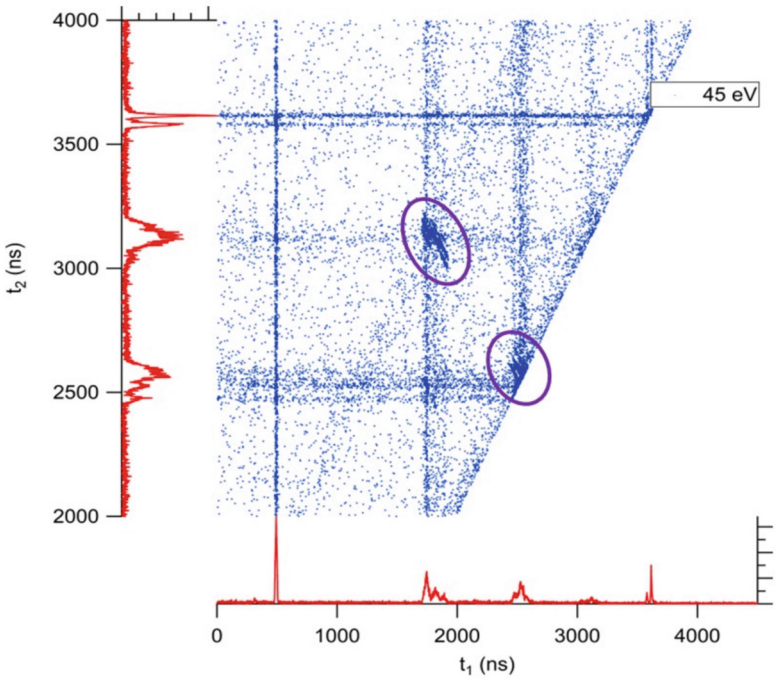

Fig. 4. The coincidence plot recorded in the double photoionization of HC_3N at a photon energy of 45.0 eV. The coincidence signals of the major open fragmentation channels are highlighted in the figure as the typical islands inside the purple ovals (see also Eqs. (2)–(10) and Sect. 4). In the figure t_1 and t_2 are respectively the arrival times of the first and second fragment ions at the detector.

In general, the analysis of PEPIPICO spectra (such as the diagram in Fig. 4), recorded as a function of synchrotron radiation photon energy, allows us to obtain important observables that are essential to fully characterize the energetics and dynamics of fragmentation that occurs following the double photoionization of the neutral precursor HC_3N. These observables are: i) the determination of all possible fragmentation channels with their corresponding threshold energies; ii) the measurement of their relative cross sections as a function of light energy; iii) the determination of the kinetic energy released (KER) of the two product ion fragments formed in each open dissociation channel; iv) the angular distribution of the product ions with respect to the direction of the

polarization vector of light; v) the evaluation of the lifetime of the intermediate dication that leads to the Coulomb explosion and subsequent fragmentation processes. This computational procedure can be performed by analyzing the shape and size of the peaks and islands (see those highlighted inside the purple ovals in Fig. 4) recorded for each ion pair produced in the coincidence spectrum, as proposed by J.H.D. Eland's group [25] who has been a leader in multiple photoionization studies.

As mentioned above, in order to confirm the reliability of our speculations on the fragmentation dynamics of the investigated systems, in our laboratory we generally perform an additional computational test, based on an alternative Monte Carlo trajectory simulation. Our computational routine is based on the determination of: i) the distribution of the delay times t_1 and t_2 of the fragment ions arriving at the TOF detector; ii) the number of recorded coincidences related to the formation of the metastable molecular dication as a function of the difference (t_2-t_1). Subsequently, a best fit of these data is performed by a Monte Carlo simulation of the ion trajectories (in general, using 10^6 trajectories) inside the TOF mass spectrometer. Finally, by minimizing the mean square values, χ^2, of the difference between the experimental data and the Monte Carlo simulation, it is possible to evaluate the lifetime of the metastable dication with its formation energy threshold. A similar procedure is applied to analyze both the distributions of the kinetic energy released (KER) of the fragment ions and their angular distributions as a function of the investigated photon energy. The reader interested in all the details of this computational procedure can refer to specific articles already published [23, 24].

4 Results and Discussion

Preliminary results concerning the double photoionization of the cyanoacetylene HC_3N molecule by synchrotron radiation in the 30–50 eV photon energy range are here presented. During the assigned beamtime at the GasPhase beamline of the Elettra Synchrotron Facility (Trieste, Italy) it was possible to perform the experiment successfully fully exploring the fragmentation microscopic dynamics of the intermediate $(HC_3N)^{2+}$ dication. The Fig. 5 shows a typical mass spectrum recorded at 45.0 eV, where all fragmentation channels are open.

Exploiting the photoelectron-photoion-photoion coincidence (PEPIPICO) device mounted in the ARPES end station (see Sect. 2 and Fig. 2), it was possible to measure accurately the threshold energy for the formation of the cyanoacetylene $(HC_3N)^{2+}$ molecular dication, obtaining the value of 31.4 ± 0.1 eV, and for the various fragmentation channels produced by double photoionization of HC_3N (see Eqs. (2)–(10) below). The measured threshold energies were obtained by accumulating 1–2 h at each investigated photon energy with a 100–200 meV energy steps. All recorded fragmentation channels and their corresponding threshold photon energies are reported in Eqs. (2)–(10) below:

$$HC_3N + h\nu \rightarrow C^+ + HCCN^+ + 2e^- \qquad h\nu \geq 33.5 \pm 0.2\ \text{eV} \tag{2}$$

$$\rightarrow CH^+ + CCN^+ + 2e^- \qquad h\nu \geq 33.5 \pm 0.2\ \text{eV} \tag{3}$$

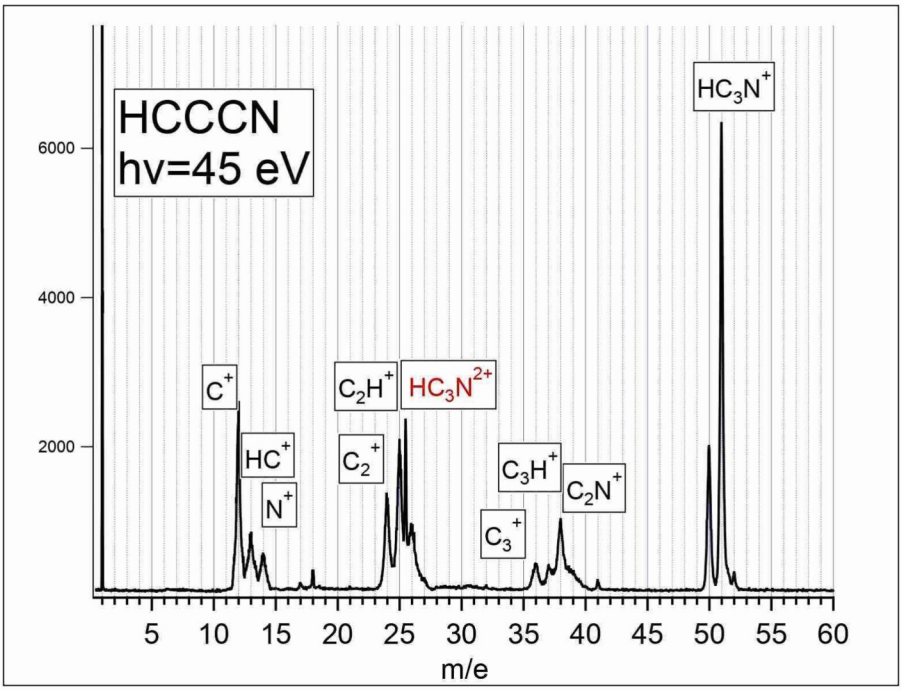

Fig. 5. The mass spectrum recorded in the double photoionization of HC_3N at a photon energy of 45.0 eV. In red is highlighted the m/e peak related to cyanoacetylene molecular dication. (Color figure online)

$$\rightarrow \text{CCCN}^+ + \text{H}^+ + 2\text{e}^- \qquad h\nu \geq 35.8 \pm 0.2 \text{ eV} \tag{4}$$

$$\rightarrow \text{C}^+ + \text{CCN}^+ + \text{H} + 2\text{e}^- \qquad h\nu \geq 37.5 \pm 0.2 \text{ eV} \tag{5}$$

$$\rightarrow \text{CCCH}^+ + \text{N}^+ + 2\text{e}^- \qquad h\nu \geq 37.6 \pm 0.2 \text{ eV} \tag{6}$$

$$\rightarrow \text{CN}^+ + \text{CC}^+ + \text{H} + 2\text{e}^- \qquad h\nu \geq 37.8 \pm 0.2 \text{ eV} \tag{7}$$

$$\rightarrow \text{CCH}^+ + \text{CN}^+ + 2\text{e}^- \qquad h\nu \geq 38.0 \pm 0.2 \text{ eV} \tag{8}$$

$$\rightarrow \text{CCN}^+ + \text{H}^+ + \text{C} + 2\text{e}^- \qquad h\nu \geq 38.2 \pm 0.2 \text{ eV} \tag{9}$$

$$\rightarrow \text{CCC}^+ + \text{N}^+ + \text{H} + 2\text{e}^- \qquad h\nu \geq 38.5 \pm 0.2 \text{ eV} \tag{10}$$

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. They were determined by using the Wannier procedure as done in previous papers [26–29].

Furthermore, by analyzing recorded coincidence plots at each investigated photon energy (see Fig. 2 – lower panel) by using the procedure described in Sects. 2 and 3, we should be able to extract the kinetic energy released (KER) for each fragment ion formation reported above as well as the relative cross sections of all the open channels (see Eqs. (2)–(10)). For this purpose, a careful analysis of the collected data is needed and this work will be done as soon as possible in order to fully characterize the microscopic dynamics of all recorded fragmentation reactions (see Eqs. (2)–(10) above).

5 Conclusions and Future Remarks

Some results obtained in a recent beamtime performed at the GasPhase beamline of the Elettra Synchrotron Facility (Trieste, Italy) and related to the double photoionization of the cyanoacetylene HC_3N molecule studied in the 30–50 eV photon energy range have been presented. A preliminary analysis based on a Monte Carlo computational routine was performed which allowed to determine the formation energy threshold for the intermediate molecular dication cyanoacetylene $(HC_3N)^{2+}$: a value of 31.4 ± 0.1 eV was measured. Moreover, such a molecular dication once formed is able to give rise to Coulomb explosion with subsequent formation of nine fragmentation channels. They were studied using photoelectron-photoion-photoion coincidence spectroscopy (PEPIPICO) coupled to time-of-flight (TOF) mass spectrometry, and the energy threshold was measured for each. Furthermore, in our ongoing work interpreting the experimental data, through a more detailed analysis of the coincidence plots recorded at each photon energy studied, we should be able to extract: i) the relative cross sections of the observed fragmentation channels as a function of photon energy; ii) the kinetic energy released for the formation of each fragment ion.

In conclusion, the new information obtained and that expected from a comprehensive and detailed analysis of the experimental data should allow us to comprehensively characterize the energetics and dynamics of the dissociation of cyanoacetylene dications due to the direct double photoionization of the precursor molecules. This is a process of astrochemical importance, as it can be induced by the interaction of neutral cyanoacetylene molecules with cosmic rays, UV and EUV photons, and synchrotron radiation, all of which are ionizing energy sources present in space. The direct approach used in this work represents the most effective method for studying the energetics of the $(HC_3N)^{2+}$ dication and the topology of its potential energy surfaces (PES). This, as already done for other systems by our research group [30–35], will constitute a further objective to be achieved. Finally, the study proposed here constitutes a first valid attempt, which will be further explored, to investigate the role of excited electronic states on the reactivity of the cyanoacetylene dication, a relevant species in space prebiotic chemistry.

Our research group, which has been involved since 2001 at the GasPhase and CiPo beamlines of the Elettra synchrotron radiation facility (see Fig. 6) in experiments studying elementary chemical processes of atmospheric and astrochemical interest [36, 37], will continue to contribute to the future development of the new MOST beamline currently under construction. We will do so by carrying on the legacy left by our colleague, collaborator, great scientist and friend Robert Richter, who has made a fundamental contribution to the development of scientific research carried out at Elettra over the past thirty years leaving an indelible mark.

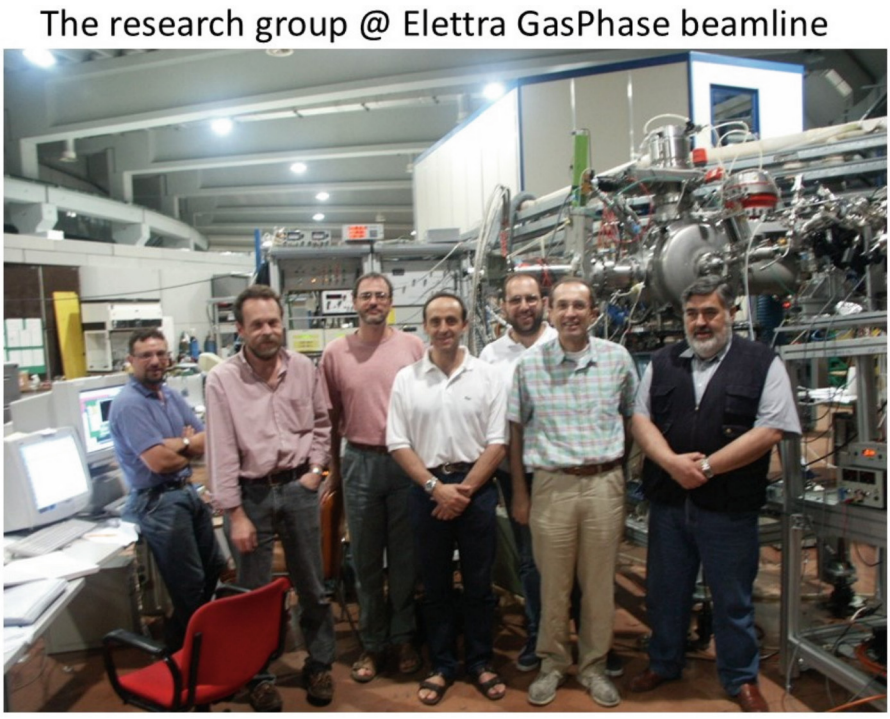

Fig. 6. From left to right: Michele Alagia, Robert Richter, Stefano Falcinelli, Stefano Stranges, Pietro Candori, Brunetto Brunetti and Franco Vecchiocattivi, during a beamtime at the GasPhase beamline of Elettra (Trieste) in the summer of 2001.

6 Disclosure of Interests

The authors have no competing interests to declare that are relevant to the content of this article.

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References

1. Sanchez, R.A., Ferris, J.P., Orgel, L.E.: Cyanoacetylene in prebiotic synthesis. Science **154**(3750), 784–785 (1966)

2. Robertson, M.P., Miller, S.L.: An efficient prebiotic synthesis of cytosine and uracil. Nature **375**, 772–774 (1995)
3. Thissen, R., Witasse, O., Dutuit, O., et al.: Doubly-charged ions in the planetary ionospheres: a review. Phys. Chem. Chem. Phys. **13**(41), 18264–18287 (2011)
4. Brunetti, B., Candori, P., Falcinelli, S., Pirani, F., Vecchiocattivi, F.: The stereodynamics of the penning ionization of water by metastable neon atoms. J. Chem. Phys. **139**(16), 164305 (2013)
5. Falcinelli, S., Rosi, M., Candori, P., Vecchiocattivi, F., et al.: Modeling the intermolecular interactions and characterization of the dynamics of collisional autoionization processes. In: Murgante, B., et al. (eds.) ICCSA 2013. LNCS, vol. 7971, pp. 69–83. Springer, Heidelberg (2013). https://doi.org/10.1007/978-3-642-39637-3_6
6. Falcinelli, S., et al.: Molecular dications in planetary atmospheric escape. Atmosphere **7**, 112 (2016)
7. Falcinelli, S., Rosi, M.: Production and characterization of molecular dications: experimental and theoretical efforts. Molecules **25**, 4157 (2020)
8. Sabzyan, H., Keshavarz, E., Noorisafa, Z.: Diatomic dications and anions. J. Iran. Chem. Soc. **11**, 871 (2014)
9. Gronoff, G., Lilensten, J., Simon, C., Witasse, O., et al.: Modelling dications in the diurnal ionosphere of Venus. Astron. Astrophys. **465**, 641–645 (2007)
10. Falcinelli, S., Pirani, F., Vecchiocattivi, F.: The possible role of penning ionization processes in planetary atmospheres. Atmosphere **6**(3), 299–317 (2015)
11. Lilensten, J., et al.: Prediction of a N_2^{++} layer in the upper atmosphere of Titan. Geophys. Res. Lett. **32**, 03203 (2005)
12. Salén, P., Schio, L., Richter, R., Alagia, M., Stranges, et al.: Electronic state influence on selective bond breaking of core-excited nitrosyl chloride (ClNO). J. Chem. Phys. **157**(12), 124306 (2022)
13. Witasse, O., Dutuit, O., Lilensten, J., et al.: Prediction of a CO_2^{2+} layer in the atmosphere of Mars. Geophys. Res. Lett. **30**, 1360 (2003)
14. Falcinelli, S., Rosi, M., Candori, P., et al.: Kinetic energy release in molecular dications fragmentation after VUV and EUV ionization and escape from planetary atmospheres. Planet. Space Sci. **99**, 149–157 (2014)
15. Falcinelli, S., Pirani, F., Alagia, M., et al.: The escape of O^+ ions from the atmosphere: an explanation of the observed ion density profiles on Mars. Chem. Phys. Lett. **666**, 1–6 (2016)
16. Miller, F.A., Lemmon, D.H.: The infrared and Raman spectra of dicyanodiacetylene. Spectrochim. Acta **23A**, 1415 (1967)
17. Parriani, M., et al.: Synthesis of chemical species relevant in environmental and astro chemistry: their production and characterization by synchrotron radiation. In: Gervasi, O., et al. (eds.) ICCSA 2025. LNCS, vol. 15888, pp. 300–314. Springer, Heidelberg (2026). https://doi.org/10.1007/978-3-031-97596-7_20
18. Teixidor, M.M., Pirani, F., Candori, P., Falcinelli, S., Vecchiocattivi, F.: Predicted structure and energetics of HCl^{2+}. Chem. Phys. Lett. **379**(1–2), 139–146 (2003)
19. Alagia, M., Brunetti, B.G., Candori, P., et al.: Threshold-photoelectron-spectroscopy-coincidence study of the double photoionization of HBr. J. Chem. Phys. **120**(15), 6980–6984 (2004)
20. Bartocci, A., Belpassi, L., Cappelletti, D., et al.: Catching the role of anisotropic electronic distribution and charge transfer in halogen bonded complexes of noble gases. J. Chem. Phys. **142**(18), 184304 (2015)
21. Pirani, F., Cappelletti, D., Falcinelli, S., et al.: Selective emergence of halogen bond in ground and excited states of noble-gas—chlorine systems. Angew. Chem. **58**(13), 4195–4199 (2019)
22. Lavollée, M.: A new detector for measuring three-dimensional momenta of charged particles in coincidence. Rev. Sci. Instrum. **70**(7), 2968–2974 (1999)

23. Falcinelli, S., Vecchiocattivi, F., Pirani, F., et al.: The fragmentation dynamics of simple organic molecules of astrochemical interest interacting with VUV photons. ACS Earth Space Chem. **3**, 1862–1872 (2019)
24. Parriani, M., Giustini, A., Alagia, M., et al.: Data analysis of molecular dications fragmentation processes by double photoionization with synchrotron radiation. In: Gervasi, O., et al. (eds.) ICCSA 2024. LNCS, vol. 14818, pp. 55–70. Springer, Heidelberg (2024)
25. Field, T.A., Eland, J.H.D.: Lifetimes of metastable molecular doubly charged ions. Chem. Phys. Lett. **211**, 436–442 (1993)
26. Wannier, G.H.: The threshold law for single ionization of atoms or ions by electrons. Phys. Rev. **90**(5), 817–825 (1953)
27. Ben Arfa, M., Lescop, B., Cherid, M., Brunetti, B., et al.: Ionization of ammonia molecules by collision with metastable neon atoms. Chem. Phys. Lett. **308**(1–2), 71–77 (1999)
28. Biondini, F., Brunetti, B.G., Candori, P., De Angelis, F., et al.: Penning ionization of N_2O molecules by $He^*(2^{3,1}S)$ and $Ne^*(^3P_{2,0})$ metastable atoms: theoretical considerations about the intermolecular interactions. J. Chem. Phys. **122**(16), 164308 (2005)
29. Falcinelli, S., Pirani, F., Vecchiocattivi, F.: Adiabatic and nonadiabatic effects in the transition states of state to state autoionization processes. Phys. Rev. Lett. **121**(16), 163403 (2018)
30. Brunetti, B., Candori, P., Falcinelli, S., Lescop, B., et al.: Energy dependence of the Penning ionization electron spectrum of $Ne^*(^3P_{2,0})$+Kr. Eur. Phys. J. D **38**(1), 21–27 (2006)
31. Alagia, M., Brunetti, B.G., Candori, P., et al.: Low-lying electronic states of HBr^2+. J. Chem. Phys. **120**(15), 6985–6991 (2004)
32. Falcinelli, S., Farrar, J.M., Vecchiocattivi, F., Pirani, F.: Quantum-state controlled reaction channels in chemi-ionization processes: radiative (optical−physical) and exchange (oxidative−chemical) mechanisms. Acc. Chem. Res. **53**(10), 2248–2260 (2020)
33. Brunetti, B., Candori, P., De Andres, J., et al.: Dissociative ionization of methyl chloride and methyl bromide by collision with metastable neon atoms. J. Phys. Chem. A **101**(41), 7505–7512 (1997)
34. Alagia, M., Biondini, F., Brunetti, B.G., Candori, P., et al.: The double photoionization of HCI: an ion-electron coincidence study. J. Chem. Phys. **121**(21), 10508–10512 (2004)
35. Balucani, N., et al.: Collisional autoionization dynamics of $Ne^*(^3P_{2,0})$–H_2O. Chem. Phys. Lett. **546**, 34–39 (2012)
36. Alagia, M., et al.: Mass spectrometric study of double photoionization of HBr molecules. J. Chem. Phys. **117**(3), 1098–1102 (2002)
37. Alagia, M., et al.: The double photoionization of hydrogen iodide molecules. J. Chem. Phys. **124**(20), 204318 (2006)