

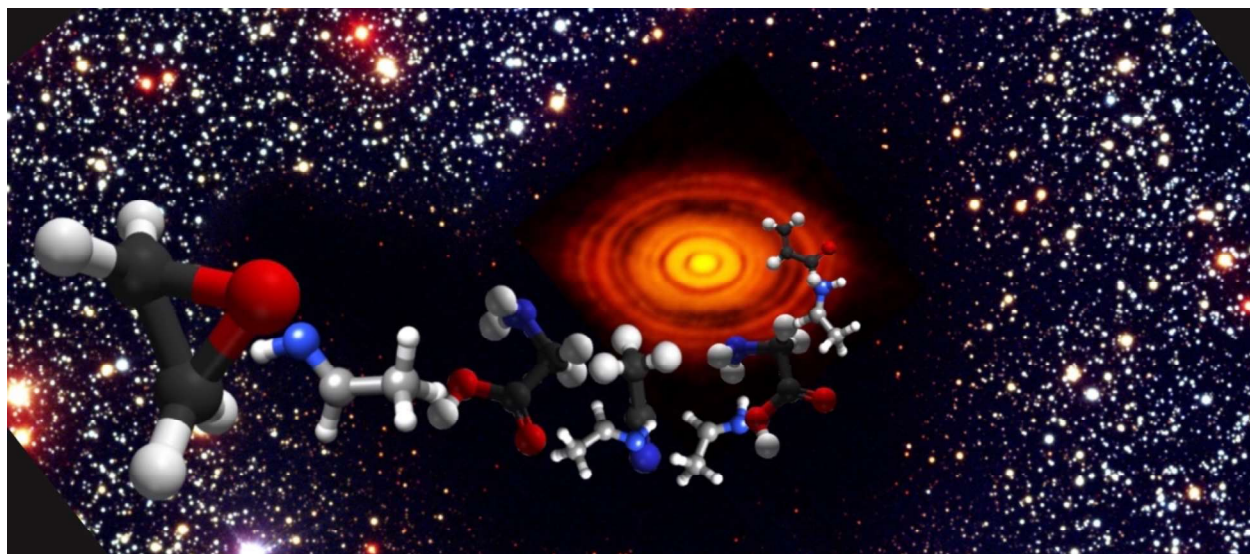
Proceedings

Astrochem2@2018

II Italian Workshop on Astrochemistry

**Chemical Evolution in our Galaxy:
Spectroscopy, Observations and Reactivity**

Follonica (GR, Italy), June 13-16 2018



Introduction: *Astrochemistry in Italy*

Vincenzo Barone¹, Claudio Codella², Cristina Puzzarini³

¹ Scuola Normale Superiore, Pisa, I-56126, Italy

² Dipartimento di Chimica “Giacomo Ciamician”, Università di Bologna, Bologna, I-40126, Italy.

³ INAF – Osservatorio Astrofisico di Arcetri, Largo E. Fermi 5, 50125, Firenze, Italy

As a continuation of the first Italian Workshop on Astrochemistry, held in March 2016 at Palazzo Strozzi (Firenze), the focus of this 2nd edition is still the synergy between astronomers and chemists to comprehend the chemical complexity and evolution in our Galaxy. The unprecedented performances offered by new observational facilities, from cm-wavelengths to the THz window, are indeed revolutionizing the census of the chemical complexity in space. Specifically, interstellar Complex Organic Molecules (iCOMs) have been observed in all the evolutionary stages leading to the formation of stars (from cold starless cores to proto-stars and proto-planetary disks). Thanks to the great advances in the modeling of gas-phase and surface chemistry through laboratory works as well as quantum chemistry calculations, we now have new tools to investigate the formation routes of iCOMs in space, building blocks of pre-biotic molecules such as amino-acids and sugars.

The previous workshop has sown important seeds in the Astrochemistry community:

- Encouraging collaborations between the chemistry and astronomy communities within the framework of two joint national projects on astrochemistry, namely “STARS in the CHAOS” and “GENESIS-SKA”.

The main goal of the 2nd Italian Workshop on Astrochemistry is to bring once again together astrophysicists and chemists working on observations, theoretical models, and laboratory experiments to present their recent advances, to discuss about the open questions, to plan further future collaborations, and to interact with European and World experts in the field.

- The birth of the first Italian Interuniversity Center in Astrochemistry, STAR (Systems and Theories for Astrochemical Research), established by Scuola Normale Superiore, University of Bologna and University of Naples Federico II. STAR aims at becoming in a near future an excellence center and the reference for astrochemical studies in Italy, thus extending the involvement to other Italian Universities and Research Institutions.
- Associated to the Interuniversity Center STAR is the first Italian Doctoral School in Astrochemistry (<http://phd.sns.it/astrochemistry/>), entirely dedicated to understand the molecular basis of the Universe evolution: the formation of small molecules in space, their evolution toward complex molecular systems, the transformation/destruction of the latter, but also the radiation-molecule interaction and the information obtainable from this.

The workshop focuses on three main topics:

- Observations of interstellar complex molecules: molecular clouds to protoplanetary systems
- Computational and molecular spectroscopy: from millimeter-waves to infra-red, from gas phase to grains
- Reactivity: from potential energy surfaces to kinetics to prebiotic chemistry



Organized in Collaboration with the Municipality of Follonica (a maritime town in the province of Grosseto, Italy), the workshop takes place in the unique environment of a former Ilva Foundry in Follonica, recently restored and with spaces destined to the Scuola Normale Superiore.

<http://smart.sns.it/astrochem2/>

Theme: *Reactivity*

Building N-containing hydrocarbons via ion-molecule reactions: isomer-selected reactivity of $C_2H_2N^+$ ions

Daniela Ascenzi¹, Claire Romanzin², Roland Thissen^{2,3}, Wolf Geppert⁴, Miroslav Polášek⁵, Jan Zabka⁵ and Christian Alcaraz^{2,3}

¹ Department of Physics, University of Trento, Trento, 38123, Italy

² LCP, CNRS-Univ. Paris-Sud 11 & Paris Saclay, Orsay Cedex, 91405, France

³ Synchrotron SOLEIL, L'Orme des Merisiers, Gif-sur-Yvette, 91192, France

⁴ Department of Physics, Stockholm University, Stockholm, 10691, Sweden

⁵ H.I.P.C. of the Czech Academy of Sciences, Prague, 18223, Czech Republic
daniela.ascenzi@unitn.it

Introduction

The recently completed *Cassini-Huygens* mission to Saturn and its satellites has unravelled the versatile and complex chemistry occurring in Titan's atmosphere [1-3]. A multitude of different positive ions of high masses were detected at ionospheric altitudes [4]. In particular, a prominent presence of nitrogen-containing compounds (especially nitriles) was found, that was not predicted by earlier models [5], and it is now well established that ionic reactions play an active role in the formation pathways of complex molecules. To improve current models of Titan's atmospheric chemistry, the identification of processes leading to the synthesis of complex ions and neutrals are pivotal, but laboratory experiments on key reactions are sparse.

We have focused our attention on the reactions of the small N-containing ions $C_2H_2N^+$ with the most abundant hydrocarbons in Titan's atmosphere, in order to assess whether they can serve as a template for building complex molecules. Although protonated nitriles are reasonably stable species, the well-known instability of CH bonds in the alpha position of nitriles might enable compounds like acetonitrile, one of the most abundant nitrogen-containing species, to undergo dissociative ionization resulting in $C_2H_2N^+$, that has been indeed observed with the Cassini Ion and Neutral Mass Spectrometer [6].

An issue that complicates the picture is that 4 different isomers of $C_2H_2N^+$ are known to be stable: one cyclic ($c-C_2H_2N^+$) and 3 linear ones (CH_2CN^+ , $HCCNH^+$ and CH_2NC^+), with the cyclic being the most stable one, followed by the cyanomethyl CH_2CN^+ cation [7]. Preliminary studies performed at Trento University on the reactivity of $C_2H_2N^+$ ions with CH_4 , C_2H_2 and C_2H_6 have led to promising results on the mechanisms of elongation of the carbon chain [8-10]. However, the electron ionization source used for $C_2H_2N^+$ production may lead to a mixture of different isomers, so further studies are here presented on the isomer selected reactivity using an alternative technique for $C_2H_2N^+$ ion generation.

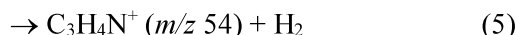
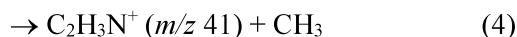
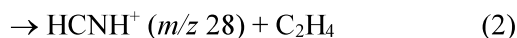
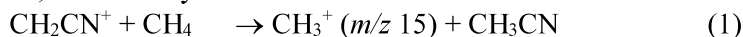
Experimental results and discussion

Experiments have been performed using the CERISES guided ion beam tandem mass spectrometer in which $C_2H_2N^+$ ions are generated via photoionization of different neutral precursors with the VUV radiation from the DESIRS beamline of the French synchrotron Soleil [11]. In particular, using CH_3CN as precursor the cyclic isomer is exclusively produced at the dissociative ionization threshold (~ 13.95 eV photon energy), while the linear CH_2CN^+ cation is formed only at photon energies higher than ~ 14.4 eV [12]. Alternatively, by starting from ICH_2CN , the CH_2CN^+ isomer is produced at the threshold for dissociative ionization of ICH_2CN (~ 12.1 eV). In addition, the exclusive production of the linear CH_2CN^+ isomer is achieved by photoionization of the cyanomethyl (CH_2CN) radical produced by pyrolysis of $ClCH_2CN$ precursor in a molecular beam source.

Using isomer selected ionic reagents cross sections, branching ratios and their dependences on collision energy have been measured for reactions with saturated and unsaturated hydrocarbons, by focussing on channels leading to molecular growth and elongation of the carbon chain. Results are presented here for CH₄, C₂H₄ and C₂H₂ neutral partners.

Reactivity of *c*-C₂H₂N⁺ and CH₂CN⁺ isomers with CH₄

With methane, the following channels have been observed, and by comparing results obtained with ICH₂CN and CH₃CN (see Fig. 1 for relative yields as a function of the photon energy) we find that the reactive isomer is the linear one, while the cyclic is non-reactive:



The product ion C₃H₄N⁺ is particularly relevant for growth processes on Titan and, by performing theoretical calculations of the most relevant stationary points along the reaction pathway, we have identified two barrierless exothermic mechanisms leading to the production of different C₃H₄N⁺ isomers (namely protonated acrylonitrile CH₂CHCNH⁺ and CH₃CHCN⁺).

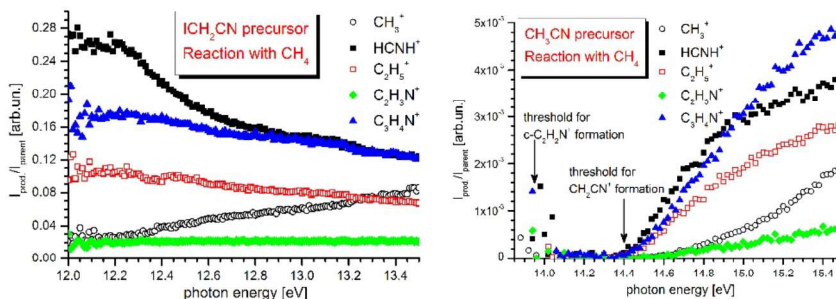
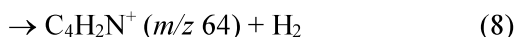


Figure 1. Relative product yields for the reaction of C₂H₂N⁺ with CH₄ as a function of the photon energy used for the production of the reagent ion

Reactivity of *c*-C₂H₂N⁺ and CH₂CN⁺ isomers with C₂H₂

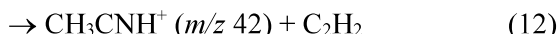
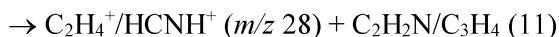
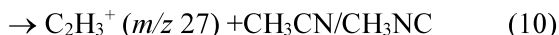
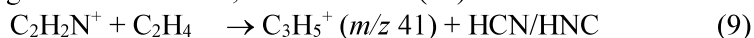
With acetylene, the following channels have been observed, with channel (7), leading to a growth by one in the number of carbon atoms, being the dominant one:



Differently from the previous case, by comparing results obtained with ICH₂CN and CH₃CN (see Fig. 2) we find that while channels (6) and (8) are formed exclusively from the linear isomer, both isomers can produce channel (7). The product ion C₃H₄N⁺ is particularly relevant for growth processes on Titan and a barrierless and exothermic pathway leading to dehydrogenated cyanoallene cation (HCCCHCN⁺) has been identified.

Reactivity of *c*-C₂H₂N⁺ and CH₂CN⁺ isomers with C₂H₄

With ethylene, the following channels have been observed, with channel (9), the equivalent of channel (7) for C₂H₂, being the dominant one, while channel (15) is the one with the smallest yield:



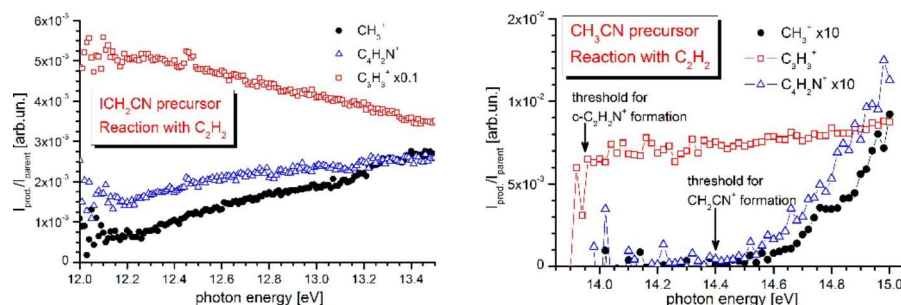
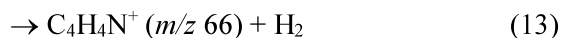


Figure 2. Relative product yields for the reaction of $\text{C}_2\text{H}_2\text{N}^+$ with C_2H_2 as a function of the photon energy used for the production of the reagent ion

Preliminary results obtained with CH_3CN as neutral precursor (see Fig. 3) indicate that channels (10)-(15) are formed exclusively from the linear isomer, while channel (9) is produced by both isomers. Channels (13), (14) and (15) are particularly relevant for growth processes on Titan. For channel (13) theoretical calculations indicate that three barrierless and exothermic pathways lead to different $\text{C}_4\text{H}_4\text{N}^+$ isomers (protonated cyanoallene $\text{CH}_2\text{CCHCNH}^+$, protonated cyanopropyne $\text{CH}_3\text{CCCNH}^+$ and dehydrogenated crotonitrile cation $\text{CH}_3\text{CCHCN}^+$). For channel (14) a possible structure of the $\text{C}_4\text{H}_5\text{N}^+$ is the pyrrole radical cation, while for channel (15) a barrierless and exothermic pathway leading to protonated cyanoacetylene HCCCNH^+ has been identified.

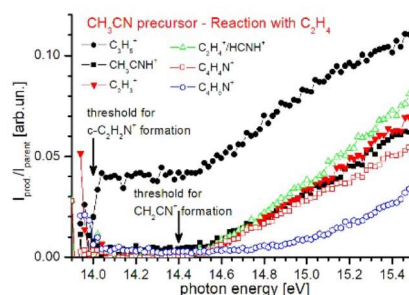


Figure 3. Relative product yields for the reaction of $\text{C}_2\text{H}_2\text{N}^+$ with C_2H_4 as a function of the photon energy used for the production of the reagent ion

References

- [1] V. Vuitton, O. Dutuit, M. A. Smith, and N. Balucani, *Titan: Interior, Surface, Atmosphere, and Space Environment*, ed. by I. Mueller-Wodarg et al. (Cambridge University Press, 2014) 224.
- [2] J. H. Westlake et al. *J. Geophys. Res. Space Physics* 119 (2014) 5951.
- [3] T. E. Cravens, R. V. Yelle, J.-E. Wahlund, D. E. Shemansky, and A. F. Nagy, *Titan from Cassini-Huygens* ed. by R. H. Brown, J.-P. Lebreton, J.H. Waite (Springer, Netherlands, 2010) 259.
- [4] J. H. Waite, D. T. Young, T. E. Cravens, A. J. Coates, et al., *Science* 316 (2007) 870.
- [5] E. H. Wilson, S. Atreya, *Planet. Space Sci.* 51 (2003) 1017.
- [6] V. Vuitton, R. Yelle, and M. J. McEwan, *Icarus* 191 (2007) 722.
- [7] S. I. Kokkila Schumacher, P. P. Bera, and T. J. Lee, *J. Phys. Chem. A* 120 (2016) 1275.
- [8] P. Fathi, W. D. Geppert, A. Kaiser, and D. Ascenzi, *Mol. Astrophys.* 2 (2016) 1.
- [9] P. Fathi, W. D. Geppert, F. Lindén, A. Cernuto, and D. Ascenzi, *Mol. AstroPhys.* 5 (2016) 9.
- [10] P. Fathi, W. D. Geppert, and D. Ascenzi, *Int. J. Mass. Spec.* 411 (2016) 1.
- [11] A. Cernuto, A. Lopes, C. Romanzin, B. Cunha de Miranda, D. Ascenzi, et al., *J. Chem. Phys.* 147 (2017) 154302.
- [12] D. Ascenzi, P. Tosi, P. Franceschi, D. Catone, S. Turchini, and K. C. Prince, *Chem. Phys.* 398 (2012) 3.