A Combined Crossed Molecular Beam and Theoretical Investigation of the CN($X^2\Sigma^+$) + HCCCN and CN($X^2\Sigma^+$) + H_2CCHCN Reactions and Astrophysical Implications

P. Liang[1], D. Marchione[1], L. Mancini[1], G. Vanuzzo[1], E. V. F. de Aragão[2], N. Faginas-Lago[1,2], M. Rosi[3], D. Skouteris[2], N. Balucani[1], P. Casavecchia[1]

[1]Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 Perugia, Italy
[2]Master-TEC s.r.l., 06128 Perugia, Italy
[3]Dipartimento Ingegneria Civile Ambientale, Università di Perugia, 06123 Perugia, Italy

Introduction

CN is one of the most abundant and widespread radicals in the interstellar medium. The fast reactions between CN and unsaturated hydrocarbons generate various nitriles[1,2], including HC_3N and H_2CCHCN, which are alleged to be prebiotic molecules. HC_3N is ubiquitous in interstellar environments. Similarly, H_2CCHCN has also been detected in numerous objects, such as the dark cloud TMC-1, massive star-forming regions Sgr B2 and Orion KL, the circumstellar envelope of the C-rich star IRC +10216, and Titan's atmosphere. Because of the wide distribution of these species, it is interesting to explore if the reactivity of CN with HC_3N and H_2CCHCN can produce more complex nitriles. Kinetics studies confirmed that the rate constant for the CN($X^2\Sigma^+$) + HC_3N reaction increases rapidly as the temperature decreases from 300 K to 22 K[3] while few studies have focused on the CN($X^2\Sigma^+$) + H_2CCHCN reaction. Furthermore, there are no experimental data on the reaction products and their branching ratios. Given these open questions, it is essential to gain further insights into these elementary reactions, both experimentally and theoretically.

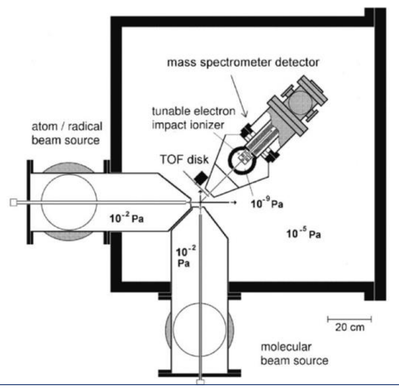
Theory

The potential energy surface of each system was investigated by locating the lowest stationary points at the B3LYP level of theory [4,5] in conjunction with the correlation consistent valence polarized set aug-cc-pVTZ [6-8]. At the same level of theory we have computed the harmonic vibrational frequencies in order to check the nature of the stationary points, i.e. minimum if all the frequencies are real, saddle point if there is one, and only one, imaginary frequency. The assignment of the saddle points was performed using intrinsic reaction coordinate (IRC) calculations [9,10]. The energy of selected stationary points was computed also at the higher level of calculation CCSD(T) using the same basis set aug-cc-pVTZ [11-13]. The CCSD(T) energies were corrected to 0 K by adding the zero point energy correction computed using the scaled harmonic vibrational frequencies evaluated at B3LYP/aug-cc-pVTZ level. All calculations were done using Gaussian 09 [14] and the optimized geometries were visualized using Avogadro Version 1.2.0 [15].

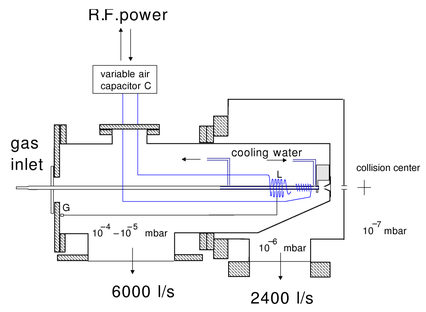
Experiment

We have investigated the **CN($X^2\Sigma^+$) + HC_3N and CN($X^2\Sigma^+$) + CH_2CHCN** reactions by the CMB method in its "universal" arrangement with mass spectrometric (MS) detection and time-of-flight (TOF) analysis by employing hard electron ionization (70eV). From product angular and velocity distribution measurements in the laboratory frame at different mass-to-charge (*m/z*) ratios, we have identified the primary product channels, derived the product angular and translational energy distributions (T(Θ) and $P(E_T)$, respectively) in the centre-of-mass frame, and determined the product branching ratios (BRs).

Perugia CMB apparatus



Lateral section of the Radio-Frequency discharge supersonic beam source

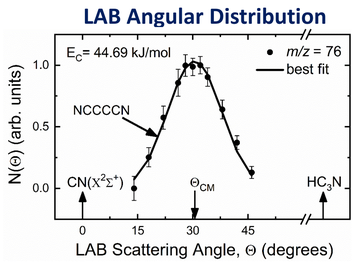


- ✓ **Continuous supersonic beams of reactants, crossing angle 90° (45° and 135° also possible)**
- ✓ **RF discharge source for cyano radical (CN)**

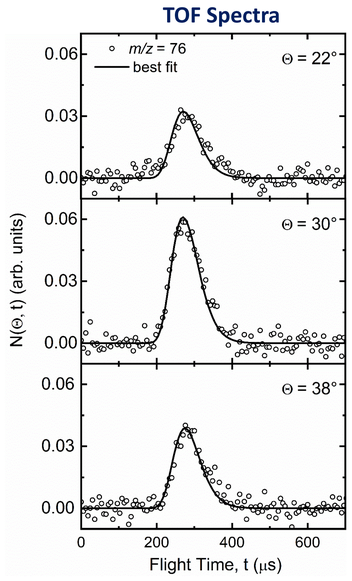
  CO_2(0.8%)/N_2(2.5%)/He
- ✓ **Rotating quadrupole mass spectrometer (MS) detector with tunable electron impact ionizer (for *soft*-ionization)**
- ✓ **TOF pseudo-random disk for product time-of-flight analysis**

The CN($X^2\Sigma^+$) + HC_3N reaction

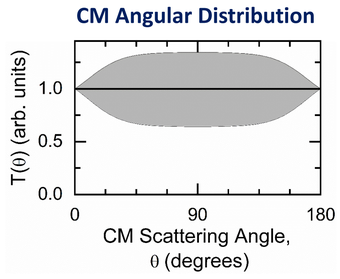
LAB Angular Distribution



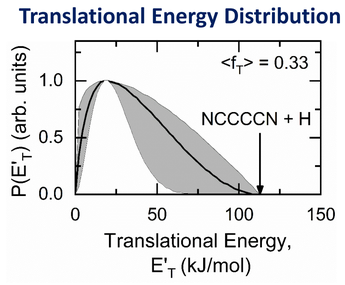
TOF Spectra



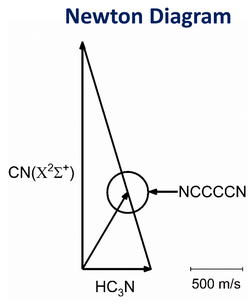
CM Angular Distribution



Translational Energy Distribution



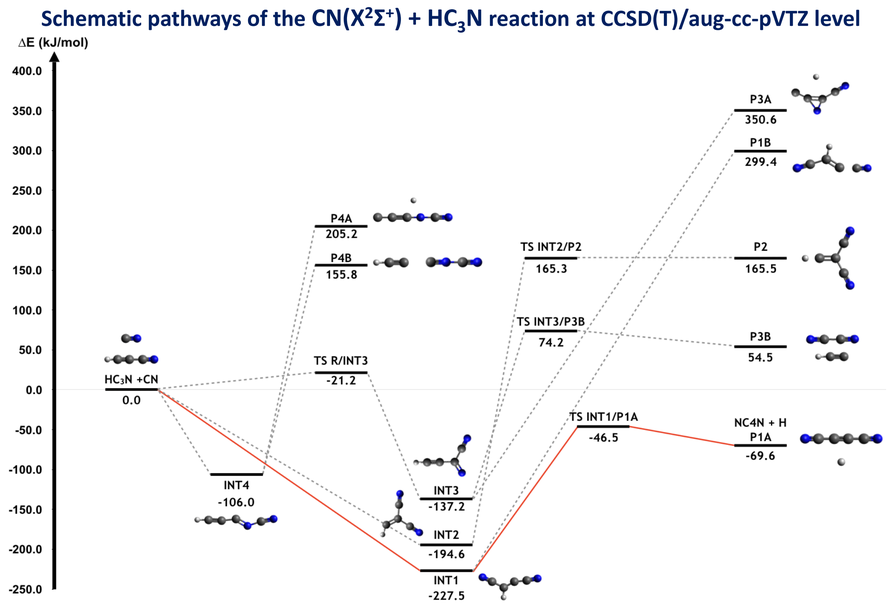
Newton Diagram



$$I_{LAB}(\Theta,v) = (v^2/u^2)\, I_{CM}(\theta,u)$$
$$I_{CM}(\theta, E_T)_{TOTAL} = \Sigma_i\, w_i \times [P(E_T)_i \times T(\theta)_i]$$

Best-fit product angular, T(Θ) , and translational energy, P(ET), distributions in the centre-of-mass (CM) frame, obtained from forward convolution analysis of the LAB angular and TOF distributions.

Schematic pathways of the CN($X^2\Sigma^+$) + HC_3N reaction at CCSD(T)/aug-cc-pVTZ level



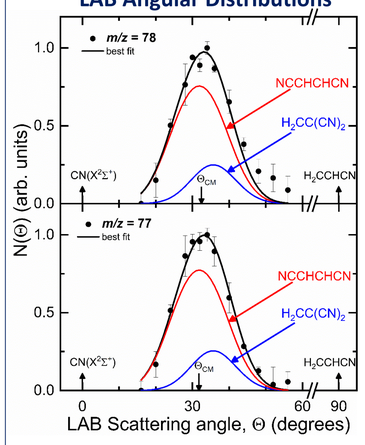
The circles superimposed on the velocity vector (Newton) diagram of the experiment delimit the maximum velocity that the indicated product can attain if all the available energy (given by E_c-ΔH) is channeled into product translational energy.

Main Results:

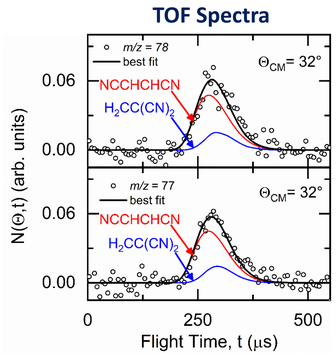
At the collision energy of 44.69 kJ/mol, the reaction of CN($X^2\Sigma^+$) with HC_3N proceed through the barrierless addition of CN by C-side to the unsaturated carbon-carbon triple bond of HC_3N leading to a bound intermediate, followed by the fission of a C-H bond to produce **2-Butynedinitrile (NCCCCN) + H** with an exit barrier. NCCCCN radical is internally very hot. From the CM T(θ) distribution, the only one exothermic channel can take place through indirect mechanism. That means the stable intermediate INT1 is able to exist for several rotational periods before dissociating to form the final product.

The CN($X^2\Sigma^+$) + CH_2CHCN reaction

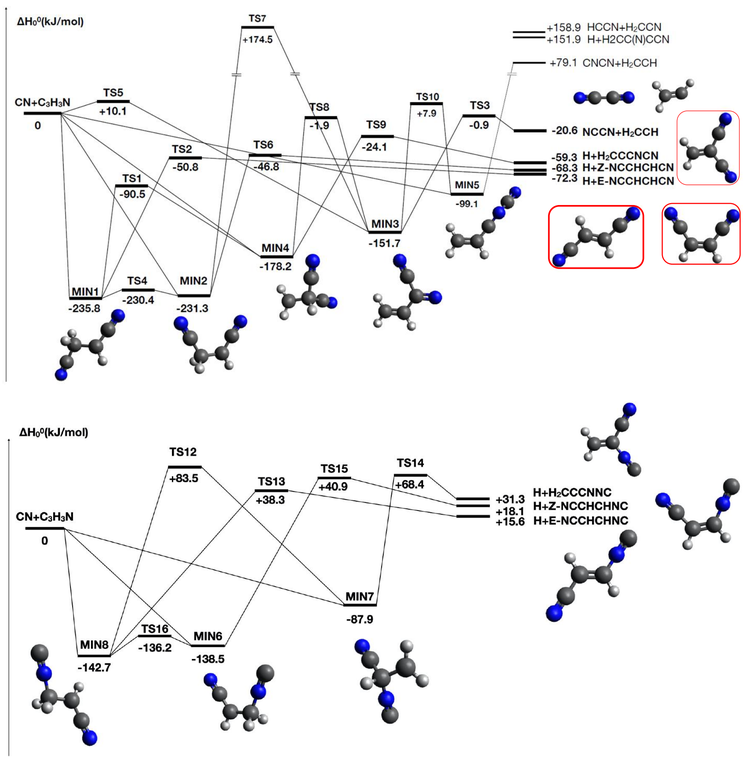
LAB Angular Distributions



TOF Spectra



Schematic potential energy diagram for the CN($X^2\Sigma^+$) + CH_2CHCN reaction originating from the attack of the CN through the C-side (Top) and N-side (Bottom)

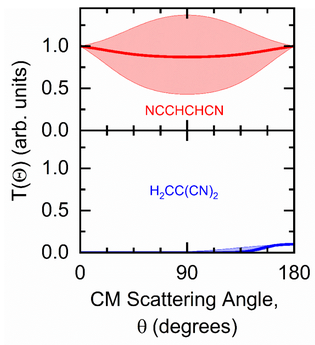


Branching Ratios

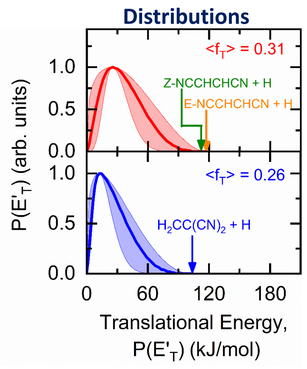
Channel	Branching Ratios				
	0.083 kJ/mol 10 K	0.78 kJ/mol 94 K	1.45 kJ/mol 175 K	2.49 kJ/mol 300 K	44.6 kJ/mol Exp. Cond.
E-NCCHCHCN + H	0.65	0.65	0.64	0.63	0.59
Z-NCCHCHCN + H	0.34	0.35	0.35	0.36	0.39
$H_2CCCNCN$ + H	1.5×10^{-3}	1.81×10^{-3}	2.35×10^{-3}	3.65×10^{-3}	1.03×10^{-2}
NCCN + H_2CCH	~0	1.38×10^{-6}	9.5×10^{-6}	8.66×10^{-5}	1.63×10^{-3}

The rate constants calculated for the CN($X^2\Sigma^+$) + CH_2CHCN reaction only consider four channels because other channels pass through a high transition-state barrier or are strong endothermic processes, which can be negligible.

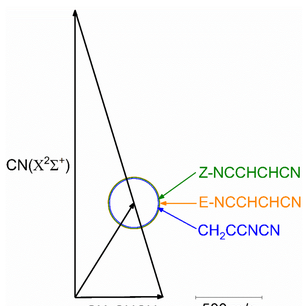
CM Angular Distributions



Translational Energy Distributions



Newton Diagram



The ratio of cross sections:
σ($H_2CCCNCN$): σ(E, Z-NCCHCHCN) = 0.1 ± 0.05

Main Results:

a) Our preliminary results indicates that the reaction of CN($X^2\Sigma^+$) with CH_2CHCN, at the collision energy of 45.52 kJ/mol, leads to three reaction channels open:
   (1) **E-but-2-enedinitrile(E-NCCHCHCN) + H**
   (2) **Z-but-2-enedinitrile(Z-NCCHCHCN) + H**
   (3) **Propanedinitrile ($H_2CCCNCN$) + H**

b) All the open channels proceed through an exit potential barrier. The E, Z-NCCHCHCN and $H_2CCCNCN$ products are internally very hot.

c) The formation of **E, Z-NCCHCHCN + H** is through indirect mechanism, **with a B.R. of about 59% and 39%, respectively**. While the formation of **$H_2CCCNCN$ + H** proceeds through direct mechanism due to the small acceptance cone of the attack of CN radical by C-side to the C atom that is already bound to a cyano group, **with a B.R. of about 1%.**

Astrophysical implications

- The CN($X^2\Sigma^+$) + HC_3N reaction is an effective process in the atmosphere of Titan and the interstellar medium (ISM), where it leads to the NCCCCN product. The first experiment to measure the primary product conducted by us verify the accuracy of the developed models in which this reaction included.
- The CN($X^2\Sigma^+$) + CH_2CHCN reaction could play a role in the formation of more complex nitriles (*i.e.* E-NCCHCHCN, Z-NCCHCHCN, and $H_2CCCNCN$) in the atmosphere of Titan and the interstellar medium (ISM). This reaction could fast below room temperatures and thus should be included in the gas-phase model.

Acknowledgements:

This work was supported by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie project grant agreement No 811312 for the project "Astro-Chemical Origins" (ACO) and the Italian Space Agency (ASI, DC-VUM-2017-034, Grant No 2019-3 U.O Life in Space).

References:

[1] I. R. Sims, *et al.*, *Chem. Phys. Lett.* **211** (4-5), 461 (1993).
[2] N. Balucani, *et al.*, *Astrophys. J.* **545** (2), 892 (2000).
[3] S. Cheikh Sid Ely, *et al.*, *J. Phys. Chem. A.* **117** (46), 12155 (2013).
[4] A. D. Becke, *J. Phys. Chem.*, **98**, 5648 (1993).
[5] P. J. Stephens, *et al.*, *J. Phys. Chem.* **98**, 11623 (1994).
[6] T. H. Dunning Jr., *J. Chem. Phys.* **90**, 1007 (1989).
[7] D. E. Woon, *et al.*, *J. Chem. Phys.*, **98**, 1358 (1993).
[8] R. A. Kendall, *et al.*, *J. Chem. Phys.* **96**,6796 (1992).
[9] C. Gonzales, *et al.*, *J. Chem. Phys.* **90**, 2154 (1989).
[10] C. Gonzales, *et al.*, *J. Phys. Chem.*, **94**, 5523 (1990).
[11] R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981).
[12] K. Raghavachari, *et al.*, *Chem. Phys Lett.* **157**, 479(1989).
[13] J. Olsen, *et al.*, *J. Chem. Phys.*, **104**, 8007 (1996).
[14] M. J. Frisch, *et al.* Gaussian09 Revision D.01.
[15] M. D. Hanwel, *et al.*, *J. Cheminformatics* **4**(1), 17 (2012).