INTERNATIONAL SYMPOSIUM AND WORKSHOP ON ASTROCHEMISTRY

Understanding extraterrestrial molecular complexity through experiments and observations

Non-thermal ion desorption from nitrile-bearing astrophysical ice analogues studied by electron and heavy ion bombardment

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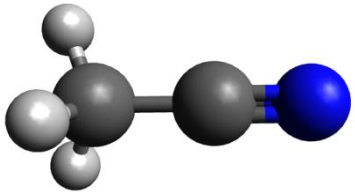
Observatório do Valongo

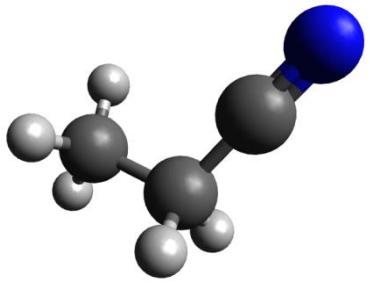
2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H_2	C_3 *	*c*-C_3H	C_5 *	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	*c*-C_6H_6 *	$HC_{11}N$
AlF	C_2H	*l*-C_3H	C_4H	*l*-H_2C_4	CH_2CHCN	$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	*n*-C_3H_7CN	C_{60} *
AlCl	C_2O	C_3N	C_4Si	C_2H_4 *	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	*l*-C_3H_7CN	C_{70} *
C_2 **	C_2S	C_3O	*l*-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$?	C_{60}^+ *
CH	CH_2	C_3S	*c*-C_3H_2	CH_3NC	CH_3CHO	C_6H_2	HC_7N	CH_3CHCH_2O 2016			
CH^+	HCN	C_2H_2 *	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CN	HCO	NH_3	CH_4 *	CH_3SH	*c*-C_2H_4O	*l*-HC_6H *	$CH_3C(O)NH_2$				
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)	C_8H^-				
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO	C_6H^-	CH_2CCHCN	C_3H_6				
CP	HOC$^+$	HNCO	HCOOH	NH_2CHO	CH_3NCO 2015	H_2NCH_2CN	CH_3CH_2SH (?)				
SiC	H_2O	HNCS	H_2CNH	C_5N		CH_3CHNH					
HCl	H_2S	HOCO$^+$	H_2C_2O	C_5NH^+							
KCl	HNC	H_2CO	H_2NCN	*l*-HC_4N							
NH	HNO	H_2CN	HNC_3	*c*-H_2C_3O							
NO	MgCN	H_2CS	SiH_4 *	H_2CCNH (?)							
NS	MgNC	H_3O^+	H_2COH^+	C_5N^-							
NaCl	N_2H^+	*c*-SiC_3	C_4H^-	HNCHCN							
OH	N_2O	CH_3 *	HC(O)CN								
PN	NaCN	C_3N^-	HNCNH								
SO	OCS	PH_3	CH_3O								
SO^+	SO_2	HCNO	NH_4^+								
SiN	*c*-SiC_2	HOCN	H_2NCO^+ (?)								
SiO	CO_2 *	HSCN	NCCNH$^+$ 2015								
SiS	NH_2	H_2O_2									
CS	H_3^+ (*)	C_3H^+									
HF	SiCN	HMgNC									
HD	AlNC	HCCO 2015									
FeO ?	SiNC										
O_2	HCP										
CF^+	CCP										
SiH ?	AlOH										
PO	H_2O^+										
AlO	H_2Cl^+										
OH^+	KCN										
CN^-	FeCN										
SH^+	HO_2										
SH	TiO_2										
HCl^+	C_2N										
TiO	Si_2C 2015										
ArH^+											
NO^+ ?											

Several organic and inorganic nitriles and isonitriles

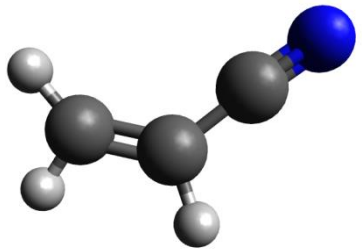
Molecules in the Interstellar Medium or Circumstellar Shells (as of 06/2016)



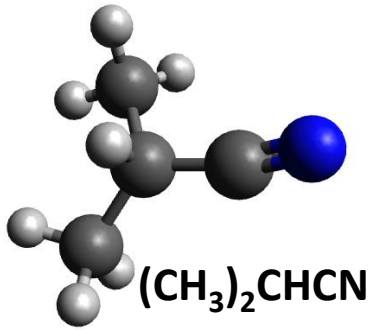
CH_3CN



CH_3CH_2CN



CH_2CHCN

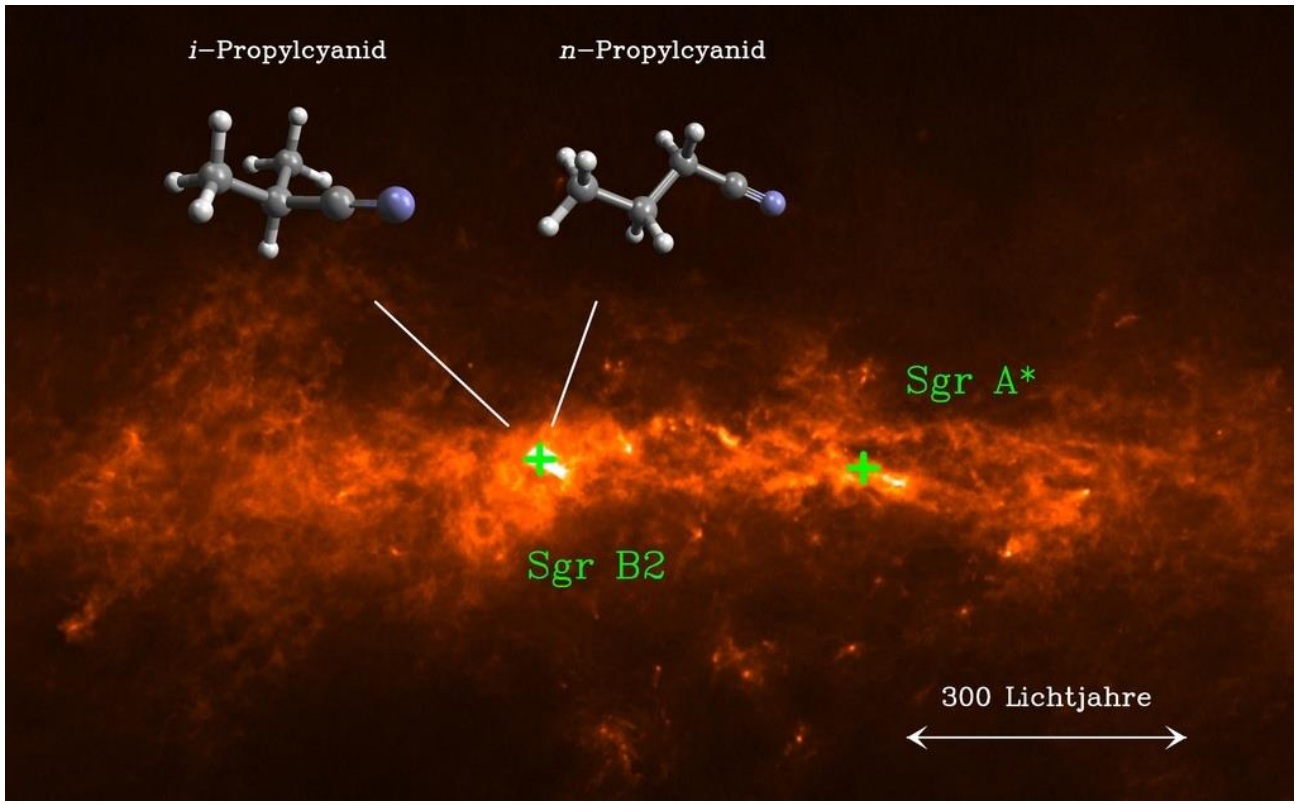


$(CH_3)_2CHCN$

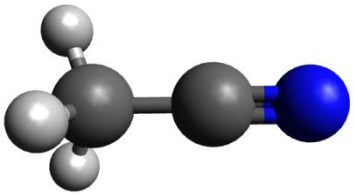
https://www.astro.uni-koeln.de/cdms/molecules

Relevant Interstellar Nitriles

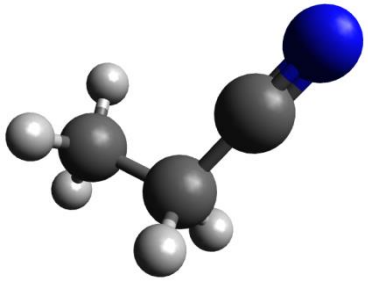
Increasing complexity of the organic **—C≡N** series



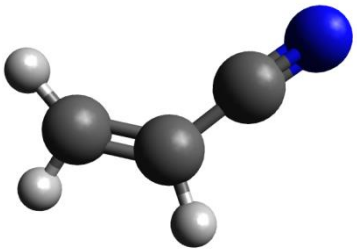
Belloche et al. *Science*, 2014 , **345**, 1584-1587



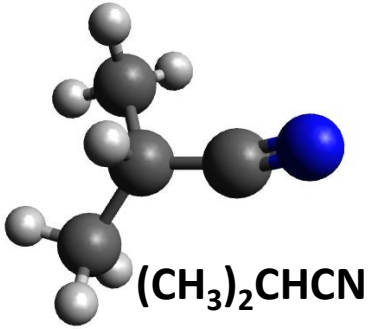
CH_3CN



CH_3CH_2CN



CH_2CHCN

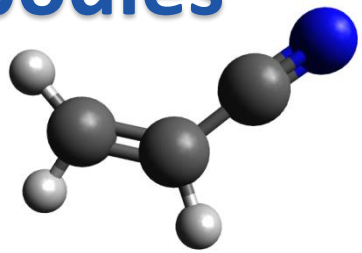


$(CH_3)_2CHCN$

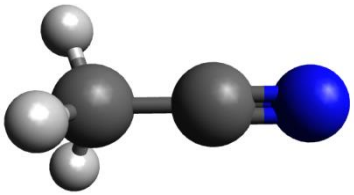
Relevant Interstellar Nitriles

- Very abundant in space (very common in **star forming regions**)
- Important in the formation of **amino acids**;
- CH_3CN is a good probe to estimate **temperature** and **column densities** based on observations of a single rotational transition.
- Tracer for Hot Molecular Cores (**HMCs**)
- Enhanced abundance of CH_3CN in **warm** (T = 100–300 K) and **dense** ($n_{H_2} = 10^6 - 10^8\ cm^{-3}$) **environments**;

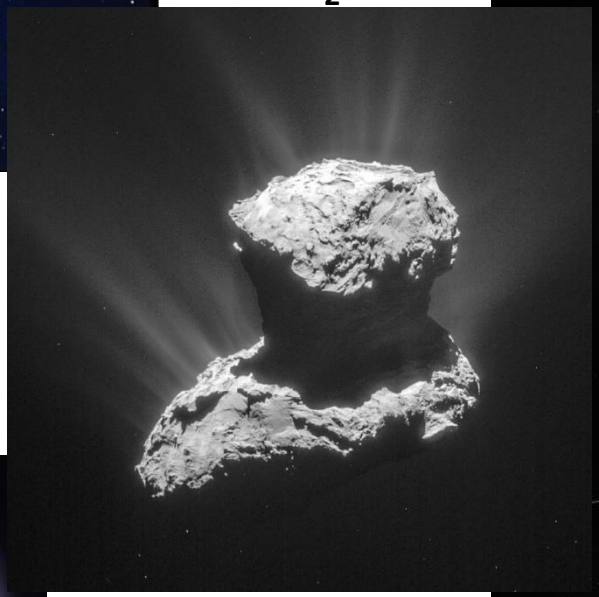
Solar System bodies

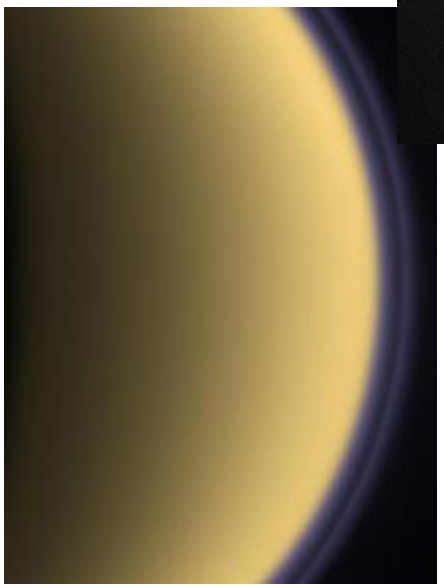


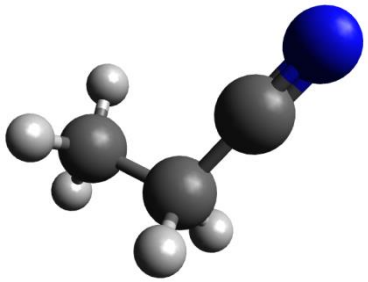
CH_2CHCN



CH_3CN







CH_3CH_2CN

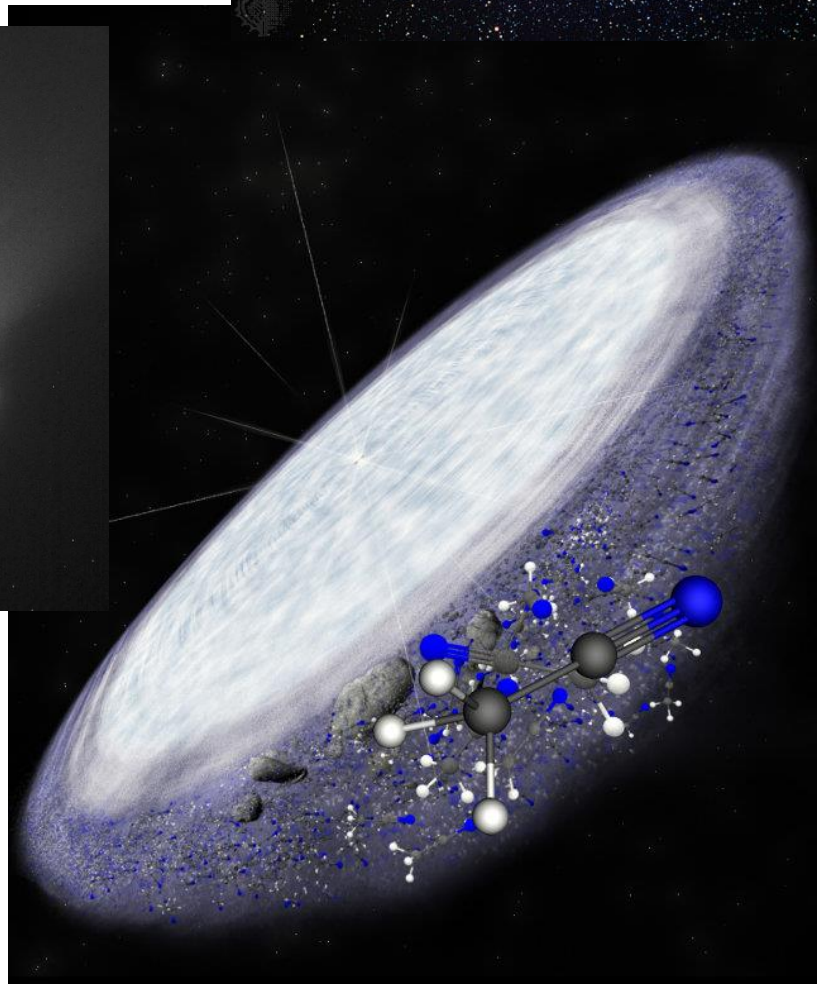


Image credit: B. Saxton / NRAO / AUI / NSF.

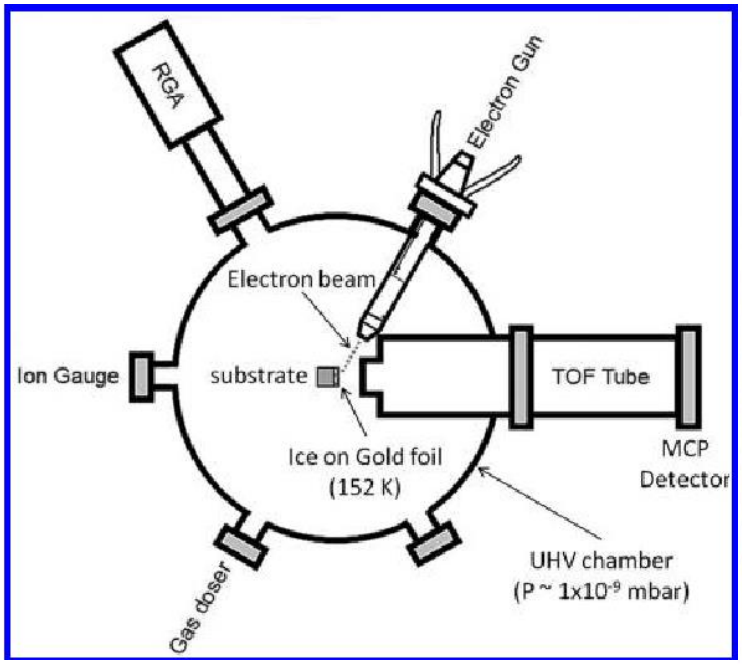
Nitrile Chemistry

Problems:

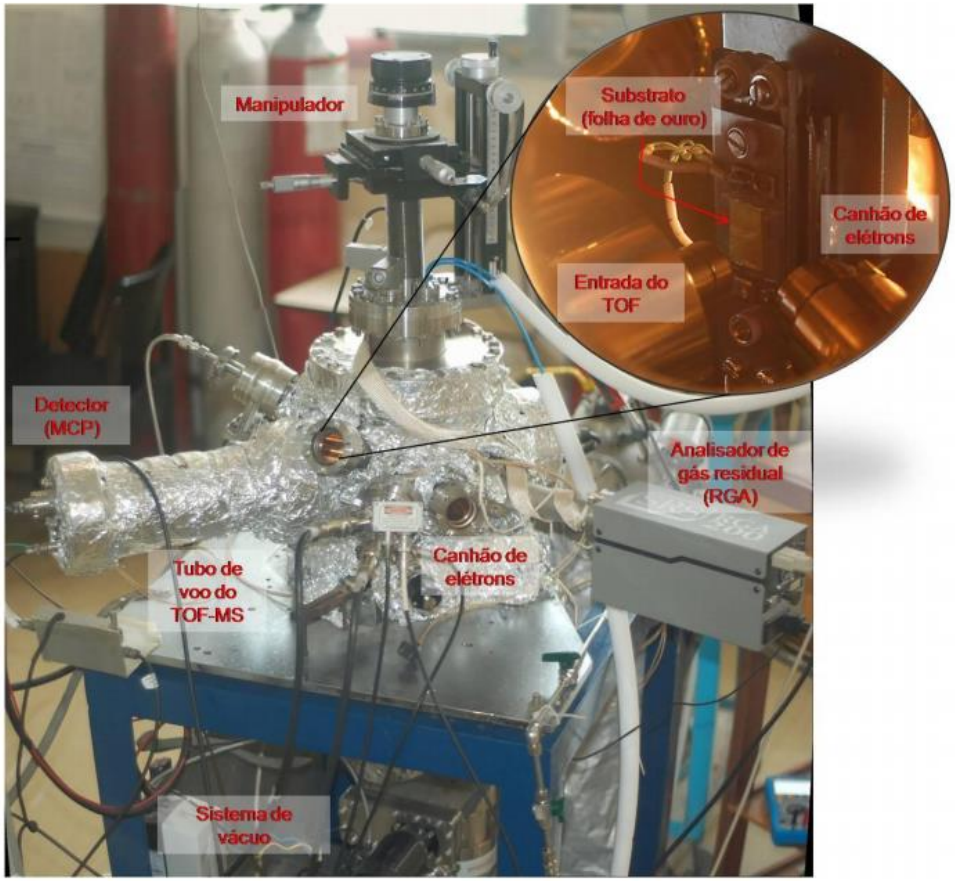
- How such **complex nitriles may be formed**?
- Not enough complex species can be produced in the **gas phase by known reaction routes**;
- What is the role played by **dust grains/ ice mantles**?
- What is the influence of **ionizing radiation**?
- Does **ion desorption** influence **gas abundances**?
- Is their **chemistry** connected?
- Is the same chemistry happening in other sources?

Laboratory work

- Surface processes are poorly known;
- Surface Science Techniques under conditions that resemble those found in the ISM;
- Non-thermal desorption processes:



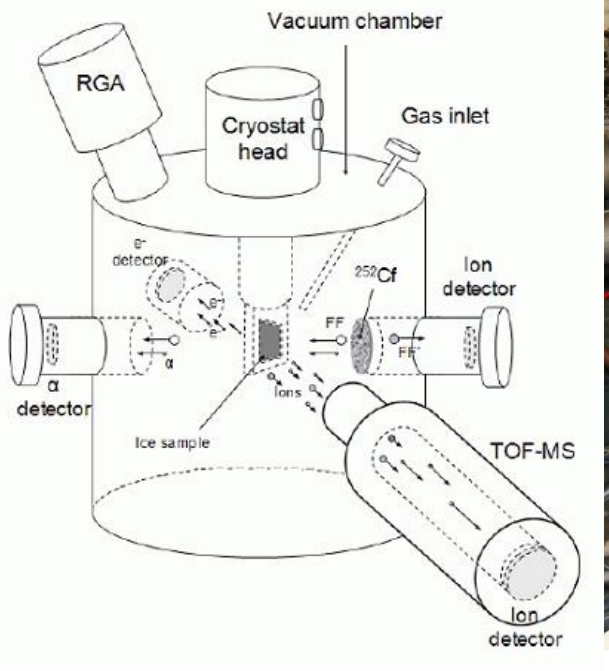
electrons in/ ions out

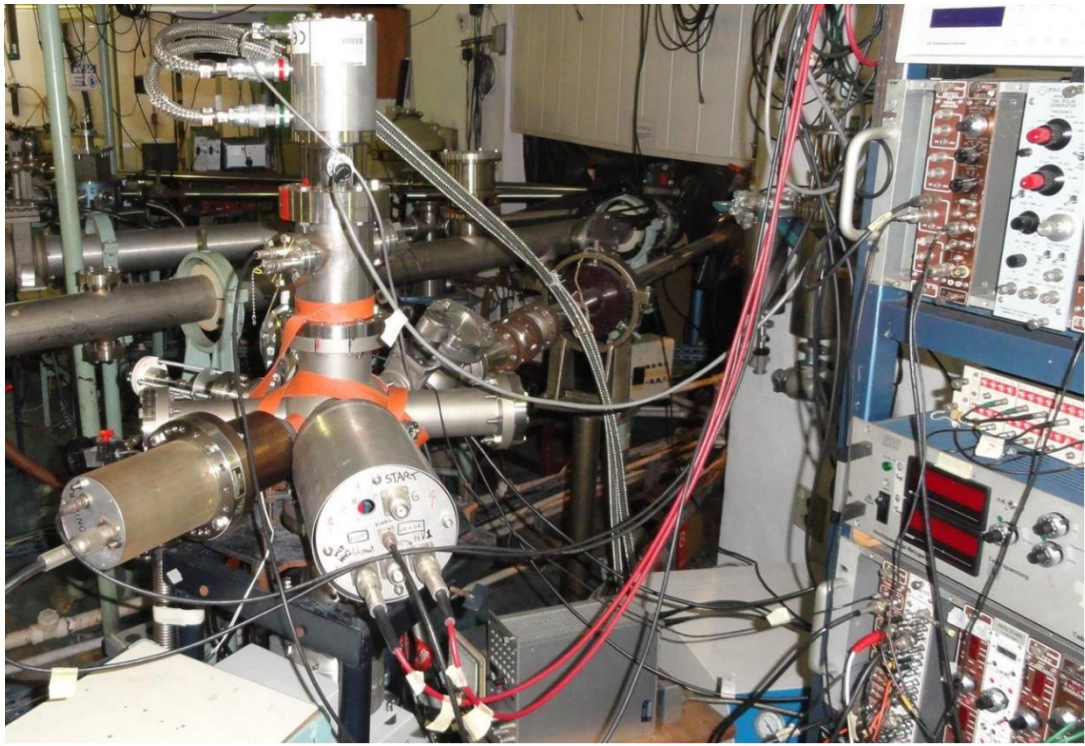


Electron Stimulated Ion Desorption (ESID)

Laboratory work

- Surface processes are poorly known;
- Surface Science Techniques under conditions that resemble those found in the ISM;
- Non-thermal desorption processes:

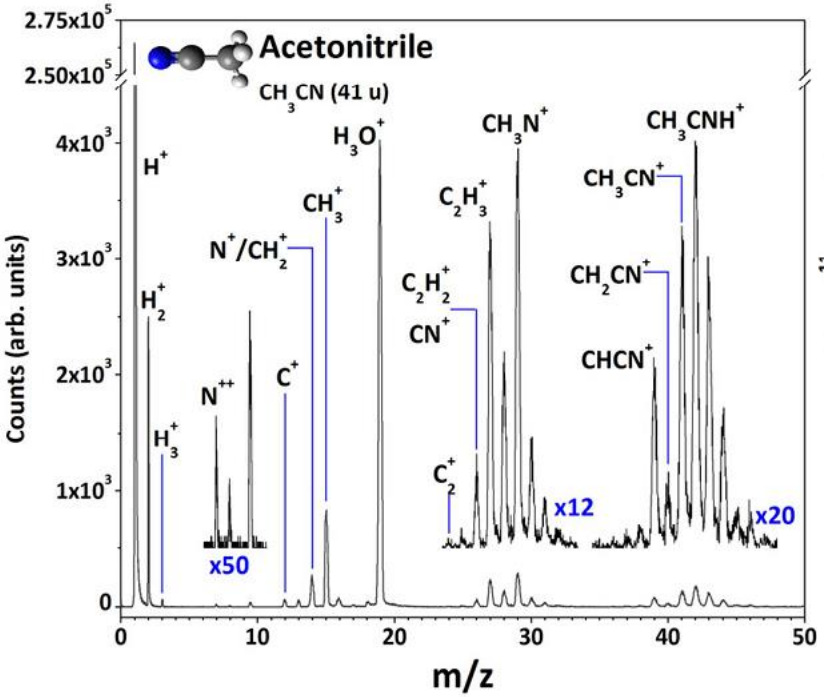


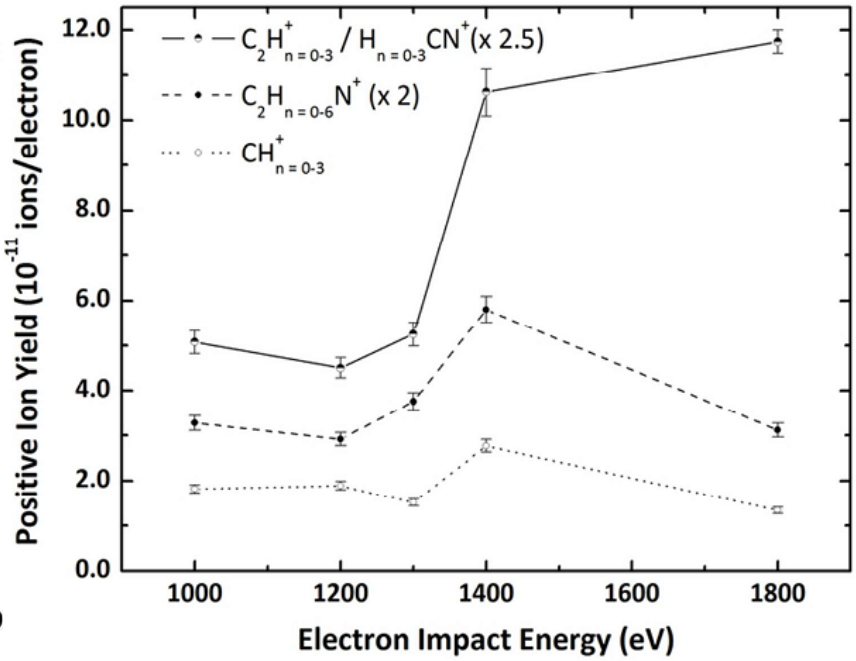


ion in/ secondary ions out

Plasma Desorption Mass Spectrometry (PDMS)

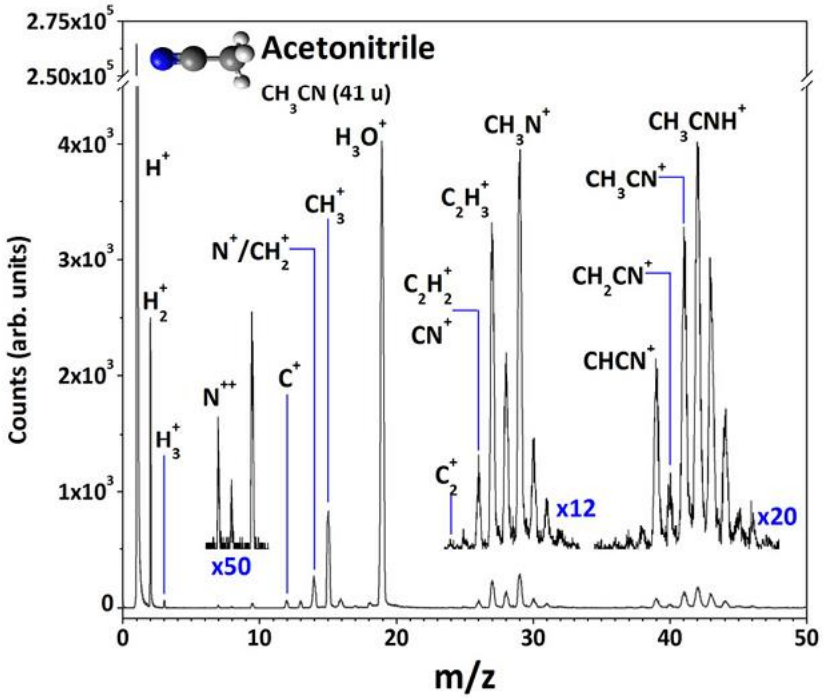
Laboratory experiments - ESID

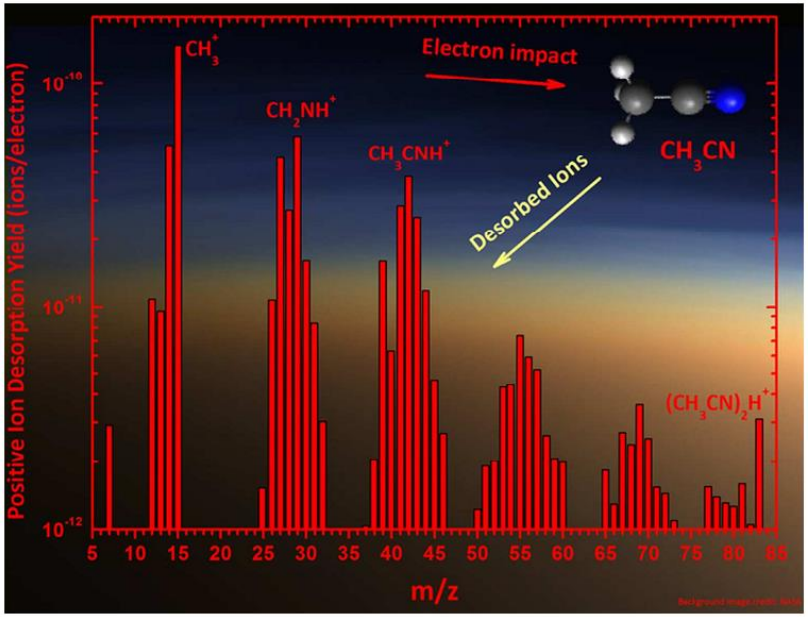


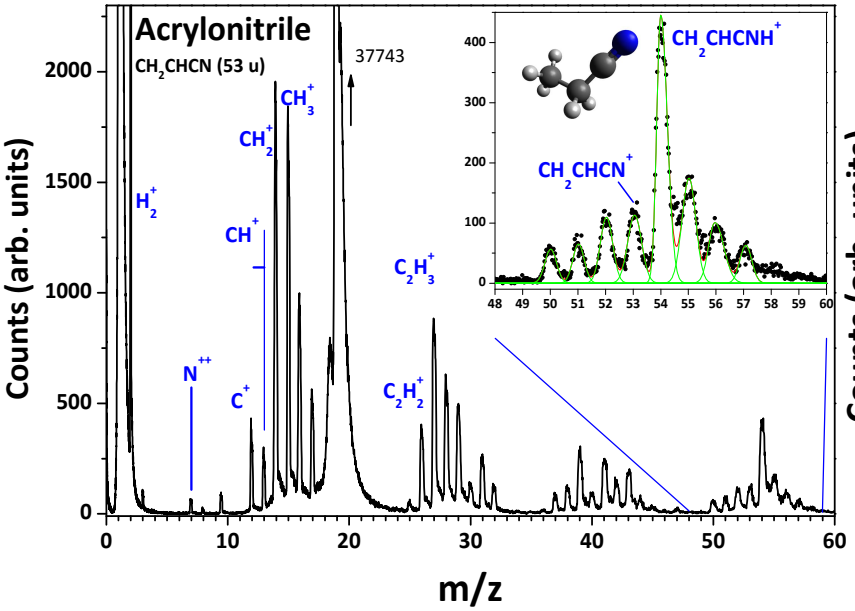


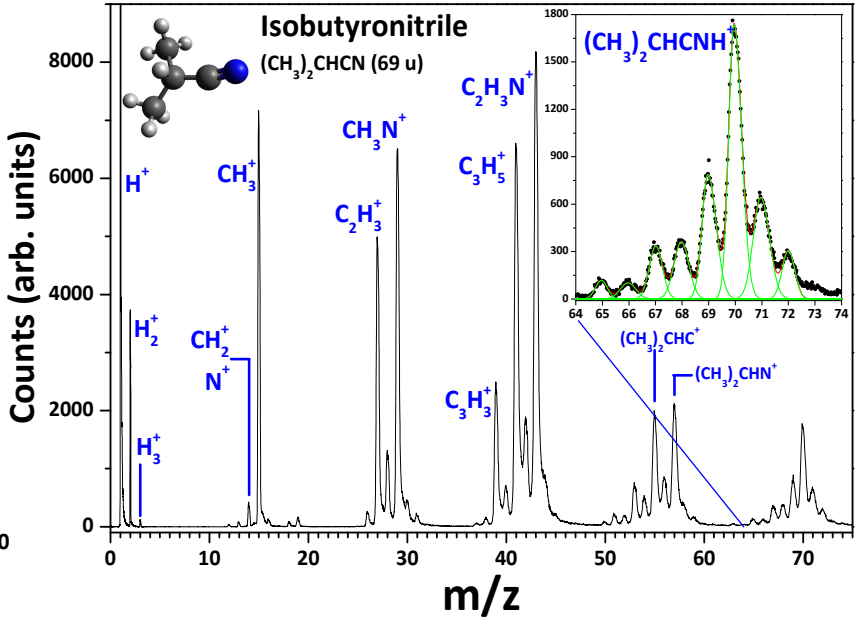
Ion desorption increases at 1400 eV, which is 3.5 times the ionization threshold for the CH_3CN N1s core level at 406 eV.

Ribeiro et al. *Phys.Chem.Chem.Phys.*, 2015, **17**, 27473

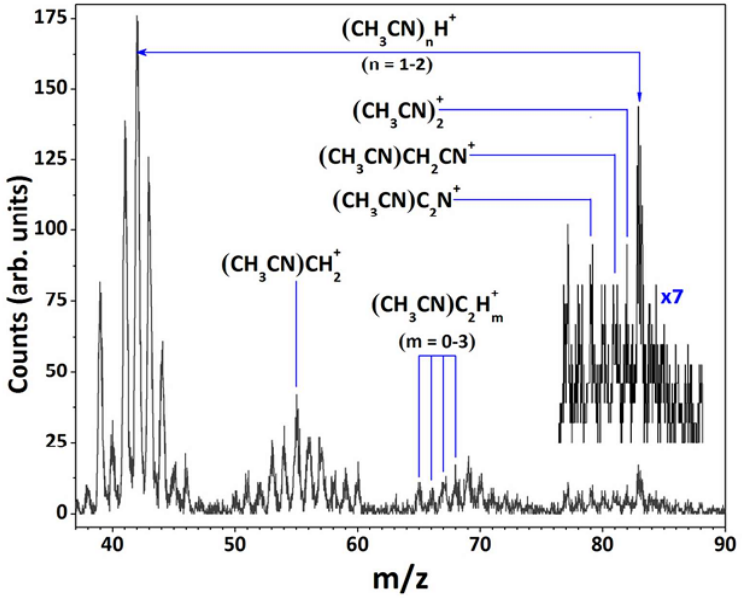

Acetonitrile
CH3CN (41 u)
Counts (arb. units)
m/z
H+
H2+
H3+
N++
N+/CH2+
CH3+
C+
H3O+
C2H3+
CN+
C2H2+
C2+
CH3N+
CH3CNH+
CH3CN+
CH2CN+
CHCN+
x50
x12
x20

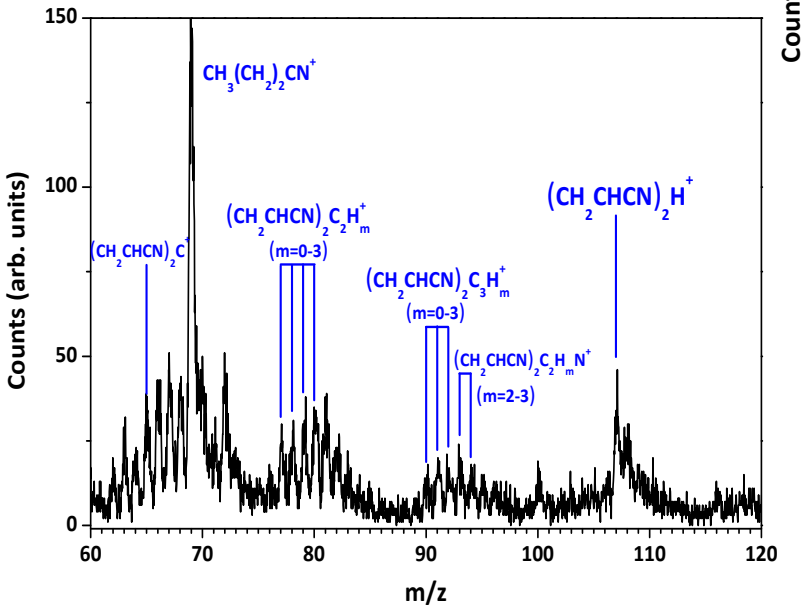

Electron impact
CH3CN
Desorbed Ions
Positive Ion Desorption Yield (Ions/electron)
m/z
CH3+
CH2NH+
CH3CNH+
(CH3CN)2H+


Acrylonitrile
CH2CHCN (53 u)
Counts (arb. units)
m/z
37743
H2+
N++
C+
CH+
CH2+
CH3+
C2H3+
C2H2+
CH2CHCNH+
CH2CHCN+

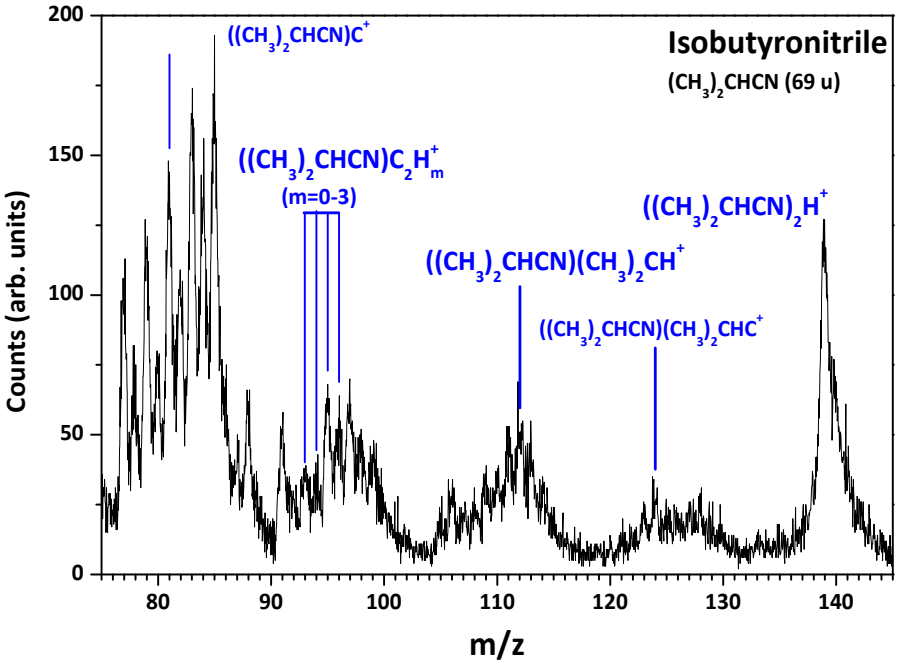

Isobutyronitrile
(CH3)2CHCN (69 u)
Counts (arb. units)
m/z
H+
H2+
H3+
CH3+
CH2+
N+
C2H3+
CH3N+
C3H5+
C2H3N+
C3H3+
(CH3)2CHNH+
(CH3)2CHC+
(CH3)2CHN+

Laboratory experiments - ESID



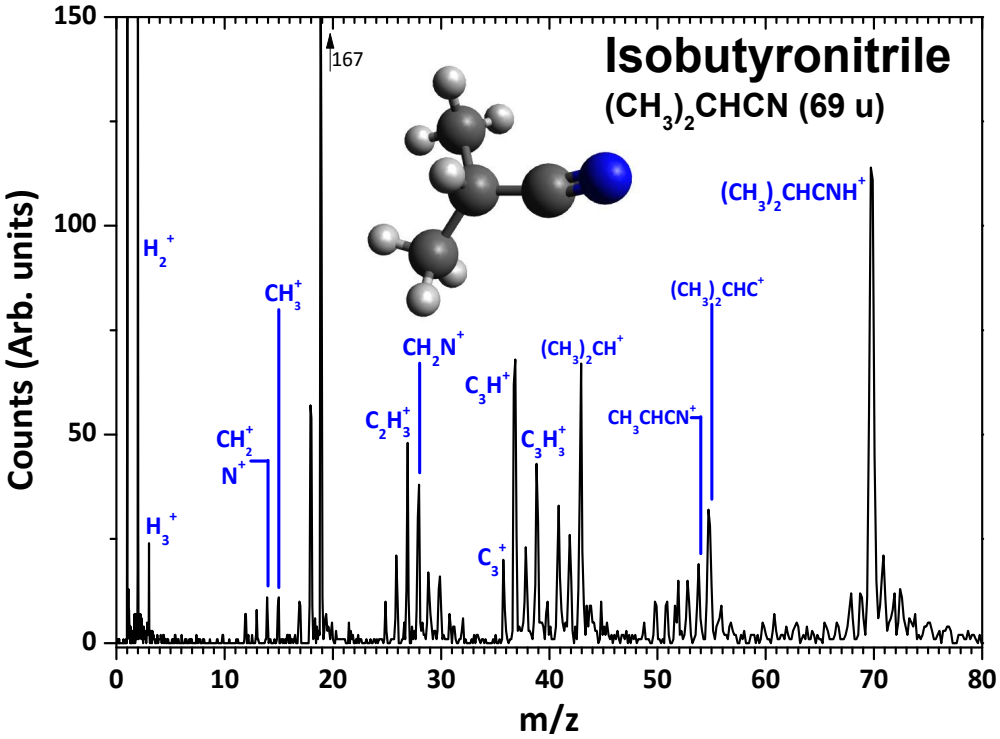


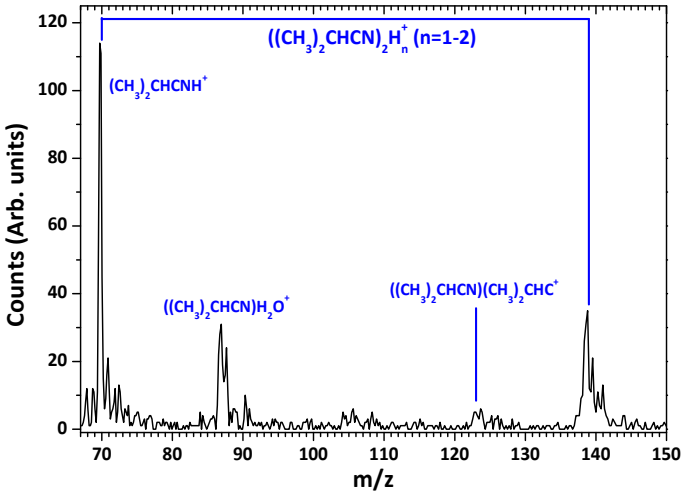
Desorption of ion clusters by electron impact (2.3 keV)



Ribeiro et al. *Phys.Chem.Chem.Phys.*, 2015, **17**, 27473

Laboratory experiments - PDMS

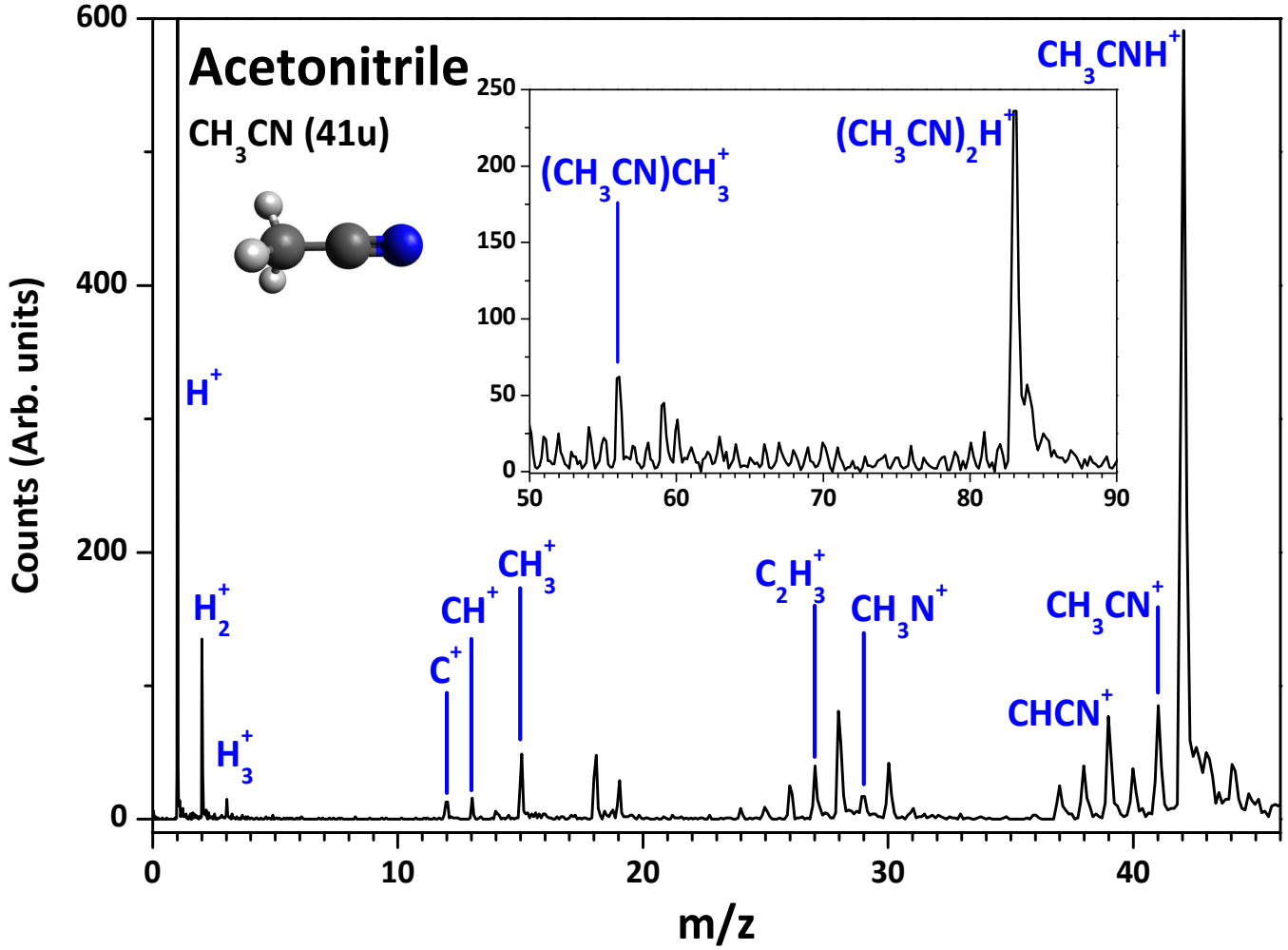




Desorption of $(CH_3)_2CHCN$ ion clusters

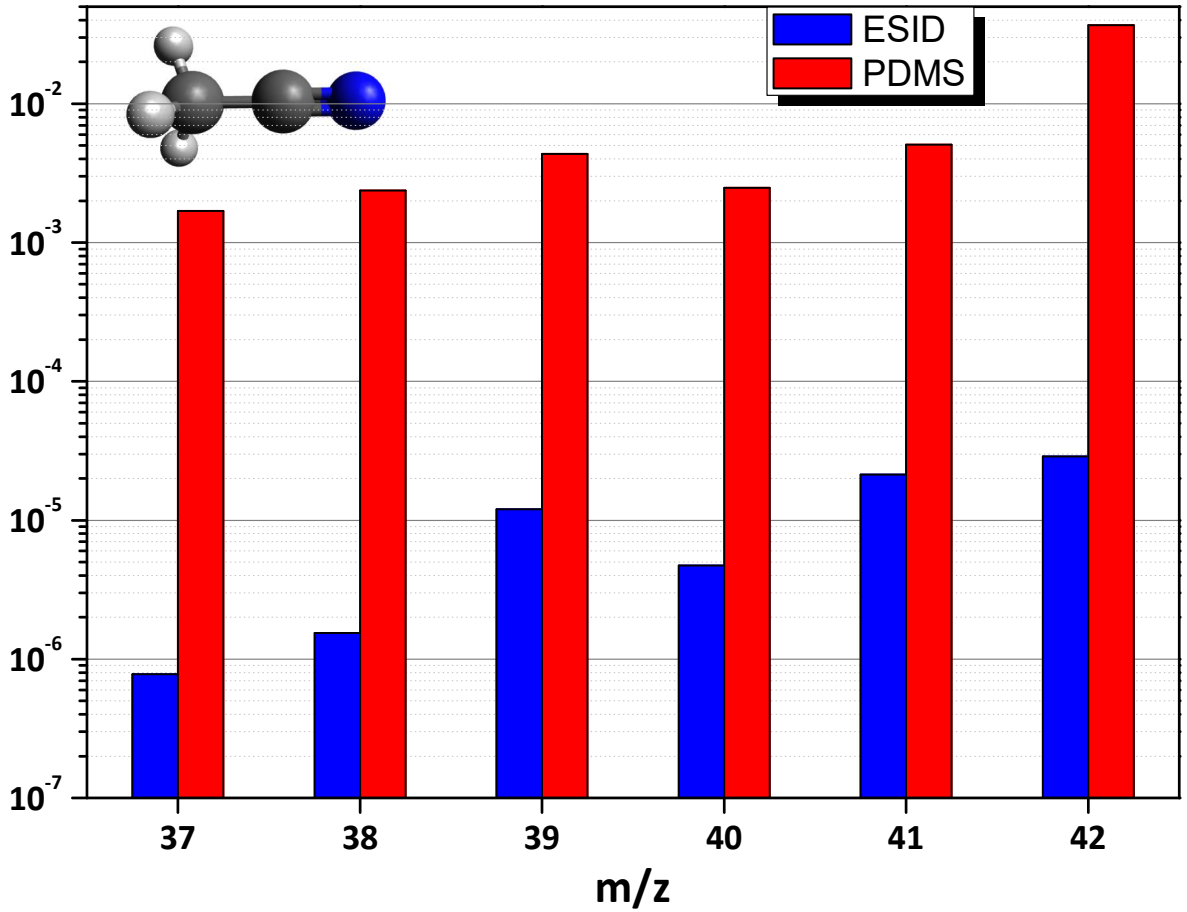
PDMS mass spectrum of $(CH_3)_2CHCN$ at 100 K

Laboratory experiments - PDMS



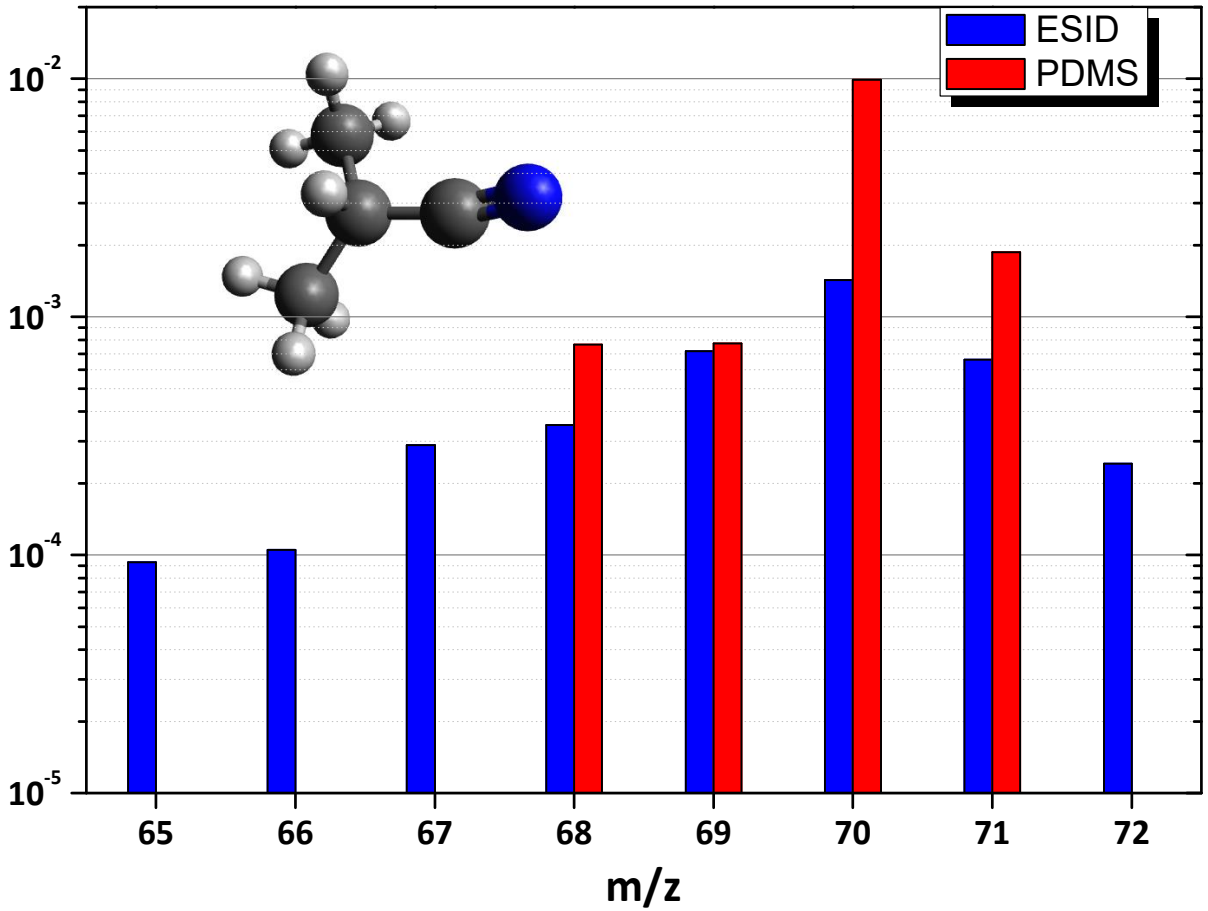
PDMS mass spectrum of CH_3CN at 100 K. Inset: Desorption of CH_3CN ion clusters

ESID and PDMS comparison



- Stronger fragmentation in **ESID**
- **Proton transfer** processes during ion desorption

ESID and PDMS comparison



- Stronger fragmentation on surface in **ESID** in respect to CH_3CN;
- Similar Ion Yield for $(CH_3)_2CHCN^+$ (m/z = 69) ion desorption in ESID and PDMS;
- **Proton transfer** processes during ion desorption.

Summary Remarks

- Strong fragmentation on surface and ion desorption is oberseved for all studied nitriles;
- Fragmentation caused by electrons is initiated by Coulomb explosion after Auger electronic decay;
- Predominance for saturated and protonated fragments desorption. The last might play a role in ion-neutral reactions on gas-phase;
- Cluster ion desorption may be a route for delivering for complex molecules (nitriles) to the cold interstellar and circumstellar material exposed to ionizing radiation
- Similar conclusions can be ascribed to the Titan atmosphere,
- where a set of complex nitriles is known to exist

Acknowledgements

Thank you for your attention!

INTERNATIONAL SYMPOSIUM AND WORKSHOP ON ASTROCHEMISTRY

Understanding extraterrestrial molecular complexity through experiments and observations

Observatório do Valongo

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CAPES

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