KINETIC DATABASE FOR ASTROCHEMISTRY

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Anion Chemistry on Titan

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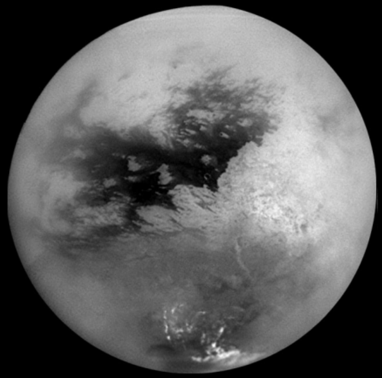
Outline



Introduction

- motivation
- Titan, Cassini – Huygens

Experimental approach

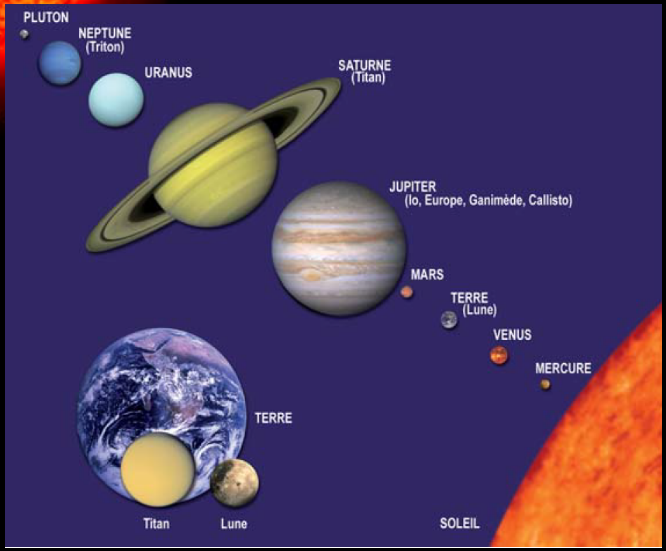
- Quattro Premier XE tandem quadrupole mass spectrometer
- atmospheric chemical ionization, T-wave collision cell

Results and Discussion

- reaction $CN^- + HC_3N$
- Proposal reaction mechanism (PRM)
- Experimental confirmation of PRM
- laboratory data vs. CAPS-Cassini spectrum

Conclusions

Titan



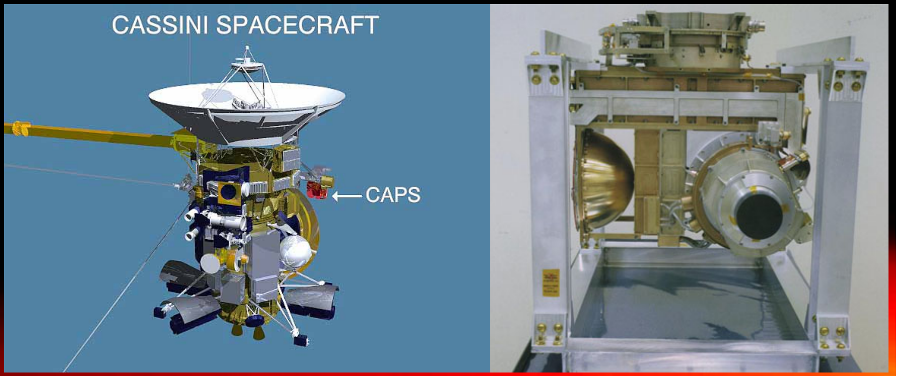
It is the only moon in the Solar System with a thick nitrogen atmosphere

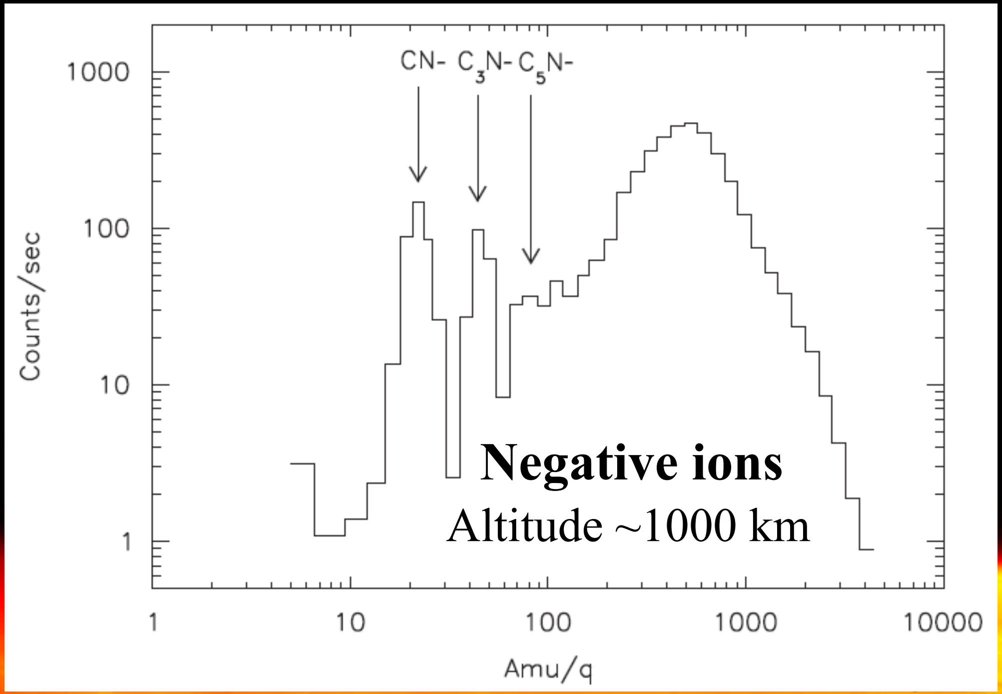
Many analogies with the early Earth and its organic chemistry with the terrestrial prebiotic chemistry

Cassini –Huygens

15.10.1997 -4.1.2005

CAPS: Cassini Plasma Spectrometer





V. Vuitton et al., 2009

Titan after Cassini - Hugens

- ionosphere ~ 950-1300 km (p ~ 10^{-4} Pa)
  positive ions ~ 100-2000cm^{-3} negative ions ~ 50-150cm^{-3}

-negative ions observed [1] in Titan's upper atmosphere, (CN^-)

- reaction $CN^- + HC_3N$ is of particular interest
- its kinetics has been experimentally investigated [2]:

$$CN^- + HC_3N \rightarrow C_3N^- + HCN \qquad k_{exp} = 4.8 \times 10^{-9}\ cm^3/s$$

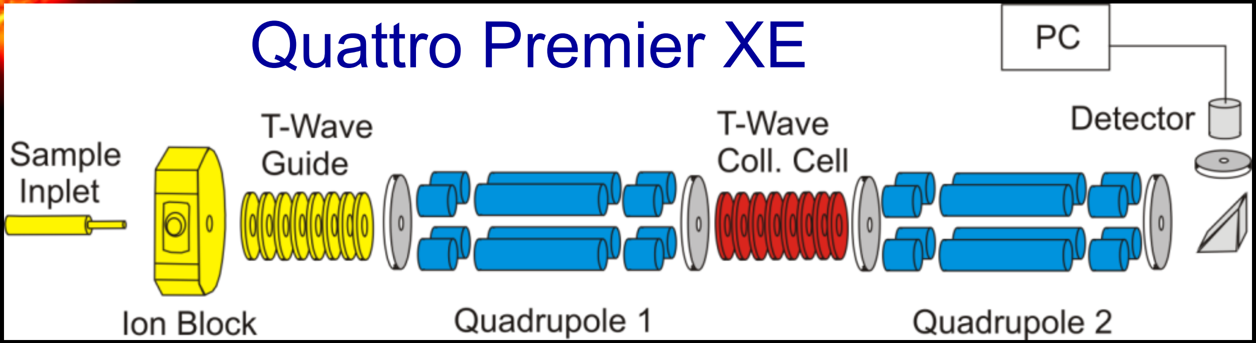
This work:

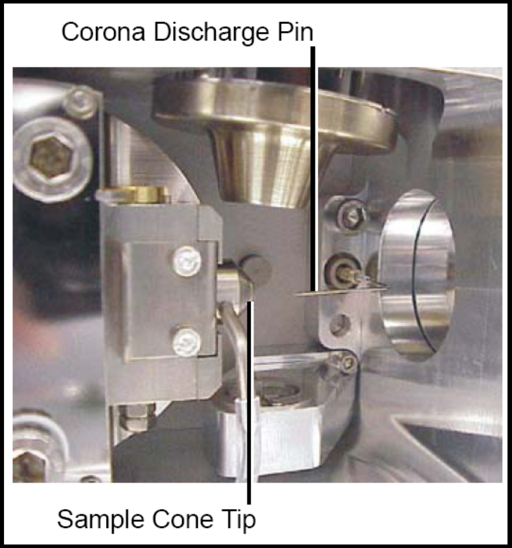
-different reaction regimes (i.e. pressure of HC_3N in the cell)
-gradual increase of carbon chain by negative ion-molecule reactions observed
-Experimental verification of proposal reaction mecanism

[1] V. Vuitton et al., *Planetary and Space Science*, 57, 13, 1558, (2009)
[2] S. Carles, F. Adjali, C. Monnerie, J.-C. Guillemin, J.-L.L. Garrec, *Icarus*, 211(1), 901-905 (2011)

Laboratory experiments

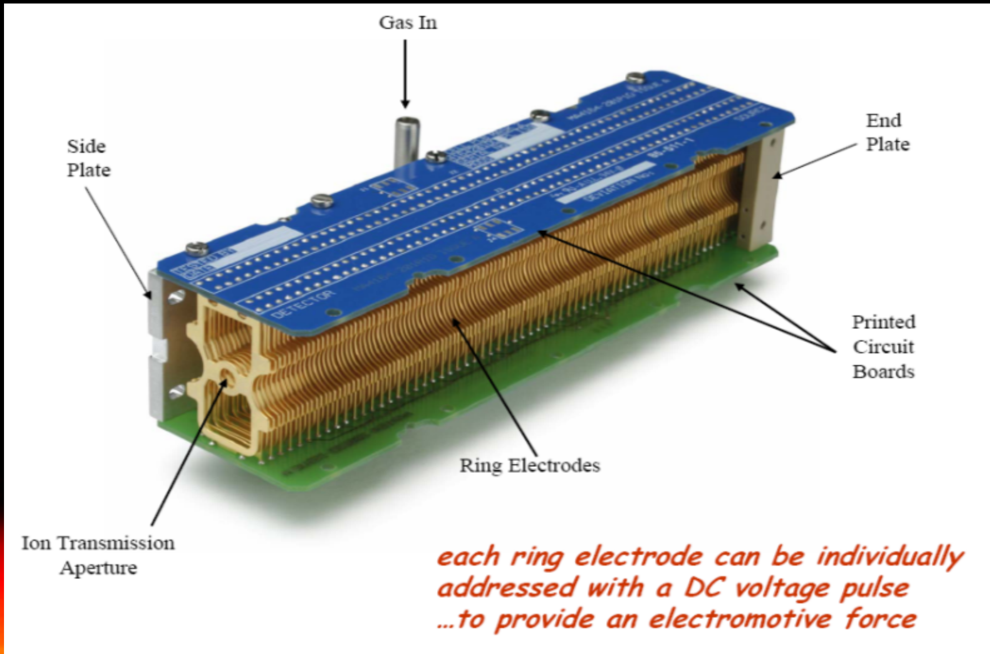
Experimental Setup





Primary ion preparation:

Atmospheric pressure chemical ionization (APCI) of CH_3CN: ☞ CN^-
APCI of acetonitrile solution of HC_3N: ☞ $C_{2n+1}N^-$, $(HC_3N)_xC_{2n+1}N^-$
etc...

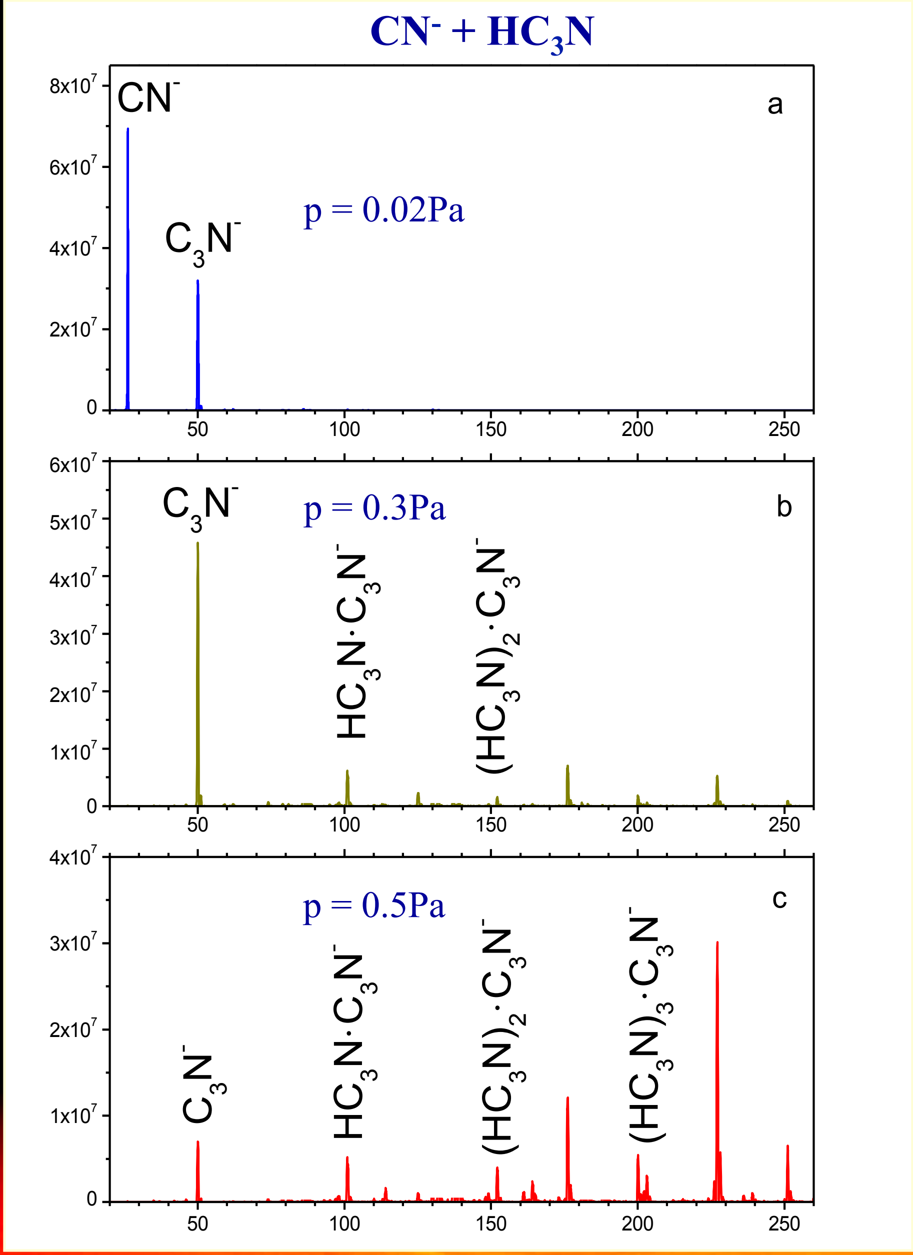


a) Proposal reaction mecanism

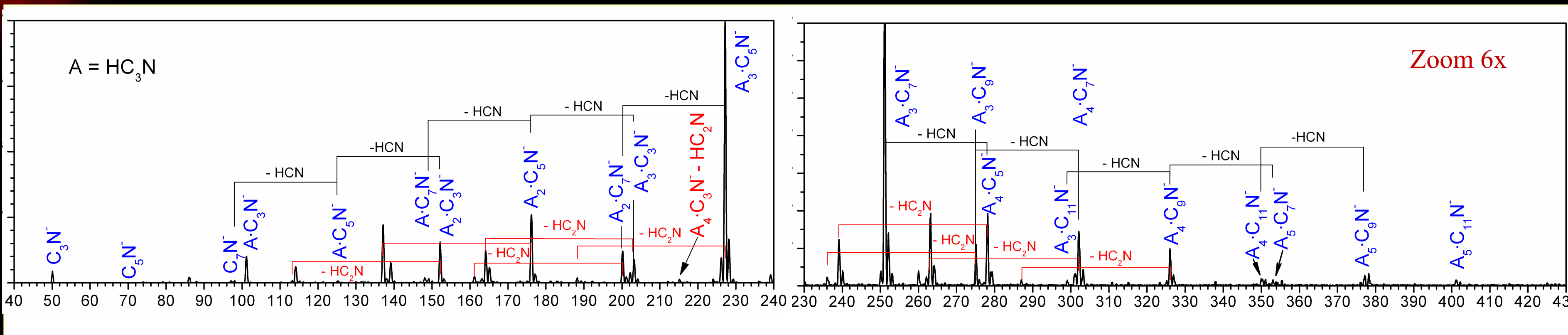
$$CN^- + HC_3N$$

J. Žabka et al. / Icarus 219 (2012) 161–167

Results and Discussion : $CN^- + HC_3N$



Results and Discussion :



50……...C_3N^-
74…... ..C_5N^-
98…..... C_7N^-

101…..[C_3N…(HC_3N)]$^-$
125…..[C_5N…(HC_3N)]$^-$
149…..[C_7N…(HC_3N)]$^-$

152…..[C_3N…($HC_3N)_2$]$^-$
176…..[C_5N…($HC_3N)_2$]$^-$
200…..[C_5N…($HC_3N)_2$]$^-$

203…..[C_3N…($HC_3N)_3$]$^-$
227…..[C_5N…($HC_3N)_3$]$^-$
251…..[C_7N…($HC_3N)_3$]$^-$
275…..[C_9N…($HC_3N)_3$]$^-$

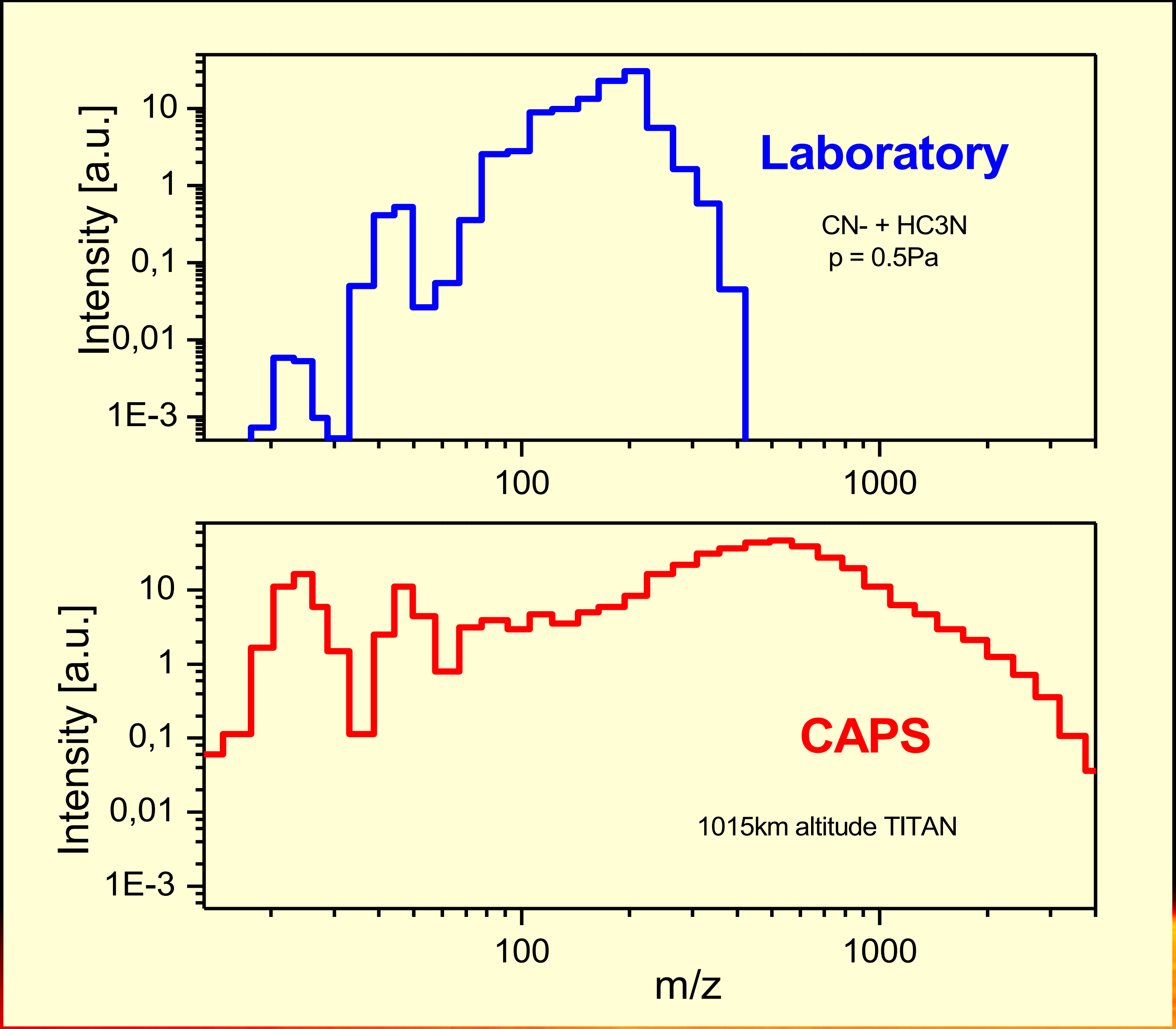
278…..[C_5N…($HC_3N)_4$]$^-$
302…..[C_7N…($HC_3N)_4$]$^-$
326…..[C_9N…($HC_3N)_4$]$^-$
350…..[$C_{11}N$…($HC_3N)_4$]$^-$

353…..[C_7N…($HC_3N)_5$]$^-$
377…..[C_9N…($HC_3N)_5$]$^-$
401…..[$C_{11}N$…($HC_3N)_5$]$^-$

$[(HC_3N)_n.C_3N^-]$ - aHCN

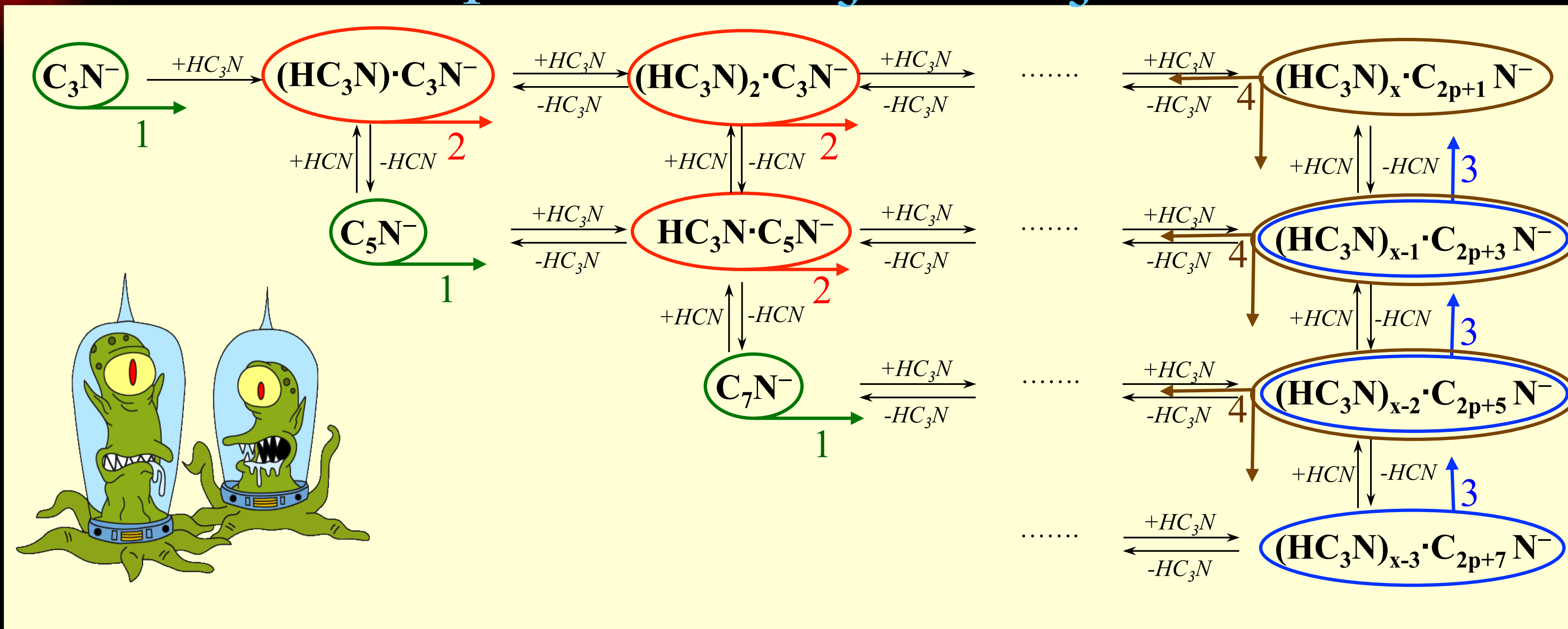
'Parent'	*-HC₂N*	'Product'	*m/z*
$(HC_3N)_2{\cdot}C_3N^-$		$HC_3N{\cdot}C_4N^-$	113
$(HC_3N)_2{\cdot}C_5N^-$		$HC_3N{\cdot}C_6N^-$	137
$(HC_3N)_2{\cdot}C_7N^-$	⟶	$HC_3N{\cdot}C_8N^-$	161
$(HC_3N)_3{\cdot}C_3N^-$		$(HC_3N)_2{\cdot}C_4N^-$	164
$(HC_3N)_3{\cdot}C_5N^-$		$(HC_3N)_2{\cdot}C_6N^-$	188
$(HC_3N)_3{\cdot}C_7N^-$		$(HC_3N)_2{\cdot}C_8N^-$	212
$(HC_3N)_3{\cdot}C_9N^-$	⟶	$(HC_3N)_2{\cdot}C_{10}N^-$	236
$(HC_3N)_4{\cdot}C_3N^-$		$(HC_3N)_3{\cdot}C_4N^-$	215
$(HC_3N)_4{\cdot}C_5N^-$		$(HC_3N)_3{\cdot}C_6N^-$	239
$(HC_3N)_4{\cdot}C_7N^-$		$(HC_3N)_3{\cdot}C_8N^-$	263
$(HC_3N)_4{\cdot}C_9N^-$		$(HC_3N)_3{\cdot}C_{10}N^-$	287
$(HC_3N)_4{\cdot}C_{12}N^-$		$(HC_3N)_3{\cdot}C_{12}N^-$	311

Results and Discussion: Laboratory v.s. Cassini



Proposal reaction scheme

First step: $CN^- + HC_3N \rightarrow C_3N^- + HCN$



1. Growth of C_xN^- anions (reaction with HC_3N)

2. Growth of $(HC_3N)_2C_xN^-$ anions (reaction with HC_3N)

3. Growth of $(HC_3N)_xC_5N^-$ anions (reaction with HCN)

4. Dissociation of $(HC_3N)_2C_xN^-$ anions

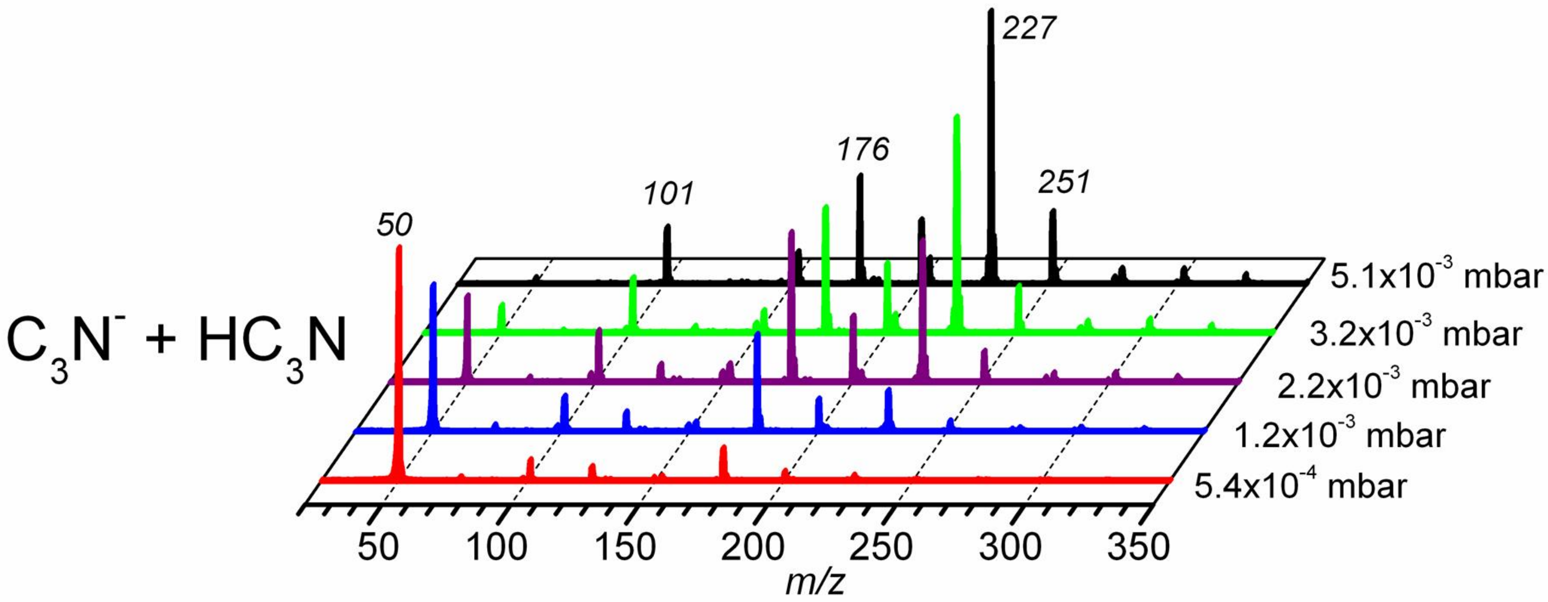
b) Verification of Proposal reaction mecanism

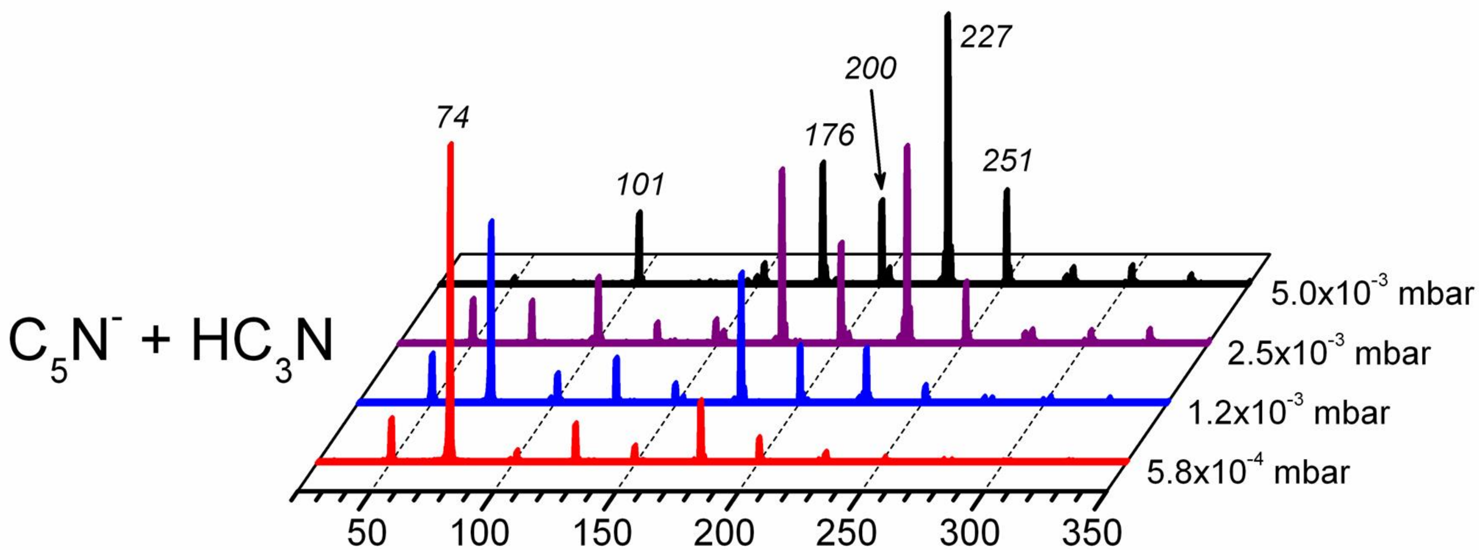
1. Growing C_xN^- anions

$$C_xN^- + HC_3N$$

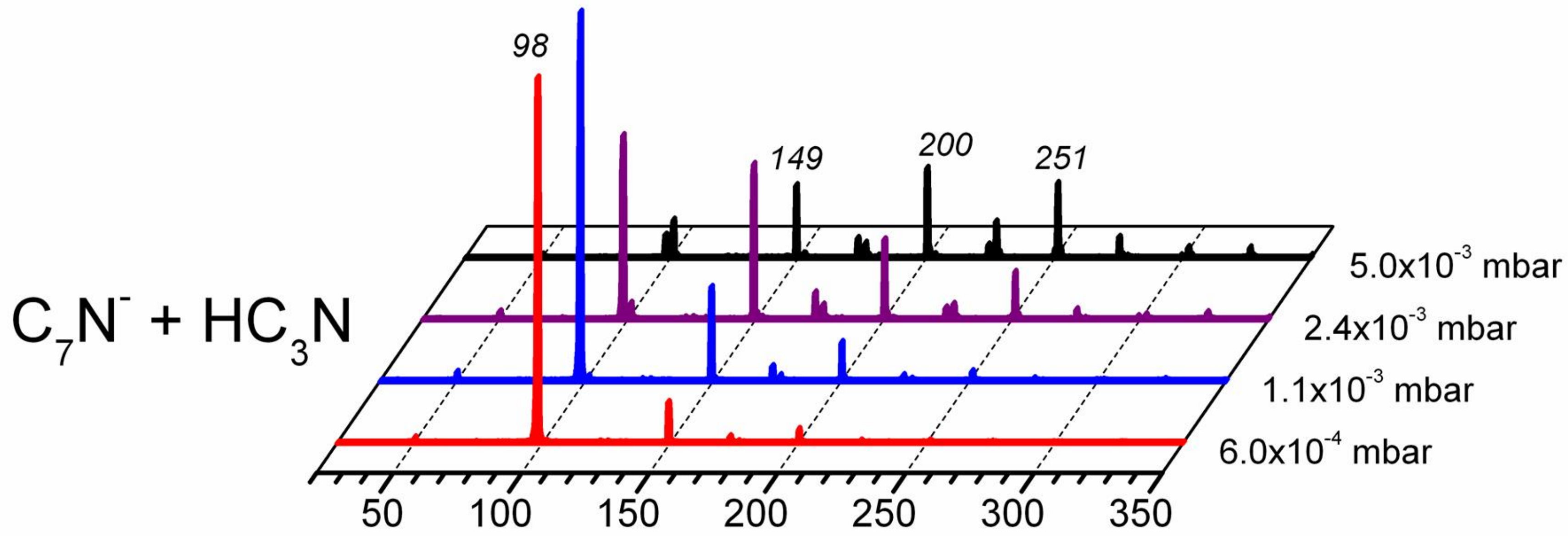
$$(x = 3,5,7,9)$$

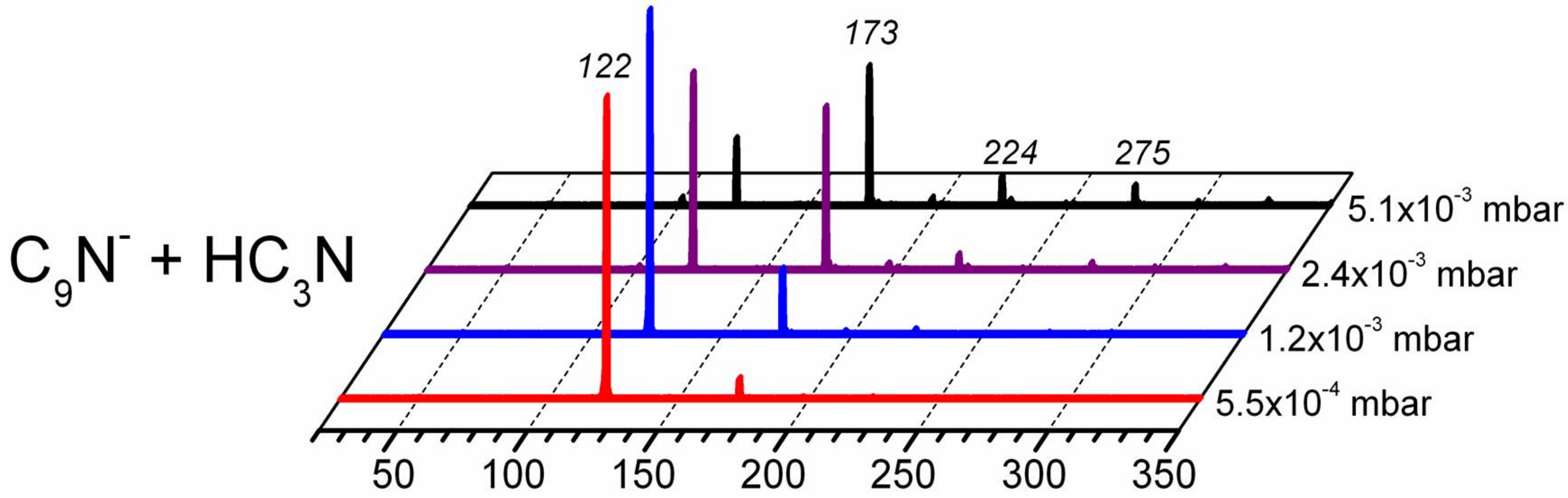
50……..C_3N^-	**101**…..[C_3N…(HC_3N)]$^-$	**152**…..[C_3N…($HC_3N)_2$]$^-$	**203**…..[C_3N…($HC_3N)_3$]$^-$	**278**…..[C_5N…($HC_3N)_4$]$^-$	**353**…..[C_7N…($HC_3N)_5$]$^-$
74…... ..C_5N^-	**125**…..[C_5N…(HC_3N)]$^-$	**176**…..[C_5N…($HC_3N)_2$]$^-$	**227**…..[C_5N…($HC_3N)_3$]$^-$	**302**…..[C_7N…($HC_3N)_4$]$^-$	**377**…..[C_9N…($HC_3N)_5$]$^-$
98…..... C_7N^-	**149**…..[C_7N…(HC_3N)]$^-$	**200**…..[C_5N…($HC_3N)_2$]$^-$	**251**…..[C_7N…($HC_3N)_3$]$^-$	**326**…..[C_9N…($HC_3N)_4$]$^-$	**401**…..[$C_{11}N$…($HC_3N)_5$]$^-$
			275…..[C_9N…($HC_3N)_3$]$^-$	**350**…..[$C_{11}N$…($HC_3N)_4$]$^-$	





50…….. C_3N^-	**101**…..[C_3N…(HC_3N)]$^-$	**152**…..[C_3N…($HC_3N)_2$]$^-$	**203**…..[C_3N…($HC_3N)_3$]$^-$	**278**…..[C_5N…($HC_3N)_4$]$^-$	**353**…..[C_7N…($HC_3N)_5$]$^-$
74…... ..C_5N^-	**125**…..[C_5N…(HC_3N)]$^-$	**176**…..[C_5N…($HC_3N)_2$]$^-$	**227**…..[C_5N…($HC_3N)_3$]$^-$	**302**…..[C_7N…($HC_3N)_4$]$^-$	**377**…..[C_9N…($HC_3N)_5$]$^-$
98…..... C_7N^-	**149**…..[C_7N…(HC_3N)]$^-$	**200**…..[C_5N…($HC_3N)_2$]$^-$	**251**…..[C_7N…($HC_3N)_3$]$^-$	**326**…..[C_9N…($HC_3N)_4$]$^-$	**401**…..[$C_{11}N$…($HC_3N)_5$]$^-$
			275…..[C_9N…($HC_3N)_3$]$^-$	**350**…..[$C_{11}N$…($HC_3N)_4$]$^-$	



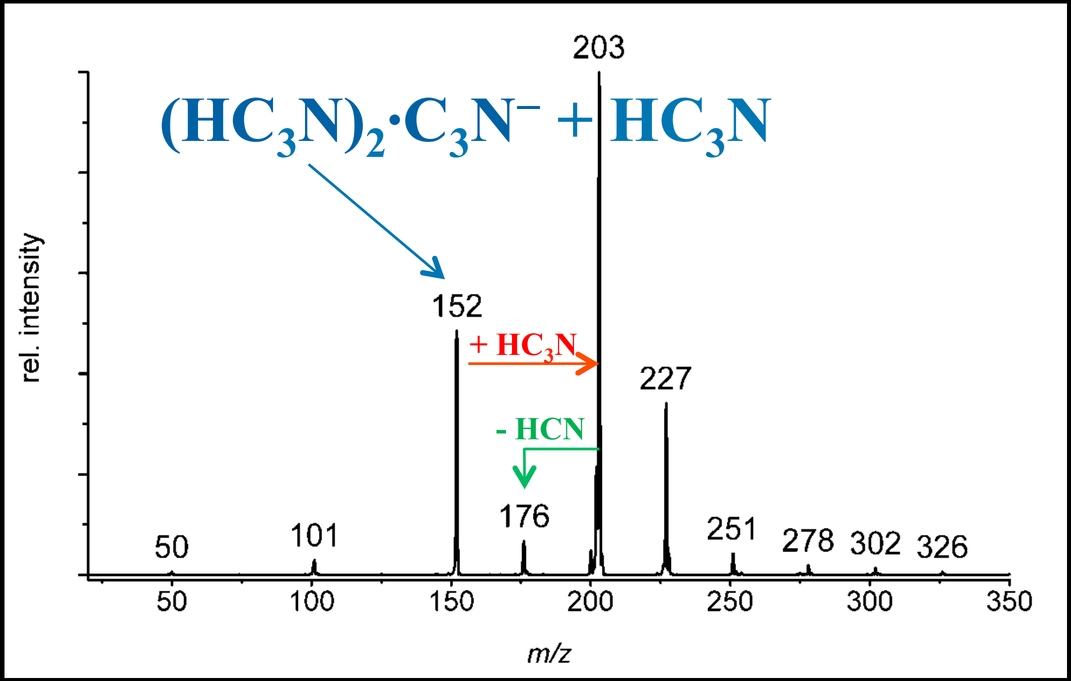


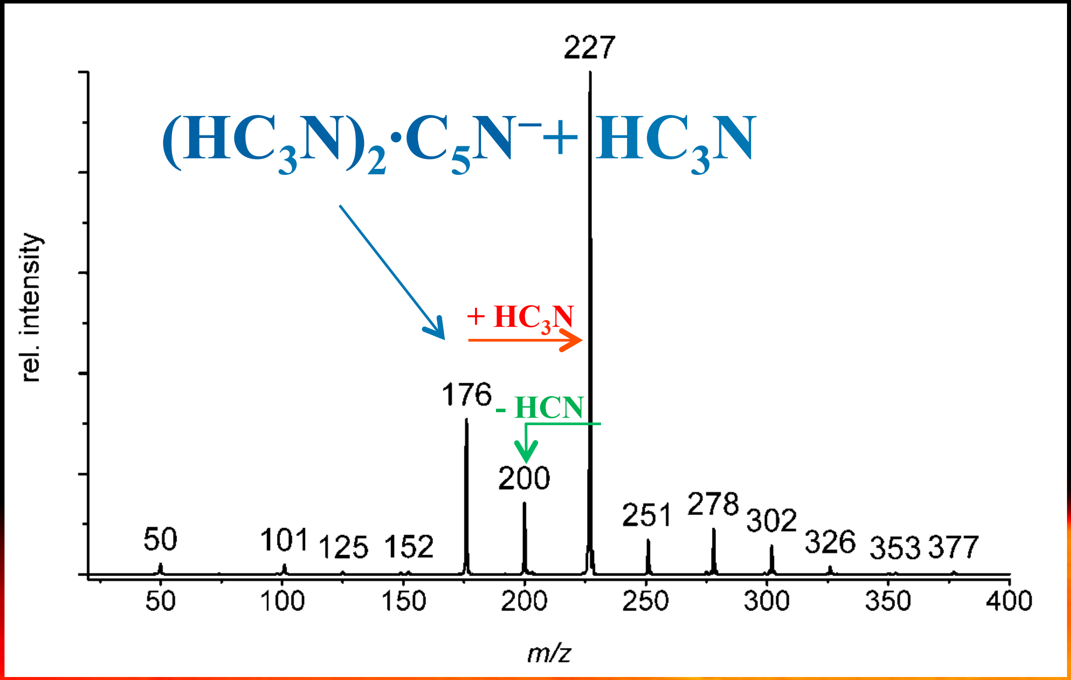
b) Verification of Proposal reaction mecanism

2. *Growing* $(HC_3N)_2C_xN^-$ anions

$$(HC_3N)_2 \,.\, C_3N^- + HC_3N$$

$$(HC_3N)_2 \,.\, C_5N^- + HC_3N$$

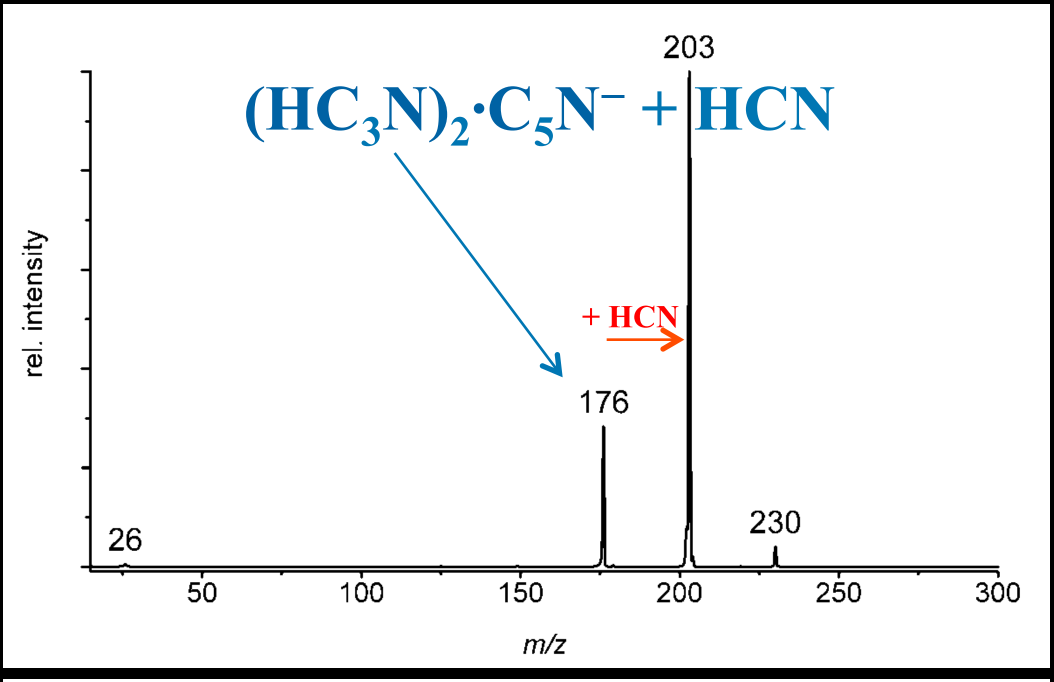

203
$(HC_3N)_2 \cdot C_3N^- + HC_3N$
152
$+ HC_3N$
227
- HCN
176
50
101
251
278
302
326
rel. intensity
50
100
150
200
250
300
350
m/z


227
$(HC_3N)_2 \cdot C_5N^- + HC_3N$
$+ HC_3N$
176
- HCN
200
50
101
125
152
251
278
302
326
353
377
rel. intensity
50
100
150
200
250
300
350
400
m/z

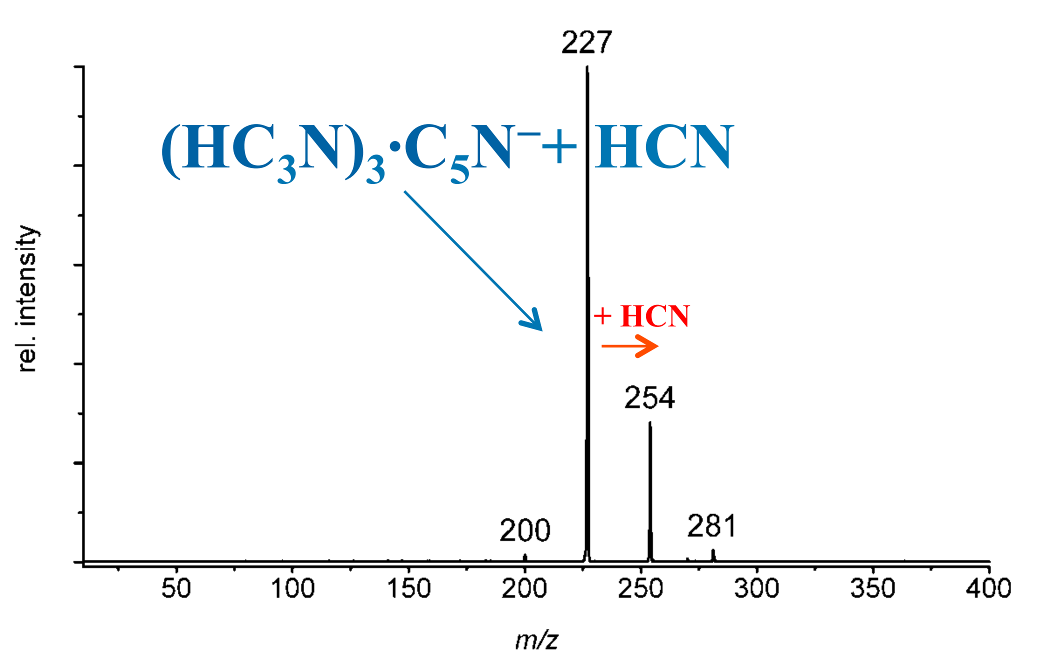
3. Growing $(HC_3N)_xC_5N^-$ anions

$$(HC_3N)_2 \,.\, C_5N^- + HCN$$

$$(HC_3N)_3 \,.\, C_5N^- + HCN$$



$(HC_3N)_2{\cdot}C_5N^- + HCN$
+ HCN
rel. intensity
203
176
230
26
50
100
150
200
250
300
m/z



$(HC_3N)_3{\cdot}C_5N^- + HCN$
+ HCN
rel. intensity
227
254
200
281
50
100
150
200
250
300
350
400
m/z

b) Verification of Proposal reaction mecanism

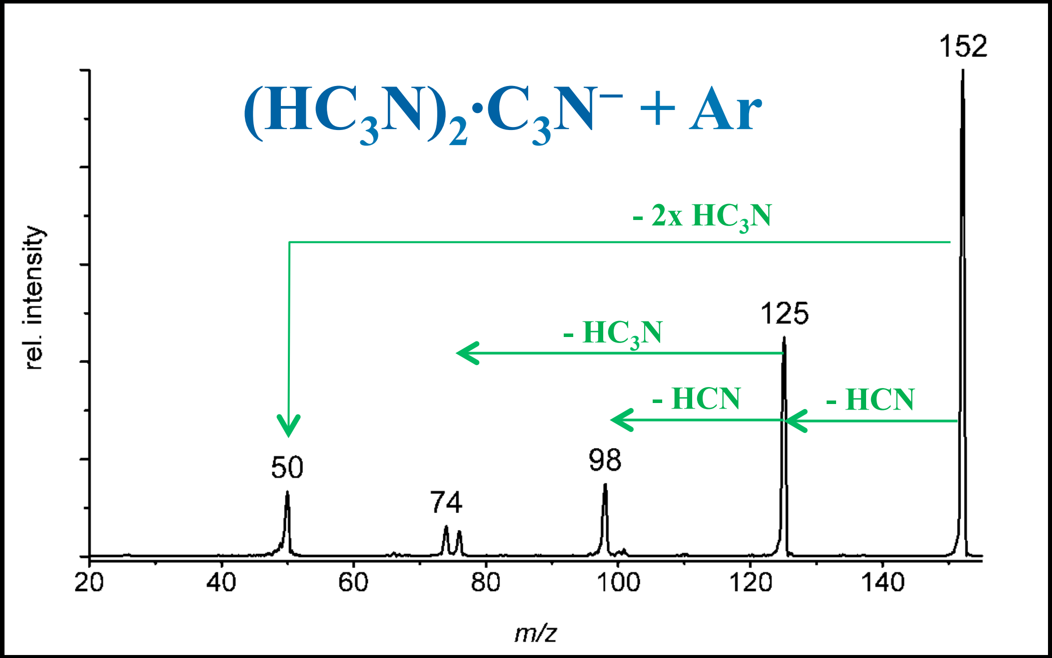
4. Dissociation of $(HC_3N)_2C_xN^-$ anions

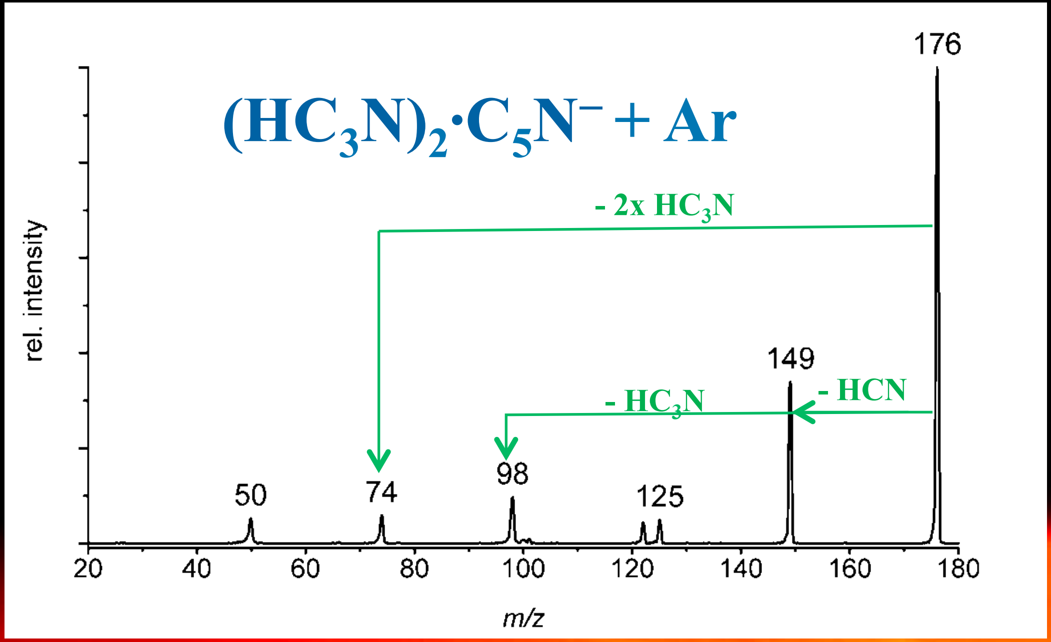
Collision Induced Dissociation (CID):

CID (Ar) ~3eV

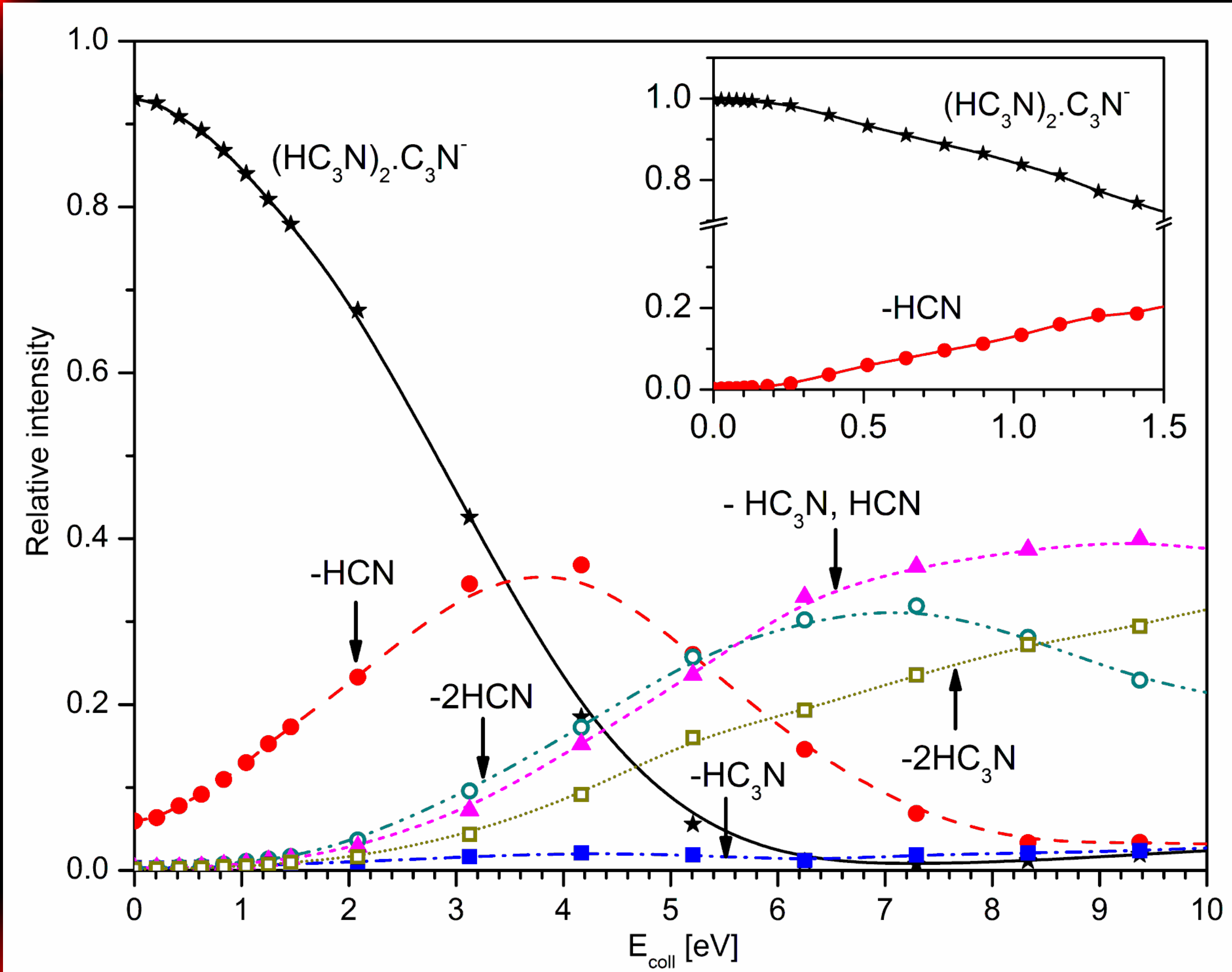
$$(HC_3N)_2 \,.\, C_3N^- \rightarrow$$

$$(HC_3N)_2 \,.\, C_5N^- \rightarrow$$



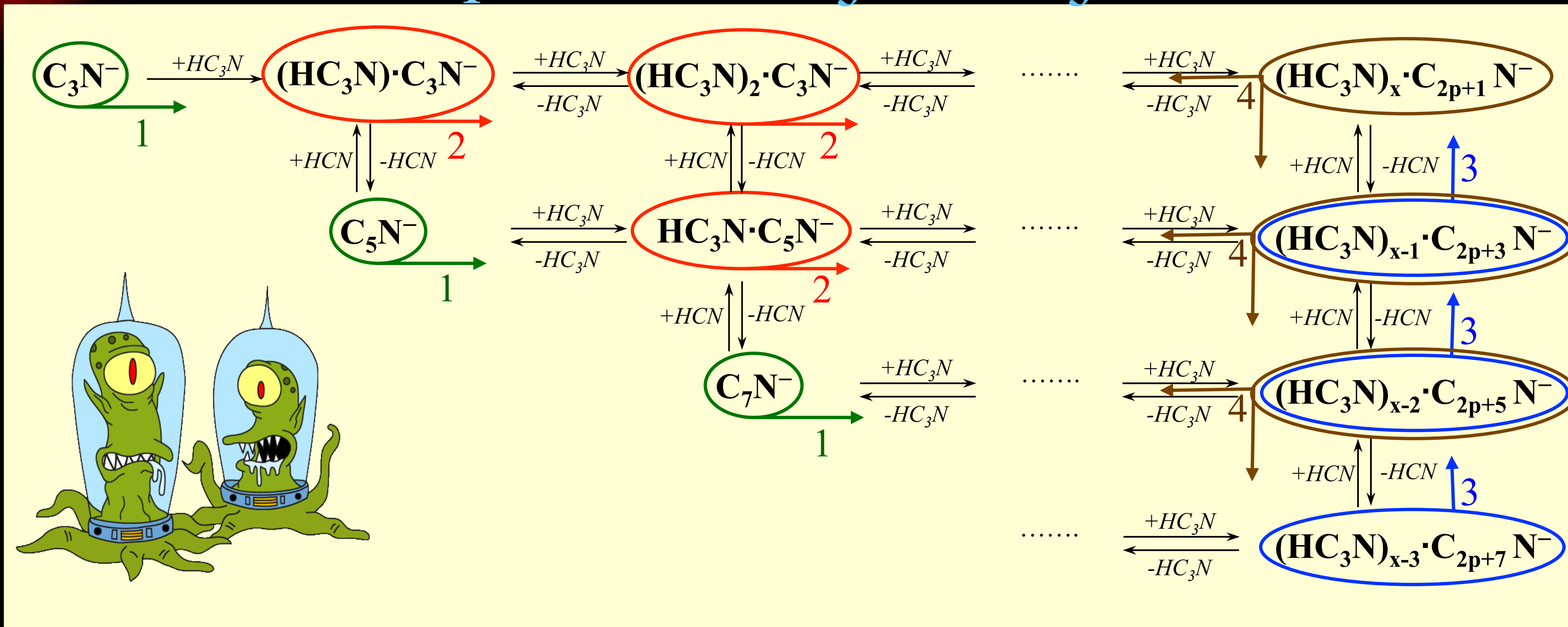


Main channel:
Elimination of HCN


1.0
0.8
0.6
0.4
0.2
0.0
Relative intensity
0
1
2
3
4
5
6
7
8
9
10
E_{coll} [eV]
$(HC_3N)_2.C_3N^-$
-HCN
-2HCN
- HC_3N, HCN
$-HC_3N$
$-2HC_3N$
1.0
0.8
0.2
0.0
0.0
0.5
1.0
1.5
$(HC_3N)_2.C_3N^-$
-HCN

Proposal reaction scheme

First step: $CN^- + HC_3N \rightarrow C_3N^- + HCN$



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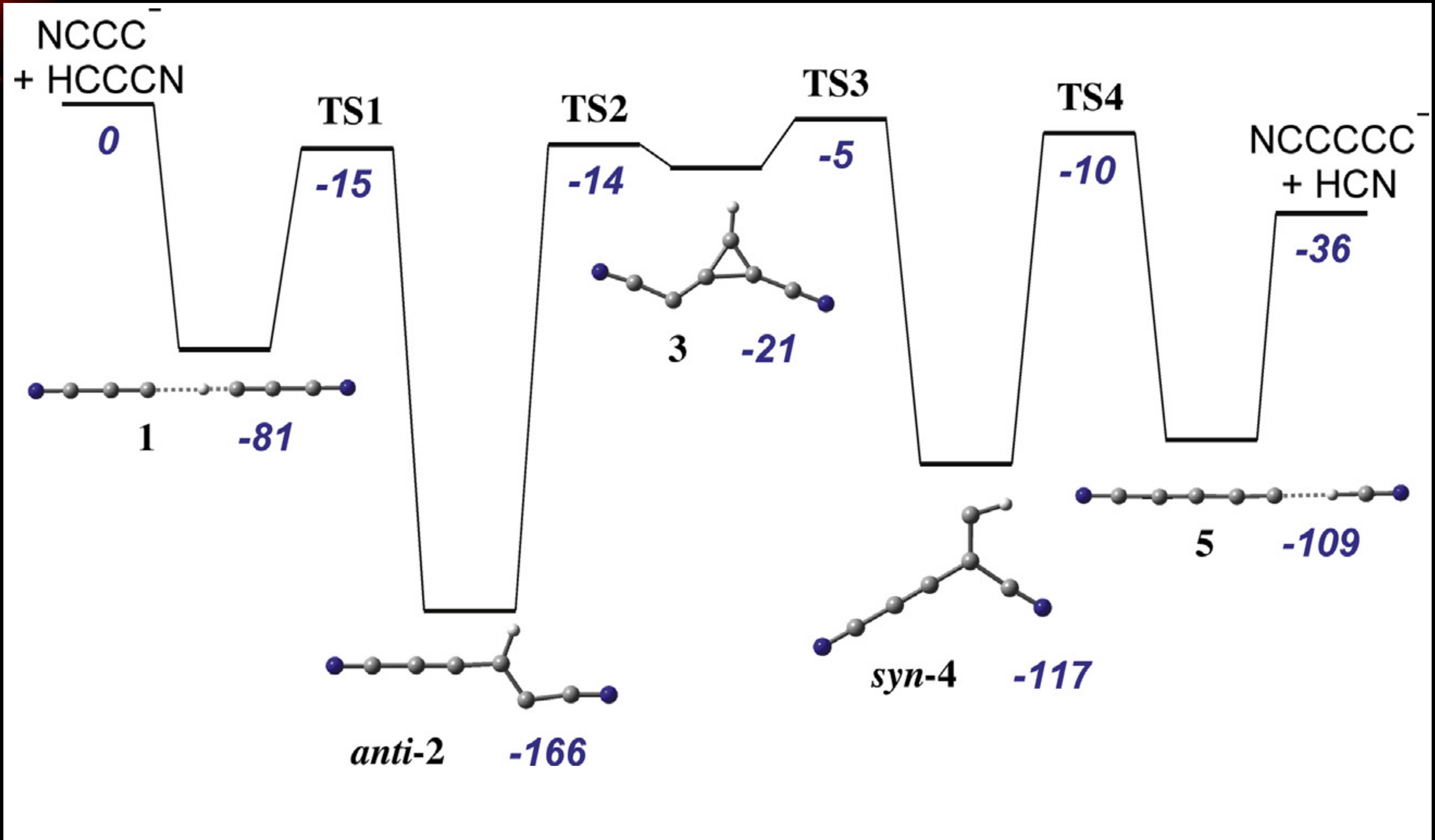
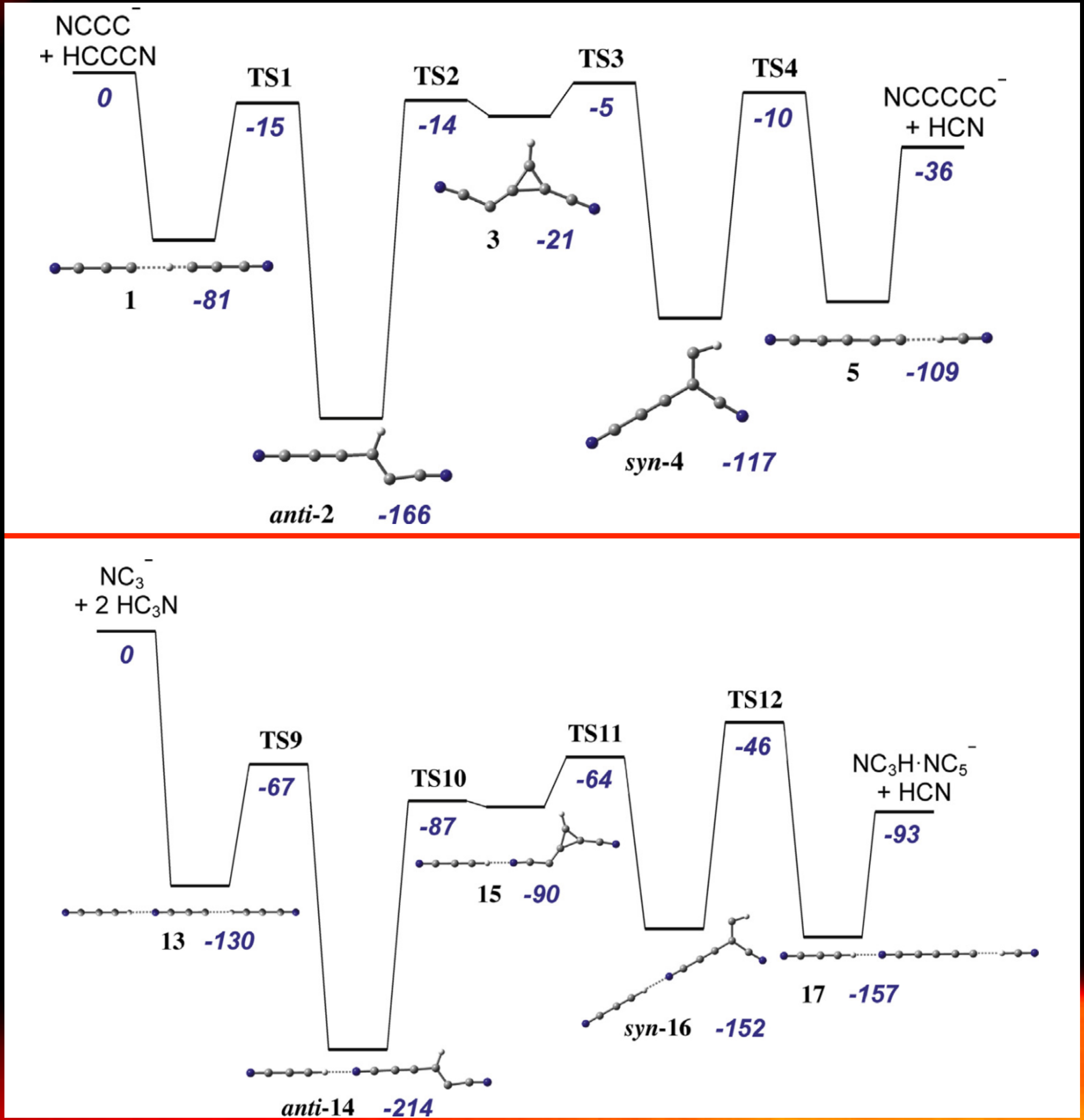
J. Žabka et al. / International Journal of Mass Spectrometry 367 (2014) 1–9

Results and Discussion: elimination of HCN



CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ , in kJ mol^{-1}, ZPVE incl.

Results and Discussion: Solvation driven reactions



CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ , in kJ mol^{-1}, ZPVE incl.

Results and Discussion: Solvation driven reactions

Destruction of anions : - photodetachment [0.4-1.0x10^{13} $cm^{-2}s^{-1}$]

- collisions with energetic heavy particles [$10^5 cm^{-2}s^{-1}sr^{-1}keV^{-1}$]
- ion-ion recombination [$I^+ \sim 10^3 cm^{-3}$ v.s. $N \sim 10^9 cm^{-3}$]

- Photodetachment cross-section for C_3N^- at 266nm is **1.43x10^{-17} cm^2** [1]
- Solar irradiation at Saturn 0.075 W/m^2 in 280-200nm ---> **0.4-1.0x10^{13} cm^{-2}s^{-1}** [2]

⇓

- Mean life time of C_3N^- in range **6600-18500 s**

- Mean free paths of C_3N^- ions at pressures of 10^{-7}mbar ~ **370m**
- Boltzmann velocity at 170K ~ **70ms^{-1}**

C_3N^- ions undergo ~ 1300-3600 collisions before are destroyed by photodetachment

Solvation driven reactions are not excluded in of Titan's ionosphere

[1] S.S. Kumar et al., Photodetachment as a destruction mechanism for CN^- and C_3N^- anions, Astrophys. J. 776 (2013) 25
[2] C.A. Gueymard, The sun's total and spectral irradiance for solar energy appli-cations, Sol. Energy 76 (2004) 423

Conclusion

- First experimental and theoretical characterization of the complex anions derived from cyanoacetylene

- Experimental results: Reaction mechanism was proposed
- bare $C_{2n+1}N^-$ anions react with HC_3N rather slowly by elimination of HCN and formation of $C_{2n+3}N^-$ anion
- When the $C_{2n+1}N^-$ anions are solvated by one or more HC_3N molecules, this reaction becomes significantly more efficient (Solvation Driven Reaction)

- Cyanoacetylene is one of the prominent N-containing organic species in Titan atmosphere → important role in the ionospheric chemistry in Titan

Possible way of formation of large anions found in the ionosphere of Titan

Future work: - Reaction mechanisms and the rate constants at temperatures 80-300K (Variable Temperature SIFT)

http://www.esa.int , http://saturn.jpl.nasa.gov, http://spaceprobes.kosmo.cz

LCP

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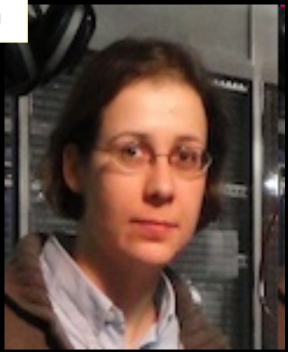

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