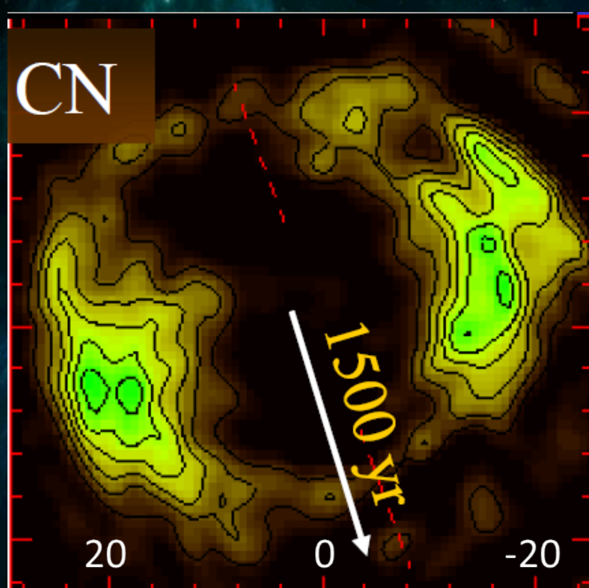
Reactions Involving Nitrile Anions in the Interstellar Medium: the CRESU Laboratory Apparatus Updates

Carles S.,
Bourgalais J., Capron M., Jamal Eddine N., Balaganesh M., Guillemin J.-C.,
Le Picard S.D., Faure A., Biennier L. and Joalland B.

Anions in the ISM

C_6H^-	C_4H^-	C_8H^-	C_3N^-	C_5N^-	CN^-
2006	*2007*	*2007*	*2008*	*2008*	*2010*
McCarthy et al	*Cernicharo et al*	*Brünken/Remijan et al*	*Thaddeus et al*	*Cernicharo et al*	*Agúndez et al*
ApJ.652,L141	*A&A.467,L37*	*ApJ.664,L43/L47*	*ApJ.677,1132*	*ApJ.688,L83*	*A&A.517,L2*
IRC+10216	*IRC+10216*	*IRC+10216*	*IRC+10216*	*IRC+10216*	*IRC+10216*

Lucas et al. Ap&SS.224,293(1995)



Main chemical pathway formation :

$e^- + CN \rightarrow CN^- + h\nu$

CN has been detected in the outer envelope of IRC +10216 (300 *R**, 100K) : $CN/H_2 = 5 \times 10^{-6}$

Alternative :

$HCN + H^- \rightarrow CN^- + H_2$

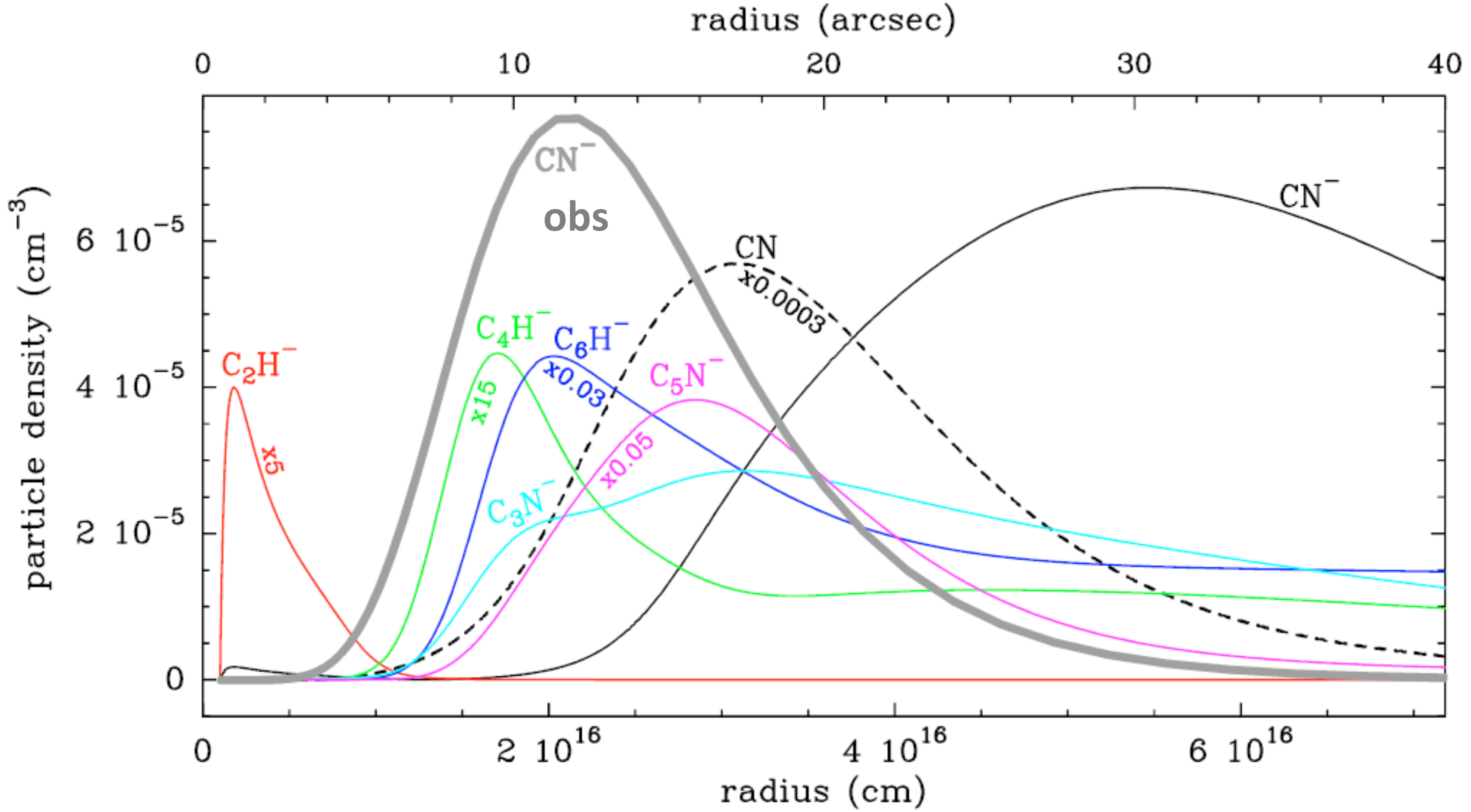
$C_x^- + N \rightarrow CN^- + C_{x-1}$

$e^- + MgNC \rightarrow CN^- + Mg$

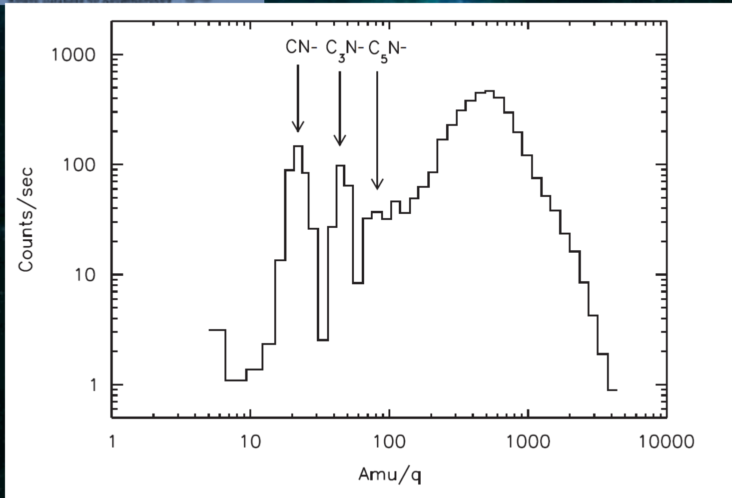
Cordiner et al. ApJ.697,68(2009)

Spatial Distribution of CN^- : Observations *vs.* models

A&A 517, L2 (2010)
M. Agúndez[1], J. Cernicharo[2], M. Guélin[3], C. Kahane[4], E. Roueff[1], J. Kłos[5], F. J. Aoiz[6], F. Lique[7], N. Marcelino[2], J. R. Goicoechea[2], M. González García[8], C. A. Gottlieb[9], M. C. McCarthy[9], and P. Thaddeus[9]



Anions in the Titan Atmosphere

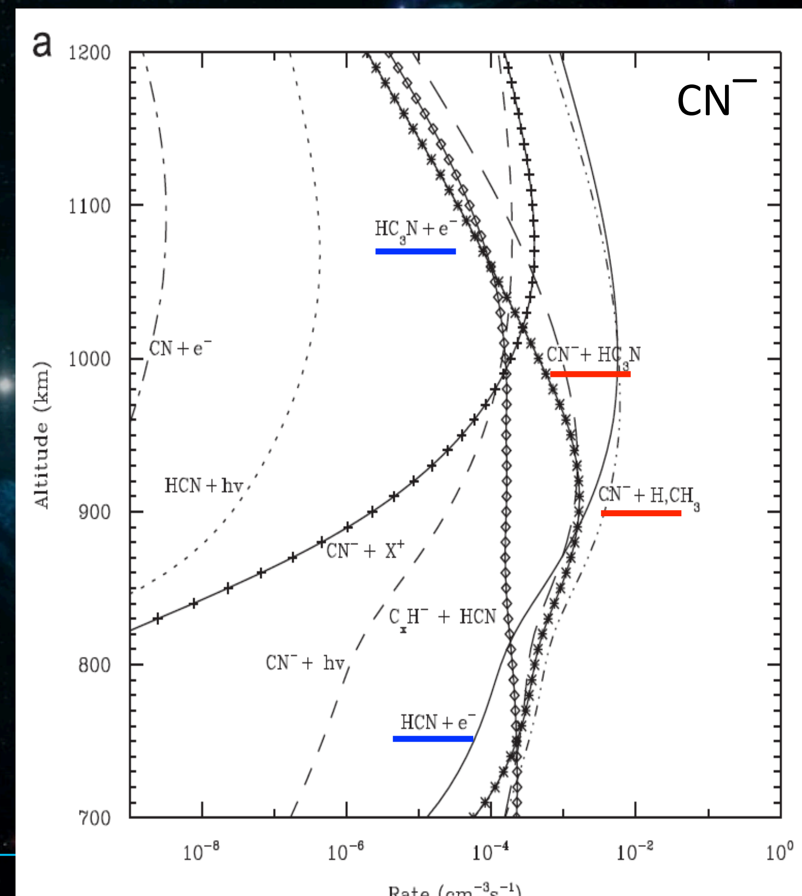


- Surprising detection of various and heavy anions - Cassini *(Waite et al. Science, 316, 870 2007)*
- Model using AE and chemistry : proposal for an identification *(Fig: Vuitton et al. Planet. Space Sci. 57,1558, 2009)*
- Ions may play a key role in the aerosol formation *(Lavvas et al. PNAS, 110, 2729, 2013)*

Altitude ≥ 900KM

	CN^-	C_3N^-
Dissociative Attachment	$HC_3N + e \rightarrow$ $HCN + e \rightarrow$	
Associative Detachment	$CN^- + H \rightarrow$ $CN^- + CH_3 \rightarrow$	$C_3N^- + H \rightarrow$ $C_3N^- + CH_3 \rightarrow$
Proton Transfer	$CN^- + HC_3N \rightarrow$	

Losses Sources

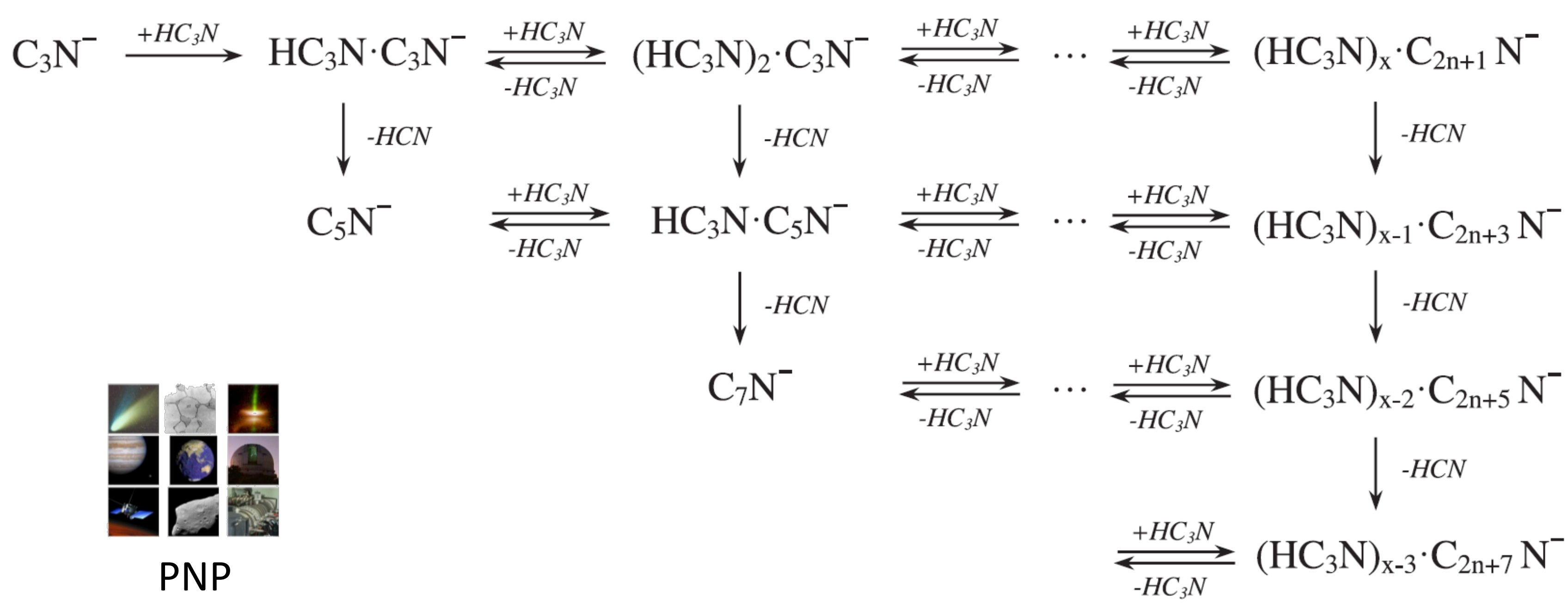


GROWTH OF NITRILES ?

$CN^- + HC_3N \rightarrow C_3N^- + HCN$ $\Delta H^0 = -0.4\ kJ.mol^{-1}$

$C_3N^- + HC_3N \rightarrow C_5N^- + HCN$ $\Delta H^0 = -48\ kJ.mol^{-1}$

(Žabka et al. Icarus, 219, 161, 2012)
(Žabka et al. Int.J.Mass Spectrom. 367, 1, 2014)



Scheme 1.

PNP

KINETIC STUDIES AT VERY LOW TEMPERATURES :

FROM 300K DOWN TO 13K

Ion Kinetic Studies In Gas Phase (Rennes)

- **Ion-molecule reactions :** 300K → 13K

  $A^{+/-} + B \rightarrow C^{+/-} + D$ CRESU

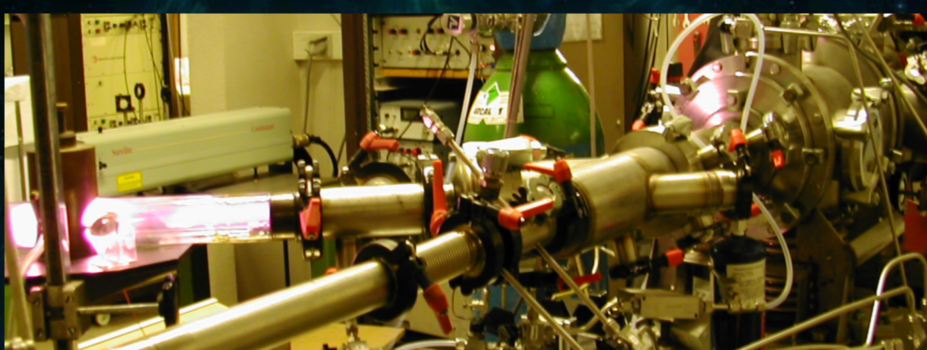
- **Electron attachment :** 300K → 13K

  $AB + e \rightarrow A^{-} + B$

- **Ion Recombination :** 300K →

  $A^{+} + e \rightarrow C + D$
  $A^{+} + B^{-} \rightarrow C + D$ A

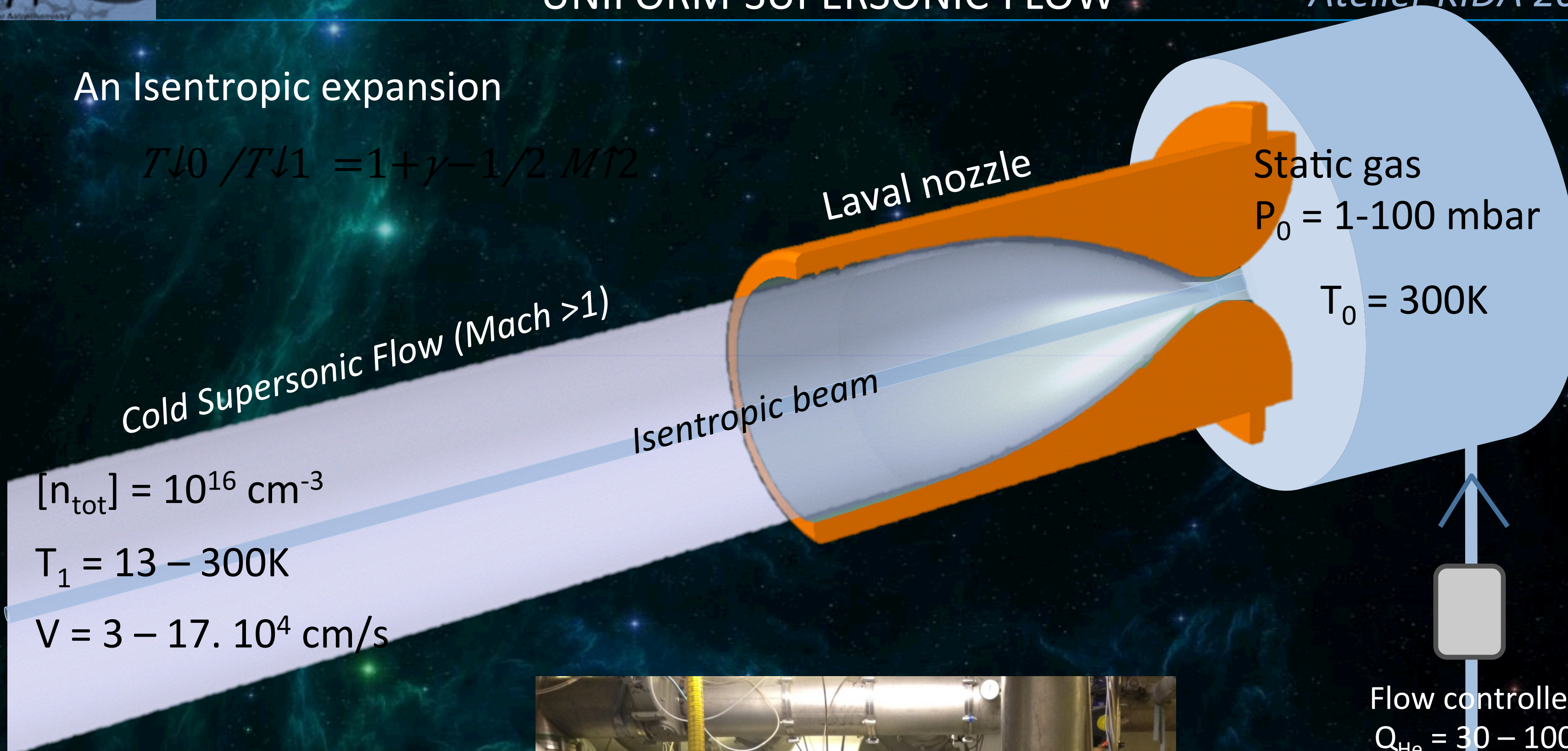
FALP SET-UP 300K



CRESU SET-UP 300K → 13K

An Isentropic expansion

$$\frac{T_0}{T_1} = 1 + \frac{\gamma - 1}{2} M^2$$

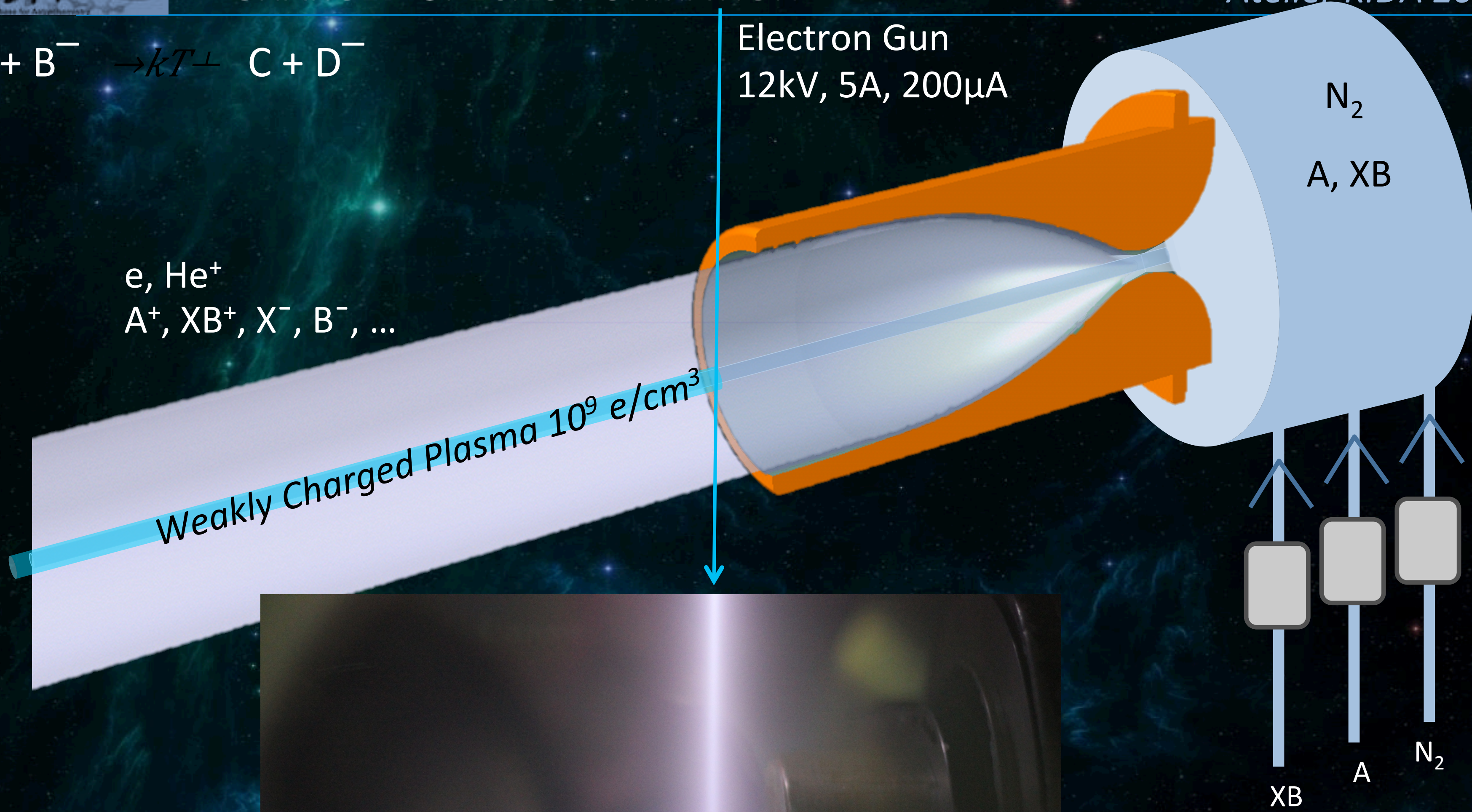


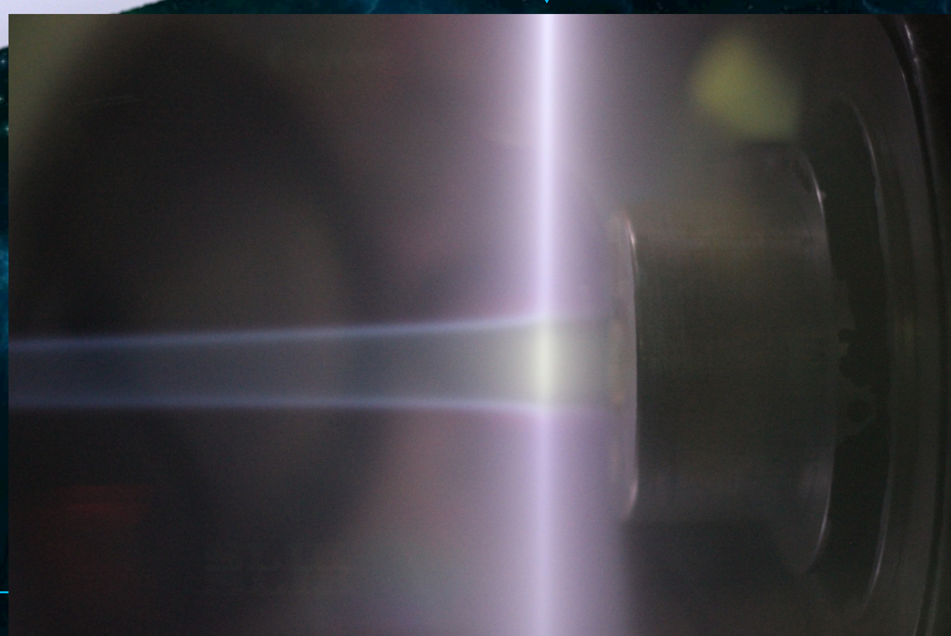
Main chamber
P_1 = 0.1 – 3 mbar

24000 m^3/h

CHARGED SPECIES FORMATION

$A + B^{-} \rightarrow kT\perp \; C + D^{-}$





Charged Species Formation

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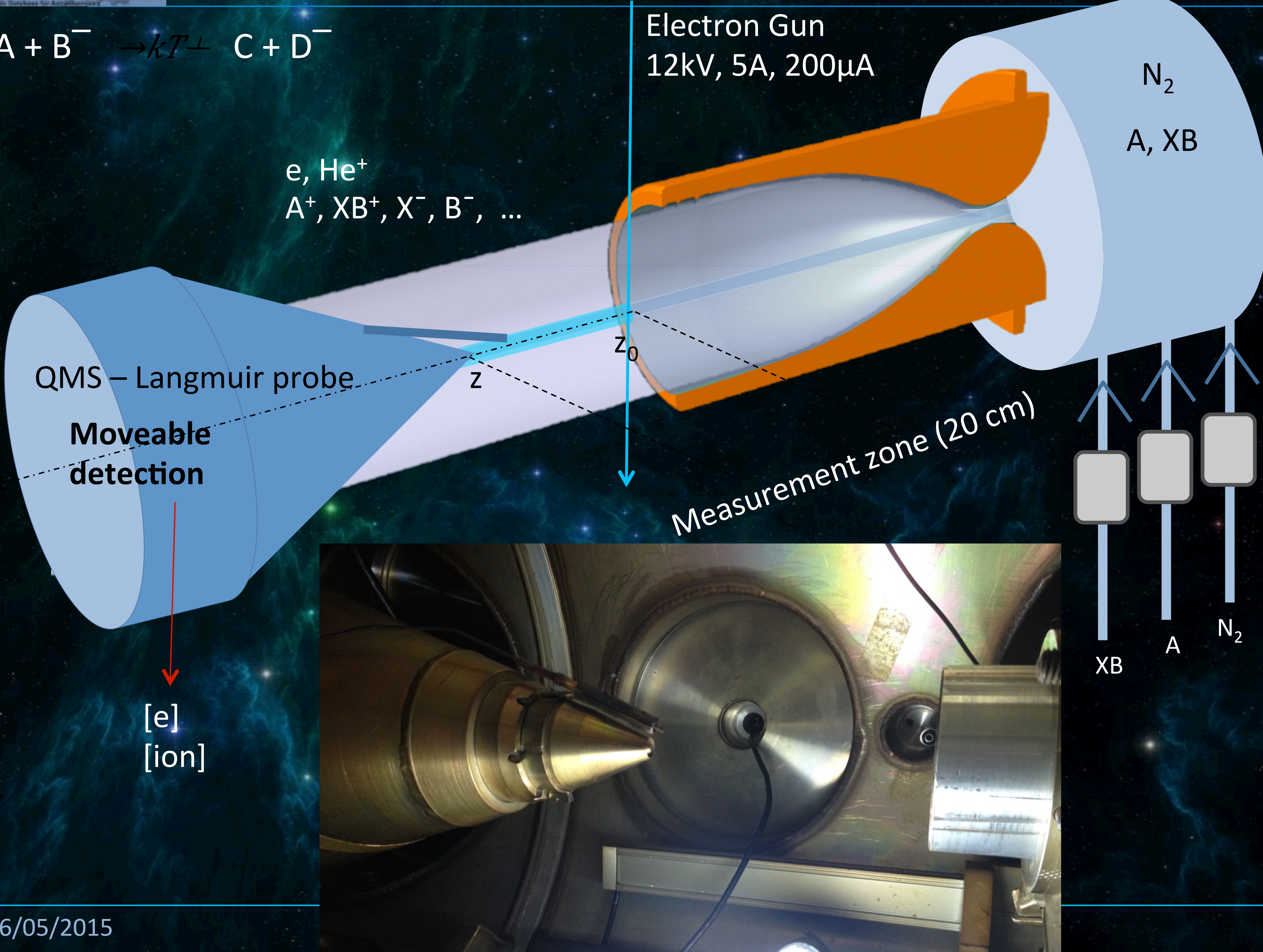
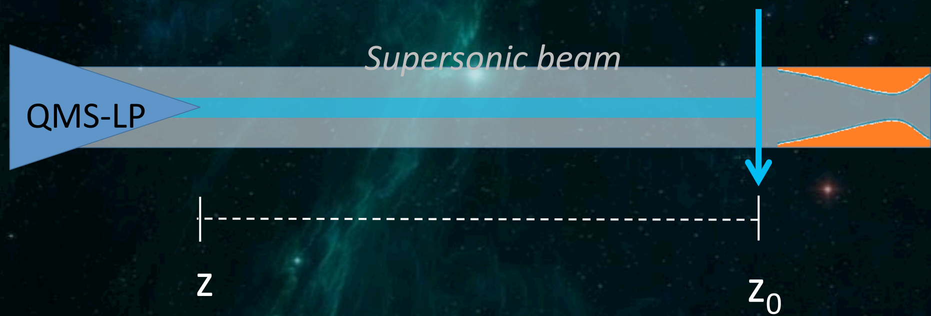


Kinetic Analyse

$$A + B^- \xrightarrow{kT} C + D^-$$



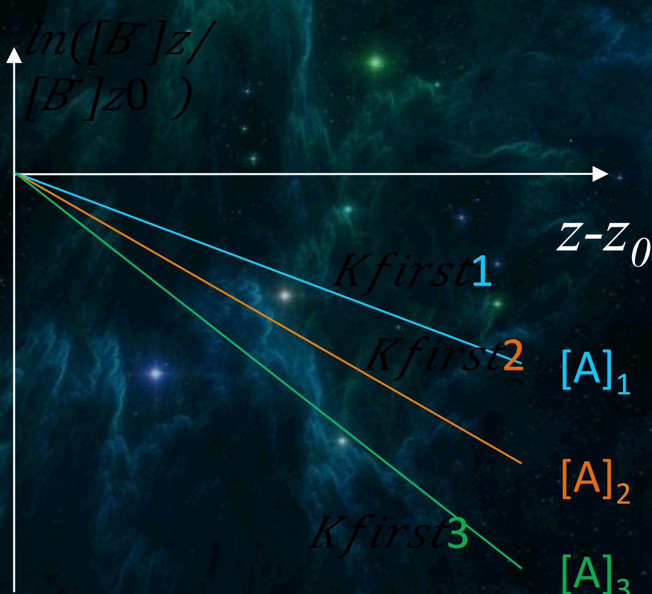
- Uniform beam

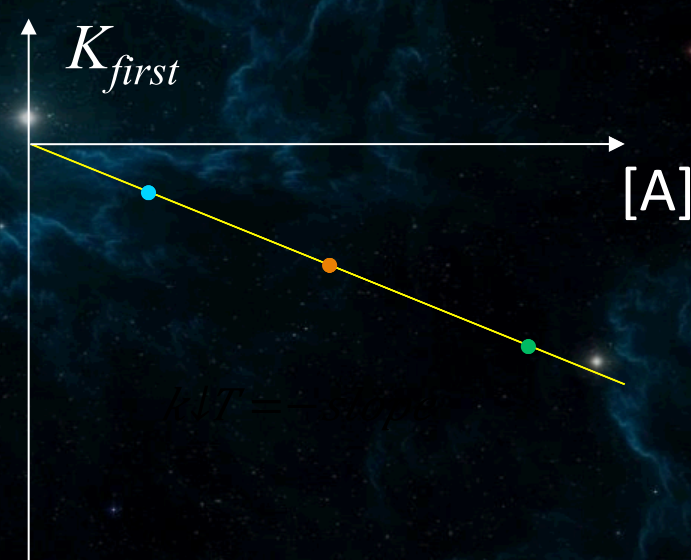
⇒ Density, Speed v, T are constant

⇒ Spatial evolution ≡ Temporal evolution

- Pseudo first order $[A] \gg [B^-]$

$$d[B^-]/dt = -kT[B^-][A] - D[B^-] \Leftrightarrow \ln([B^-]_z/[B^-]_{z0}) = -kT[A]/v\,(z - z_0) - D$$

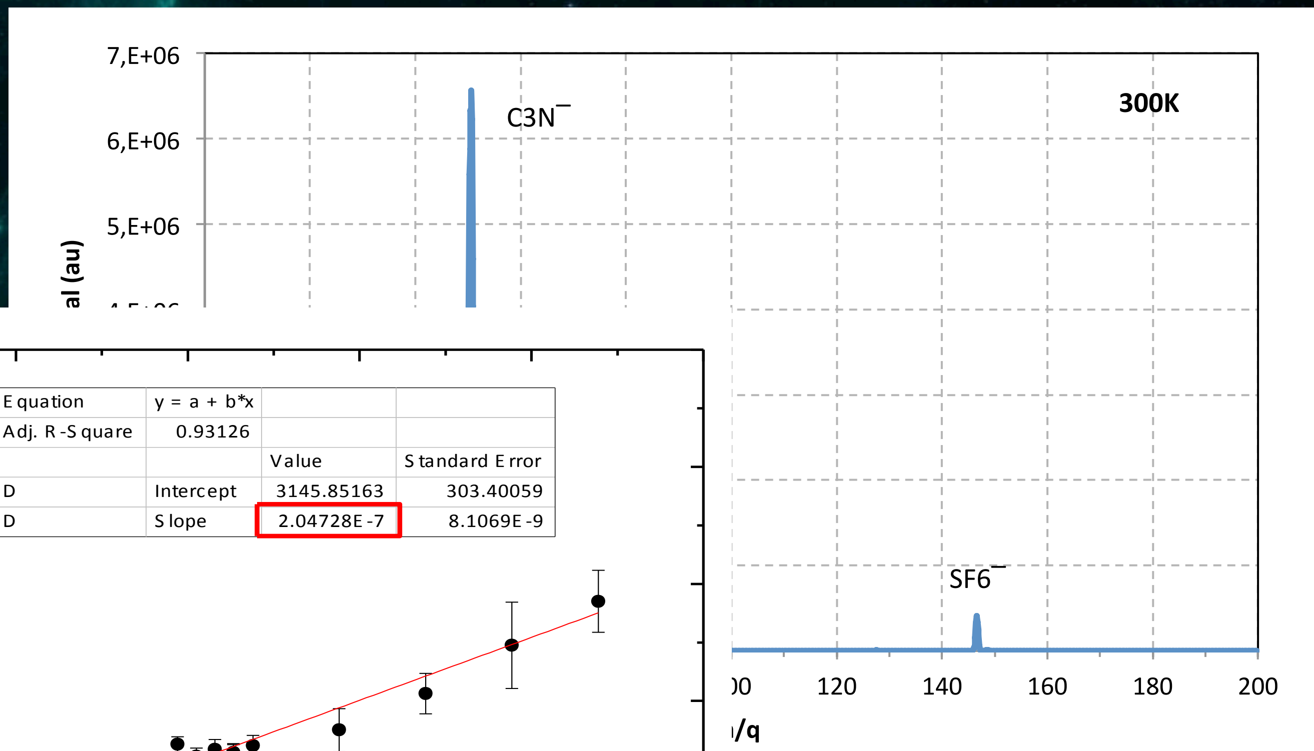


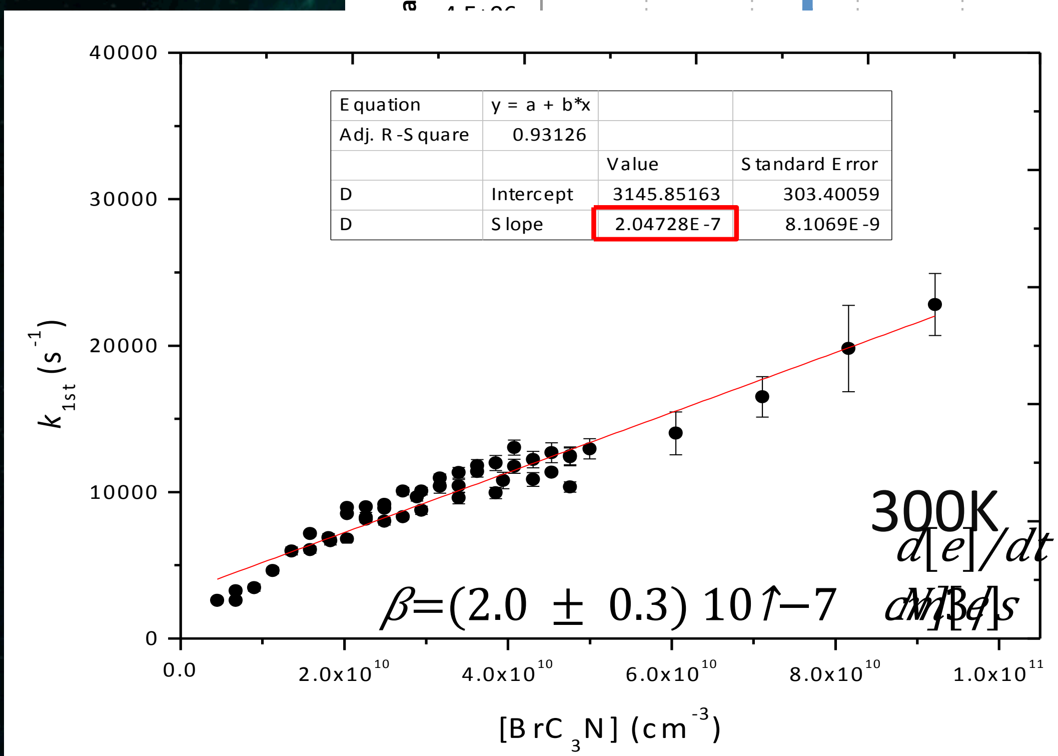


$HC_3N + C_3N^-$ Reaction

C_3N^- Anion Formation

$$BrC_3N + e\ (\leq 0.5\ \text{eV}) \rightarrow Br + C_3N^-$$
$$\rightarrow Br^- + C_3N$$





300K

$d[e]/dt = -D/\Lambda 2\,[e] \ldots$

$\beta = (2.0 \pm 0.3)\ 10^{-7}\ cm^3/s$

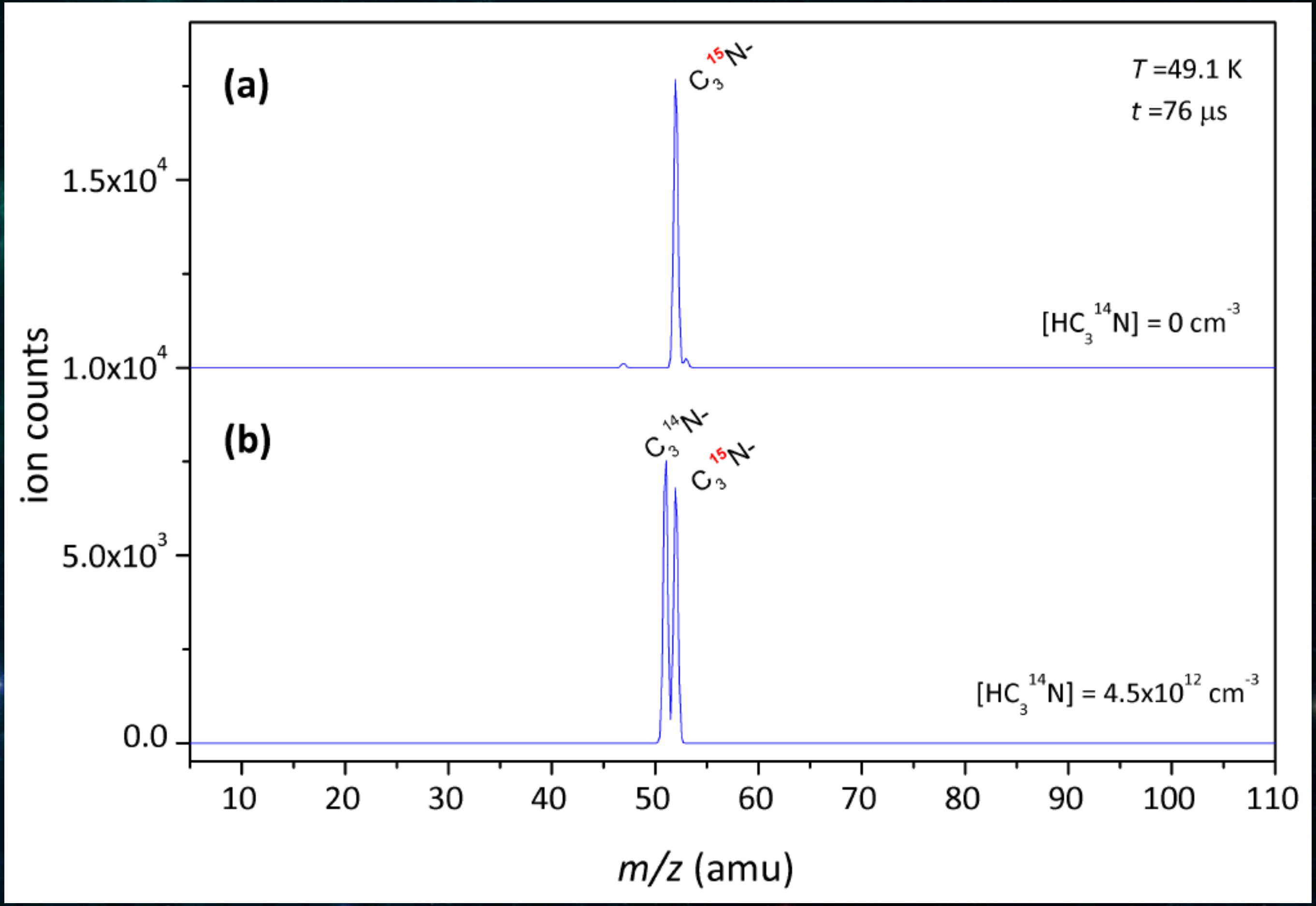
Ambipolar diffusion

(Carles et al. AIP Conf. Proceedings, 2015)

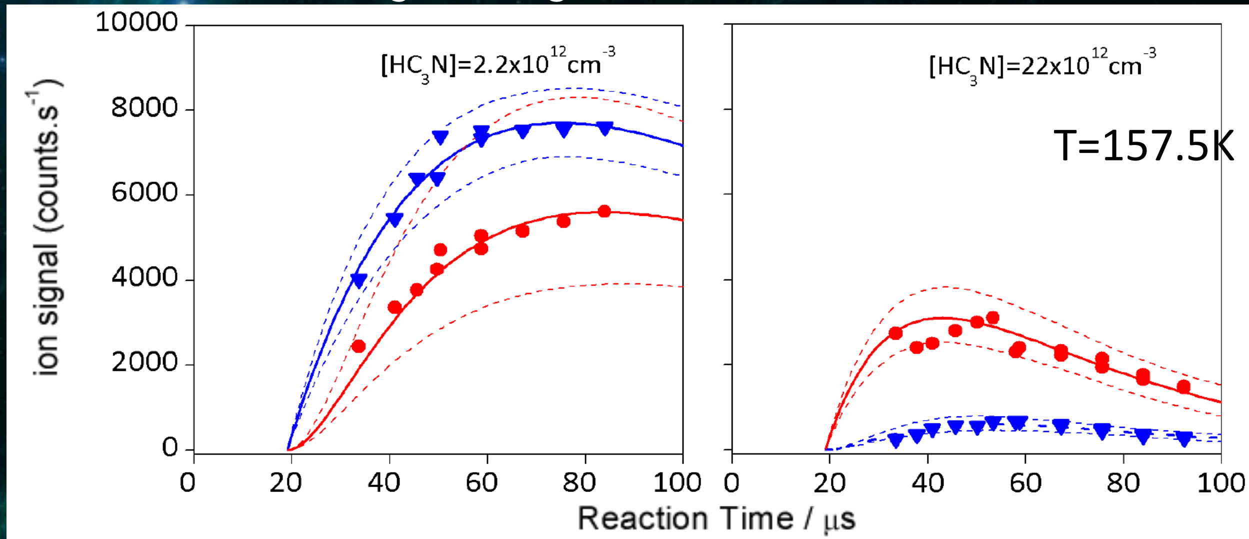
$HC_3N + C_3{}^{15}N^-$ Reaction

(Biennier et al. In preparation)

$$BrC_3{}^{15}N + e\ (\leq 0.5\ eV) \rightarrow Br + C_3{}^{15}N^-$$
$$\rightarrow Br^- + C_3{}^{15}N$$



$HC_3N + C_3{}^{15}N^-$ Reaction



$C_3{}^{15}N^- + HC_3N \xrightarrow{k1} C_3N^- + HC_3{}^{15}N$ ● $\Delta H^0 = 0\ kJ.mol^{-1}$

$C_3N^- + HC_3N \xrightarrow{k3} e + \text{neutral species}$ ● Reactive Detachment

$$\frac{dC_3{}^{15}N^-}{dt} = +k_2[BrC_3{}^{15}N][e^-] - k_1[HC_3N]C_3{}^{15}N^- - D_1C_3{}^{15}N^-$$

$$\frac{dC_3N^-}{dt} = +k_1[HC_3N]C_3{}^{15}N^- - D_2C_3N^- - k_3[HC_3N]C_3N^-$$

$$\frac{d[BrC_3{}^{15}N]}{dt} = -k_2[BrC_3{}^{15}N][e^-]$$

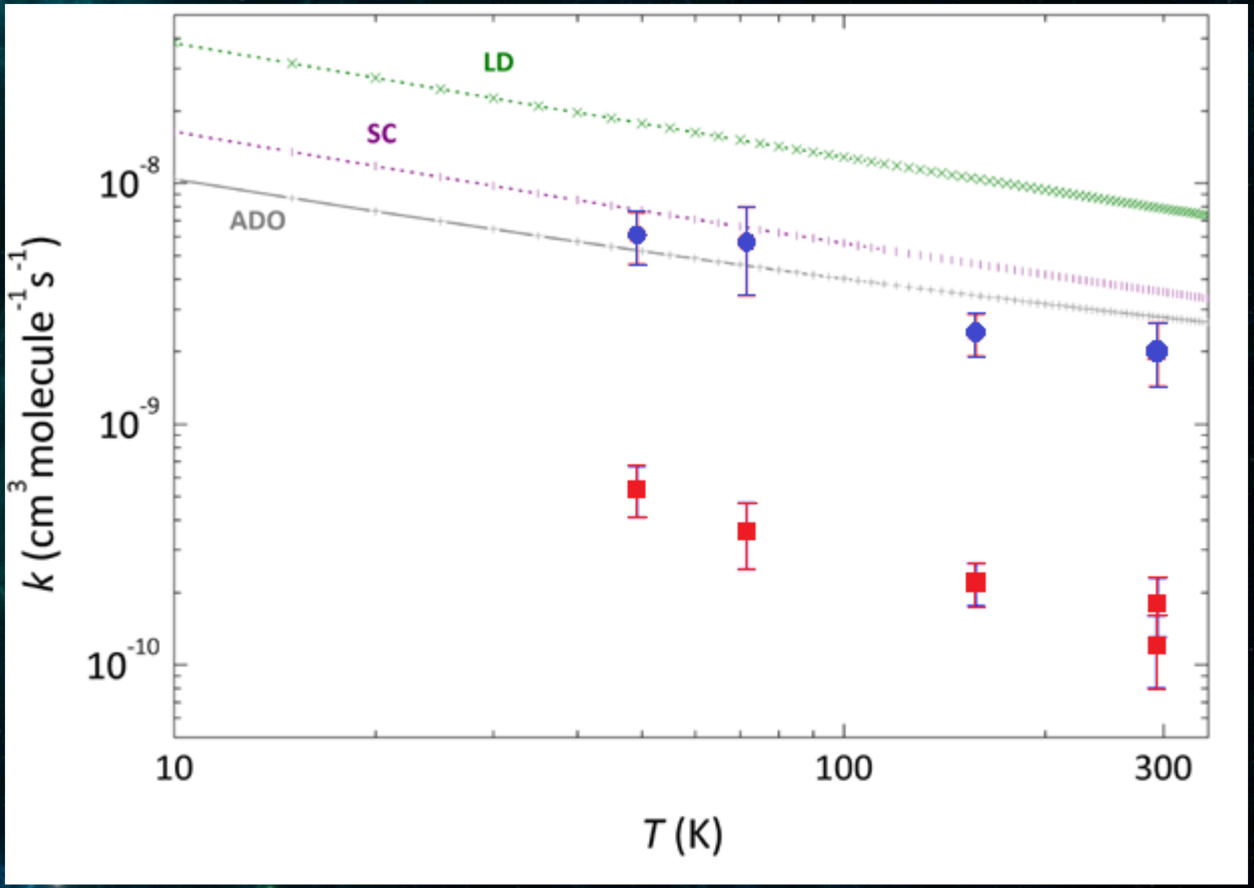
$$\frac{d[e^-]}{dt} = -k_2[BrC_3{}^{15}N][e^-]$$

Dissociative Attachment

$$\frac{d[HC_3N]}{dt} = -k_1[HC_3N]C_3{}^{15}N^- - k_3[HC_3N]C_3N^-$$

T K	k_1 $\times10^{-9}$ cm^3·molecule^{-1}·s^{-1}	k_3	n_{tot} $\times10^{16}$cm^{-3}	[HC_3N] $\times10^{12}$cm^{-3}
49.1	6.1± 1.5	0.54±0.13	10.4	3.1–25
71.6	5.7±2.3	0.36±0.11	6.01	1.2 – 11
157 .5	2.4±0.5	0.22±0.04	13.0	2.2 – 22
294	2.0±0.6	0.18±0.05	7.47	3.2–51.8
293	1.98± 0.12	0.12±0.04	1.74	0.44 – 15.2

$HC_3N + C_3{}^{15}N^-$ Reaction



$C_3{}^{15}N^- + HC_3N \xrightarrow{k1} C_3N^- + HC_3{}^{15}N$ ● $\Delta H^0 = 0$ kJ.mol^{-1}

$C_3N^- + HC_3N \xrightarrow{k3}$ e + neutral species ● Reactive Detachment

X^- + A Reaction Study : Limitations

Studied Reaction is : $A + B^- \rightarrow C^- + D$

$\rightarrow E^- + F$

The B^- anion is formed by dissociative electron attachment inside the uniform supersonic flow:

$BX + e \rightarrow X^- + B$ ①

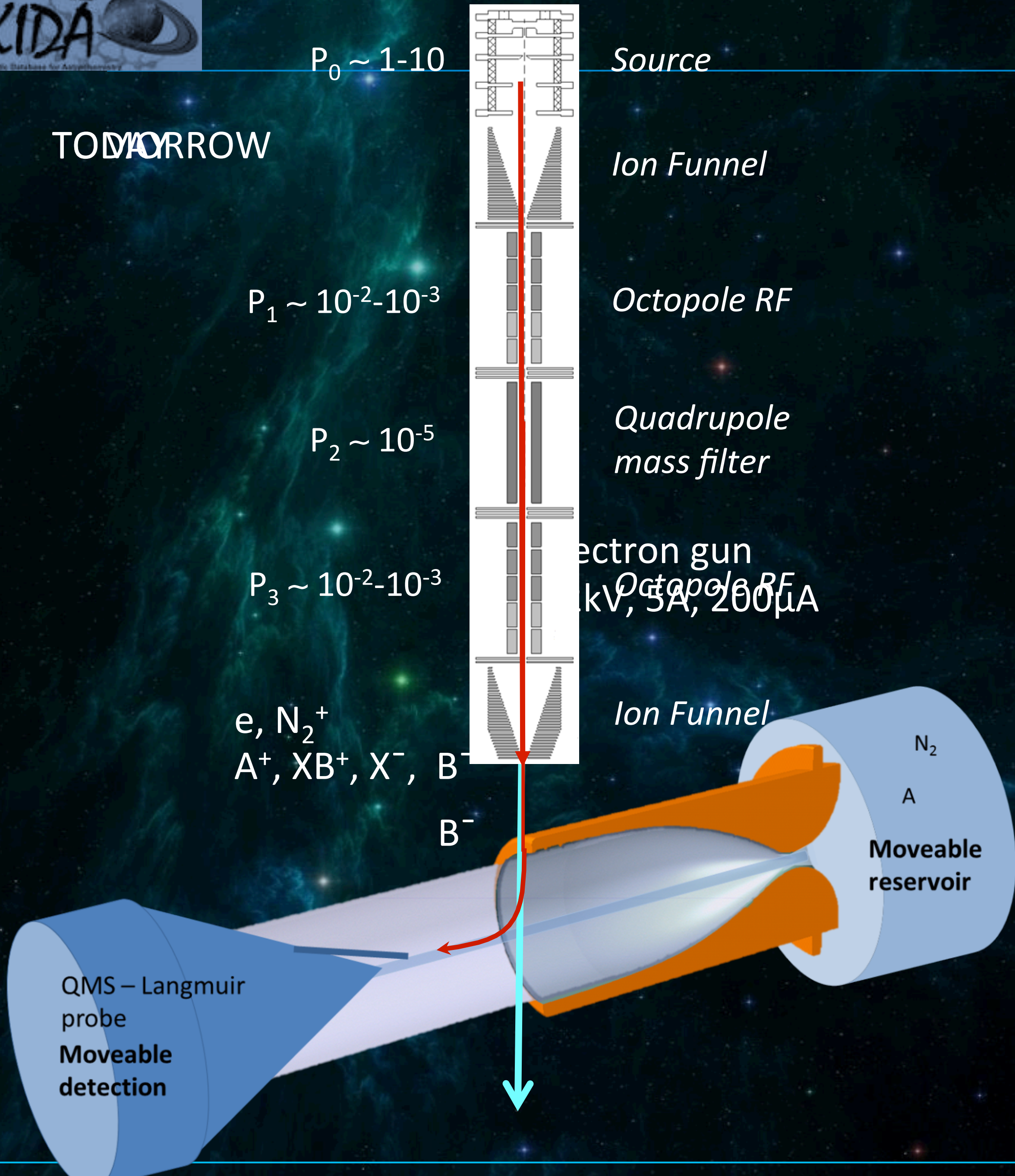
$\rightarrow B^- + X$ ②

- The vapor pressure of BX must be high at room temperature
- The electron attachment (EA) must be efficient at E(e)= 0 eV
- The electron attachment (EA) must be efficient / τ_{hydro}
- The main exit channel must be the ②
- A lot of charged species generate several undesirable reactions

Today :

- $BrCN + e \rightarrow Br + CN^-$
- $BrC_3N + e \rightarrow Br + C_3N^-$

CONCLUSION – PERSPECTIVES: FUTUR CRESU SET-UP



$$A + B^- \rightarrow C^- + D$$
$$\rightarrow E^- + F$$

The B^- anion is directly formed and selected outside the uniform supersonic flow ⇒

Only 1 constraint

- The vapor pressure of BX must be high at room temperature

Several advantages

- Only B^-
- Various B^-
  C_xH^- ; $C_{x>3}N^-$; C_x^-
- *k(T)*
- ***Branching Ratio (T)***

STAFF - SPONSORS

Ludovic BIENNIER

Sébastien LE PICARD

Nour JAMAL EDDINE

Michaël CAPRON

Jérémy BOURGALAIS

Baptiste JOALLAND

Jean-Claude GUILLEMIN

- Daniel Cordier (UTINAM Lab., Besançon)
- Alexandre Faure, Véronique Vuitton, Rolland Thissen (IPAG Lab., Grenoble)
- Christian Alcaraz, Claire Romanzin, Joël Lemaire, Essyllt Louarn (LCP Lab., Orsay)
- Ján Žabka, Miroslav Polášek (J. Heyrovský Institut of Physical Chemistry, Czech Republic)

Thanks For Your Attention