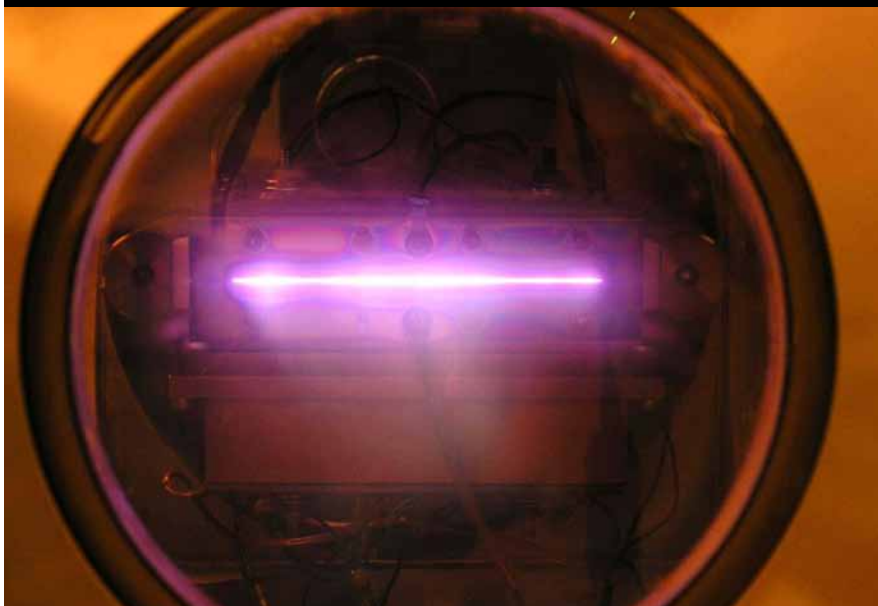
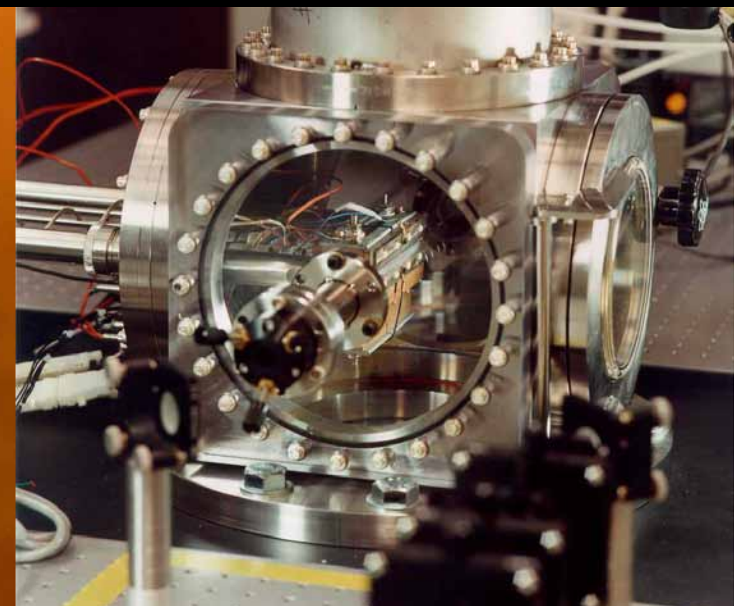
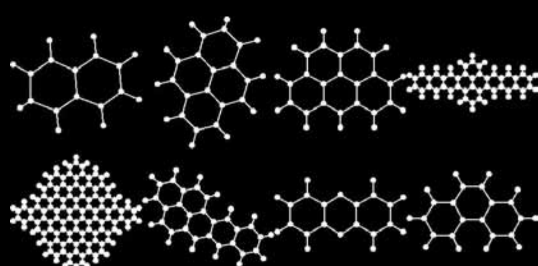
The formation of solid particles from their gas-phase molecular precursors in cosmic environments

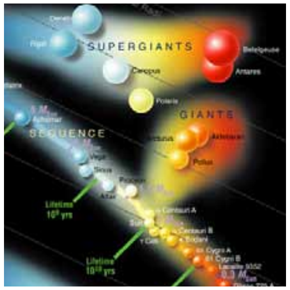




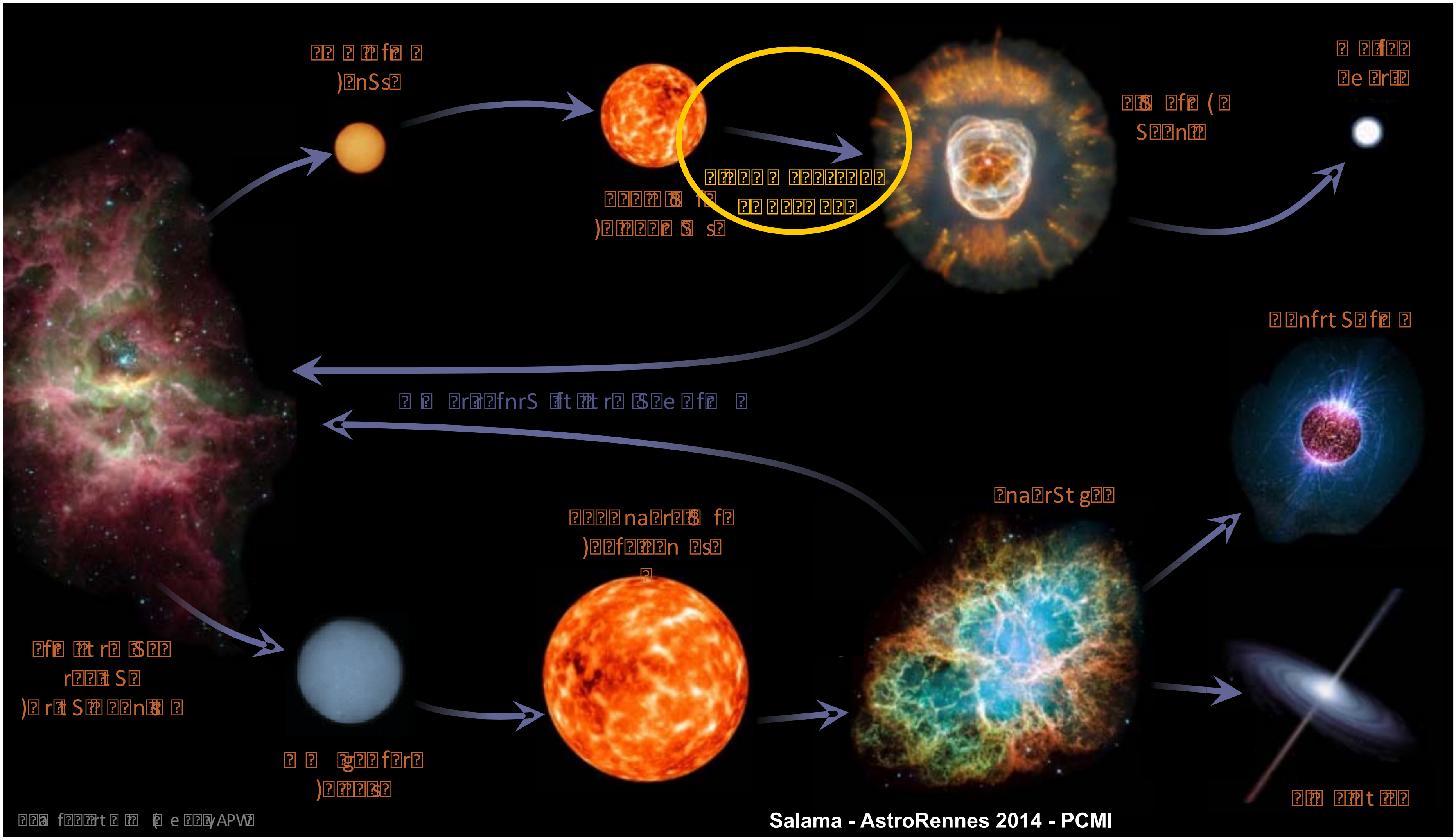
Farid Salama
NASA Ames Research Center



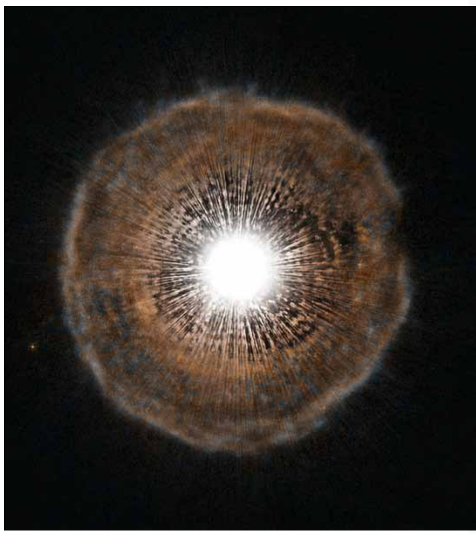
Ames Research Center

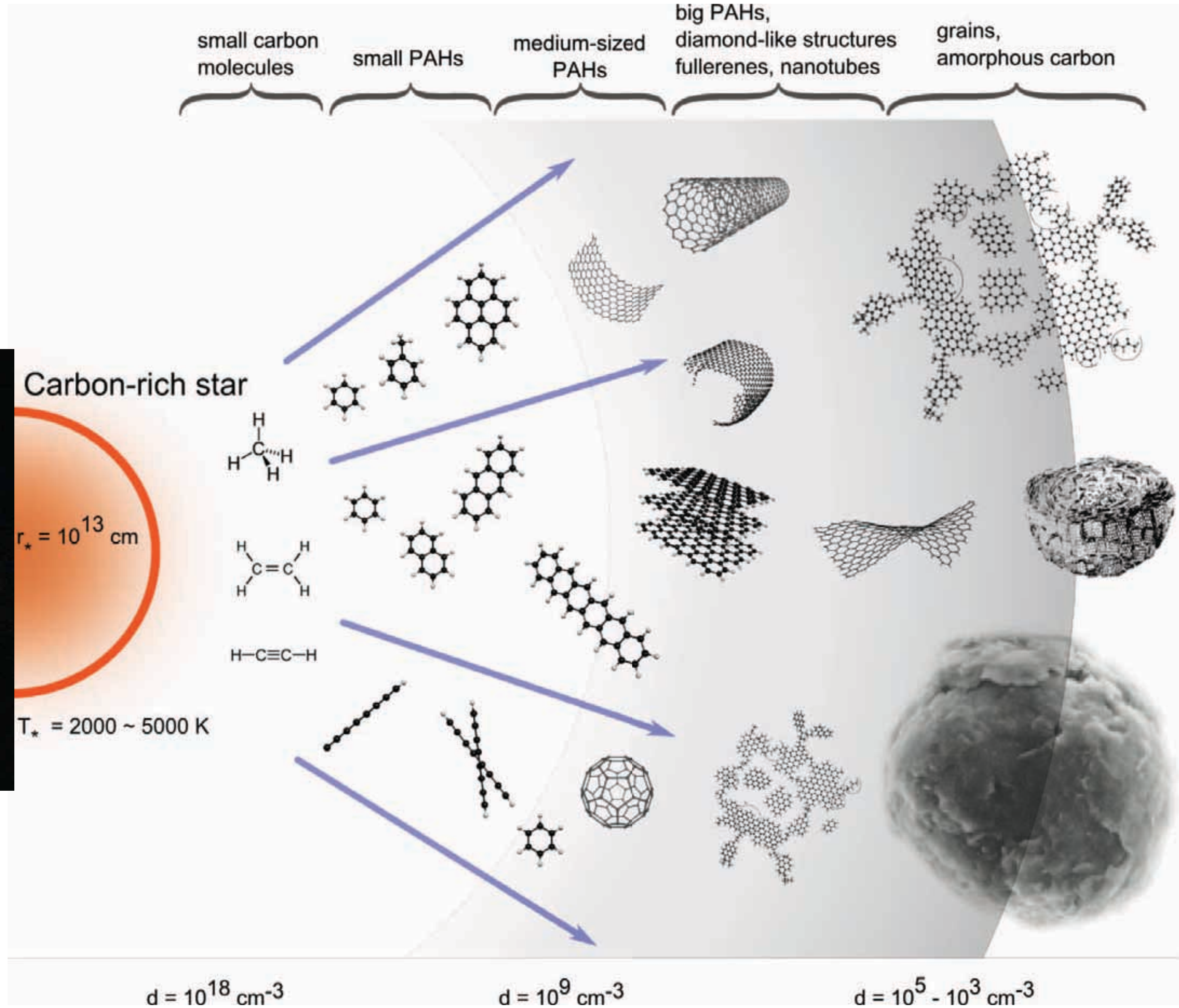


AGB STELLAR EVOLUTION

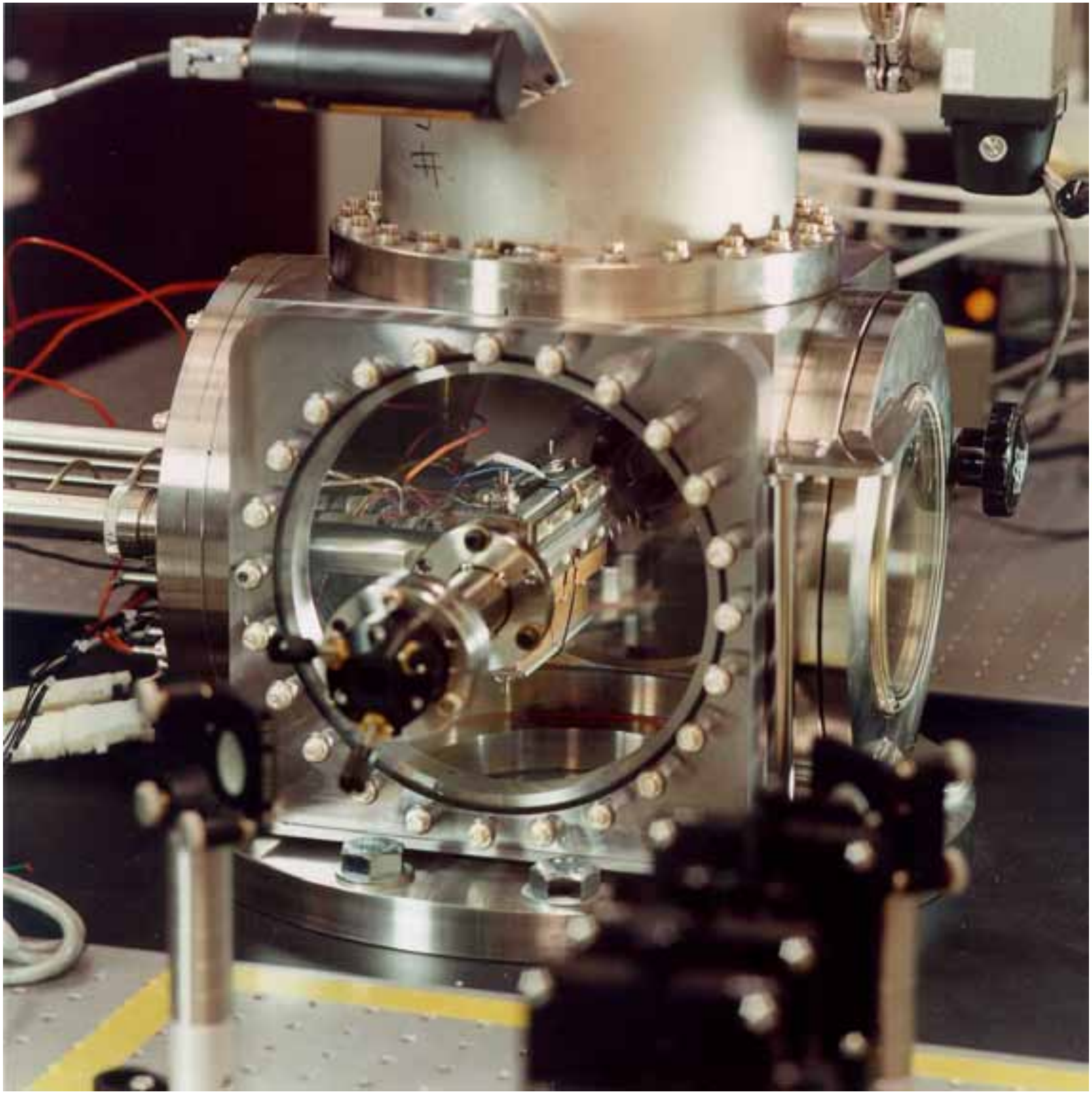


Carbon in the Galaxy – Project 1 Investigations



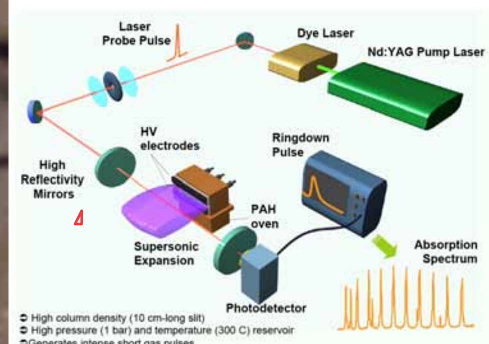


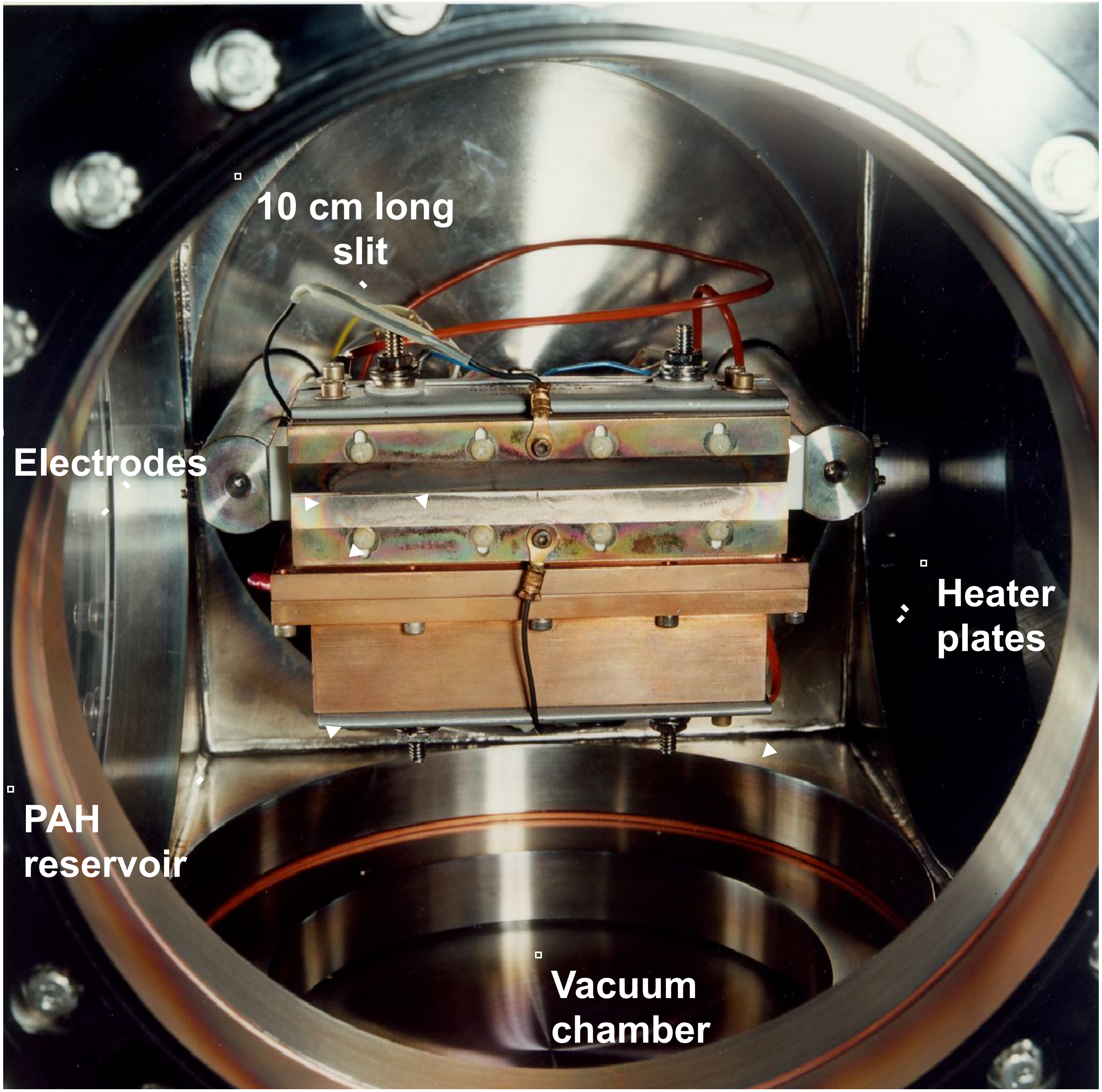
Contreras & Salama, ApJS (2013), adapted from G. Pascoli, A. Polleux, A&A (2000)



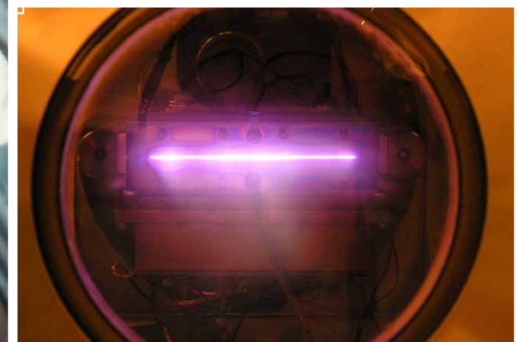
TOOLS

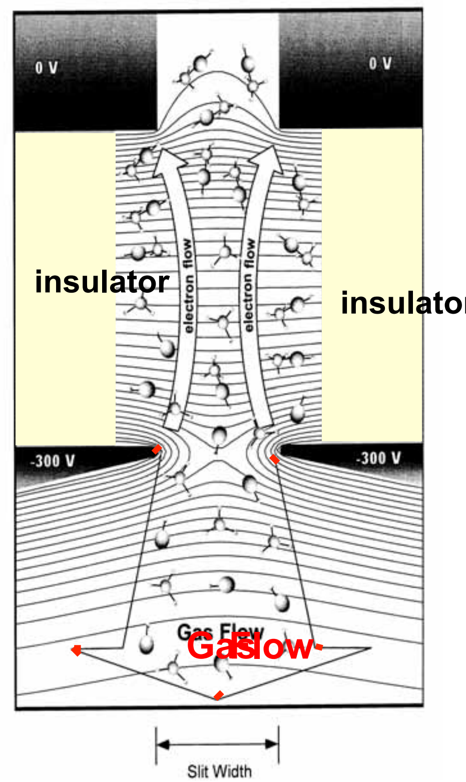
Simulation Chamber

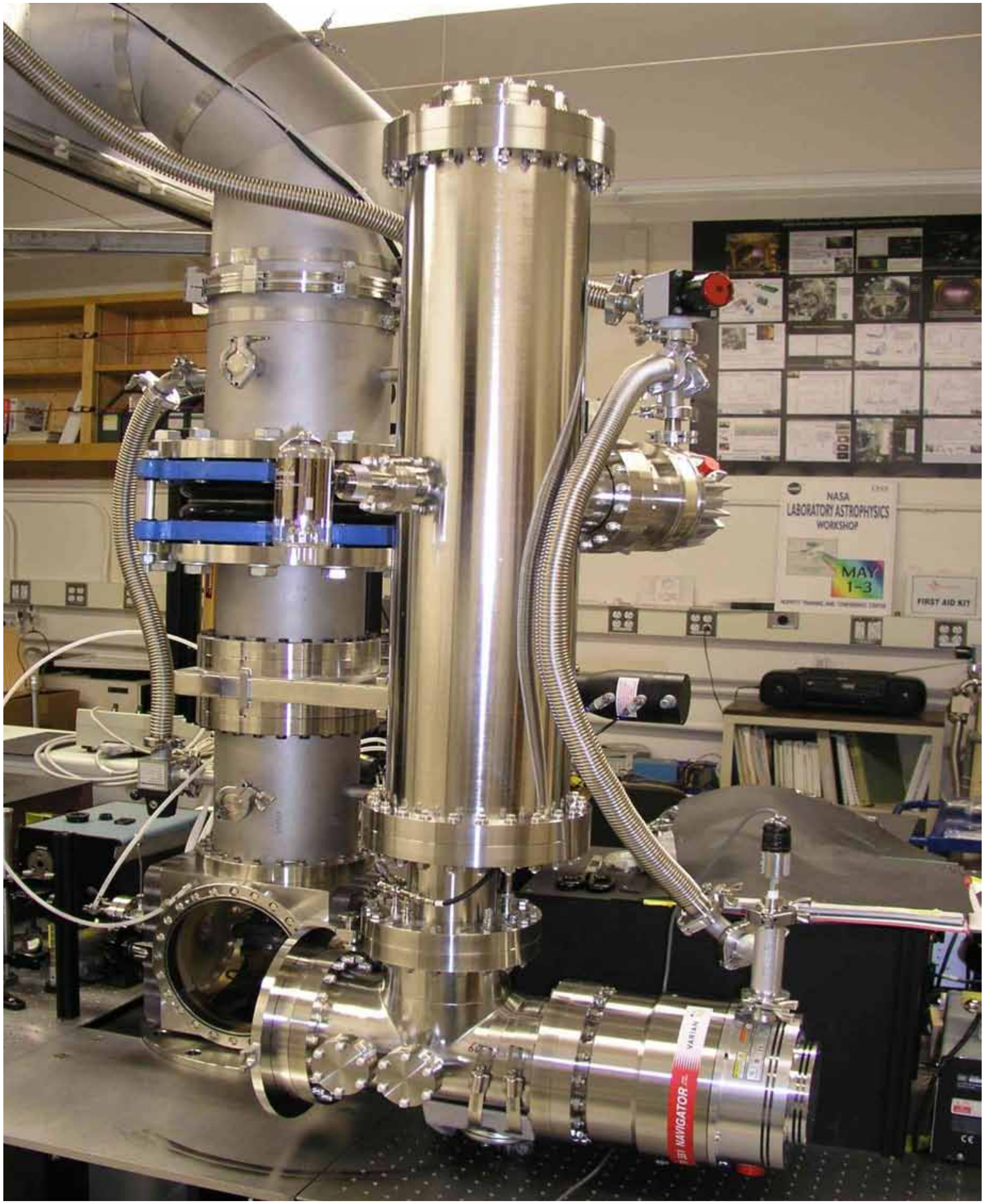


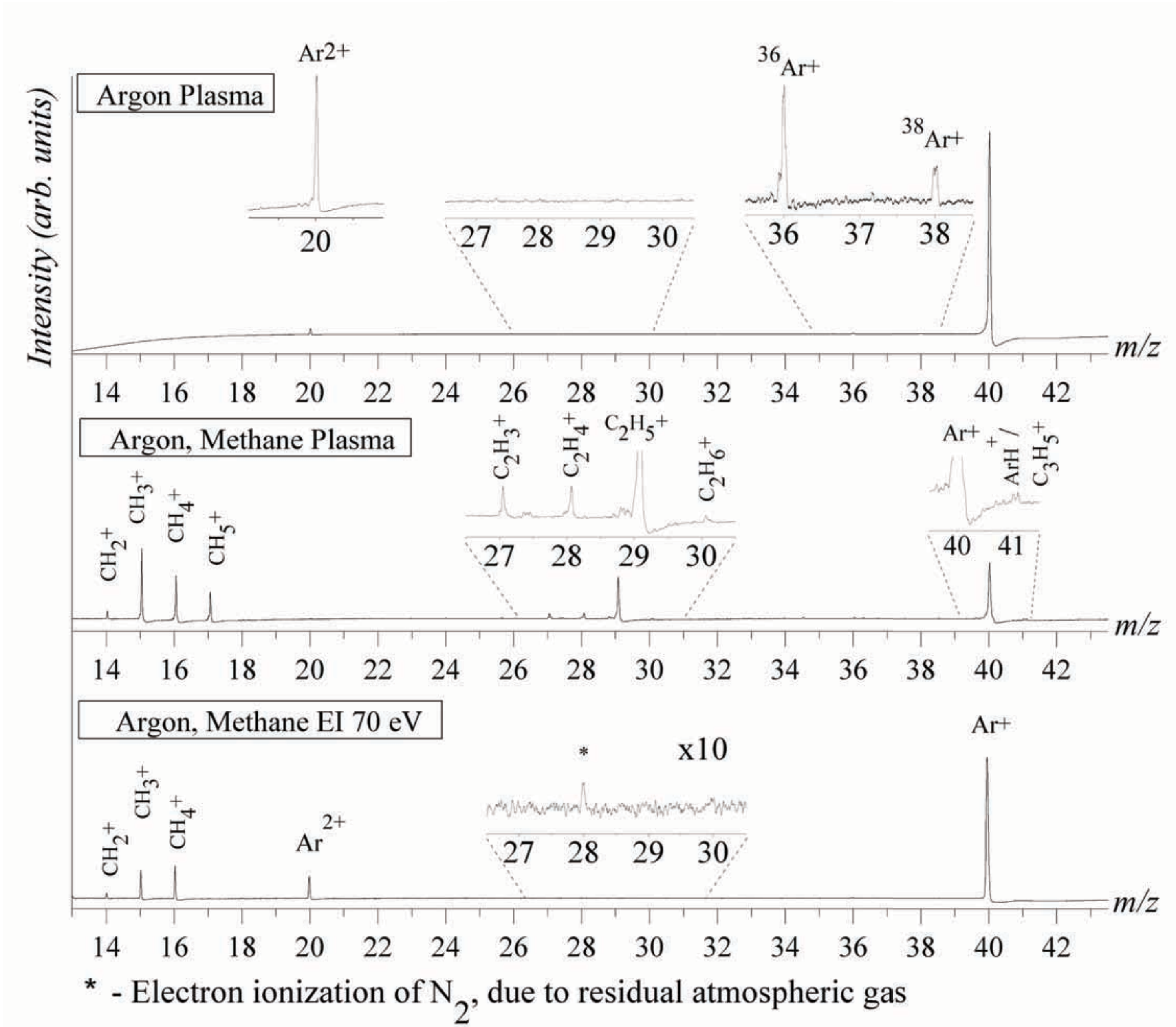


Simulation Chamber






NASA
LABORATORY ASTROPHYSICS
WORKSHOP
MAY
1-3
FIRST AID KIT
VARIAN
NAVIGATOR

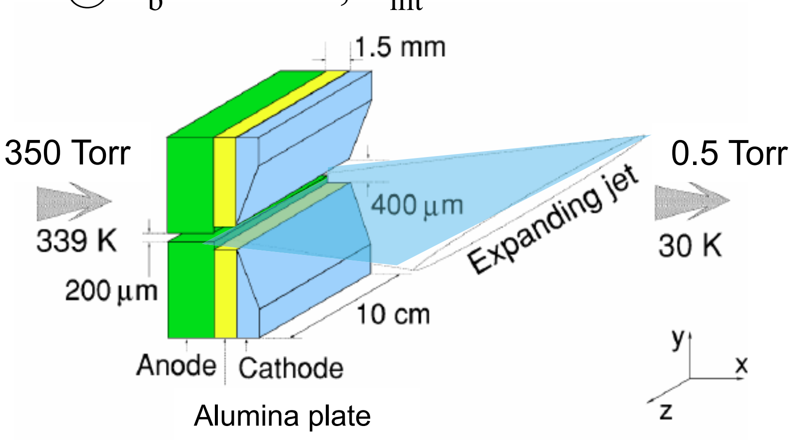


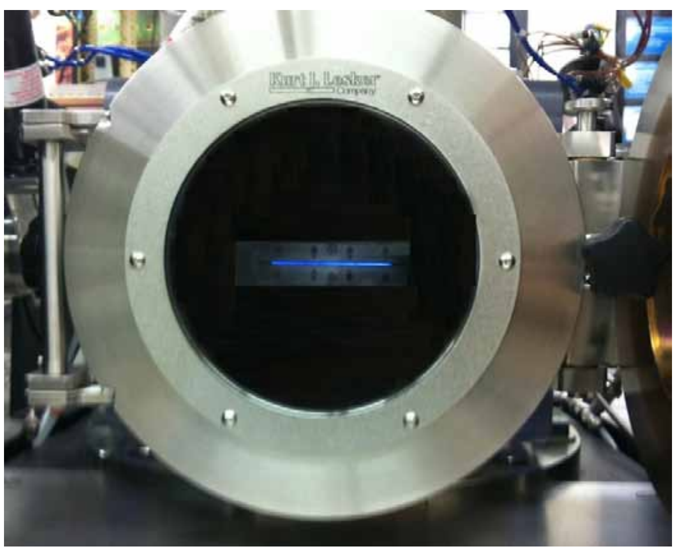
Rickets, Contreras & Salama, IJMS 300 (2011)

Pulsed Nozzle Discharge

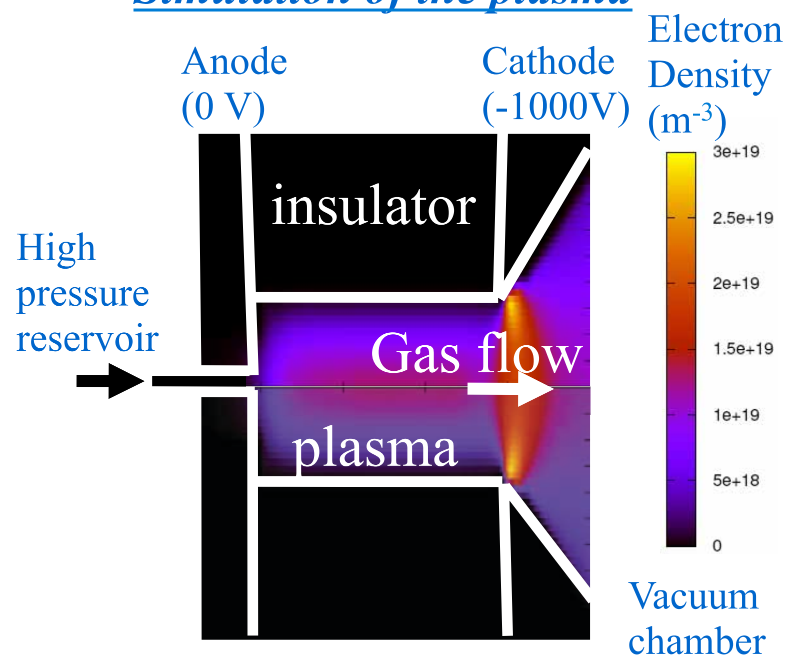
High energy discharge setup

- Plasma characteristics: -500 to -800V
  T_e 1000 – 2000 K, T_{rot} 50 – 200 K
  @ P_b 350 Torr, P_{int} 100 mTorr

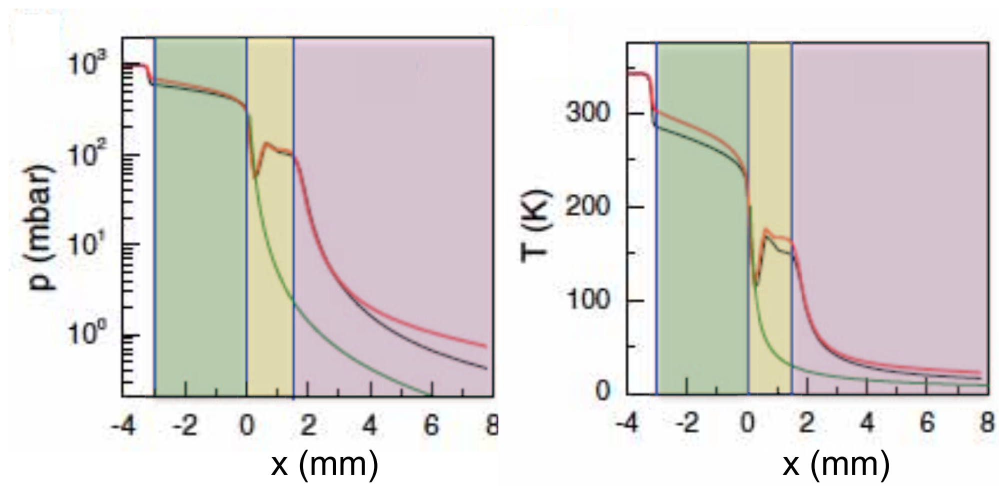




Simulation of the plasma

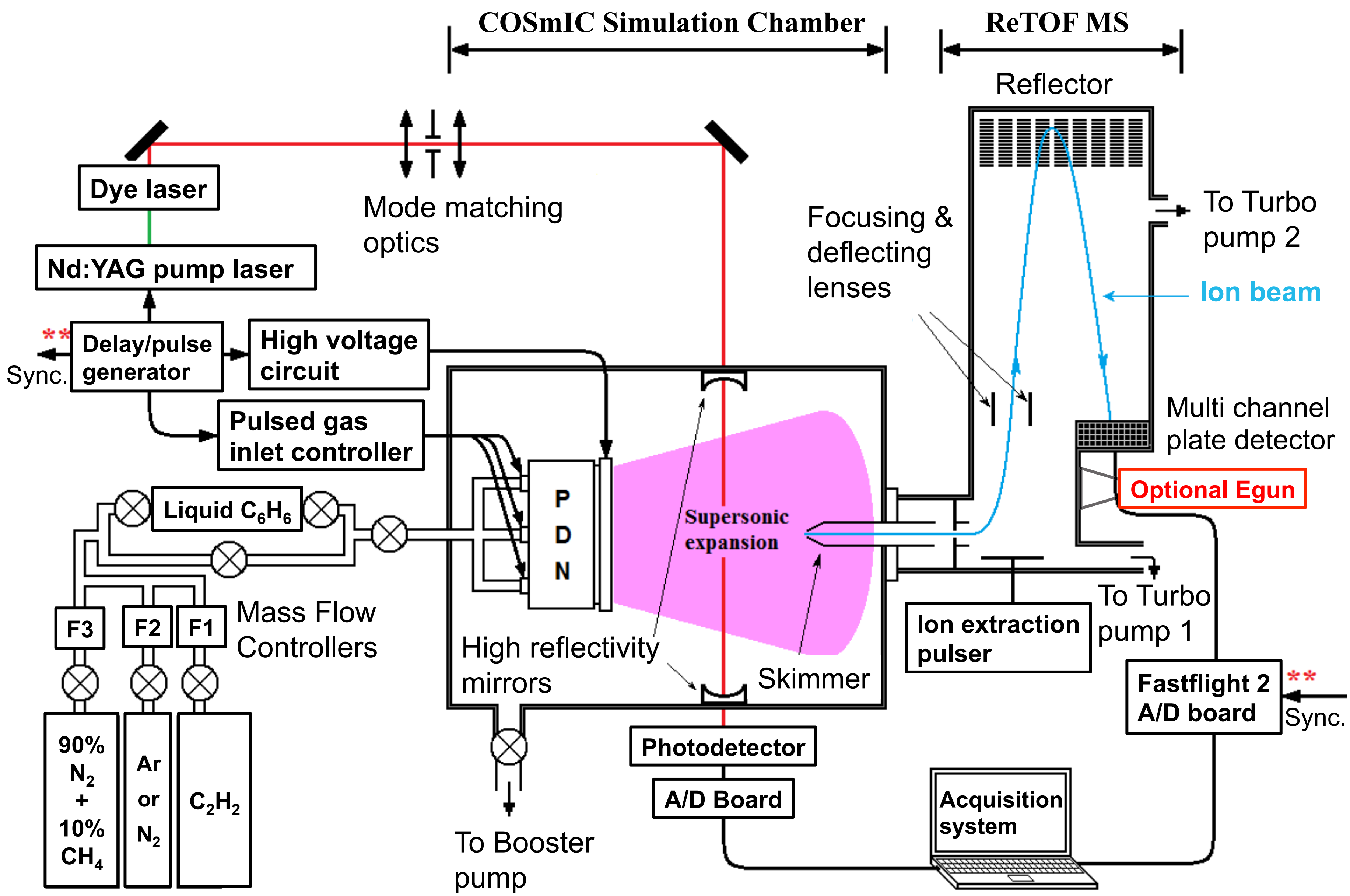


B. Broks et al., Phys. Rev. E, (2005)

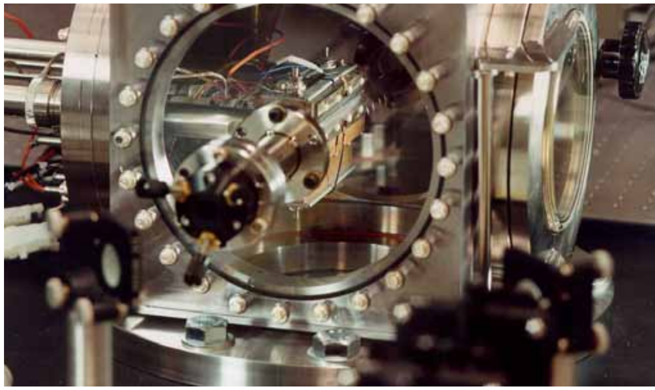


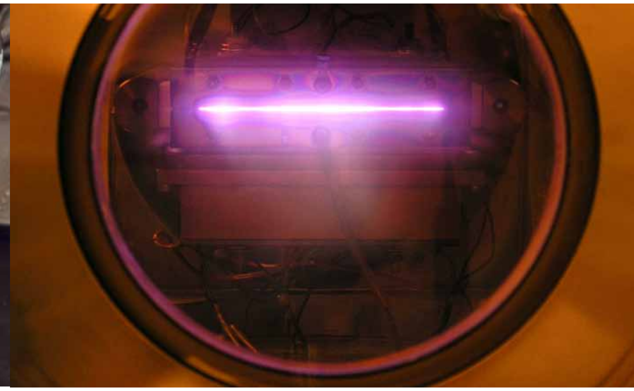
Biennier et al., J. Chem. Phys. (2006)

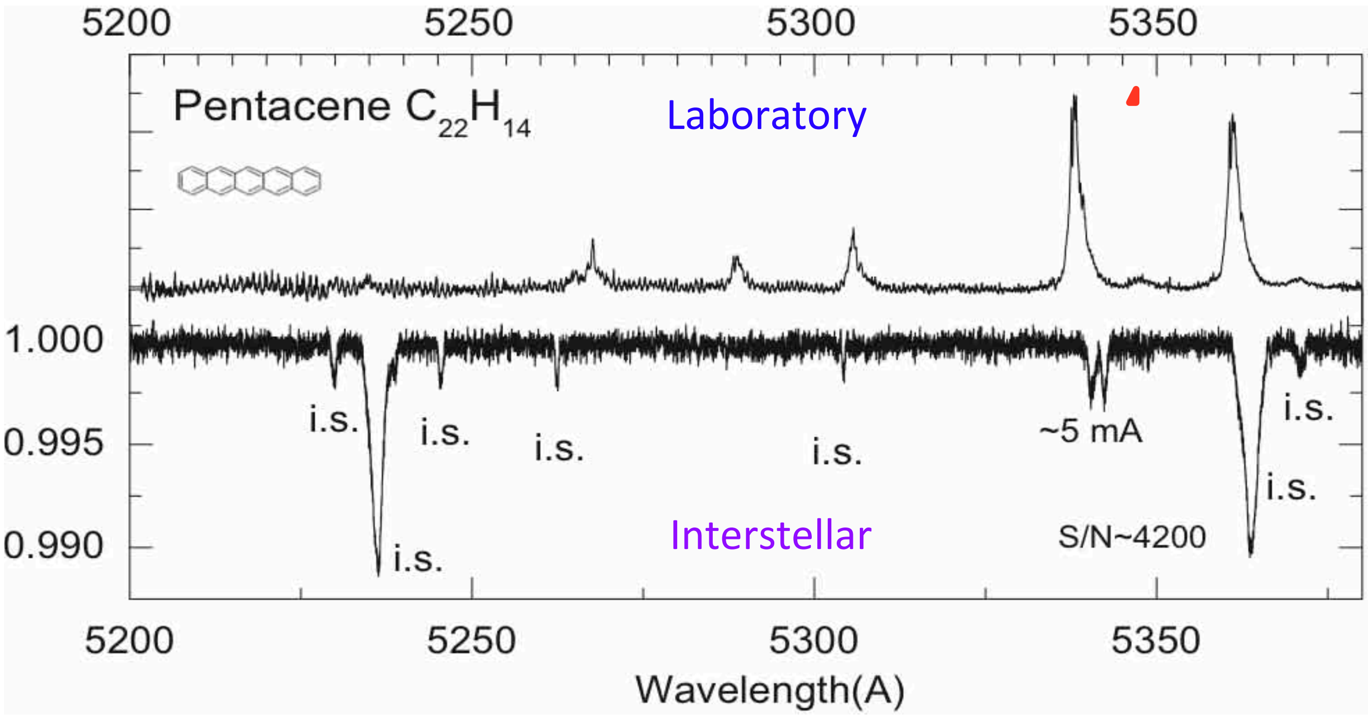
Pulsed Discharge Nozzle (PDN) + Cavity Ring-Down Spectroscopy + ReTOF Mass Spectrometer

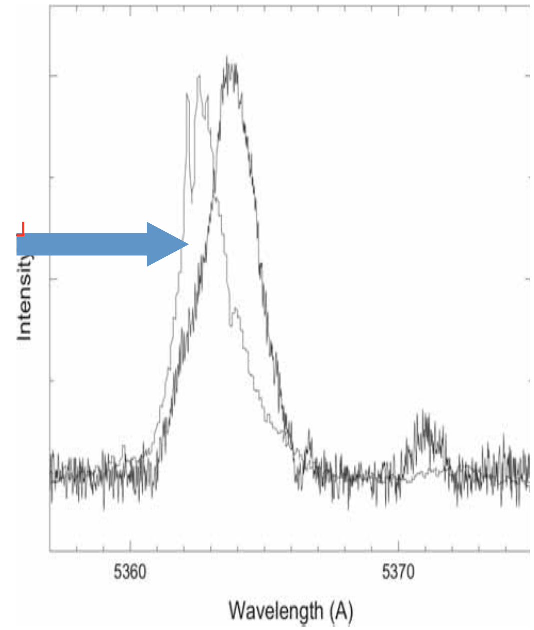


Ricketts, Contreras & Salama, 2011, IJMS





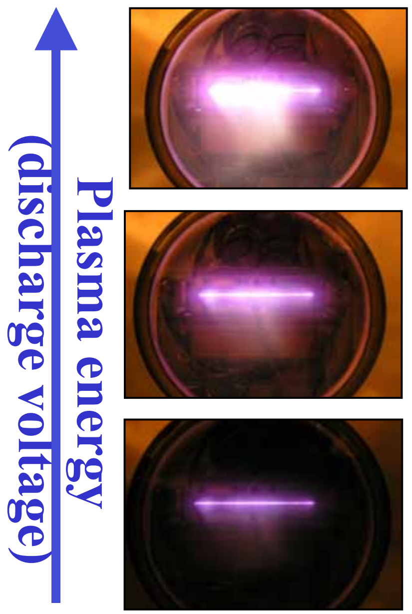

5200
5250
5300
5350
Pentacene $C_{22}H_{14}$
Laboratory
1.000
0.995
0.990
i.s.
i.s.
i.s.
i.s.
i.s.
~5 mA
i.s.
i.s.
Interstellar
S/N~4200
5200
5250
5300
5350
Wavelength(A)

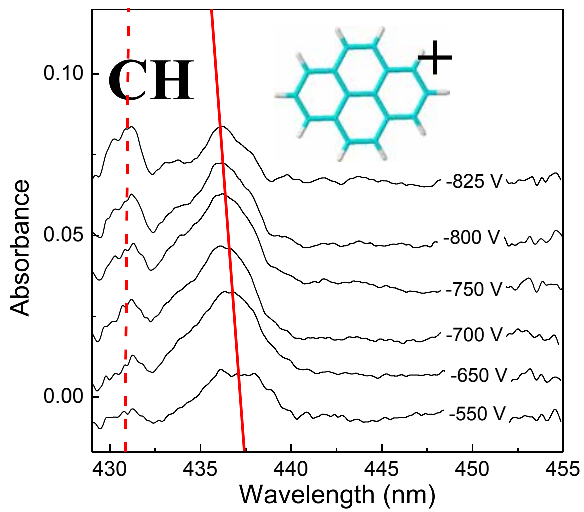

Intensity
5360
5370
Wavelength (A)


Salama - AstroRennes 2014 - PCMI

Cosmic Simulation Chamber

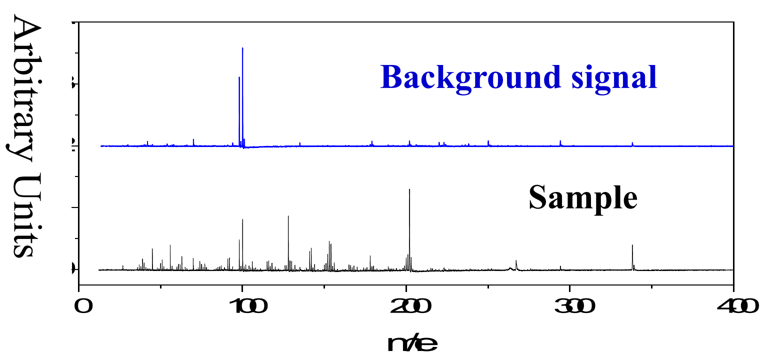
CRDS Spectrum of Pyrene ($C_{16}H_{10}^{+}$) versus Discharge Energy





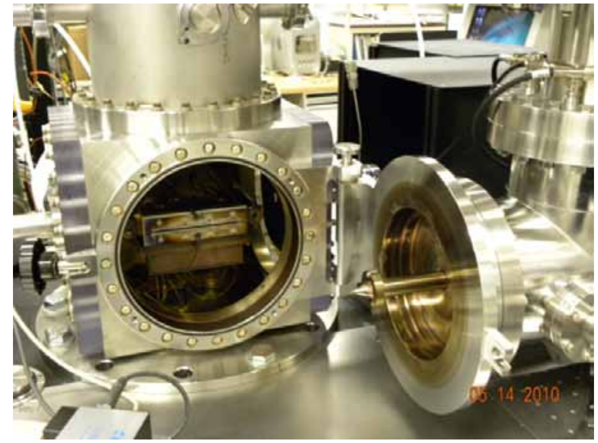
Biennier *et al.* - 2005

μL²MS of soot formed from $C_{12}H_{10}$ (154 amu) precursor

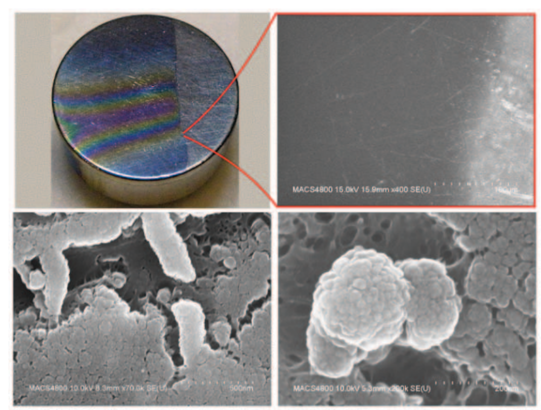


Sabbah, Zare, Stanford, 2006-2010

Observation and collection of soot



Electrodes



ReTOF-MS Results - Summary of Experiments

Precursor category and types

Hydrocarbons

Alkanes
- Methane (CH_4)
- Ethane (C_2H_6)

Alkenes
- Ethylene (C_2H_4)

Alkynes
- Acetylene (C_2H_2)

Aromatics
- Benzene (C_6H_6)
- Toluene ($C_6H_5CH_3$)
- Pyridine (C_5H_5N)

Polycyclic Aromatic Hydrocarbons

Homogenous PAHs
- Naphthalene ($C_{10}H_8$)
- 1-Methylnaphthalene ($C_{10}H_7CH_3$)
- Acenaphthene ($C_{12}H_{10}$)

Heterogeneous PAHs
- Quinoline (C_9H_7N)
- 2,3-Benzofuran (C_8H_6O)
- Thianaphthene (C_8H_6S)

Mixtures of Precursors

Benzene Analogs & Hydrocarbons

Benzene (C_6H_6) &
- Methane (CH_4)
- Ethane (C_2H_6)
- Ethylene (C_2H_4)
- Acetylene (C_2H_2)

Toluene ($C_6H_5CH_3$) &
- Methane (CH_4)
- Ethylene (C_2H_4)
- Acetylene (C_2H_2)

Pyridine
- Methane (CH_4)
- Acetylene (C_2H_2)

PAH & Hydrocarbons

Naphthalene ($C_{10}H_8$) &
- Methane (CH_4)
- Ethane (C_2H_6)
- Ethylene (C_2H_4)
- Acetylene (C_2H_2)

1-Methylnaphthalene ($C_{10}H_7CH_3$)
- Methane (CH_4)
- Ethane (C_2H_6)
- Ethylene (C_2H_4)
- Acetylene (C_2H_2)

Acenaphthene ($C_{12}H_{10}$) &
- Methane (CH_4)
- Ethane (C_2H_6)
- Ethylene (C_2H_4)
- Acetylene (C_2H_2)

Quinoline (C_9H_7N) &
- Acetylene (C_2H_2)

2,3-Benzofuran (C_8H_6O) &
- Acetylene (C_2H_2)

Thianaphthene (C_8H_6S) &
- Acetylene (C_2H_2)

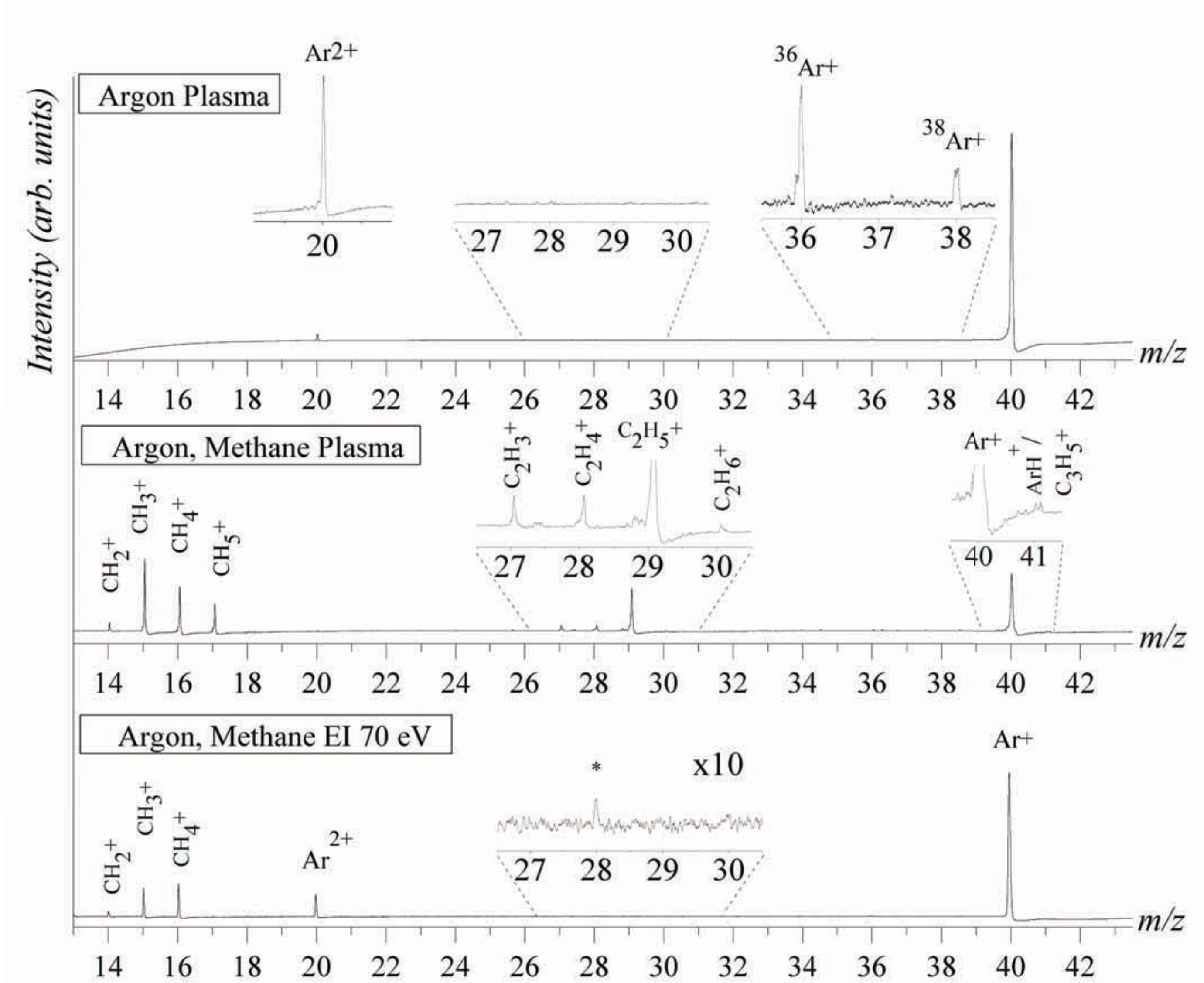
*Contreras and Salama, ApJ Supplement, **2013**,208, 6*

ReTOF-MS Results – Hydrocarbons: Methane

Comparison of Mass Spectra between ionization types

Plasma –
Major products for Methane:
By addition of CH_x

EI – Electron Ionization
No recombination products (expected)



* - Electron ionization of N_2, due to residual atmospheric gas

Contreras and Salama, ApJ Supplement, 2013, 208, 6

ReTOF-MS Results – Hydrocarbons

Argon plasma experiments

Chemical formulas of ions detected:

#C	Methane (CH_4)
0	H
1	C, CH, CH_2, CH_3, CH_4, CH_5
2	C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6
3	C_3H_4, C_3H_5
4	C_4H_6

#C	Ethane (C_2H_6)
0	H
1	CH, CH_2, CH_3
2	C_2, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6
3	C_3H_3, C_3H_4, C_3H_5, C_3H_6, C_3H_7
4	C_4H_7

#C	Ethylene (C_2H_4)
0	---
1	CH_2
2	C_2H, C_2H_2, C_2H_3, C_2H_4
3	C_3H_3, C_3H_4, C_3H_5
4	C_4H_5, C_4H_6, C_4H_7
5	C_5H_7, C_5H_8, C_5H_9

#C	Acetylene (C_2H_2)
0	H
1	C, CH, CH_3
2	C_2, C_2H, C_2H_2, C_2H_3, C_2H_4
3	C_3H_3, C_3H_4, C_3H_5
4	C_4H, C_4H_2, C_4H_3, C_4H_4
5	C_5H_6 \ C_4H_2O
6	C_6H_2, C_6H_3, C_6H_4, C_6H_5

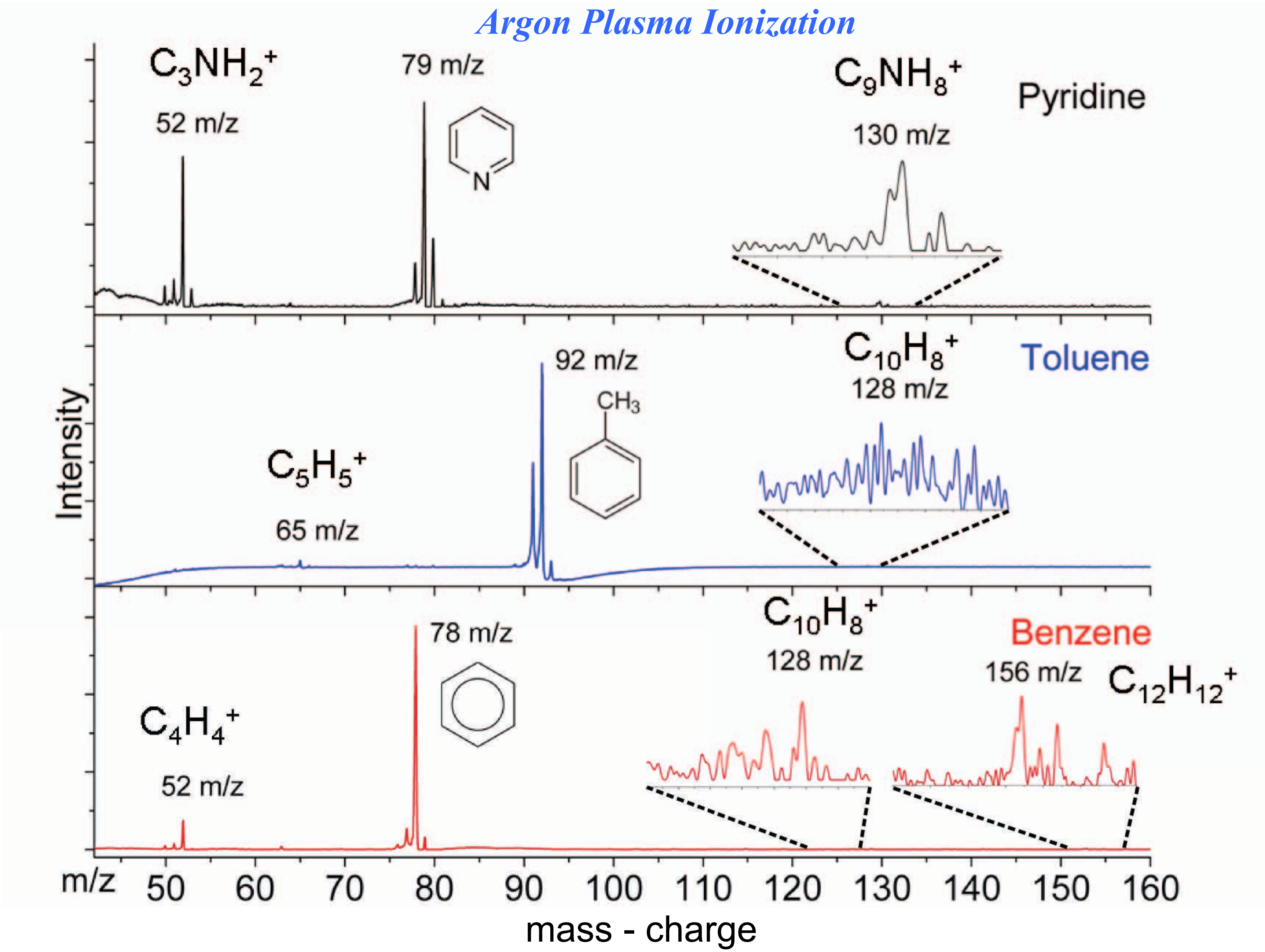
Methane, Ethane, Ethylene
Show gradual increase of the #H as the #C increases

Acetylene
H:C ratio is similar as #C increases

Acetylene
Mixed with Acetone (stability)
Peaks in blue are mainly from Acetone

Acetylene recombination
Growth as C_2H_x

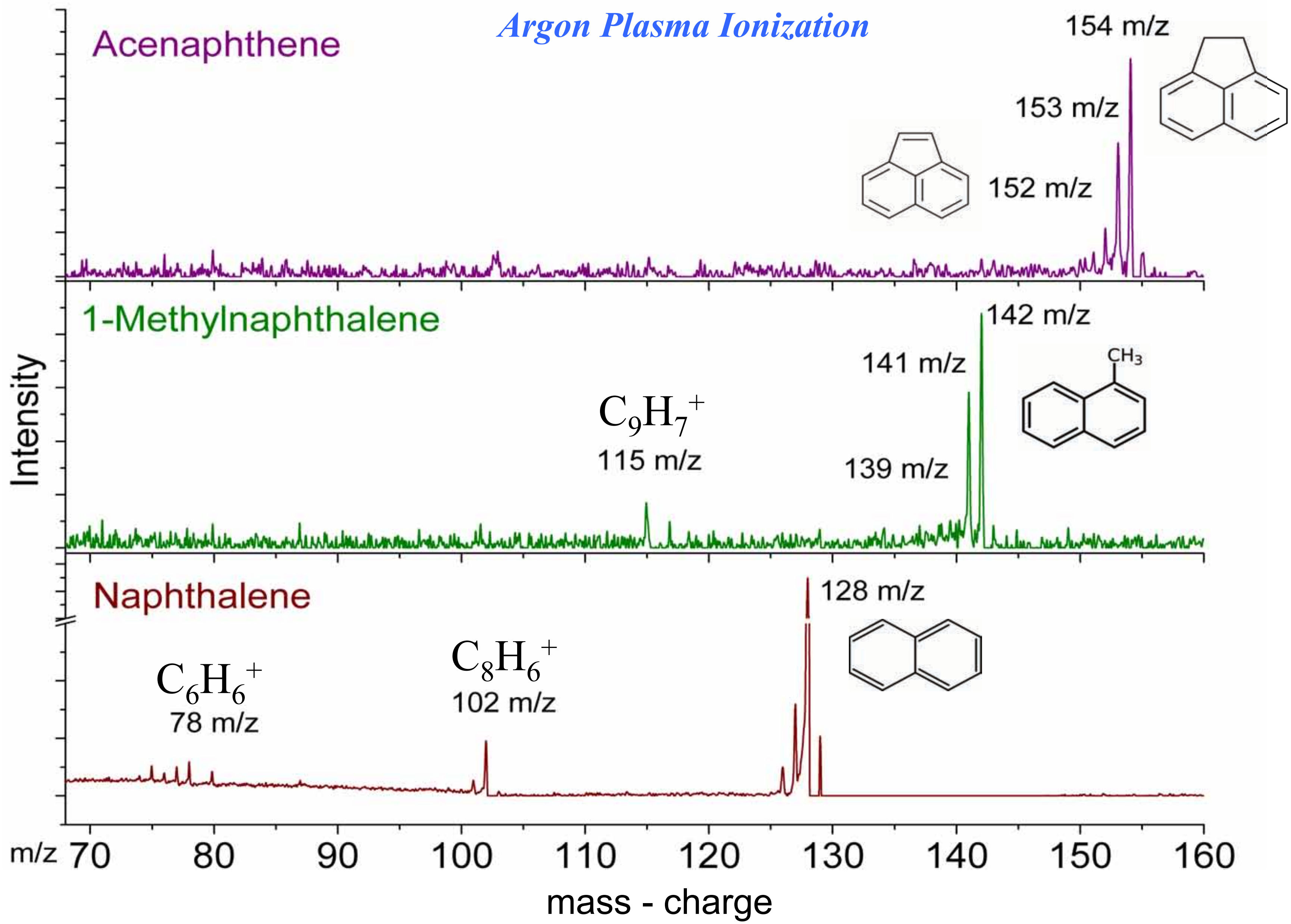
ReTOF-MS Results – Single Ring Aromatics



Contreras and Salama, ApJ Supplement, 2013, 208, 6

ReTOF-MS Results – Homogeneous PAHs

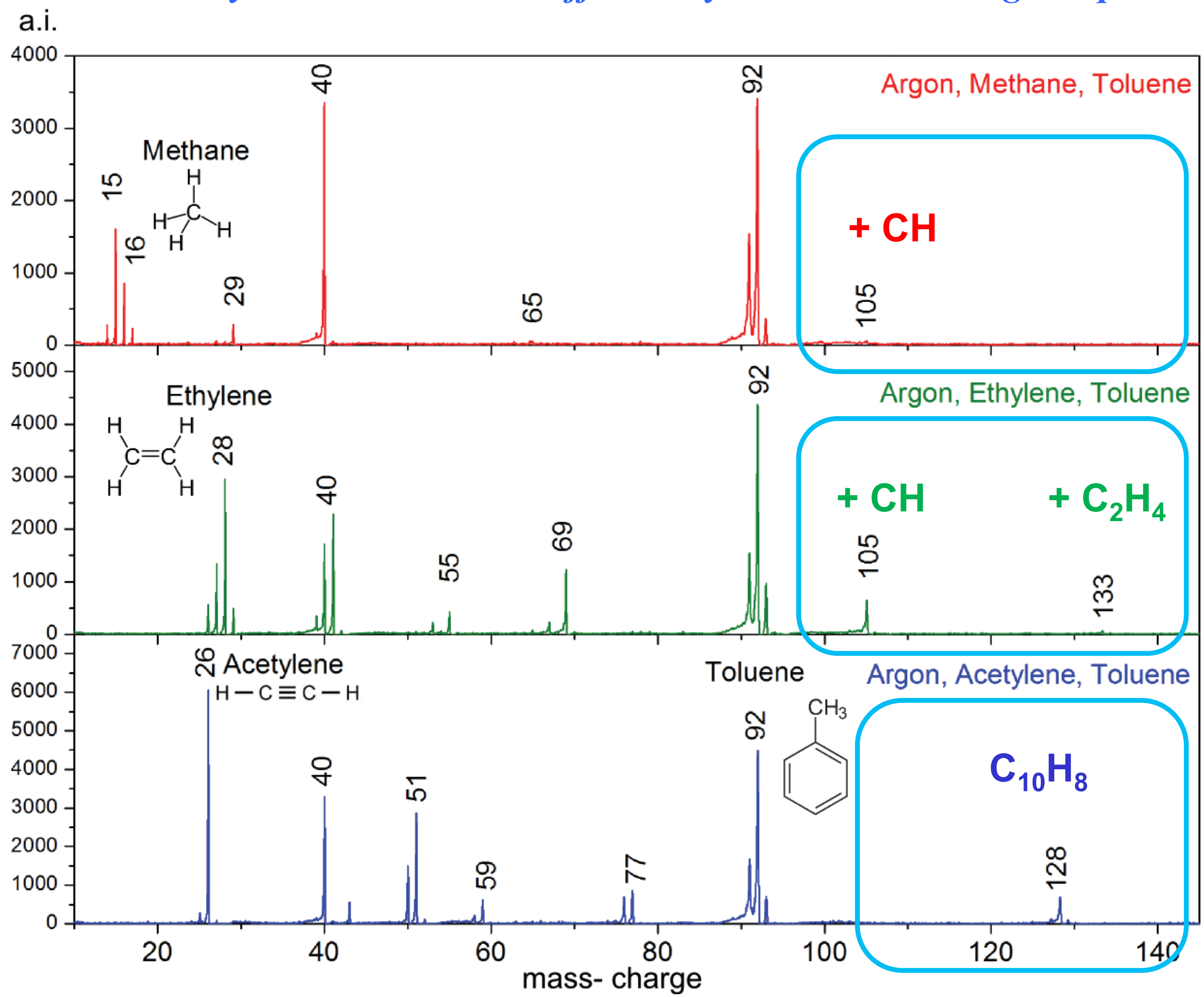
Argon Plasma Ionization



Contreras and Salama, ApJ Supplement, 2013, 208, 6

ReTOF-MS Results – Mixtures: Toluene/Hydrocarbons

Distinct chemistry occurs with each different hydrocarbon starting compound



Contreras and Salama, ApJ Supplement, 2013, 208, 6

ReTOF-MS Summary

Hydrocarbons

- Methane, Ethane, Ethylene show sequential CH_x growth
- Acetylene major growth involves C_2 groups
- Acetylene experiments show growth up to C_6H_5 ions

Single-ring aromatics

- Benzene, toluene, pyridine all show recombination product ions
- Benzene forms ions $C_{10}H_8^+$ (128m/z) and $C_{12}H_{12}^+$ (156 m/z)
- Toluene also forms $C_{10}H_8^+$ (128 m/z)
- Pyridine has an analogous ion at 130 m/z, $C_9H_8N^+$

PAHs

- Acenaphthene shows 2 H losses
- 1-Methylnaphthalene shows further fragmentation and ring cleavage
- Naphthalene fragment peaks are comparable to benzene, toluene, acetylene

Mixtures

- Product ions seems dependent on the type of hydrocarbon precursor used.

Contreras and Salama, ApJ Supplement, 2013, 208, 6

High Resolution Microscopy on Soot Material

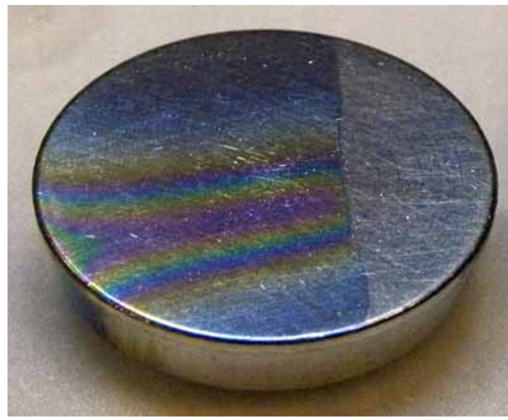
- Further characterization of soot nanoparticles and micrograins from the plasma experiments was obtain by depositing argon hydrocarbon plasma products on solid aluminum and copper mesh grid substrates

- Imaging of the grains was obtained with SEM (Hitachi S4800),
  x80k – 200k magnification

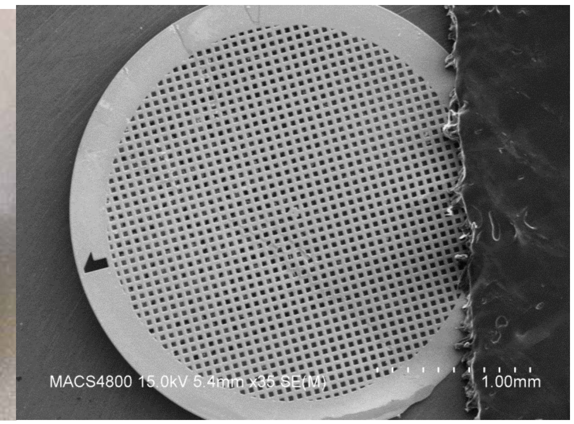
- Deposition studies were obtained from the following precursors:
  Ar-Methane (CH_4)
  Ar-Acetylene (C_2H_2)
  Ar-Methane-Acetylene

Substrates used

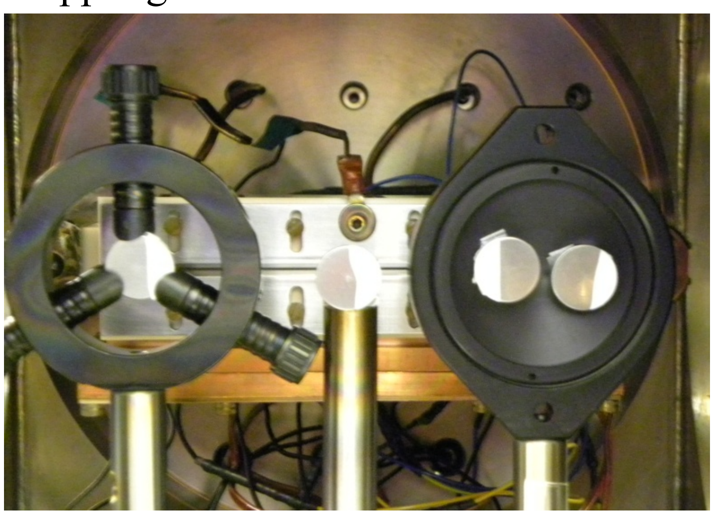
- Aluminum SEM disc
- Aluminum foil on disc
- TEM copper grid w/ C web

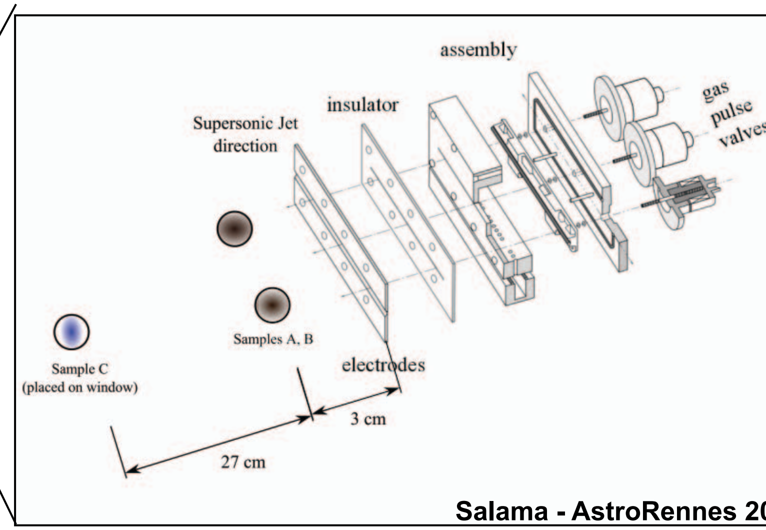


SEM disc



TEM copper grid

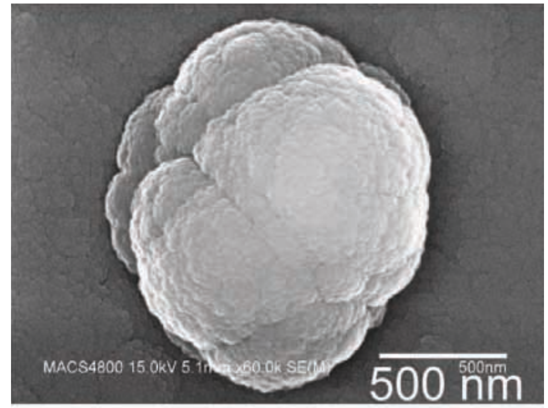




SEM Soot Summary

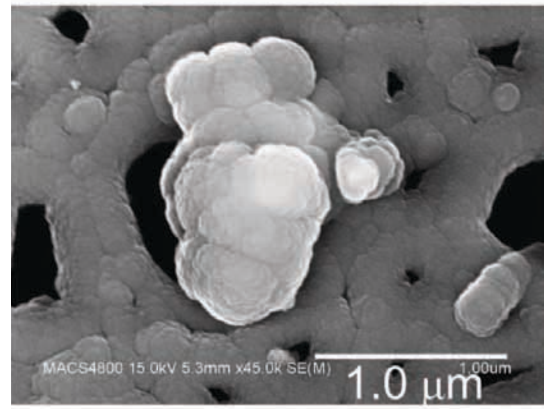
Grains

- Size: 20 – 400 nm, a few larger (1 μm diameter)
- Most are spheroid shape
- Cauliflower like pattern
- Many exhibit depression/void patterns on surrounding surface



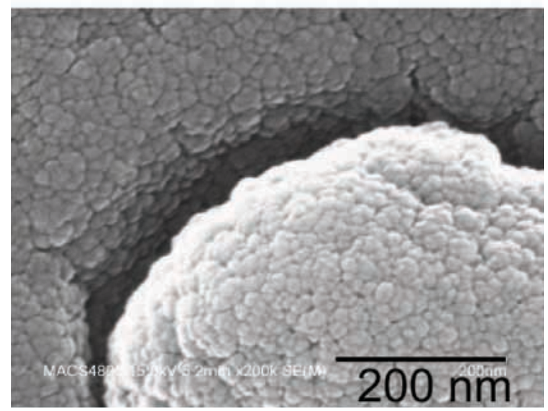
Agglomerates

- Size: 200 – 2.0 μm
- Cauliflower like pattern
- Due to nanoparticle accumulation and/or over-concentration of molecules



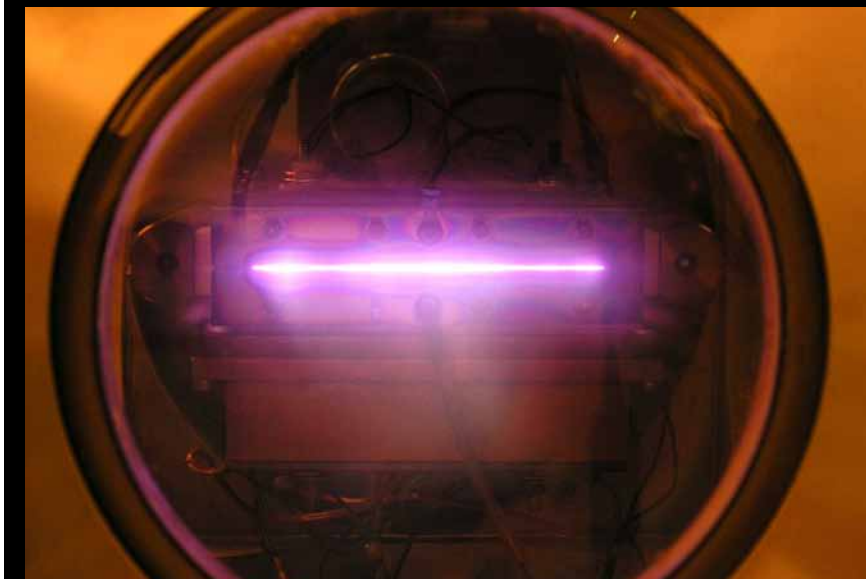
Deposited Layers

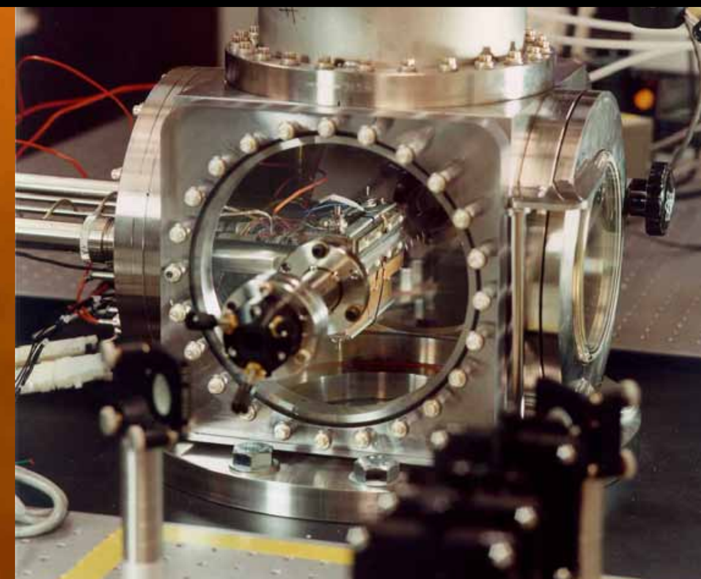
- Cauliflower like pattern
- Resolvable diameters ~ 5 – 50 nm
- Graininess factor varies with precursor?
- Multi-layered deposition, similar to amorphous carbon structure?

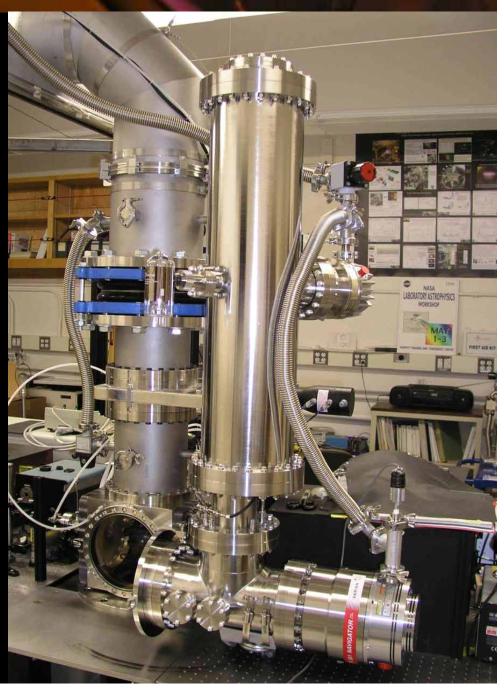


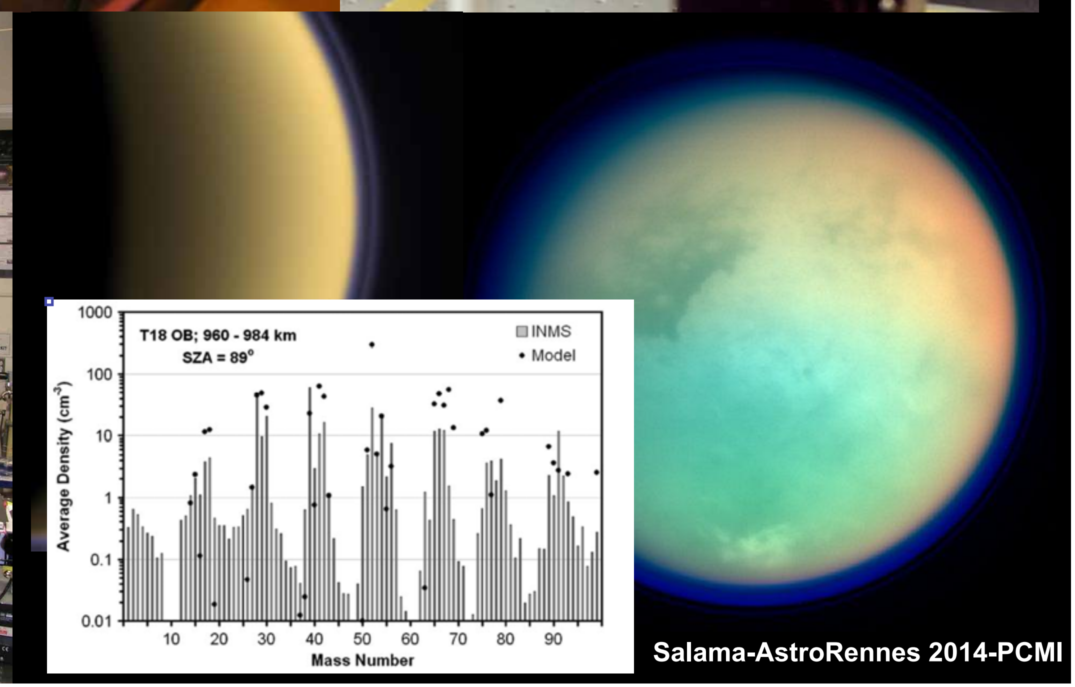
Formation of Carbon Aerosols on Titan

Ion Neutral Mass Spectrometer (INMS) - Cassini.









Ames Research Center

Salama-AstroRennes 2014-PCMI

Motivation: Titan's atmospheric chemistry

Major components: N_2 **(94-98%)** *(UV, e-)* → **Complex organic chemistry** → **aerosols**

CH_4 **(1.8-6%)**

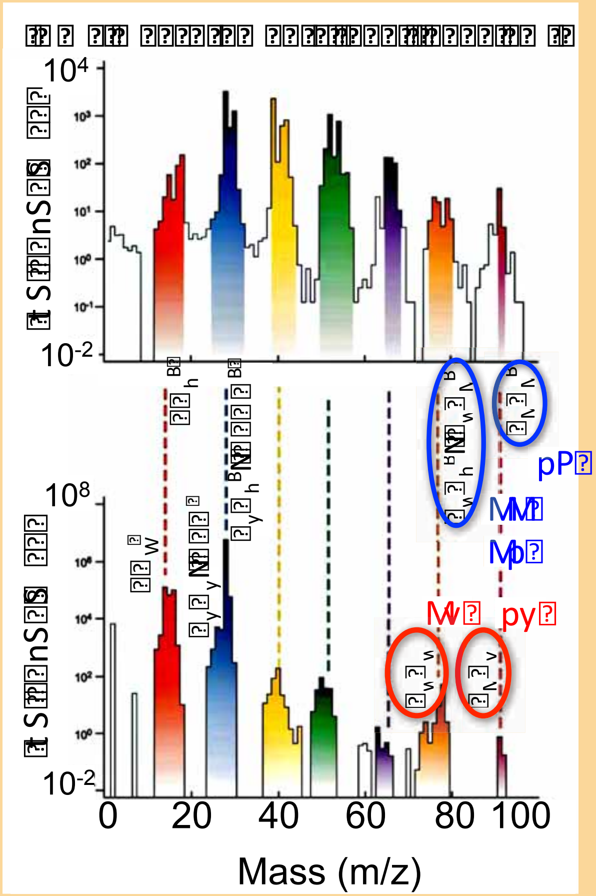
Atmospheric temperatures: 70 K < T < 180 K

Detection of benzene and toluene (precursors of Polycyclic Aromatic Hydrocarbons (PAH)) **and heavy ions by Cassini/Huygens in Titan's upper atmosphere.** *(Waite et al. 2007, Vuitton et al. 2008)*

+ Results from numerical models *(Ricca et al. 2001, Wilson & Atreya 2003, Lebonnois 2005, Vuitton et al. 2007, Lavvas et al. 2011)*

+ Results from experimental simulation *(Khare et al 2002, Imanaka et al. 2004, Trainer et al. 2004, Gautier et al. 2011)*

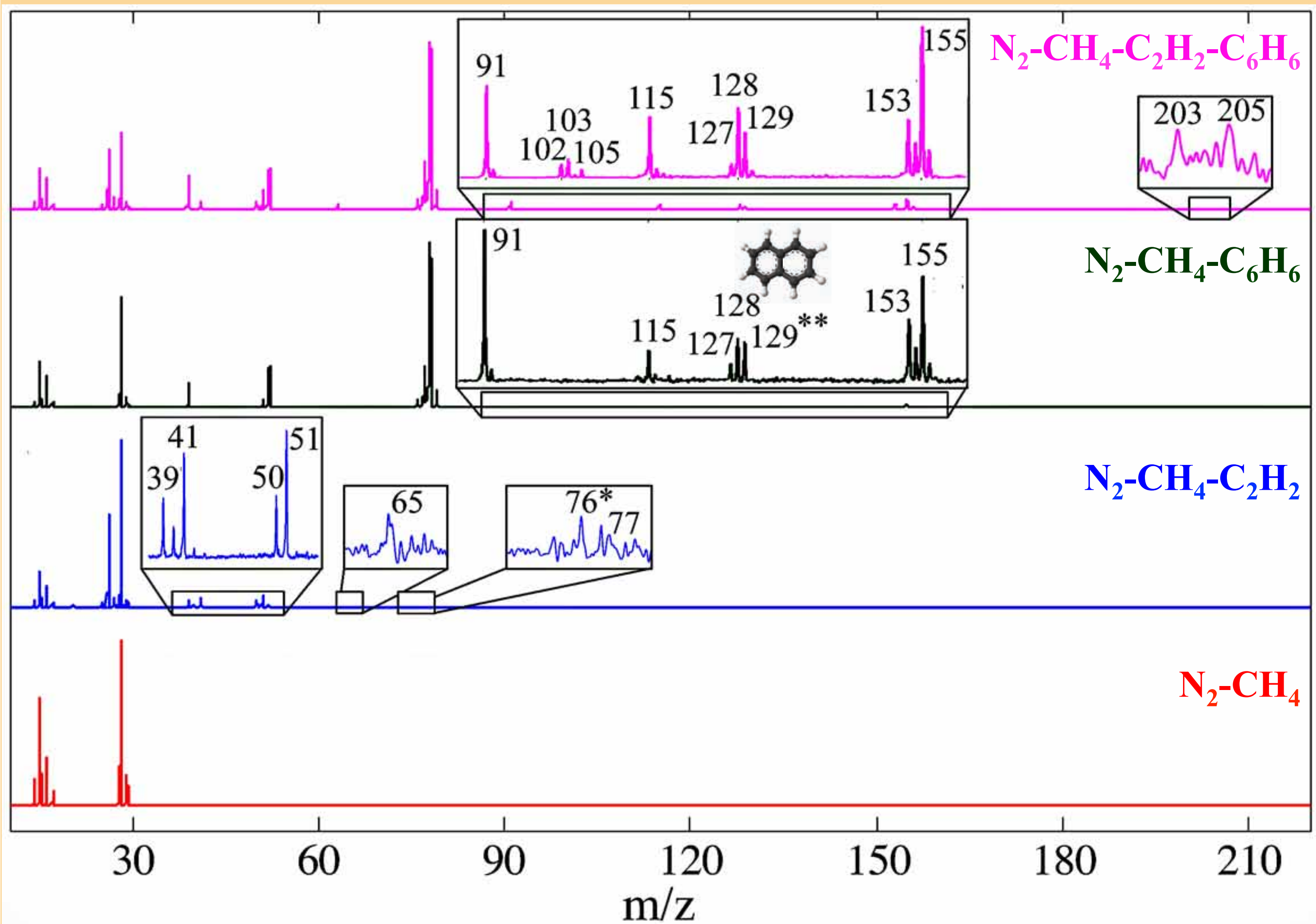
→ **suggest that PAHs and PANHs might play a role in the formation of aerosols.**



Sciamma, Ricketts & Salama, Icarus 2014

GAS PHASE: ReTOF-MS analysis

Probing the first and intermediary steps of Titan's chemistry:



→ up to **205** m/z

+ new peaks at 102-105 m/z

→ up to **156** m/z

(91 = ion associated with formation of toluene?
*** 129 = protonated naphthalene?)*

→ up to **77** m/z

(77 = ion associated with formation of benzene?
** 76 = cyclic $C_6H_4^+$?)*

→ up to **42** m/z

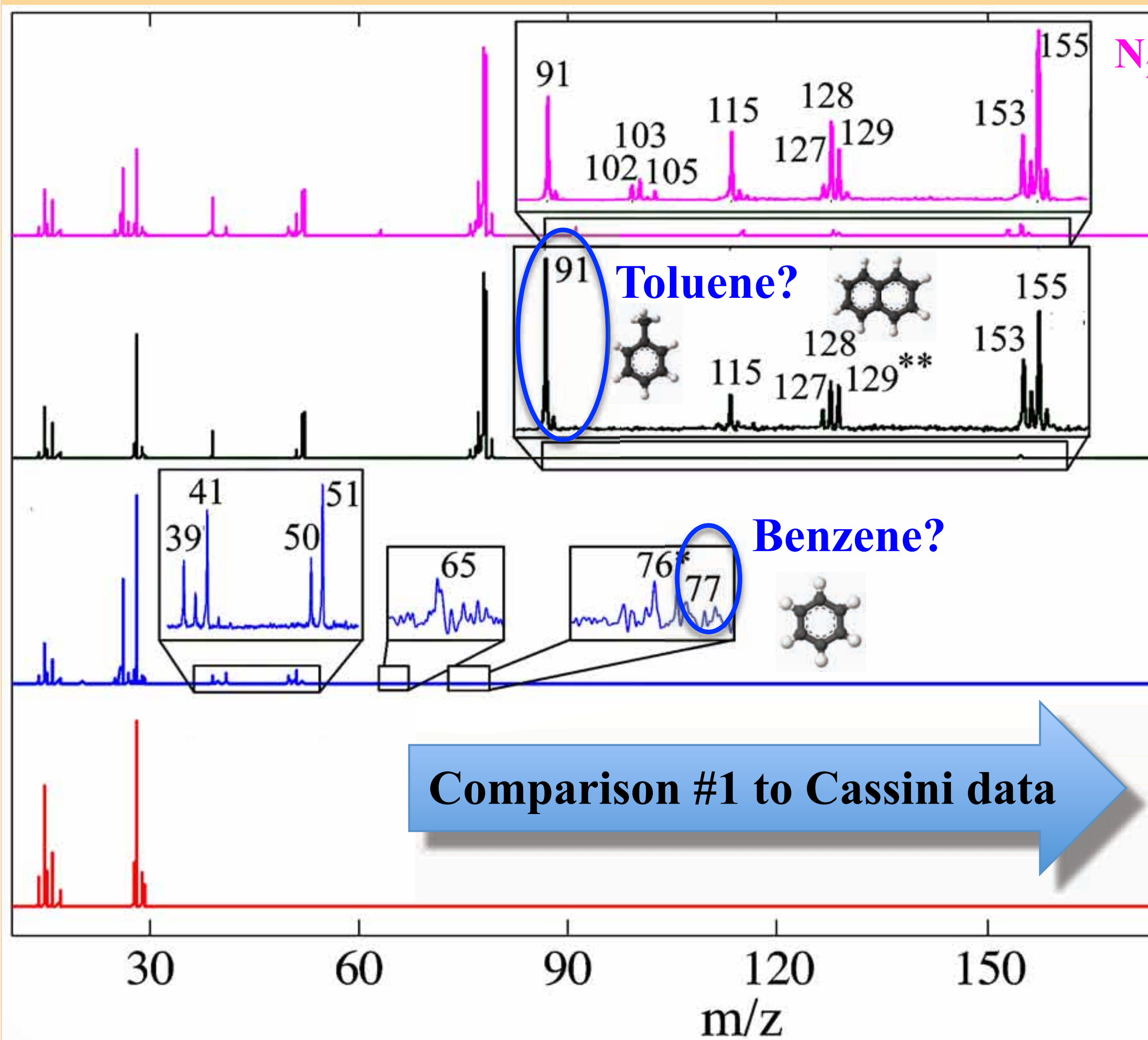
Due to short residence time in pulsed plasma

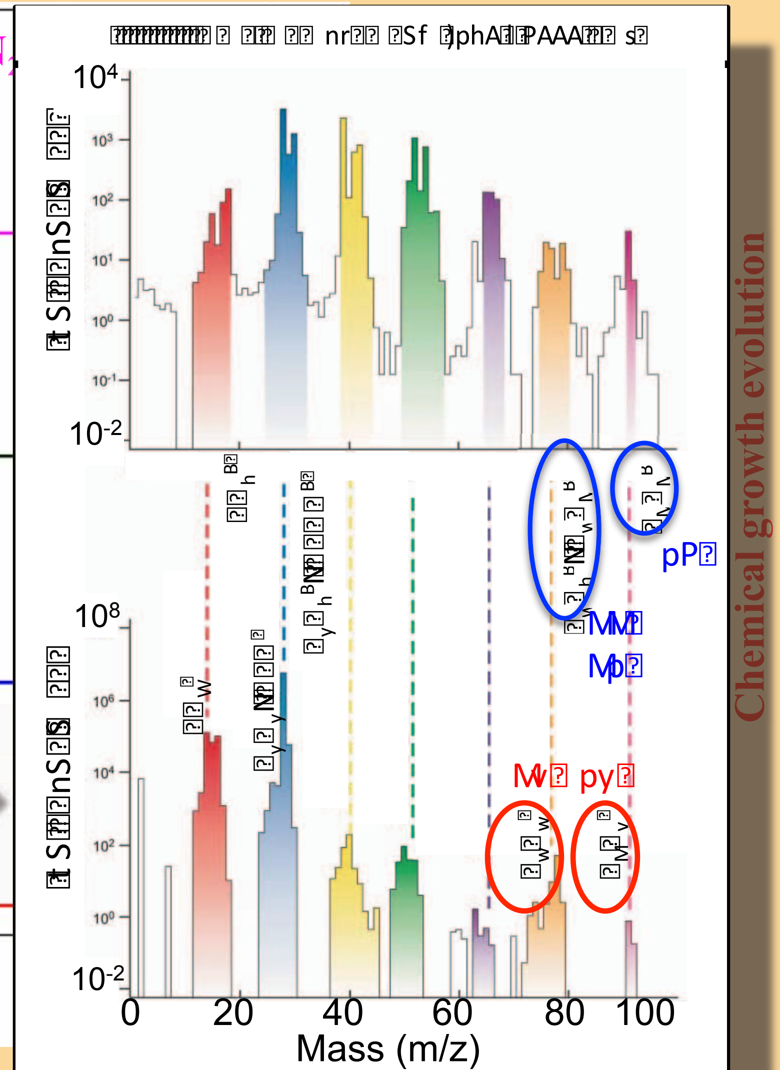
Chemical growth evolution

Sciamma, Ricketts & Salama, Icarus 2014

GAS PHASE: ReTOF-MS analysis

Probing the first and intermediary steps of Titan’s chemistry:





Sciamma, Ricketts & Salama, Icarus 2014

(Waite et al., 2007)

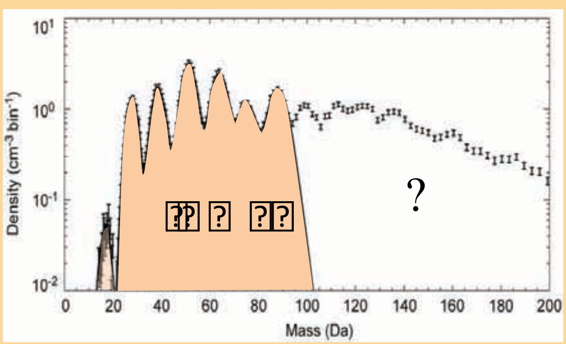
GAS PHASE: ReTOF-MS analysis

Comparison to CAPS – IBS: best match

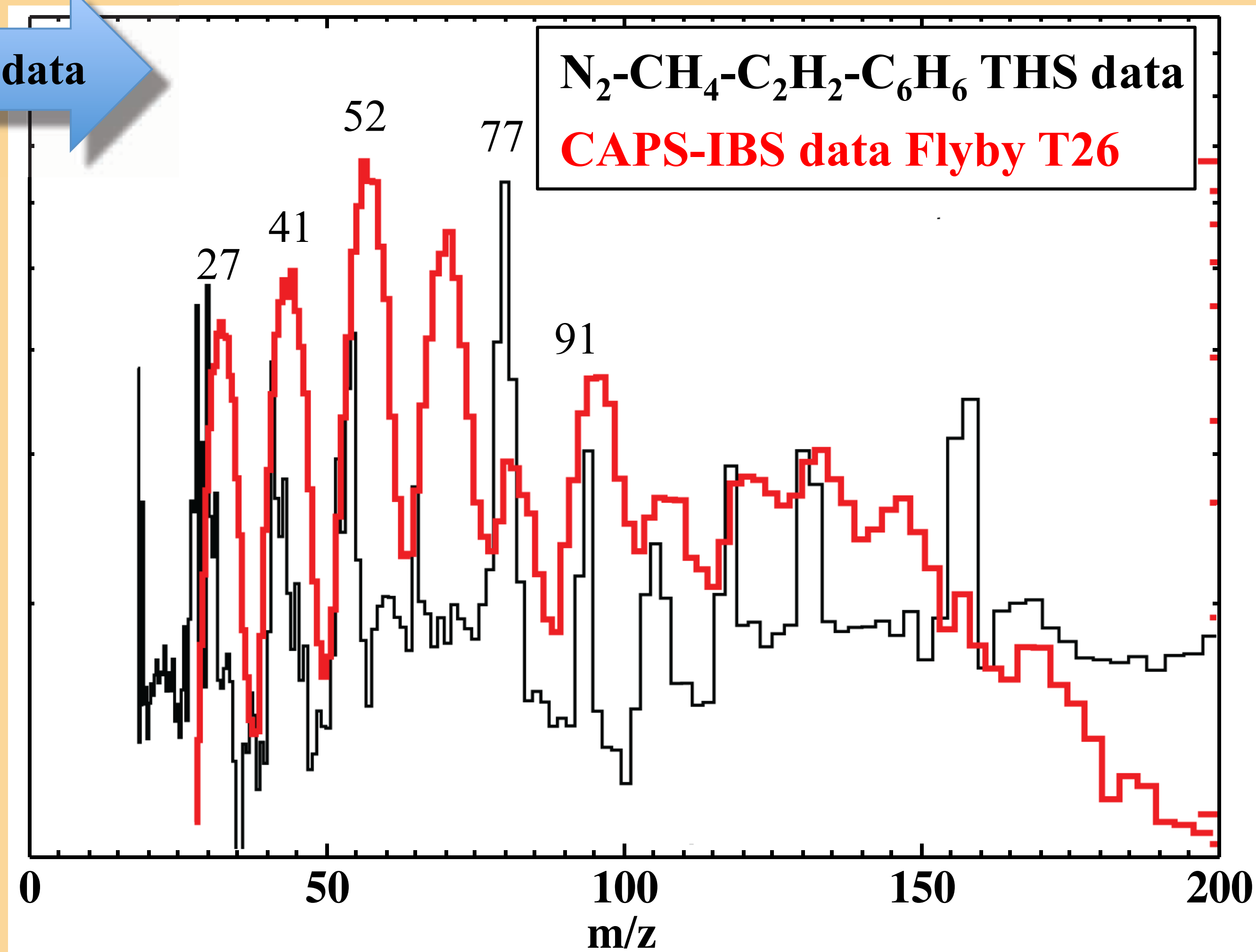
Comparison #2 to Cassini data

Peaks observed in THS experiments match regions of positive ion spectrum in CAPS-IBS:

- **below 100 m/z** (also in agreement with INMS)



(CAPS-IBS data - Crary et al., 2009)



Sciamma, Ricketts & Salama, Icarus 2014

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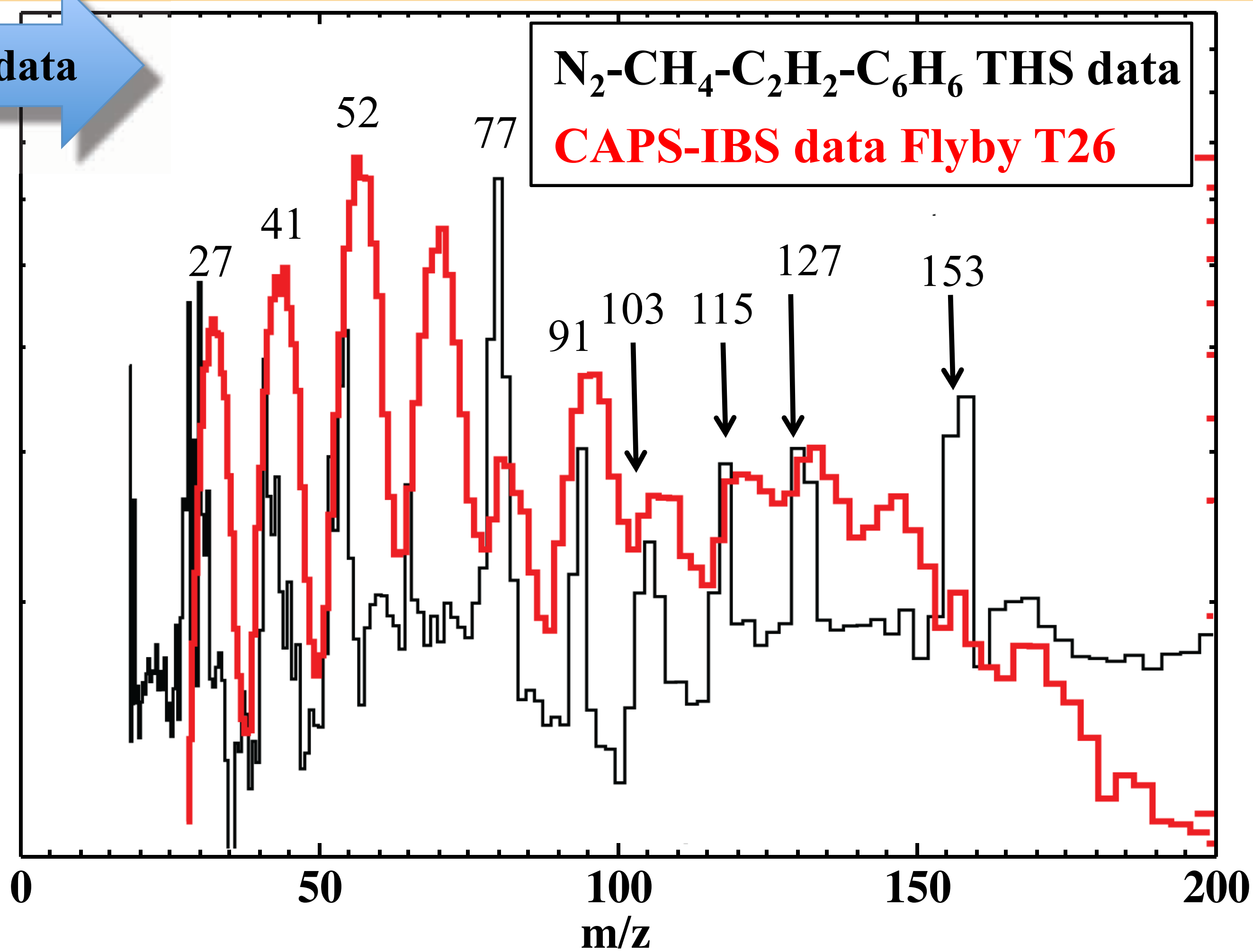
  → most probably due to aromatic compounds



Sciamma, Ricketts & Salama, Icarus 2014

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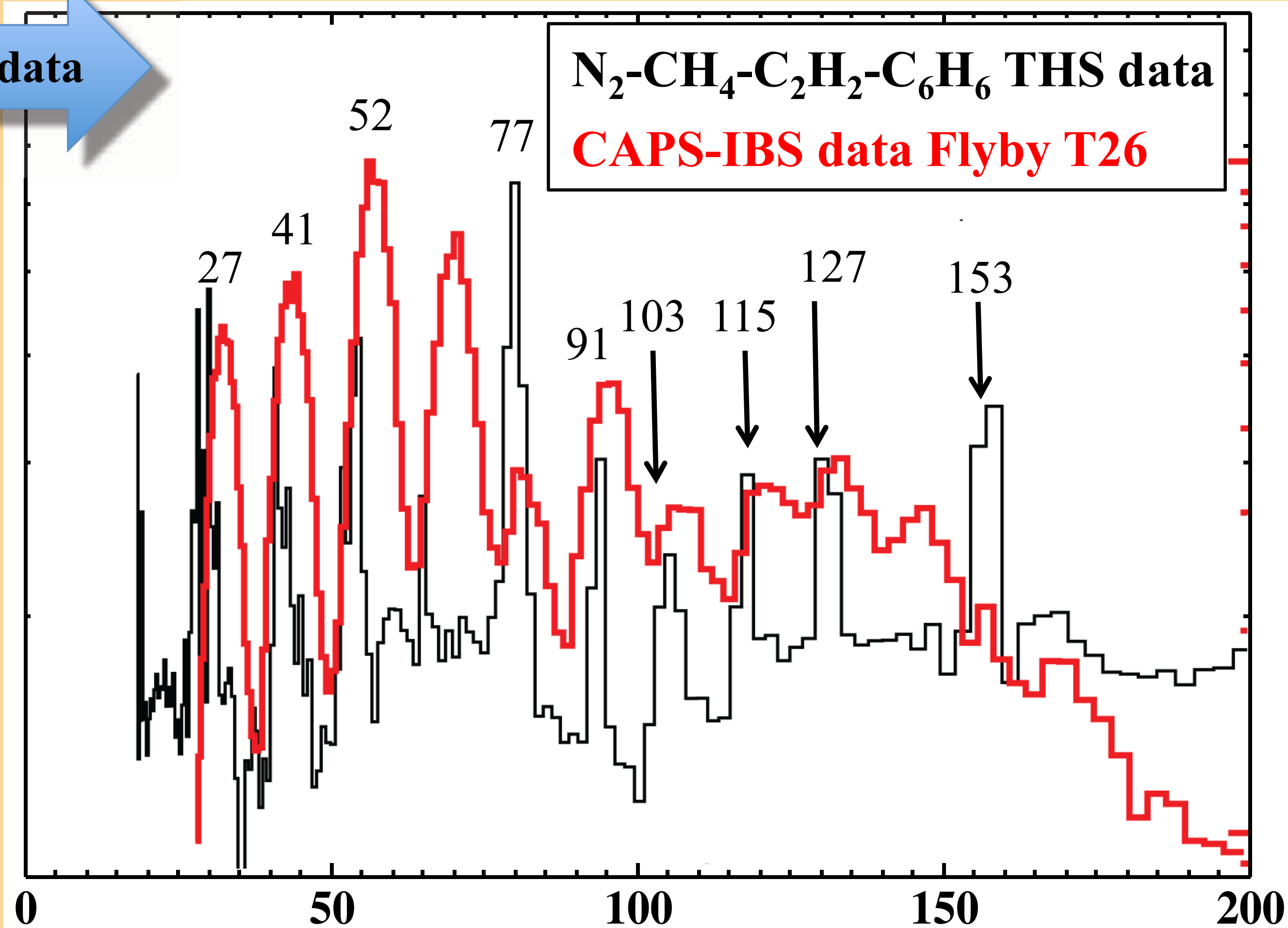


(CAPS-IBS data - Crary et al., 2009)

NEXT:

- **Missing regions: due to aliphatic compounds?**

Sciamma, Ricketts & Salama, Icarus 2014

CONCLUSION

Probing different steps of the Titan chemistry at low temperature

The THS experiment can be used to **monitor** **different time and chemical windows** in the chain of chemical reactions in Titan's atmospheric chemistry.

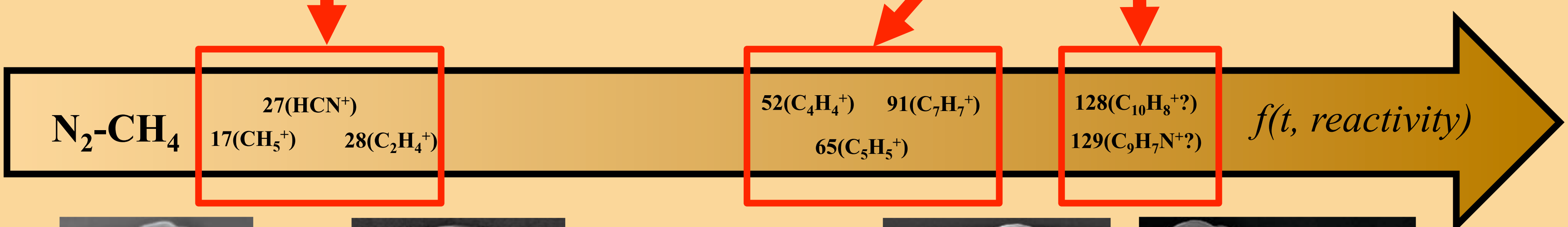
First steps

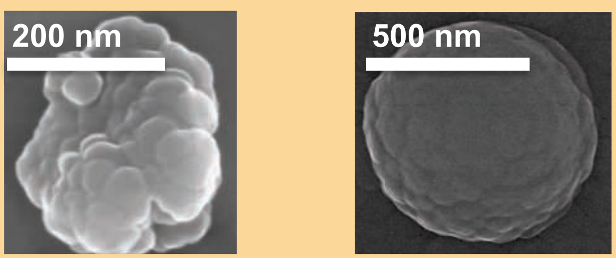
Short plasma + N_2 - CH_4 mixture:

⇒ **Probing the initial products of the N_2 - CH_4 chemistry**

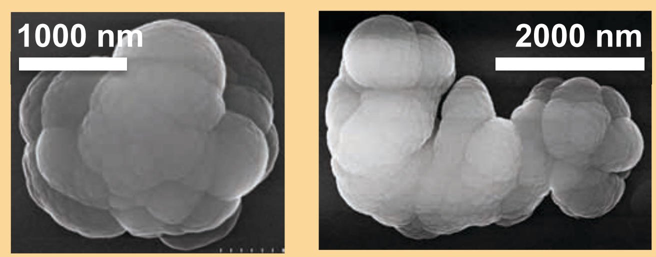
Intermediary steps

⇒ **probing next steps of chemistry and specific chemical pathways**





100 - 500 nm grains



1000 - 5000 nm grains

Sciamma, Ricketts & Salama, Icarus 2014

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