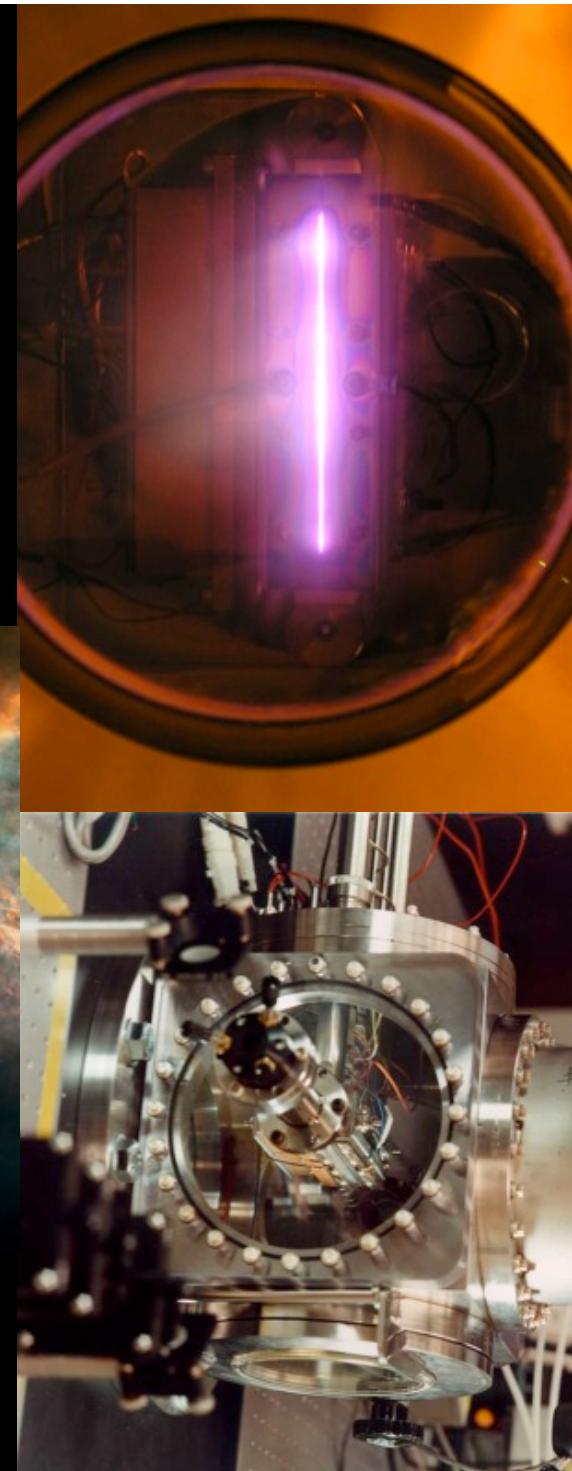
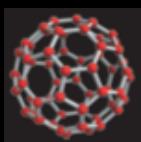
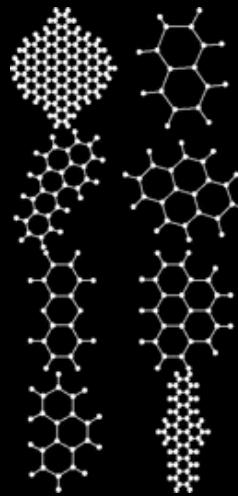


# Organic Carbon in the Molecular Universe Laboratory Astrophysics Studies of Cosmic Dust Analogs

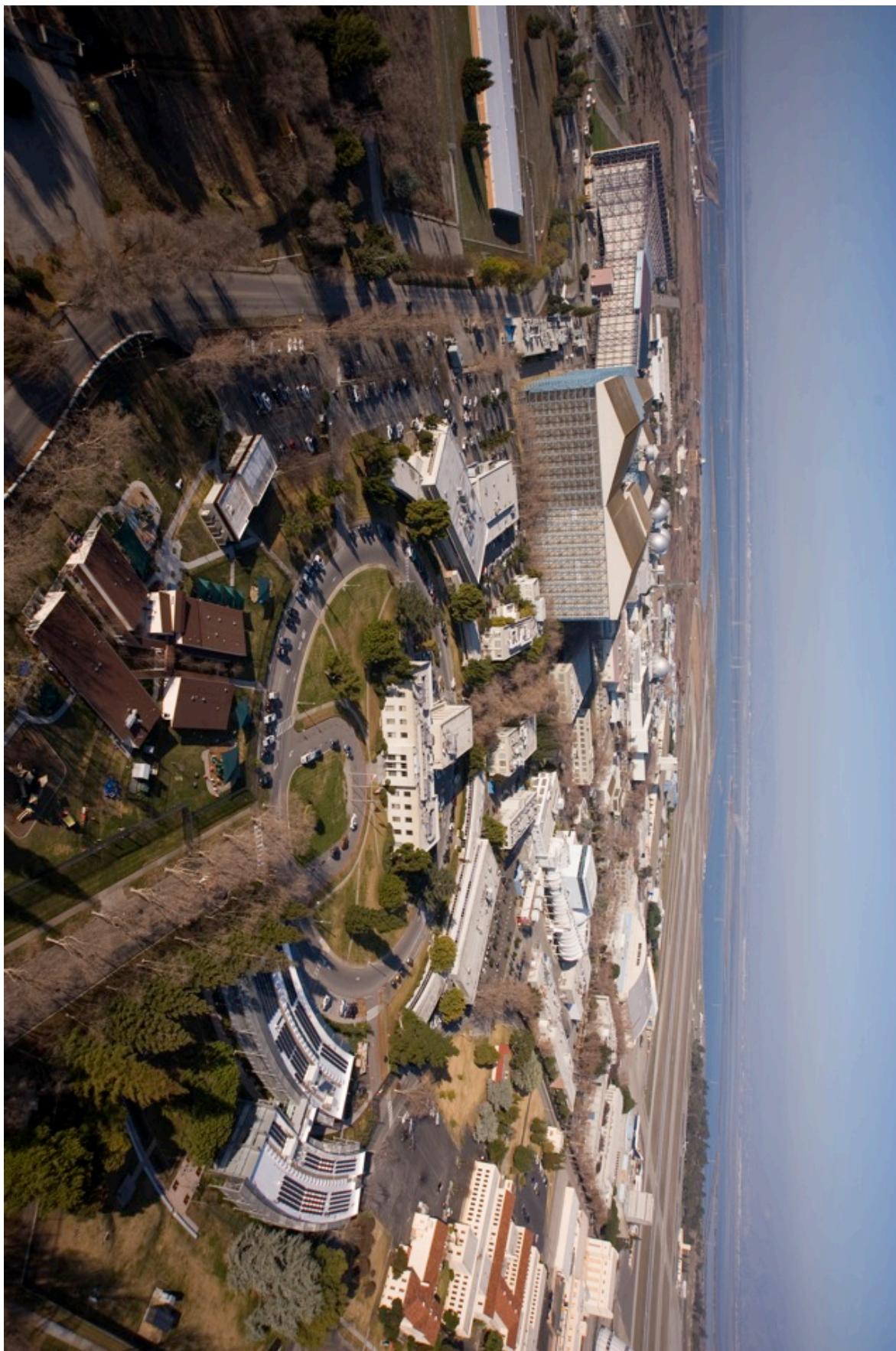


**Farid Salama**  
*NASA Ames Research Center*

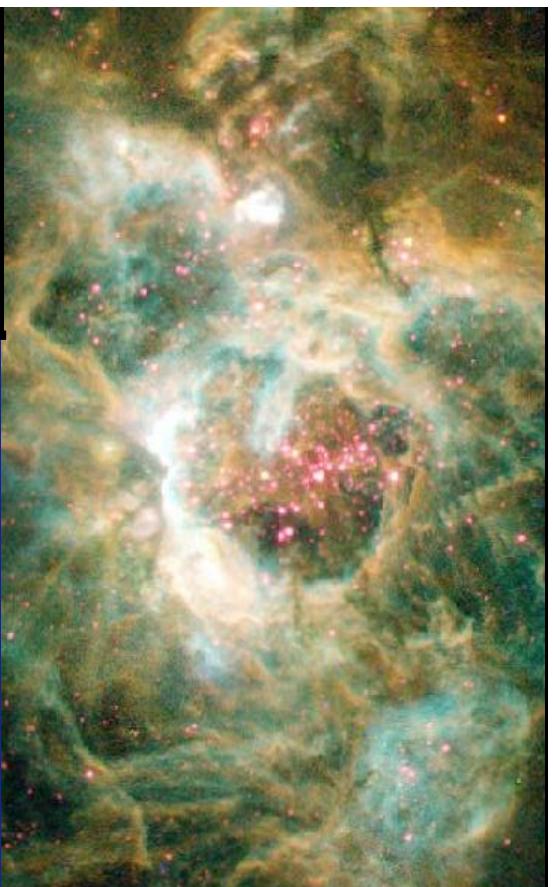


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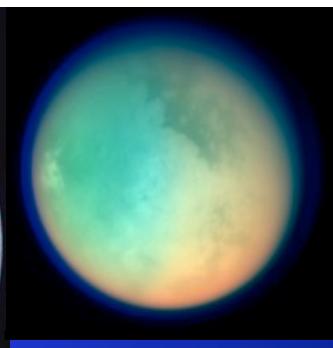
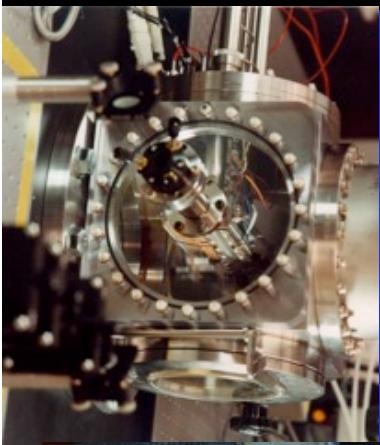
# Space Environments



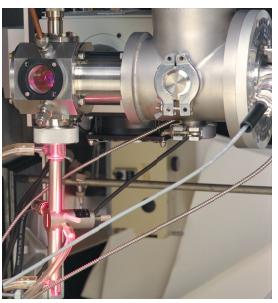
## Interstellar Medium & Star-Forming Regions

Earth-Moon System, Outer Planets & Moons  
(Titan) and Interplanetary Space

## Laboratory & Space Exposure



# Laboratory Astrophysics & Astrochemistry: Cosmic Simulation Chamber (COSmIC) UV-Vis-NIR, MS Lab Facility



Simulation Chambers for the Formation/Processing and the Analysis of Interstellar, Planetary and Lunar materials

## Research Theme: The Molecular Universe

### Current Research Projects:

#### Astrophysics & Astrochemistry:



- Search for the signature of carbon molecules (PAHs, fullerenes,...) UV/Vis/NIR
- Nature molecular carriers contributing to Galactic and Extragalactic extinction
- Molecular carriers of the Diffuse Interstellar Bands (DIBs) UV/Vis/NIR (HST/COS; JWST; VLT/EDIBLES)

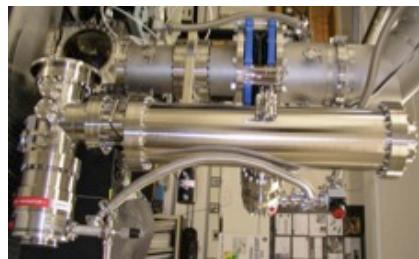
- Formation of circumstellar and interstellar carbon grains from molecular precursors (HST/COS; JWST).
- Complex organic molecules in space (ISS/EXPOSE-R/EXOcube).

#### Solar System:

- Formation of aerosols in the atmosphere of Titan (Cassini).
- Complex organic molecules in space (ISS/EXPOSE-R/EXOcube).

#### Lunar:

- Dust Activation/Mitigation (surface reactivity).



## Astrophysics:

- Energy budget and signature of aromatic carbon molecules
- PAHs & Grain formation

## Planetary:

- Titan's atmosphere (haze)

## ISS:

- Exposure experiments on complex organic molecules

Astrophysics:

- Energy budget and signature of aromatic carbon molecules
- PAHs & Grain formation

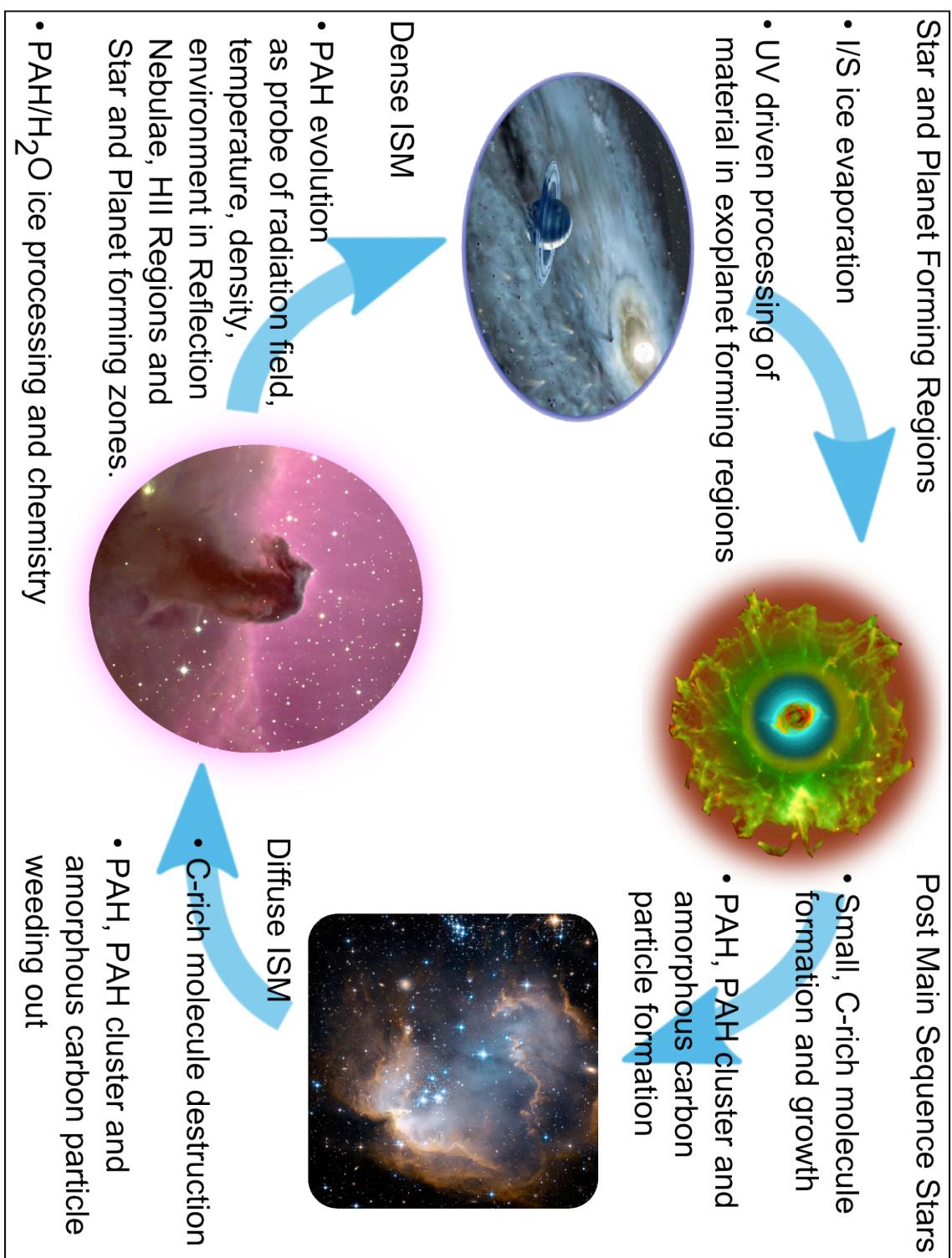
Planetary:

- Titan's atmosphere (haze)

ISS:

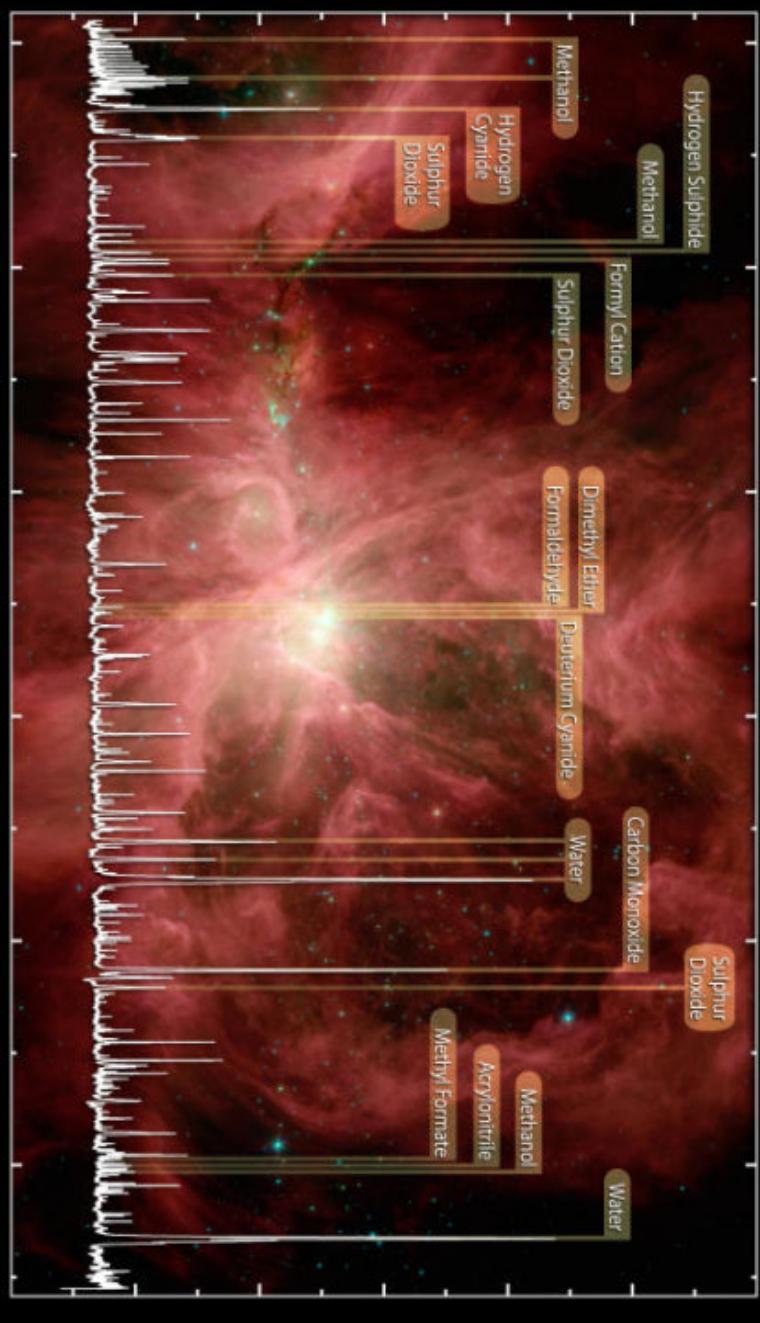
- Exposure experiments on complex organic molecules

# The Stellar Life Cycle and Evolution of Cosmic Carbon

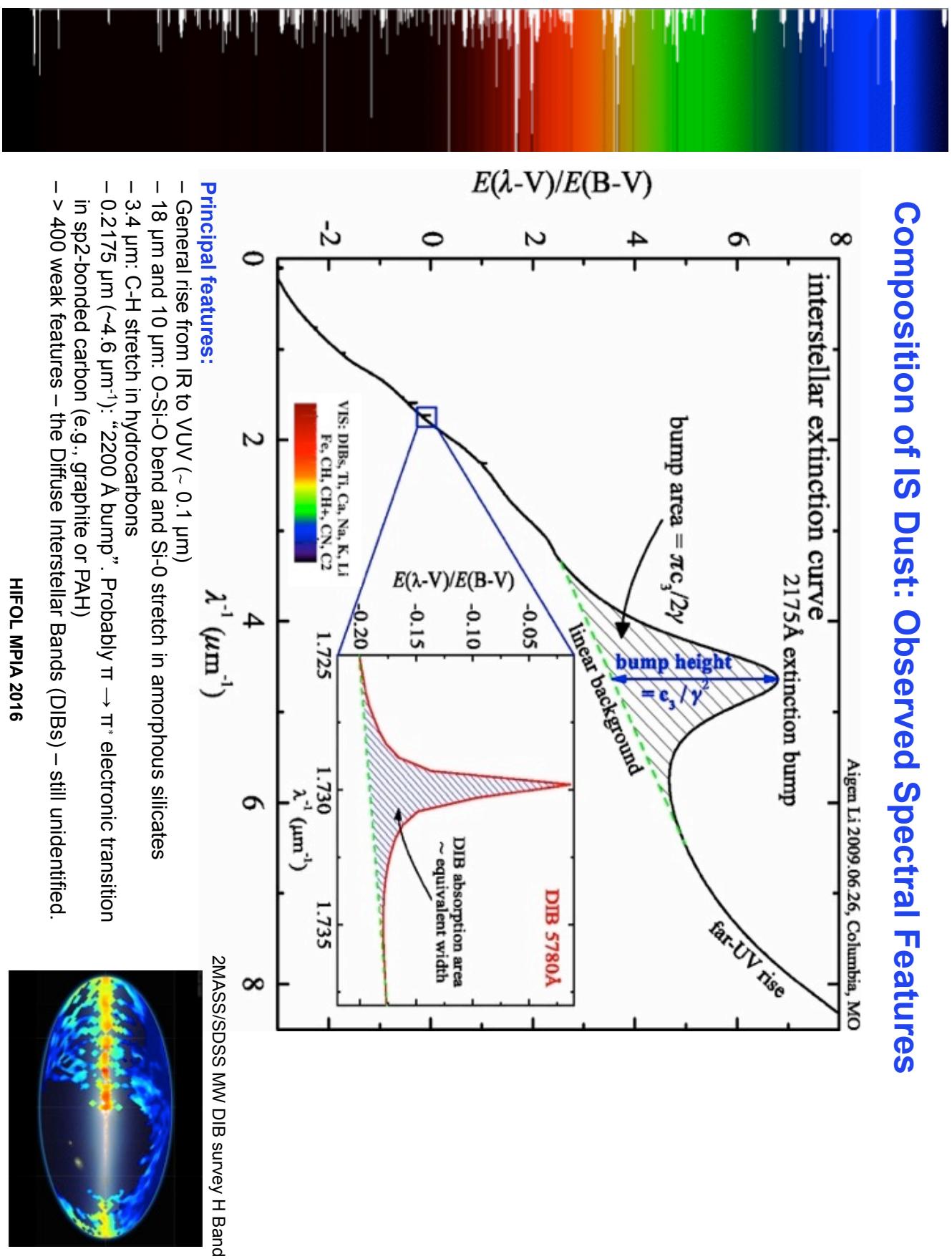


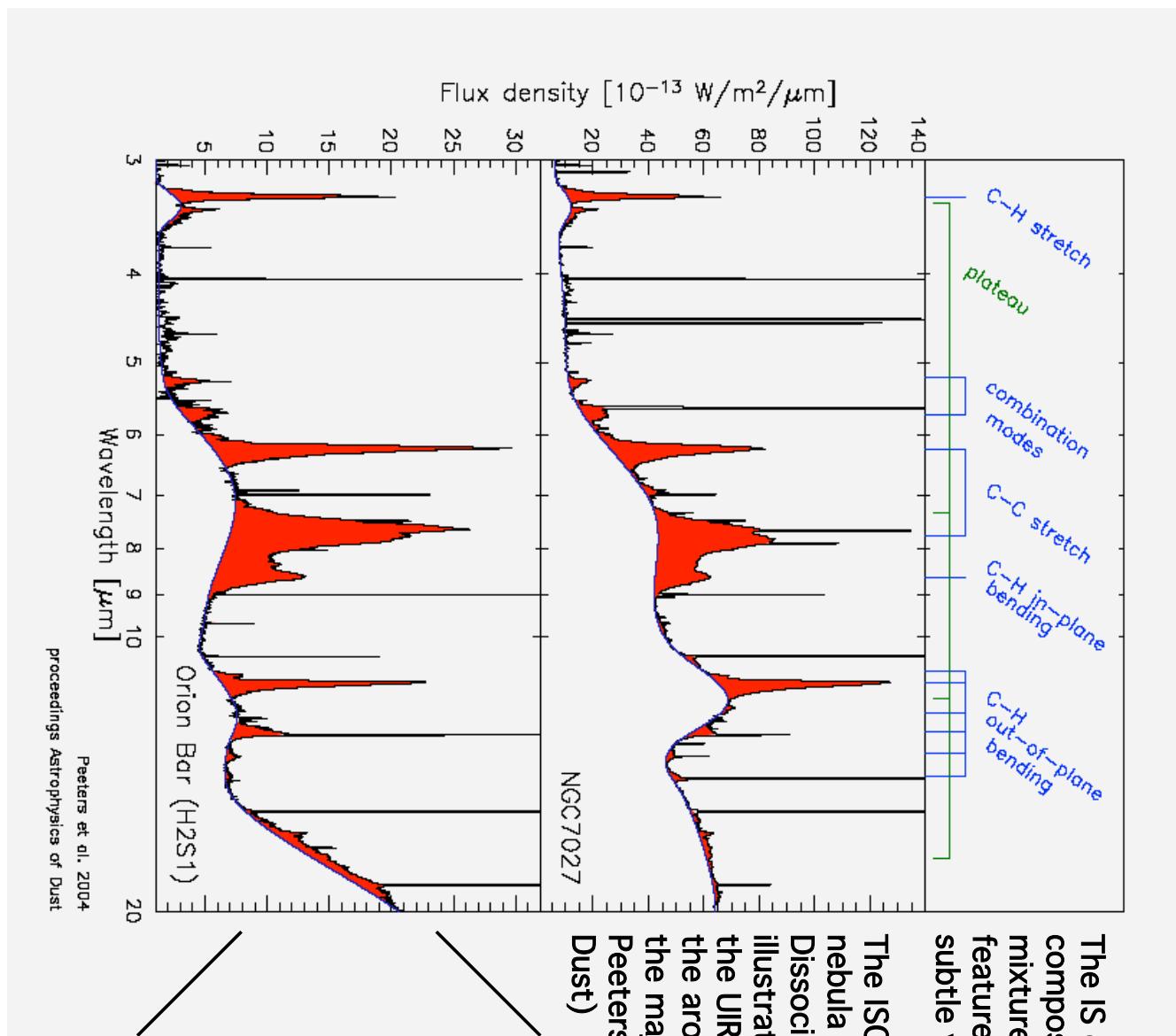
## HIFI Spectrum of Water and Organics in the Orion Nebula

© ESA, HEXOS and the HIFI consortium  
E. Bergin



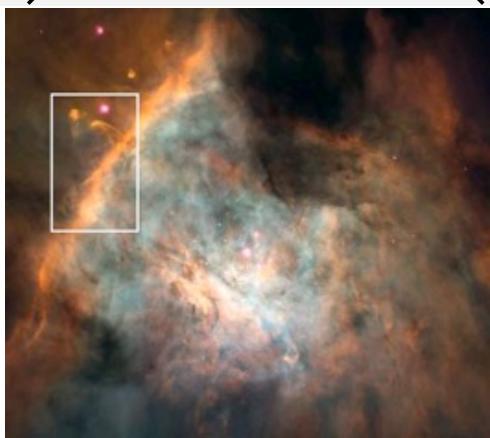
# Composition of IS Dust: Observed Spectral Features



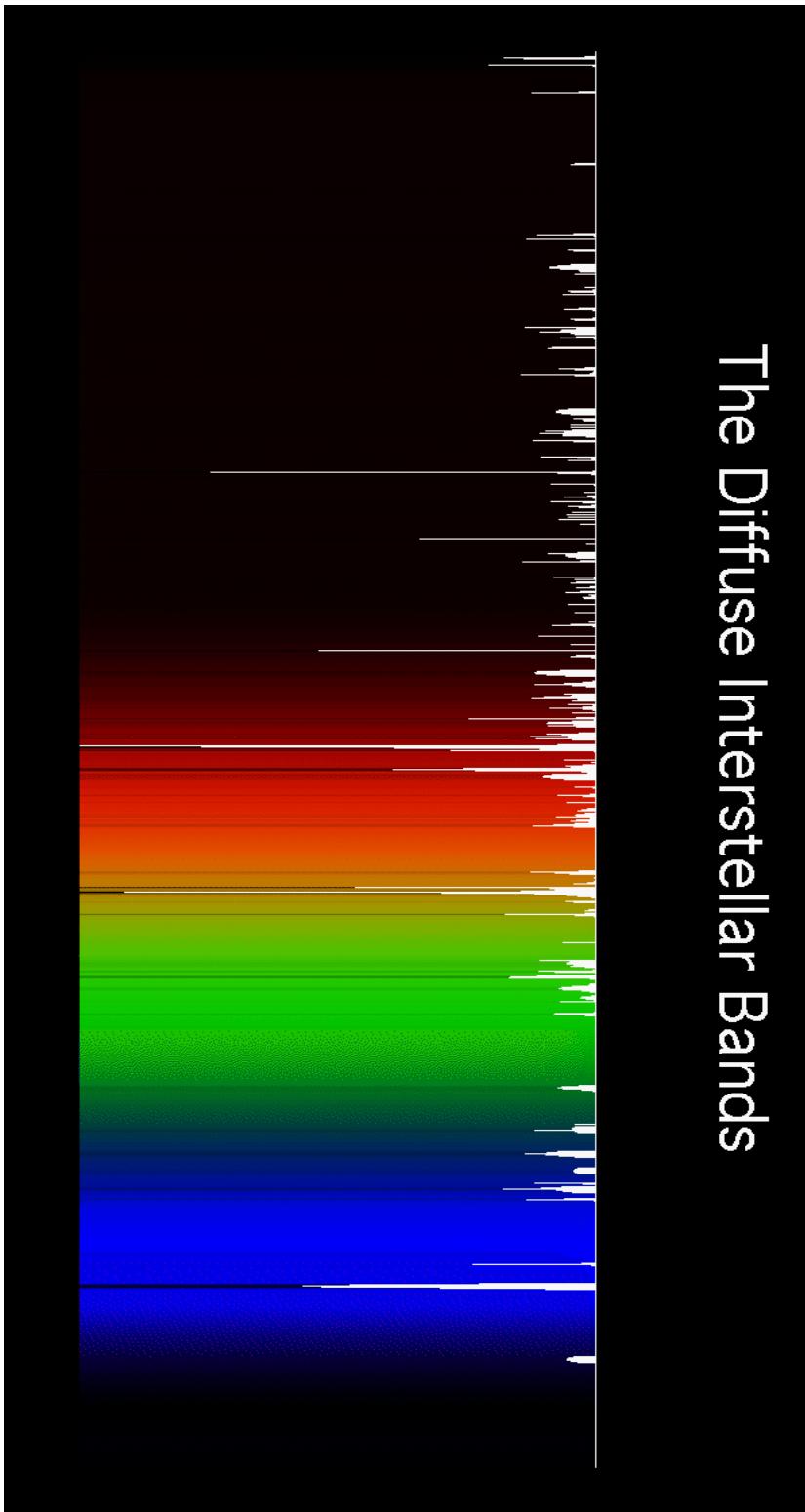


The IS emission spectra represent the composite emission of a complex mixture of aromatic compounds. The features are not resolvable, but show subtle variations.

The ISO-SWS spectra of the planetary nebula NGC 7027 and the Photo-Dissociation region at the Orion Bar illustrate the richness and variety of the UIR spectrum. Also indicated are the aromatic mode identifications of the major UIR features (Adapted from Peeters *et al.*, 2004, *Astrophysics of Dust*)

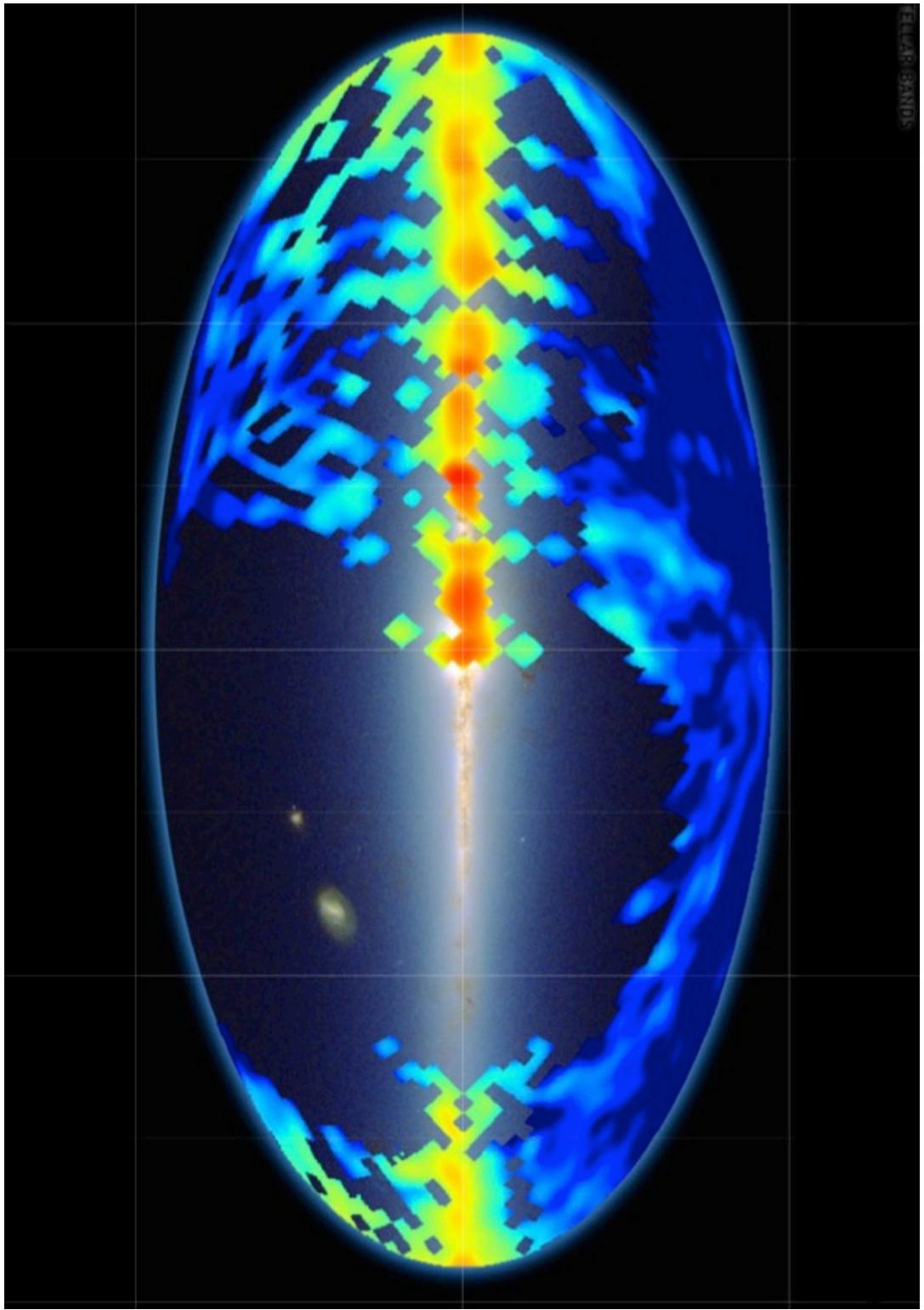


# The Diffuse Interstellar Bands



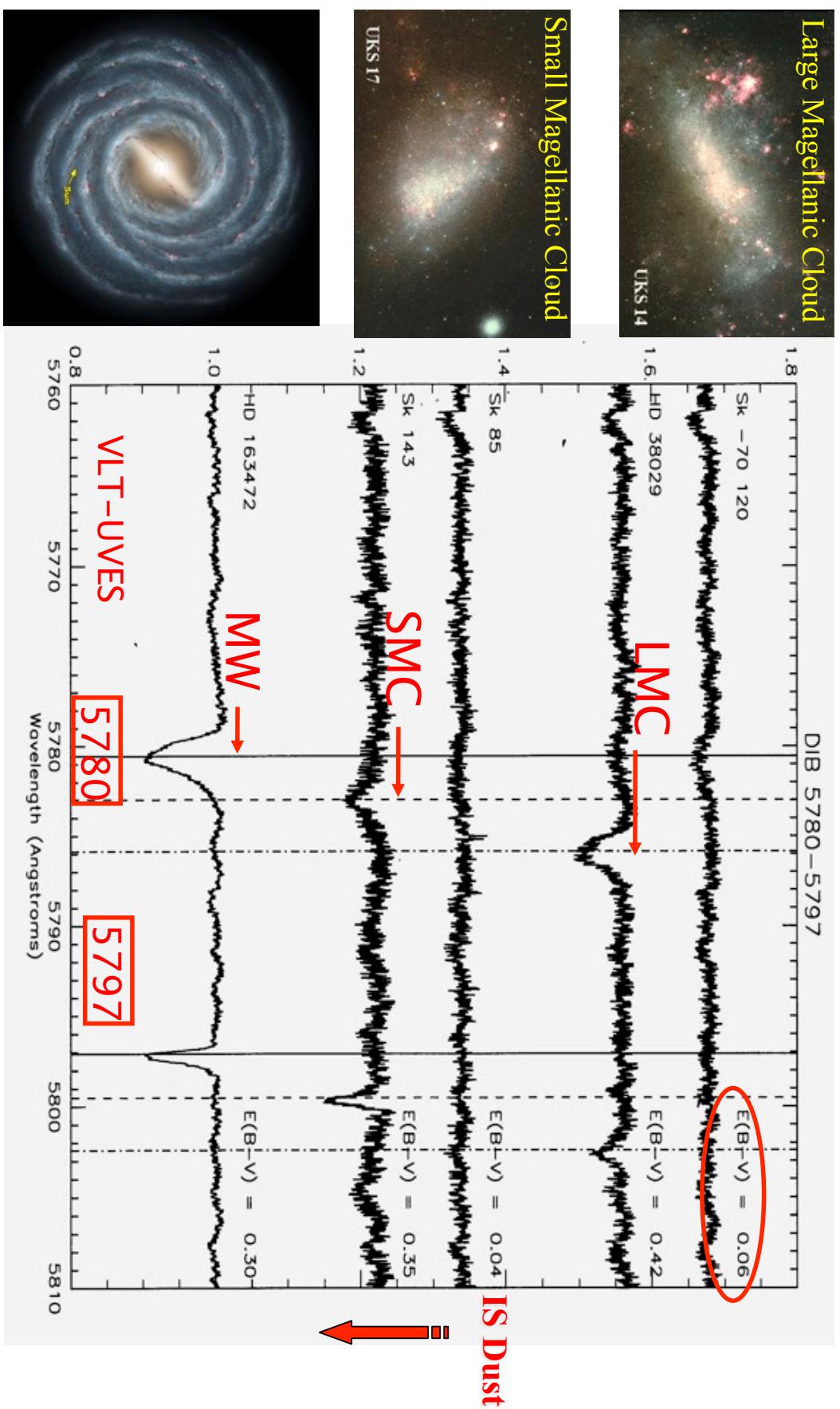
- First discovered in 1922
  - Of interstellar origin - ubiquitous carrier(s) - very stable
  - Currently > 300 known DIBs (Narrow: 1-2 Å to Broad: 20 Å)
  - DIBs fall at constant wavelengths
  - Spectral fingerprint of molecules in space
  - Superimposed on IS extinction curve
- |                        |       |
|------------------------|-------|
| 1922: Heger            | 2     |
| 1934: Merrill          | 4     |
| 1975: Herbig           | + 39  |
| 1995: Herbig           | + 127 |
| 2000: O'Tuairisg + 226 |       |
| 2003: York > 400       |       |

# Map of the Diffuse Interstellar Bands in the Milky Way



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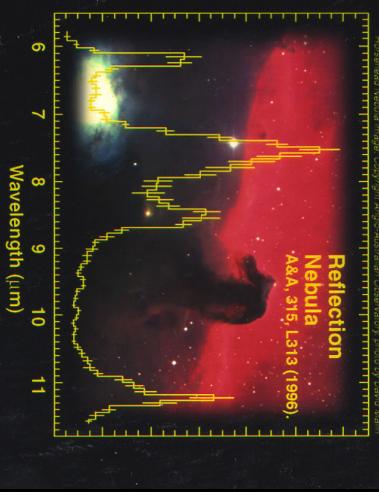
# Diffuse Interstellar Bands in the Magellanic Clouds



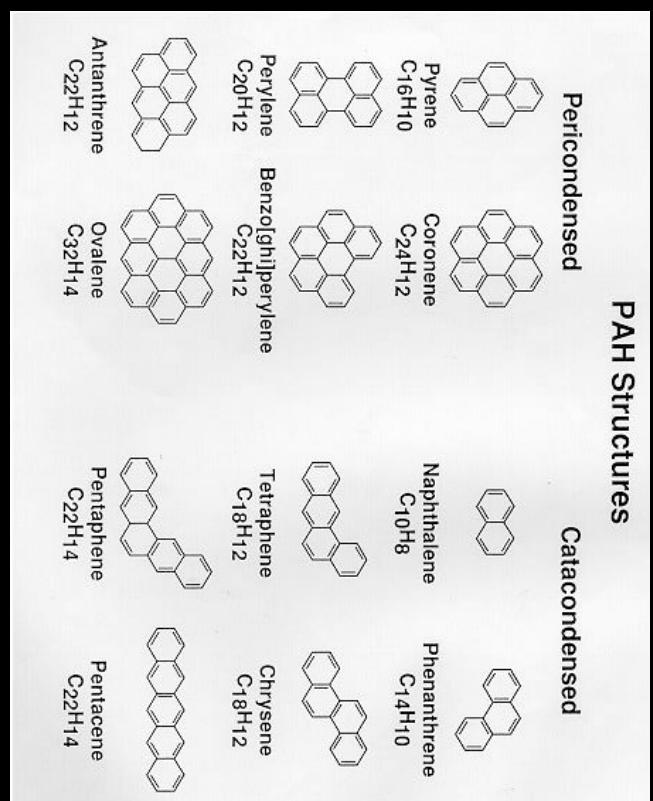
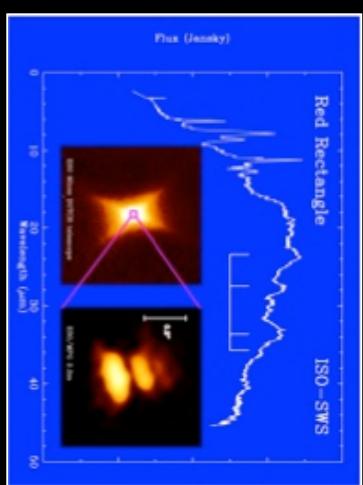
Salama et al. ApJ 1999; Ehrenfreund et al. ApJ 2002

# PolyCyclic Aromatic Hydrocarbons

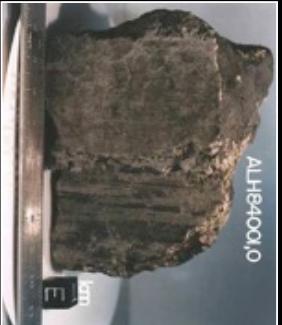
Emission (MJy/Sr)



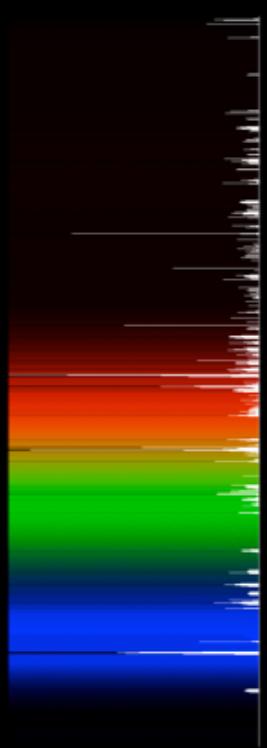
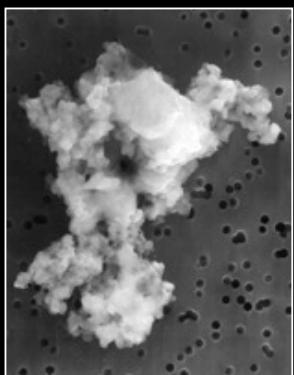
## ISM Infrared Emission



## Meteorites



## IDPs



## RR Blue Luminescence

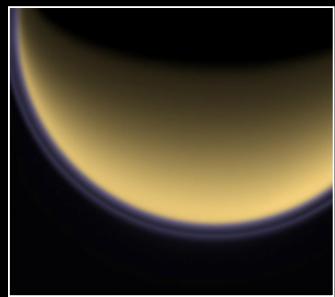


DIBs

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Comets

Planetary Atmospheres,  
Rings & Surfaces

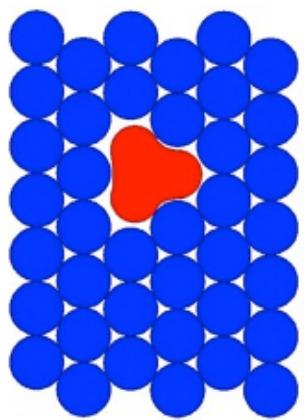


## Measuring laboratory spectra under astrophysically relevant conditions -

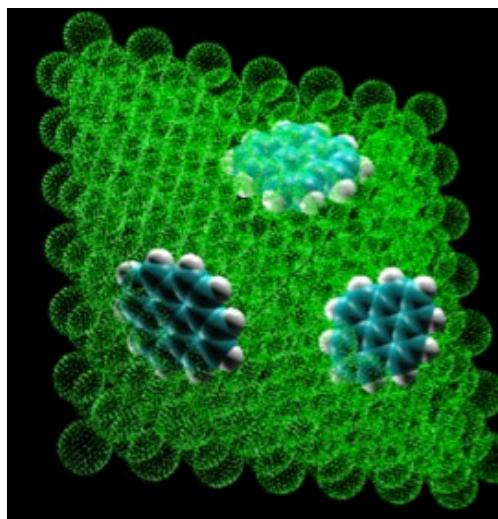
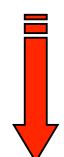
**Requirements:** Molecules & Ions: **1: Free** - **2: Cold** - **3: Exposed to VUV photons**

Matrix Isolation Spectroscopy (MIS) provides:

- Low temperature (5 K)
- Low density (molecule/ion fully isolated)
- High-energy photons (VUV)
- Solid phase



Ne Matrix-embedded molecules



A. Christie (Slimfilms.com)  
in Bernstein et al. 1999

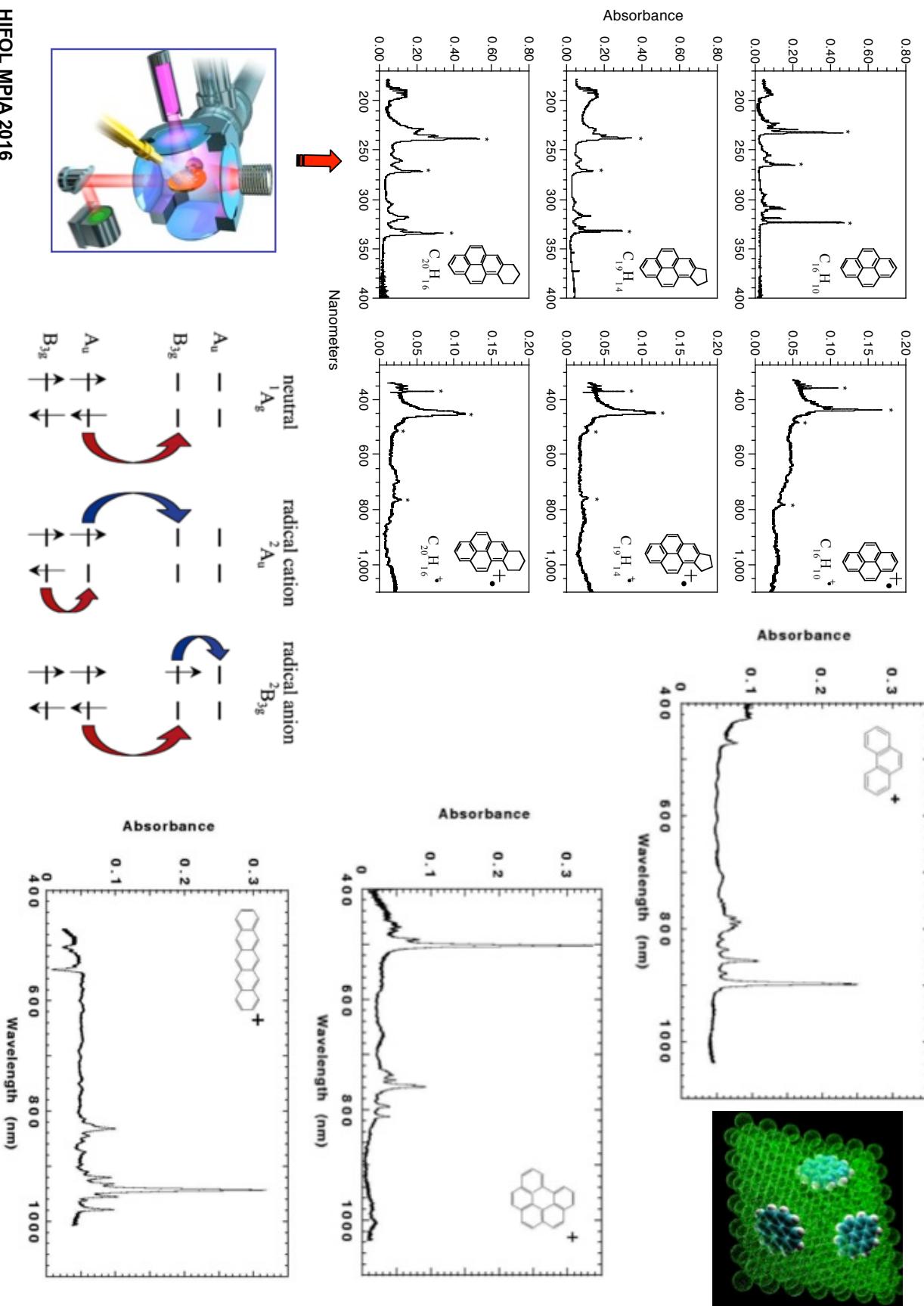
Adapted from Honeycutt et al. 2003



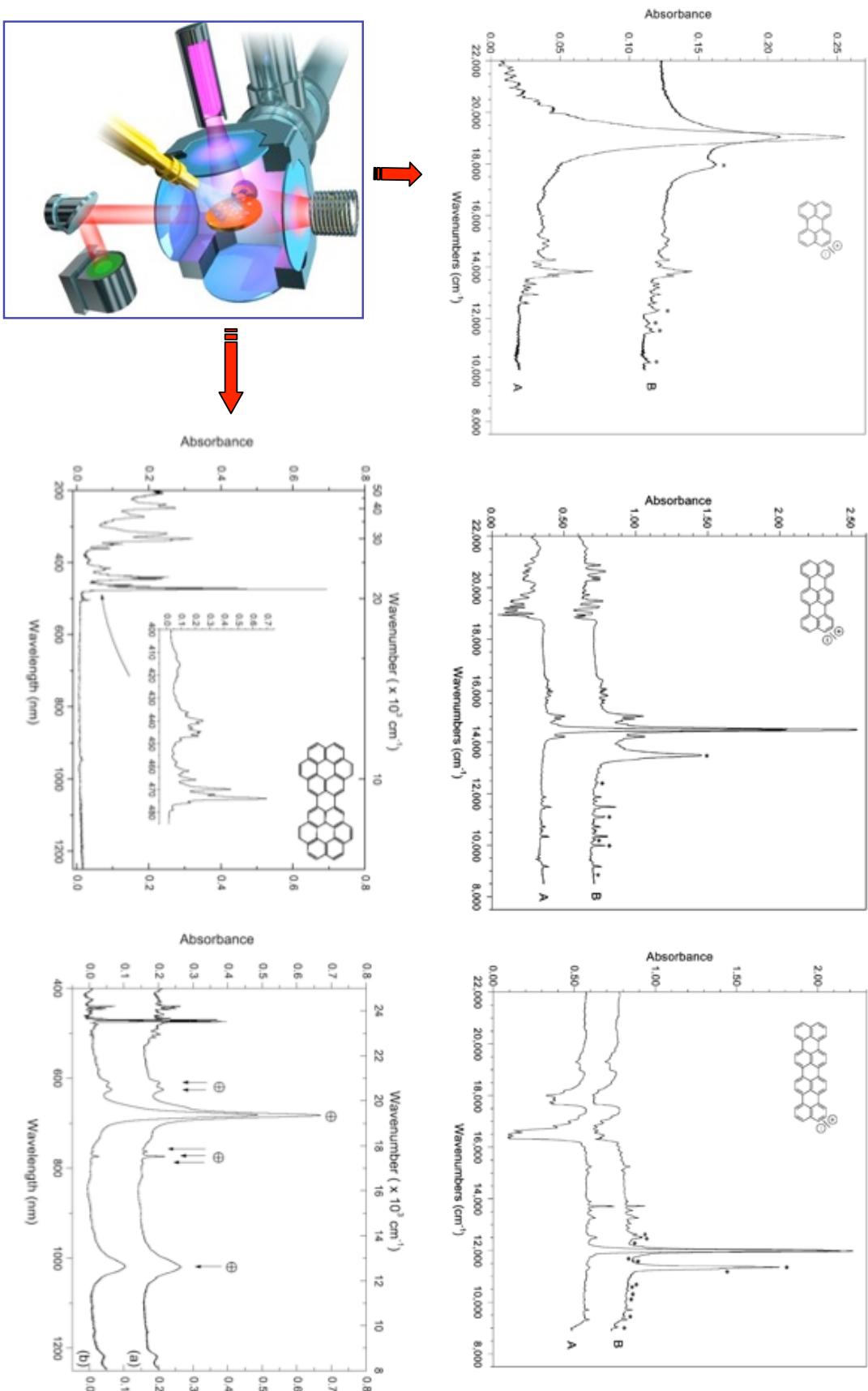
Matrix Isolation Spectroscopy (MIS) Chamber

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# Preparatory Investigations: MIS Electronic Absorption Spectra of PAH Neutrals & ions



# Preparatory Investigations: MIS Electronic Absorption Spectra of $\text{C}_{20}\text{H}_{12}$ , $\text{C}_{30}\text{H}_{16}$ , $\text{C}_{40}\text{H}_{20}$ and $\text{C}_{48}\text{H}_{20}$ Cations (+) and Anions (-)



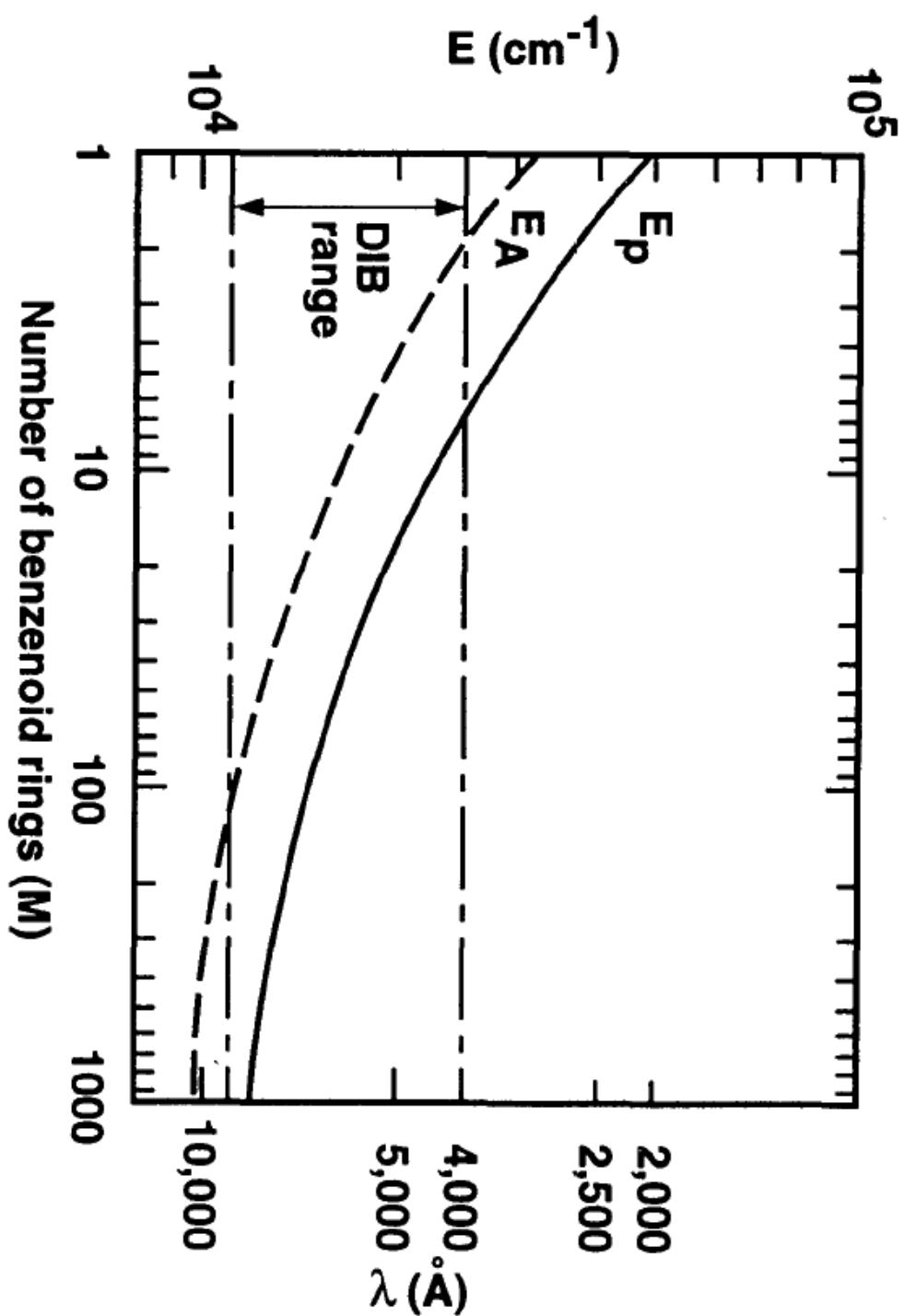
COMPARISON OF DIBs WITH THE ABSORPTION BANDS OF PAH CATIONS ISOLATED IN NEON MATRICES

$\lambda$ PAH <sup>+</sup> (Ne matrix data)	HD 207198 Sp = O9 Iie $E(B - V) = 0.60$	BD +40°4220 Sp = O7e $E(B - V) = 1.96$	HD 195592 Sp = O9.5 Ia $E(B - V) = 1.14$	HD 190603 Sp = B1.5 Iae $E(B - V) = 0.72$	HD 187459 Sp = B0.5 I $E(B - V) = 0.41$
3442 TetraB .....	...	Blended with interstellar Ca I (4226,734, 9.5%, 18 mÅ)	...	Interstellar Ca I 4226,73, 5.5% 4 mÅ	Interstellar Ca I 4226,73, 10 mÅ
4277 Bl[ep]yrA .....	...	...	...	DB 4428,88, 4.5%, 400 mÅ	DB 4428,88, ... 3%, 200 mÅ
4395 PyreneA .....	...	...	...	DB 4428,88, 4.5%, 400 mÅ	DB 4428,88, ... 3%, 200 mÅ
4442 IMePyrA .....	...	...	...	DB 4501.8, 3.5%, 100 mÅ	DB 4501.8, 2.5%, 63 mÅ
4456 4MePyrA .....	...	...	...	DB 4501.8, 3.5%, 100 mÅ	DB 4501.8, 2.5%, 63 mÅ
4499 COHPyrA .....	...	...	...	DB 4501.8, 3.5%, 100 mÅ	DB 4501.8, 2.5%, 63 mÅ
4580 4MePyrB .....	...	...	...	DB 4963,96, 1.5%, 15 mÅ	DB 4963,96, 2%, 15 mÅ
4590 CoronA .....	...	...	...	DB 4969,67, 1.2%, 10 mÅ	DB 4969,67, 1.2%, 10 mÅ
4987 COHPyrB .....	...	...	...	DB 4984,73, 3%, 13 mÅ	DB 4984,73, 2%, 8 mÅ
5022 bg[ep]perA .....	...	...	...	DB 4984,73, 2%, 8 mÅ	DB 4984,73, 1.5%, 3 mÅ
5251 PerI/A .....	...	...	...	DB 4984,73, 2%, 8 mÅ	DB 4984,73, 1.5%, 3 mÅ
6120 Nap[ph]B2 (projected value)*	...	...	...	DB 6116,65, 2.5%, 19 mÅ	DB 6116,65, 2%, 19 mÅ
6489 Nap[ph]B1* .....	...	...	...	DB 6491,88, 2%, 22 mÅ	DB 6491,88, 2%, 22 mÅ
6706 Nap[ph]A* .....	...	...	...	DB 6699,37, 3%, 35 mÅ	DB 6699,37, 2%, 19 mÅ
7229 peryIB1 .....	...	...	...	DB 6701,98, 2.2%, 4 mÅ	DB 6701,98, 1%, 6.5 mÅ
7256 peryIB2 .....	...	...	...	DB 7249,26, 2.8%, 43 mÅ	DB 7224,18, 8%, 125 mÅ
7580 1MePyrB .....	...	...	...	DB 7257,35, 1%, 15 mÅ	DB 7224,18, 15%, 200 mÅ
		DIB 7276,7, 6%, 33 mÅ	DIB 7276,7, 3%, 15 mÅ	DB 7276,7, 2.5%, 20 mÅ	DB 7224,18, 8%, 125 mÅ
		DIB 7581,24, 5%, 39 mÅ	DIB 7582,24, 6%, 100 mÅ	DB 7582,24, 1.5%, 26 mÅ	DB 7562,24, 3.5%, 30 mÅ
7584 bg[ep]perB .....	See above	See above	See above	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
7588 4MePyrC .....	See above	See above	See above	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
8321 PentacB .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
8308 PhenantB* .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
8648 TetraC .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
8839 1,benzanthA .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
8919 PhenanthA* .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
9124 Bl[ep]YRB .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
9310 MePhenA .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
9433 PentacA .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
9470 CoronB .....	...	...	...	DB 7585,63, 1.5%, 30 mÅ	DB 7585,63, 1.5%, 30 mÅ
		DIB 9577, 10%, 380 mÅ	DIB 9577, 5%, 200 mÅ	DIB 9577, 5%, 180 mÅ	DIB 9577, 5%, 180 mÅ
		DIB 9632, 11%, 280 mÅ	DIB 9632, 7.5%, 215 mÅ	DIB 9632, 7.5%, 215 mÅ	DIB 9632, 7.5%, 215 mÅ

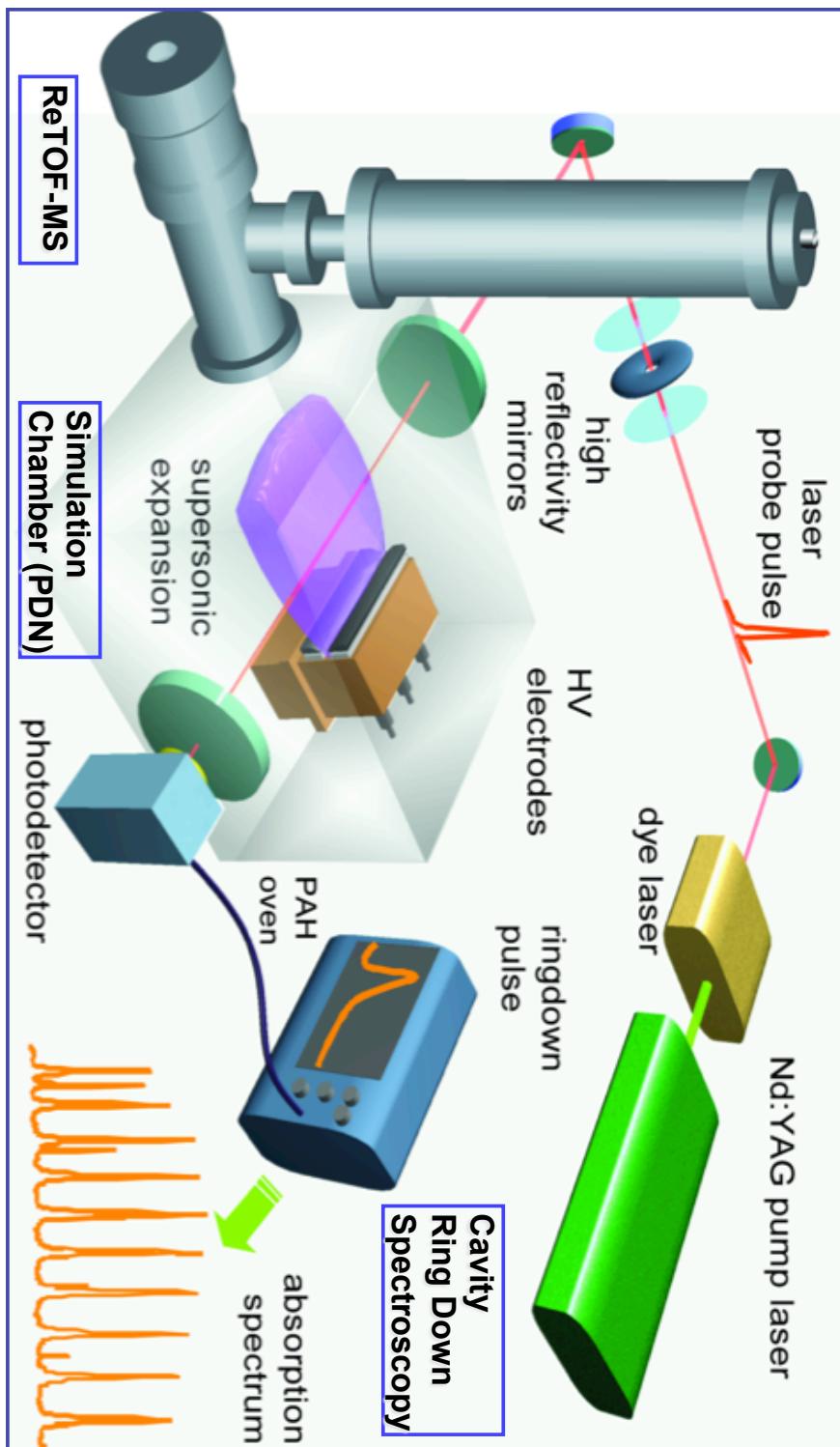
## Comparison of DIBs with PAH Cation Bands. PAHs Isolated in Neon Matrices

PAH <sup>+</sup>	$\lambda_{\text{peak}} \text{ (nm)}$	DIBs (nm)
Pyrene ( $\text{C}_{16}\text{H}_{10}^+$ )	439.5 (443.0 in Ar)	442.9
1-Methylpyrene ( $\text{CH}_3 - \text{C}_{16}\text{H}_9^+$ )	444.2	442.9
4-Methylpyrene ( $\text{CH}_3 - \text{C}_{16}\text{H}_9^+$ )	(457.7) 482.8 757.6	482.4 758.1
Naphthalene ( $\text{C}_{10}\text{H}_8^+$ )	674.2 652.0	674.1 652.0
Phenanthrene ( $\text{C}_{14}\text{H}_{10}^+$ )	898.3 856.8	857.2
Tetracene ( $\text{C}_{18}\text{H}_{12}^+$ )	864.7	864.8
Benzog(hi)perylene ( $\text{C}_{22}\text{H}_{12}^+$ )	502.2 758.4 755.2 794.3	503.9 (?) 758.1; 758.6 755.8 (?); 756.2 793.5 (prob.)
Coronene ( $\text{C}_{24}\text{H}_{12}^+$ )	459.0 946.5	459.5 946.6

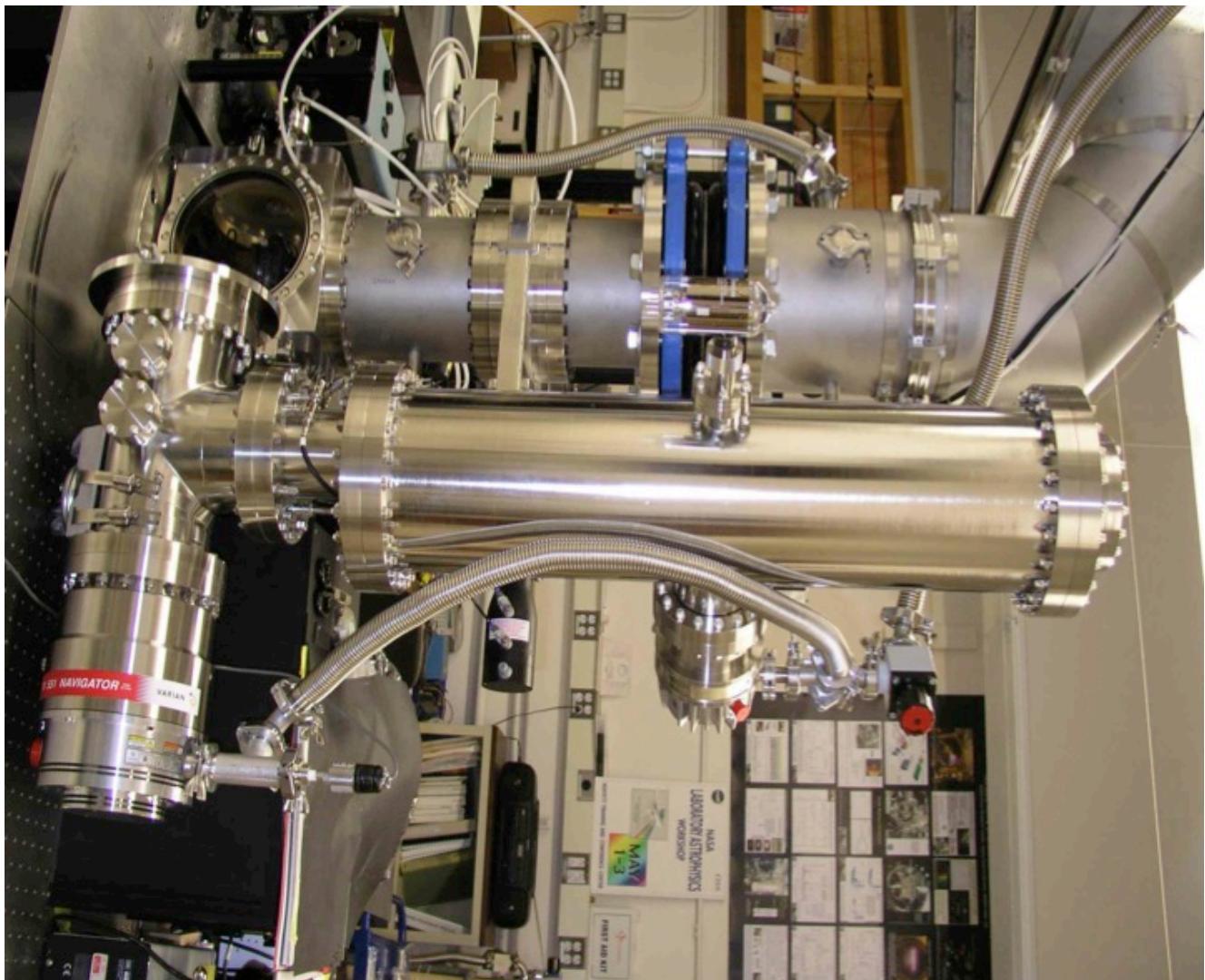
- + General conclusions: - spectral characteristics as function of charge state
- molecular size and structure (compact vs. non-compact; etc...).

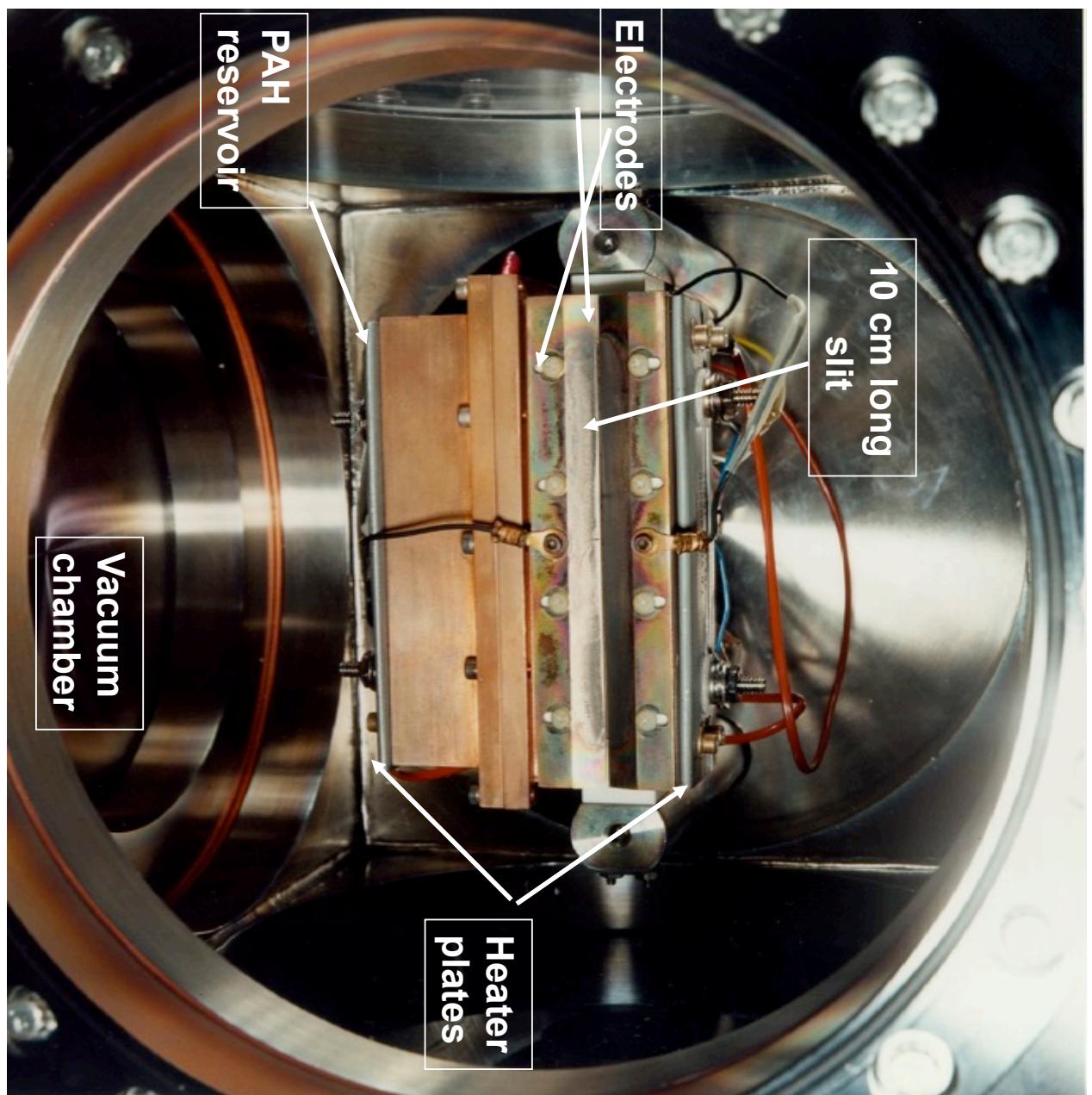


# Measuring Laboratory Spectra Under Astrophysically Relevant Conditions: Combine PDN + CRDS + o-ReTOF-MS: Free jet expansion + cavity ringdown spectroscopy + time-of-flight mass spectrometry

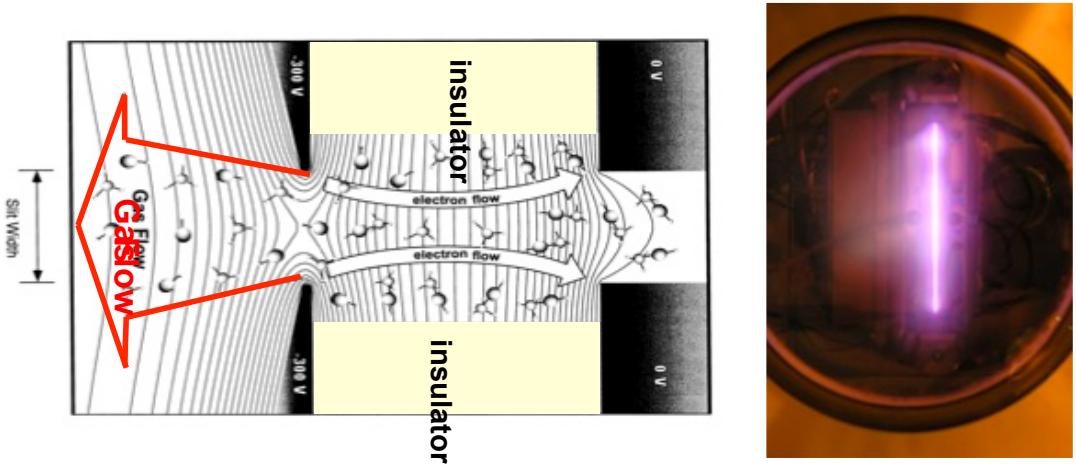


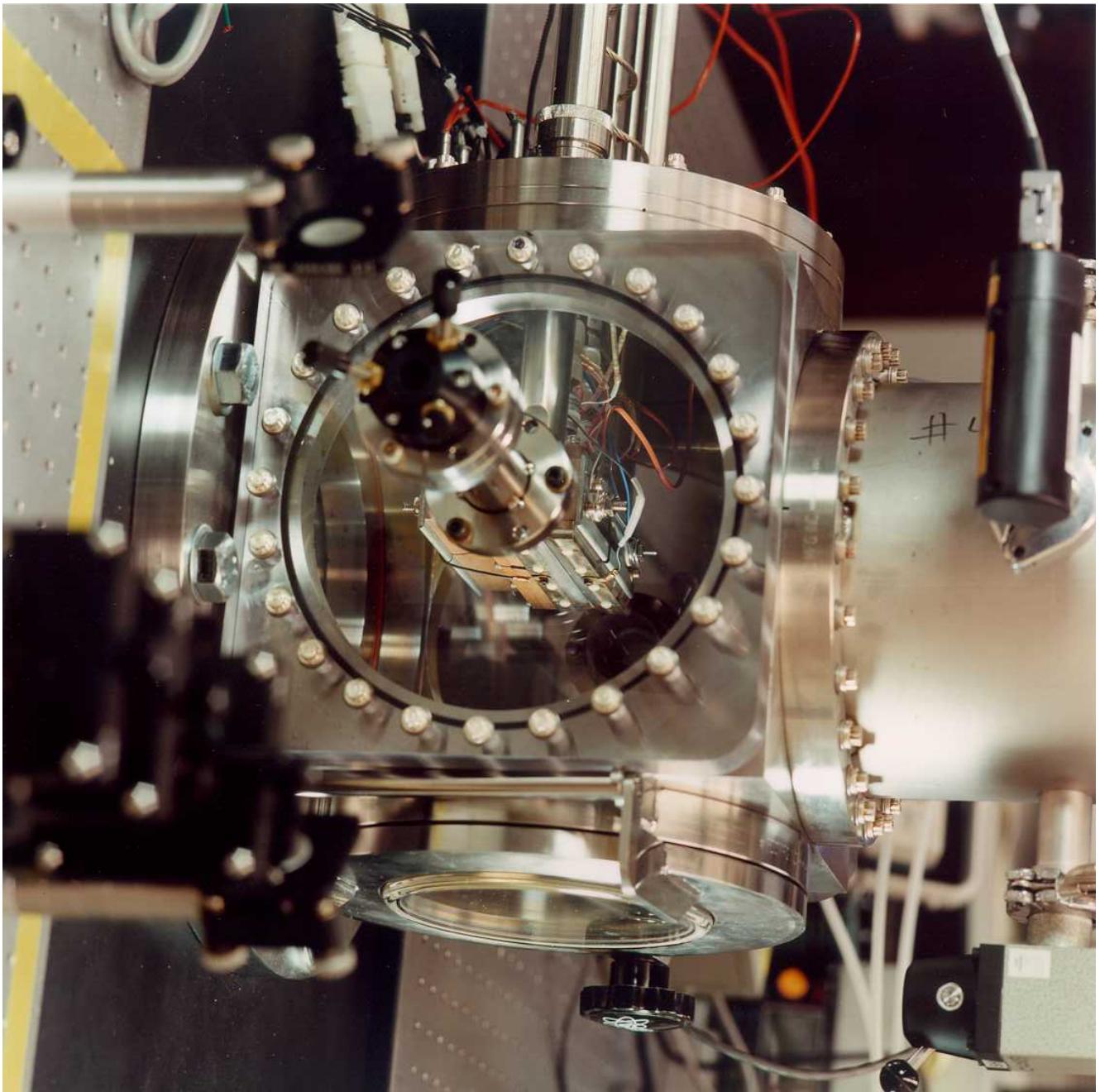
- High column density (10 cm-long slit)
- High pressure (1 bar) and temperature (300 C) reservoir
- Generates intense short gas pulses
- Generates (plasma) and stabilize (supersonic expansion) transient species





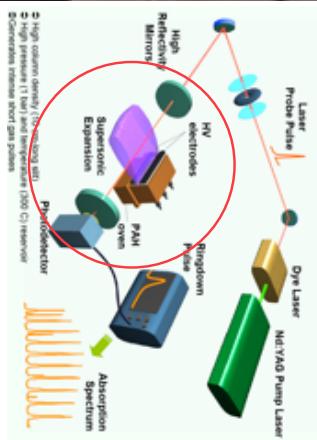
Simulation  
Chamber



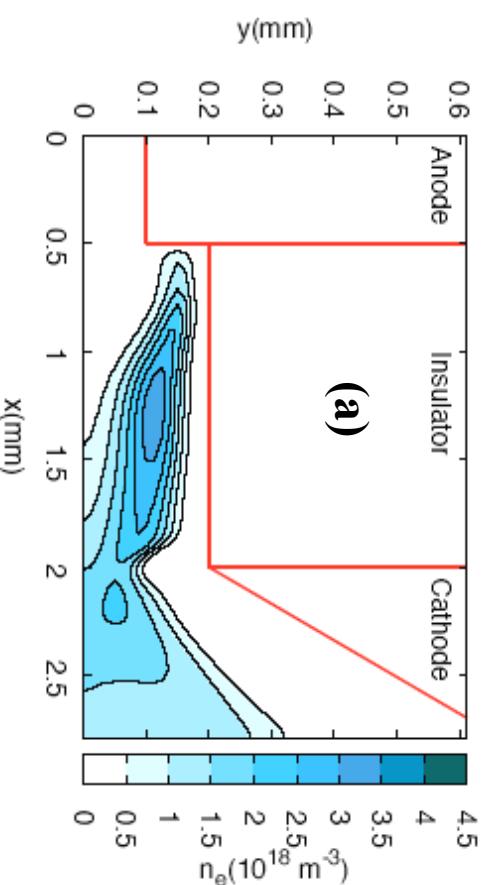


# Simulation Chamber

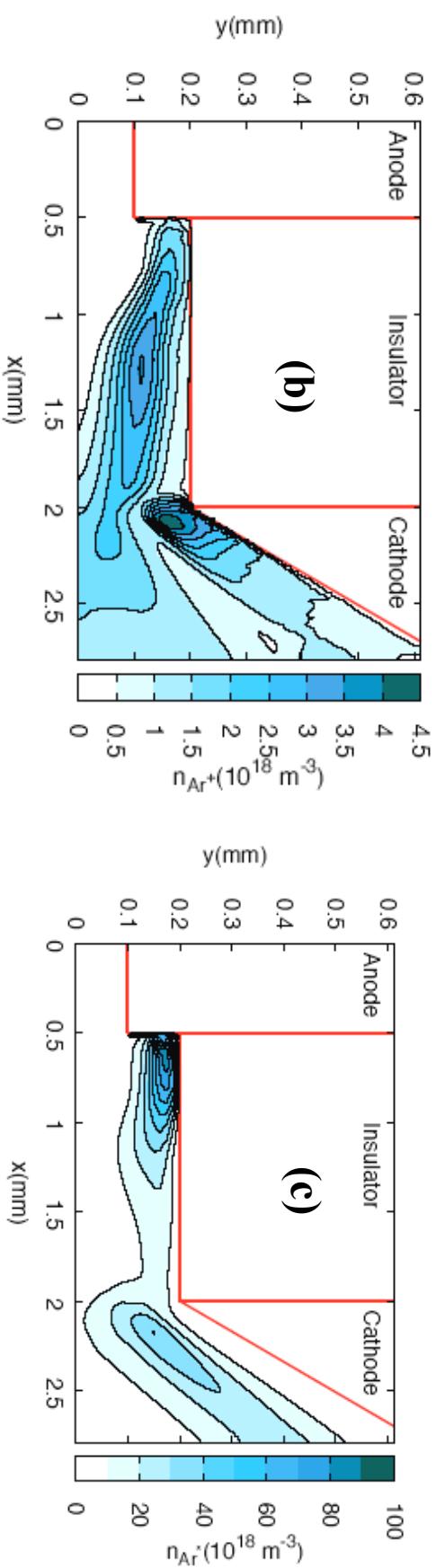
TOOLS



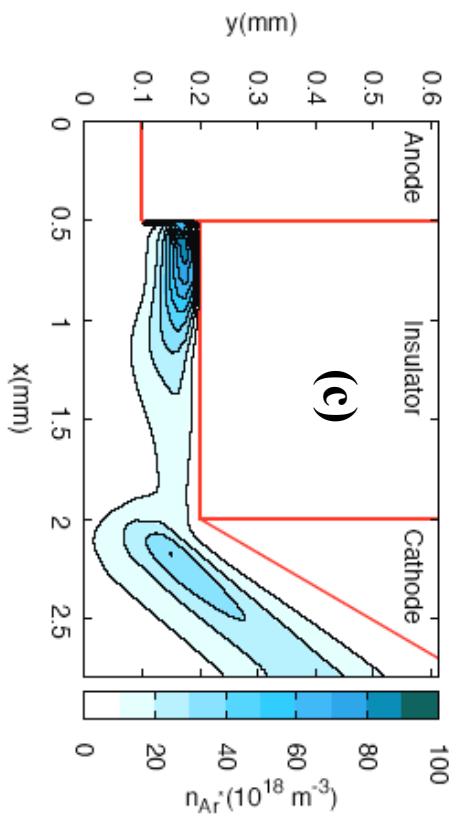
## Results: Simulation of the Plasma Glow Discharge



**(a)**



**(b)**



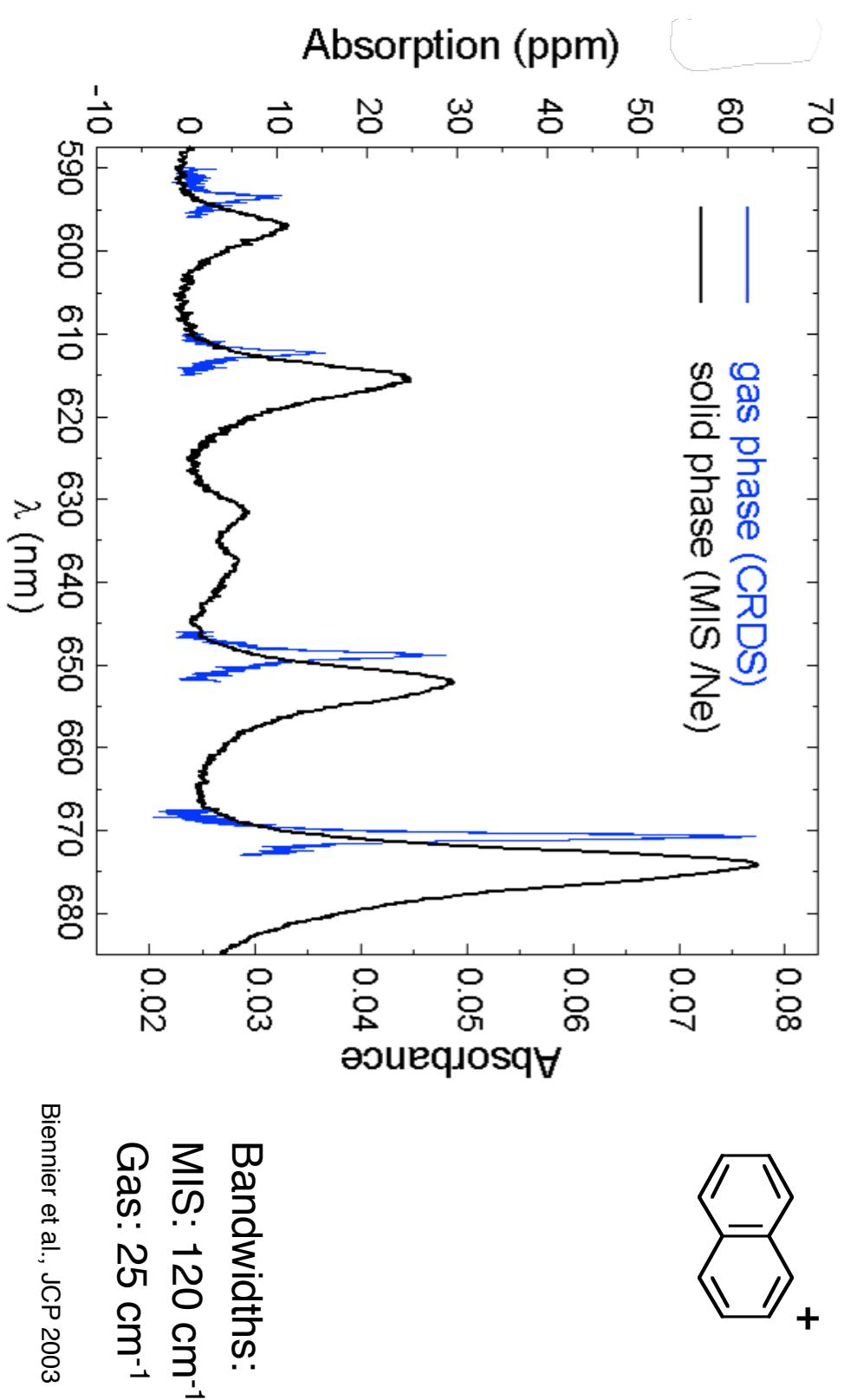
**(c)**

The (a) steady-state electron density, (b)  $\text{Ar}^+$  density and (c)  $\text{Ar}^*$  density of the pulsed discharge nozzle for a source voltage of -500 V.

**Ar\* atoms in the expansion region >> electrons and ions. PAH ions are dominantly formed through Penning ionization of the neutral molecular precursors seeded in the supersonic expansion of Ar gas.**

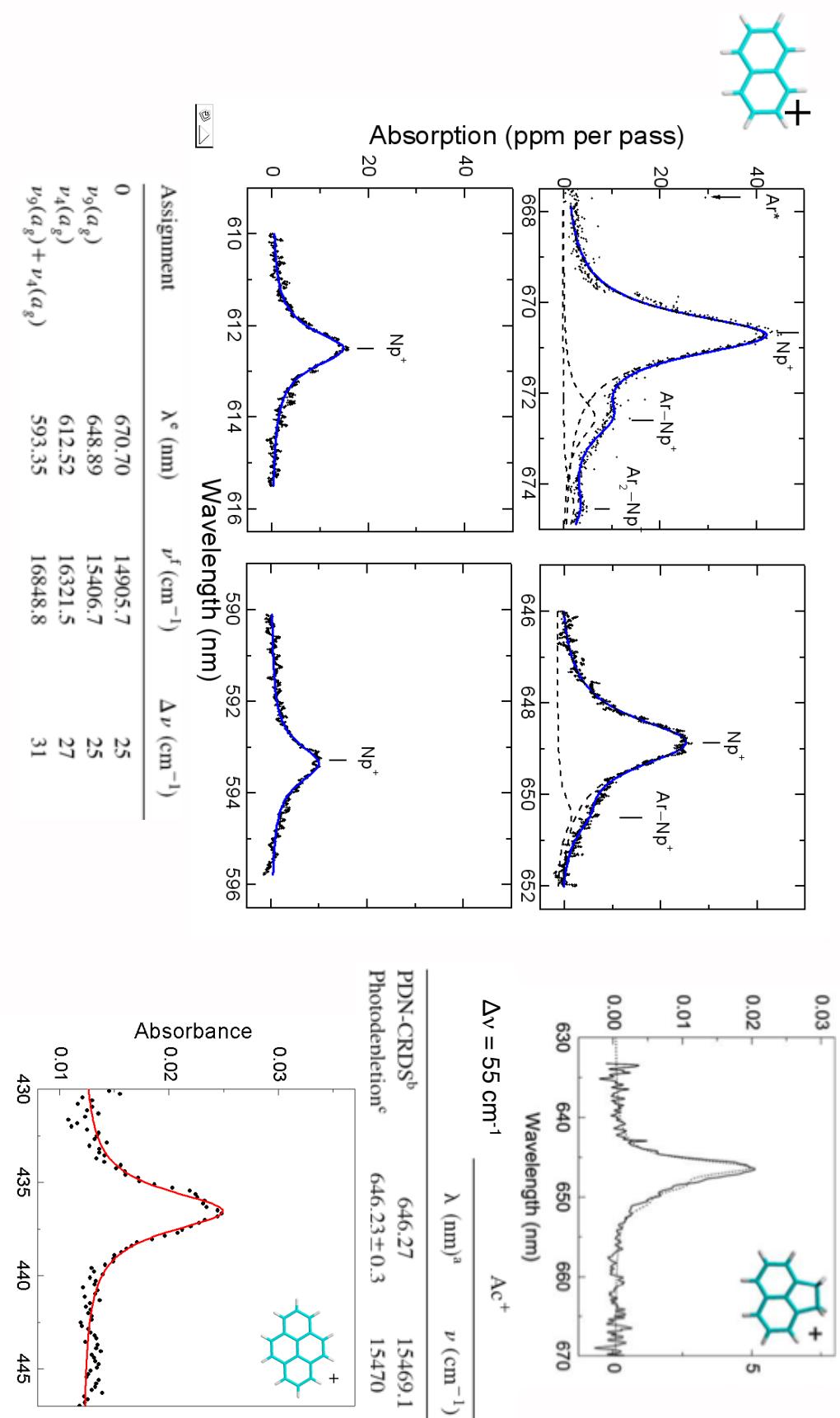
Remy, Biennier, Salama, IEEE 2005; Benidar, Biennier, Salama, Chem. Phys. 2006; Broks et al., Phys. Rev. E 2005; Broks et al. Spectrochim. Acta A 2005

## Cavity Ringdown Gas-Phase Spectra of the PAH Ions compared to MIS



Intrinsic band profiles and peak positions can now be measured in the laboratory to search for specific PAHs ( neutrals and/or ions) in interstellar and circumstellar spectra.

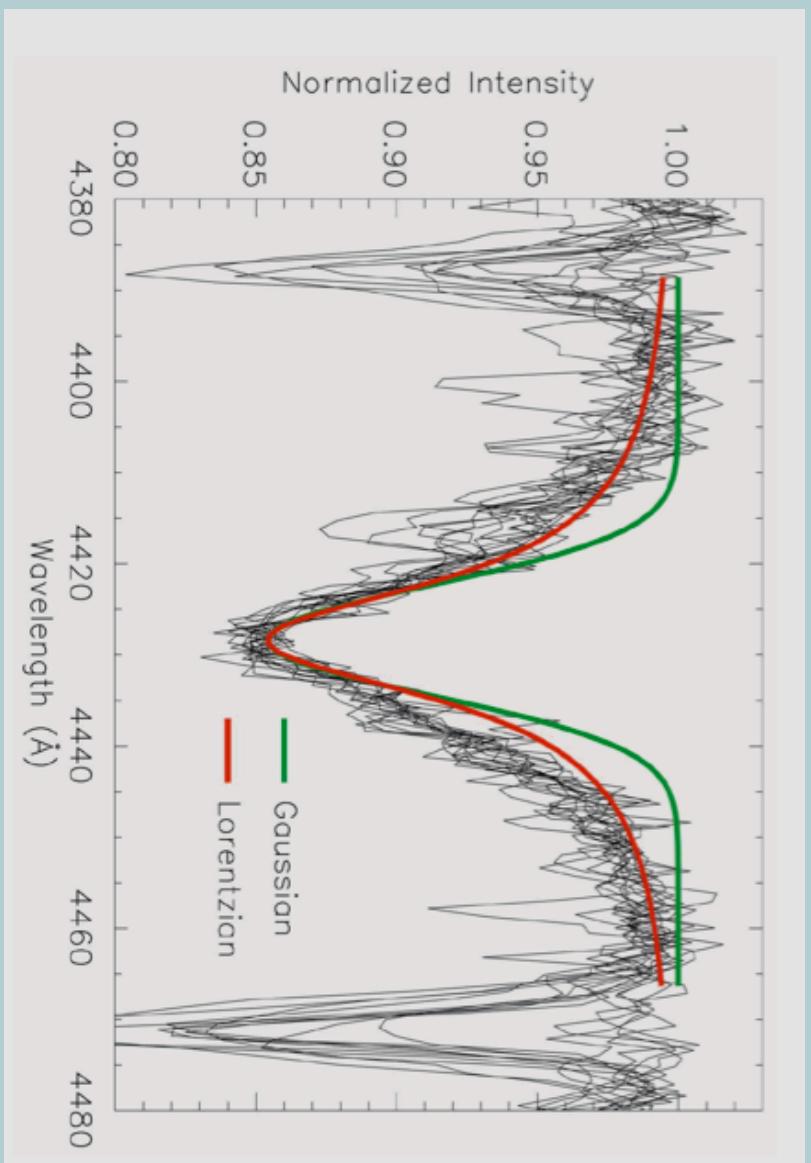
## CRDS Electronic Absorption Spectra of PAH ions In the Gas Phase



Biennier et al. 2003, 2004

**The vibronic bands of PAH ions are broad.**

## THE INTRINSIC PROFILE OF THE 4428 Å DIFFUSE INTERSTELLAR BAND



35 OB Stars  
High extinction  
Spectral Resolving  
Power ~2000  
 $\lambda$ 4428: 60 fs  
Molecular carrier  
Fast relaxation

### Fit of $\lambda$ 4428 to the Gaussian and Lorentz profiles.

- The Lorentz profile is a perfect fit to the observations of the 4428 Å DIB.
- Proposal that the broad 4428 Å DIB is a molecular feature whose width is explained by very rapid internal conversion. (Snow et al. ApJ 2002)

**Table 1.** Electronic state peak positions and band widths of cold gas-phase PAH ions measured in the laboratory are compared to the characteristics of the strong broad 4428 Å DIB

Molecular ion	Electronic State	$\lambda(\text{\AA})$	$\Delta\lambda(\text{\AA})$
Naphthalene <sup>+</sup> [C <sub>10</sub> H <sub>8</sub> <sup>+</sup> ] <sup>a,1</sup>	D <sub>2</sub>	6707.7	10
Naphthalene <sup>+</sup> [C <sub>10</sub> H <sub>8</sub> <sup>+</sup> ] <sup>b,2</sup>	D <sub>3</sub>	4548.5	19
Acenaphthene <sup>+</sup> [C <sub>12</sub> H <sub>14</sub> <sup>+</sup> ] <sup>a,1</sup>	D <sub>2</sub>	6462.7	22
Fluorene <sup>+</sup> [C <sub>13</sub> H <sub>10</sub> <sup>+</sup> ] <sup>c,2</sup>	D <sub>3</sub>	6201.7	53
Phenanthrene <sup>+</sup> [C <sub>14</sub> H <sub>10</sub> <sup>+</sup> ] <sup>d,2</sup>	D <sub>2</sub>	8919.0	12
Anthracene <sup>+</sup> [C <sub>14</sub> H <sub>10</sub> <sup>+</sup> ] <sup>e,1</sup>	D <sub>2</sub>	7087.6	47
Pyrene <sup>+</sup> [C <sub>16</sub> H <sub>10</sub> <sup>+</sup> ] <sup>f,1</sup>	D <sub>5</sub>	4362.0	28
Pyrene <sup>+</sup> [C <sub>16</sub> H <sub>10</sub> <sup>+</sup> ] <sup>g,2</sup>	D <sub>4</sub>	4803.3	30
Pyrene <sup>+</sup> [C <sub>16</sub> H <sub>10</sub> <sup>+</sup> ] <sup>g,2</sup>	D <sub>2</sub>	7786.6	97
Methylpyrene <sup>+</sup> [C <sub>17</sub> H <sub>12</sub> <sup>+</sup> ] <sup>h,1</sup>	D <sub>5</sub>	4411.3	10
Pyrene(COH) <sup>+</sup> [C <sub>17</sub> H <sub>10</sub> O <sup>+</sup> ] <sup>h,1</sup>	D <sub>8</sub>	(4413.3; 4409.3)	20
Pyrene(COH) <sup>+</sup> [C <sub>17</sub> H <sub>10</sub> O <sup>+</sup> ] <sup>h,1</sup>		4457.8	
Pyrene(COH) <sup>+</sup> [C <sub>17</sub> H <sub>10</sub> O <sup>+</sup> ] <sup>h,1</sup>		4442.7	
<i>4428 Å DIB<sup>i</sup></i>		<i>4428.4 ± 1.4</i>	<i>17.3 ± 1.64</i>

Also C78H26+

Salama, in *Molecules in Space* 2008

**\*\*PAH ions:**

- Band widths versus broad DIBs
- Naphthalene<sup>+</sup>?
- Anthracene<sup>+</sup>?
- Column densities ~ 10<sup>13</sup>

**\*\*Hydrocarbons:**

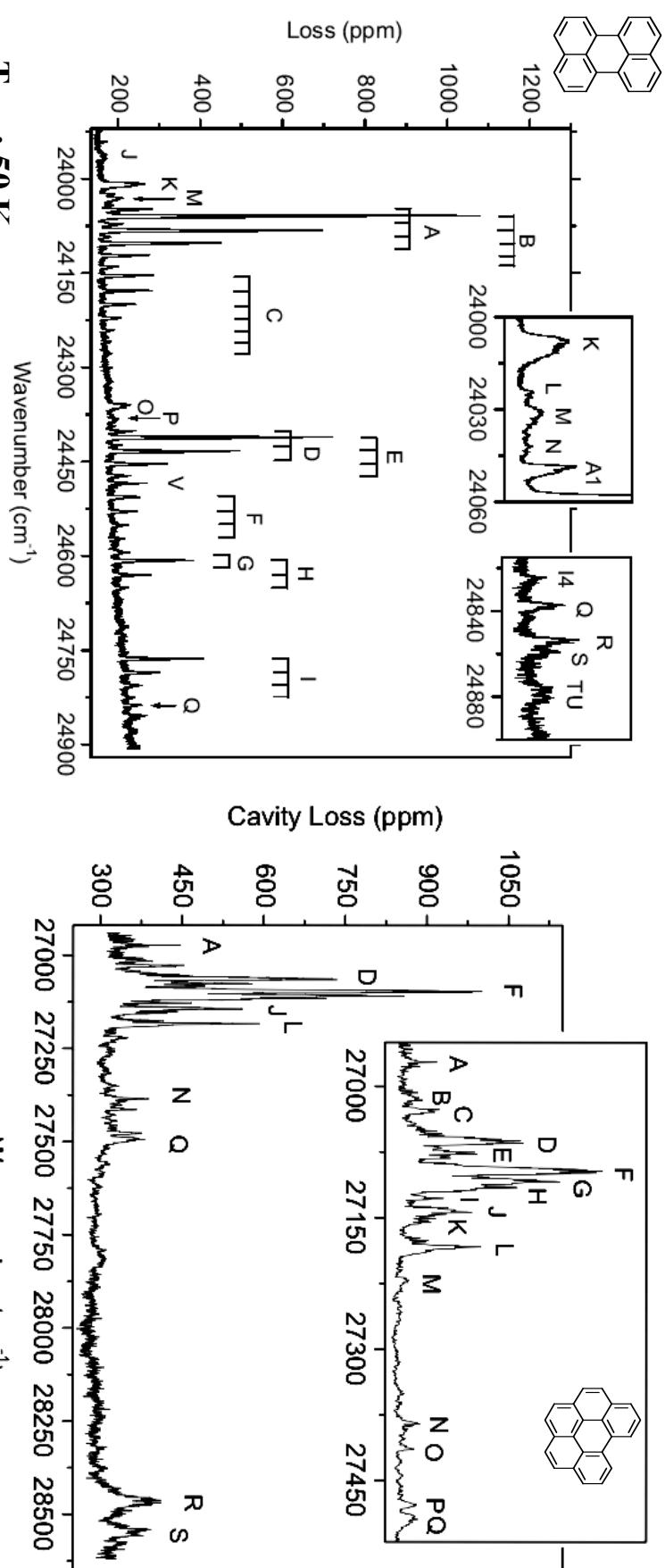
- Diacetylene<sup>+</sup>?
- Plasma product
- H<sub>2</sub>CCCC (I-C<sub>3</sub>H<sub>2</sub>)
- **\*\* Fullerenes**
- C<sub>60</sub>+

**Criteria for Identification of Carrier:**

- 2+ objects
- absent in unreddened stars
- 1+ instrument confirmed stationary (in spec. binary)
- 2+ transitions (preferred)
- Match wavelength + profile

# Electronic Absorption Spectra of Neutral PAHs In the Gas Phase

CRDS - Neutral Perylene ( $C_{20}H_{12}$ ) & Neutral Benzoperylene ( $C_{22}H_{12}$ )



T<sub>ROT</sub>: 50 K.

Range: 4000 – 4200 Å

Range: 3500 – 3700 Å

The vibronic bands of neutral PAHs range between 2 and 10  $\text{cm}^{-1}$ .

### Stellar Data

Star HD	Sp/L	<i>V</i>	<i>B</i> – <i>V</i>	<i>E(B</i> – <i>V</i> )	<i>v</i> sin <i>i</i>	<i>rv</i> <sup>a</sup>
110432	B2pe	5.3	0.26	0.47	200	+7.7
115842	B0.5 Iab	6.02	0.30	0.50	70	+8.7
136239	B2Iae	7.82	0.92	1.08	60	-14.0
144217	B0.5V	2.50	-0.07	0.17	100	-9.1
147165	B1 III	2.90	0.14	0.35	50	-4.4
147889	B2 V	7.90	0.84	1.05	100	-7.2
148184	B2 Ve	4.42	0.28	0.49	100	-10.8
148379	B2Iab	5.32	0.54	0.70	60	-11.3 <sup>b</sup>
149404	O9 Iab	5.48	0.39	0.62	100	+1.7
149757	O9.5V	2.57	0.02	0.29	400	-14.7
151932	WN7	6.48	0.26	0.55		+2.0
152236	B1Iae	4.72	0.48	0.67	60	+2.2
152249	O9.5 Iab	6.47	0.20	0.43	80	+3.7
154368	O9.5 Iab	6.13	0.51	0.74	70	-1.7
154445	B1 V	5.62	0.14	0.37	130	-15.0
170740	B2 V	5.72	0.24	0.45	25	-7.6
163800	O7.5	6.98	0.28	0.57	138	-5.6

### Notes.

<sup>a</sup> *rv* is the heliocentric radial velocity (km s<sup>-1</sup>) of the main component of the interstellar CH 4300.31 Å band.

<sup>b</sup> Mid-position between two components.

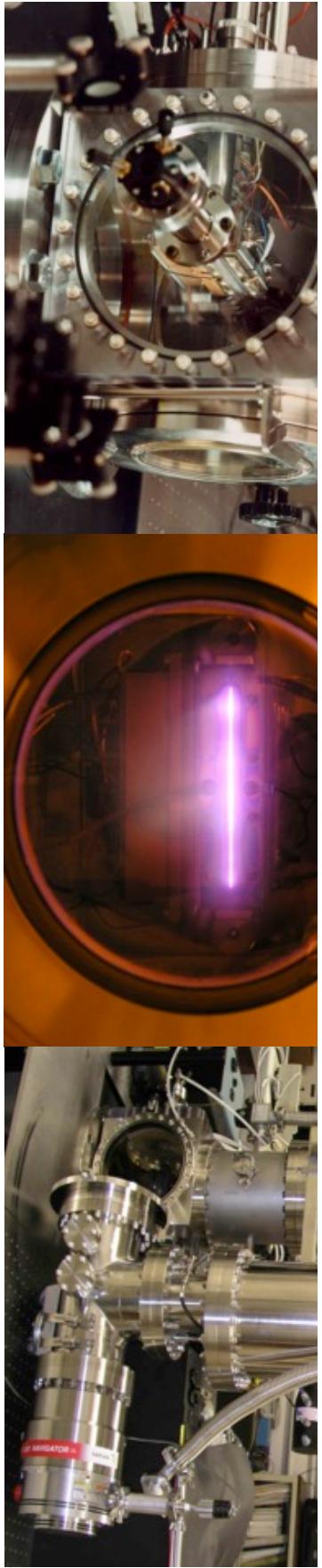
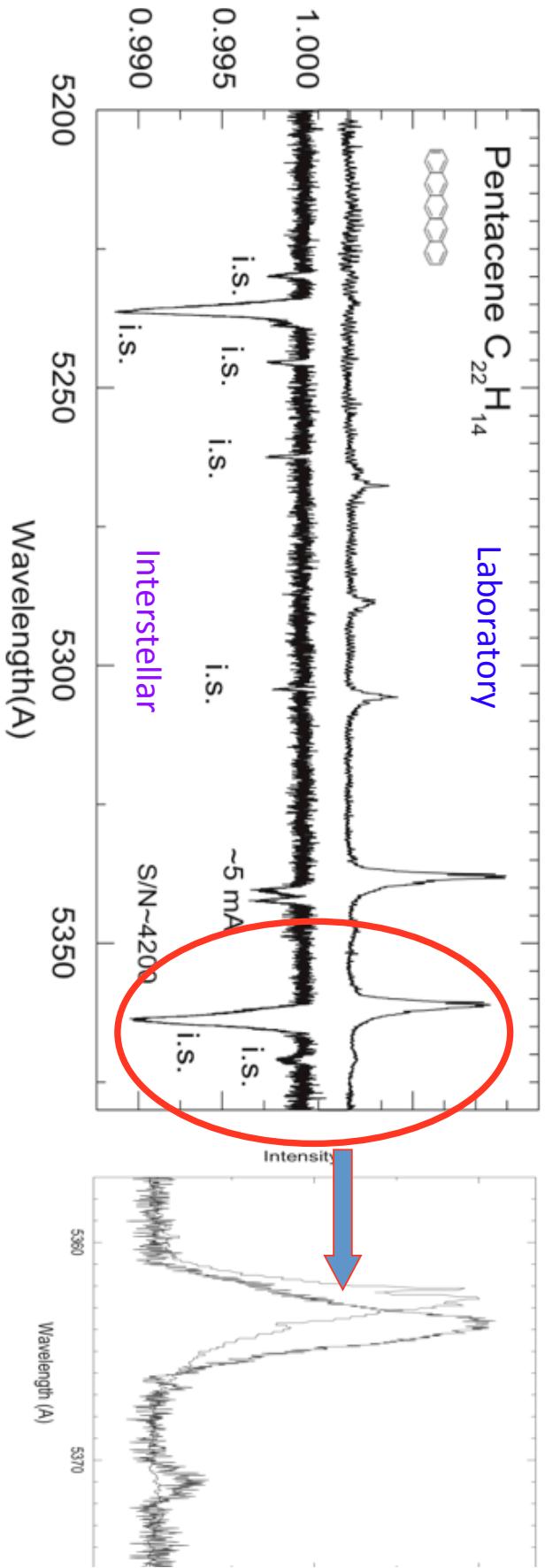
Salama et al. ApJ 2011

Upper Limits of PAHs Abundance Measured in the Spectra of the Individual Program Stars of Table 1 and in the Average Spectrum in the Wavelength Region Corresponding to the Strongest PAH Absorption Feature(s)

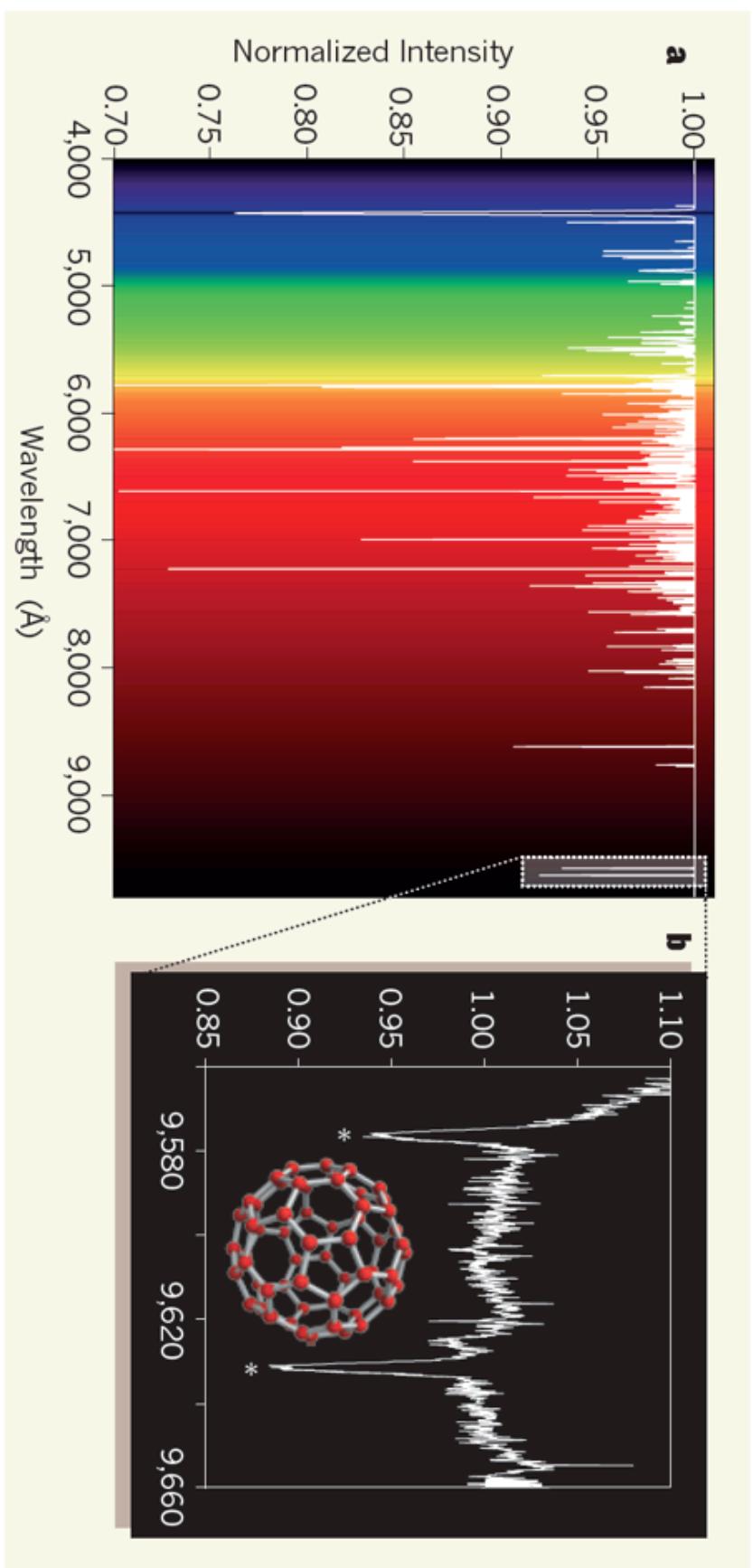
HD	Acenaphthene <sup>a</sup> λ Peak: 3175.0 Å Δλ: 3174.55–3175.52	Benzol[ghi]perylene <sup>b</sup> λ Peak: 3689.4 Å Δλ: 3685.9–3690.9	2-Methylnaphthalene <sup>a</sup> λ Peak: 3152.7 Å Δλ: 3152.2–3153.2	Pentacene <sup>a</sup> λ Peak: 5339.5 Å Δλ: 5339.3–5342.2	Pentacene <sup>a</sup> λ Peak: 5362.8 Å Δλ: 5359.3–5365.0	Perylene <sup>c</sup> λ Peak: 4155.0 Å Δλ: 4154.4–4155.7
	$f = 2.2\text{E}(-3)^d$	$f = 1.4\text{E}(-1)^d$	$f = 2.3\text{E}(-3)^d$	$f = 4.1\text{E}(-1)^d$	$f = 4.1\text{E}(-1)^d$	$f = 2.4\text{E}(-1)^d$
110432	330.0.0027 1.7290E13	840.0.0053 0.31295E12	410.0.0021 1.04052E13	1170.0.0050 0.48221E12	1100.0.0077 1.27304E12	760.0.0014 0.38276E11
115842	330.0.0024 1.7290E13	880.0.0046 0.27162E12	470.0.0020 0.99098E13	940.0.0132 1.27304E12	1280.0.0052 0.50150E12	900.0.014 0.38276E11
136239						
144217	500.0.0018 1.7290E13	1100.0.0044 0.25981E12	640.0.014 0.69368E13	1130.0.0073 0.70403E12	1100.0.0385 0.36681E12	970.0.0012 0.32808E11
147165	300.0.0028 1.57650E13	700.0.0060 0.35428E12	390.0.0022 1.09008E13	1100.0.0048 0.46295E12	1090.0.0073 0.66979E12	920.0.0014 0.38276E11
148184	280.0.0031 1.22052E13	700.0.0060 0.35428E12	350.0.0024 1.18917E13	1000.0.0110 1.06087E12	1750.0.0311 0.29736E12	980.0.0011 0.30074E11
148379						
149404	210.0.0037 1.93248E13	640.0.0068 0.40152E12	280.0.030 1.48647E13	1130.0.0073 0.70403E12	1390.0.0203 0.19409E12	840.0.0013 0.35545E11
149757	410.0.0021 1.18818E13	900.0.0044 0.25981E12	490.0.0019 0.94142E13	1100.0.0048 0.46295E12	1970.0.0073 0.66979E12	930.0.0012 0.32808E11
151932	260.0.0038 1.88163E13	600.0.0077 0.45466E12	370.0.0023 1.13962E13	1090.0.0073 0.70403E12	1600.0.0247 0.23616E12	740.0.0013 0.35542E11
152236	350.0.0024 1.62775E13	800.0.0056 0.30666E12	440.0.0020 0.99098E13	1080.0.0070 0.67509E12	2050.0.0130 0.12453E12	1060.0.0012 0.332808E11
152249	260.0.0031 1.42394E13	730.0.0057 0.33657E12	350.0.026 1.28827E13	1160.0.0075 0.72332E12	1250.0.0124 0.11856E12	890.0.0013 0.35542E11
154368	240.0.0034 0.91539E13	580.0.0075 0.44285E12	290.0.033 1.63511E13	1160.0.0075 0.72332E12	1250.0.0124 0.11856E12	760.0.0014 0.38276E11
154445	250.0.0034 1.22052E13	660.0.0076 0.44876E12	430.0.024 1.18917E13	1300.0.0060 0.57865E12	1400.0.0208 0.19887E12	710.0.0016 0.43744E11
170740	260.0.0034 1.37308E13	560.0.0080 0.47238E12	330.0.027 1.33792E13	1400.0.0050 0.48221E12	4300.0.0236 0.22565E12	780.0.0014 0.38276E11
average	1000.0.0006 0.30513E13	2500.0.0021 0.12399E12	930.0.010 0.49549E13	4100.0.0050 0.48221E12	2100.0.0007 0.19138E11	
HD	Pheanthrene <sup>a</sup> λ Peak: 3408.4 Å Δλ: 3407.7–3409.1	Pyrene <sup>a</sup> λ Peak: 3205.8 Å Δλ: 3199.0–3215.2	C <sub>42</sub> H <sub>18</sub> <sup>e</sup> λ Peak: 4264.1 Å Δλ: 4263.35–4264.85	C <sub>42</sub> H <sub>18</sub> <sup>e</sup> λ Peak: 4335.2 Å Δλ: 4334.45–4335.95	Benzofluorene <sup>f</sup> λ Peak: 3345.1 Å Δλ: 3345.45–3345.2	Anthracene <sup>g</sup> λ Peak: 3611.8 Å Δλ: 3611.6–3612.0
	$f = 2.3\text{E}(-2)^d$	$f = 1.6\text{E}(-1)^d$	$f = 8.5\text{E}(-4)$	$f = 2.4\text{E}(-4)$	$f = 2.4\text{E}(-2)$	$f = 1.0\text{E}(-2)$
110432	830.0.0015 0.63444E12	400.0.0359 0.24609E13	950.0.0013 9.46039E13	660.0.0020 0.492834E14	650.0.0003 1.26232E12	860.0.0004 3.46490E12
115842	845.0.0017 0.71903E12	430.0.0315 0.21593E13	950.0.0015 1.09158E14	610.0.0022 5.45216E14	560.0.0003 1.26232E12	780.0.0004 3.46490E12
136239						
144217	1250.0.0009 0.38066E12	570.0.0250 0.17137E13	520.0.0076 1.89208E14	315.0.0041 1.01031E15	180.0.0012 5.04929E12	330.0.0011 9.52848E12
144217						
147165						
148184	870.0.0015 0.63444E12					
148379						
149404	760.0.0017 0.71903E12	300.0.0459 0.31464E13	480.0.0311 0.21319E13	1030.0.0014 1.01881E14	1110.0.0012 8.73267E13	1220.0.0002 8.41548E11
149757	1100.0.0013 0.54985E12					
151932	840.0.0014 0.59214E12	370.0.0352 0.24129E13	910.0.0015 1.09158E14	50.0.0022 3.30691E14	630.0.0023 1.67355E14	670.0.0004 2.75918E12
152236	1020.0.0012 0.59755E12	420.0.0331 0.22690E13	1210.0.0011 8.00495E13	500.0.0024 3.60754E14	500.0.0024 3.60754E14	220.0.0009 6.20815E12
152249	910.0.0013 0.54985E12	370.0.0367 0.25158E13	880.0.0015 1.09158E14	59.0.0021 3.15660E14	440.0.0003 2.06938E12	670.0.0005 4.33113E12
154368	550.0.0024 1.01511E12	320.0.0414 0.28379E13	820.0.0017 8.23758E13	510.0.0026 3.90817E14	510.0.0026 3.90817E14	780.0.0004 3.46490E12
154445	880.0.0014 0.59214E12	380.0.0380 0.26049E13	930.0.0014 6.78392E13	500.0.0025 3.75786E14	570.0.0003 2.06938E12	580.0.0005 4.33113E12
170740	665.0.0019 0.80362E12	320.0.0425 0.29133E13	850.0.0015 1.09158E14	500.0.0027 4.05848E14	380.0.0005 3.44897E12	1730.0.0003 2.59868E12
average	2250.0.0005 0.21148E12	1000.0.0141 0.09665E13	2790.0.0011 8.00495E13	2000.0.0010 1.50314E14	1900.0.001 6.89793E11	

Notes. Signal-to-noise ratio (S/N), equivalent width (EW in Å), and corresponding column density (c.d. in cm<sup>-2</sup>) values are given for each PAH band. Δλ represents the wavelength range that was used to derive upper limits for the column densities of the strongest features.

<sup>a</sup> This work; <sup>b</sup> Tan & Salama (2005b); <sup>c</sup> Tan & Salama (2005a); <sup>d</sup> Tan et al. (2010); <sup>e</sup> Kokkin et al. (2008); <sup>f</sup> Staicu et al. (2006); <sup>g</sup> Hermine (1994).



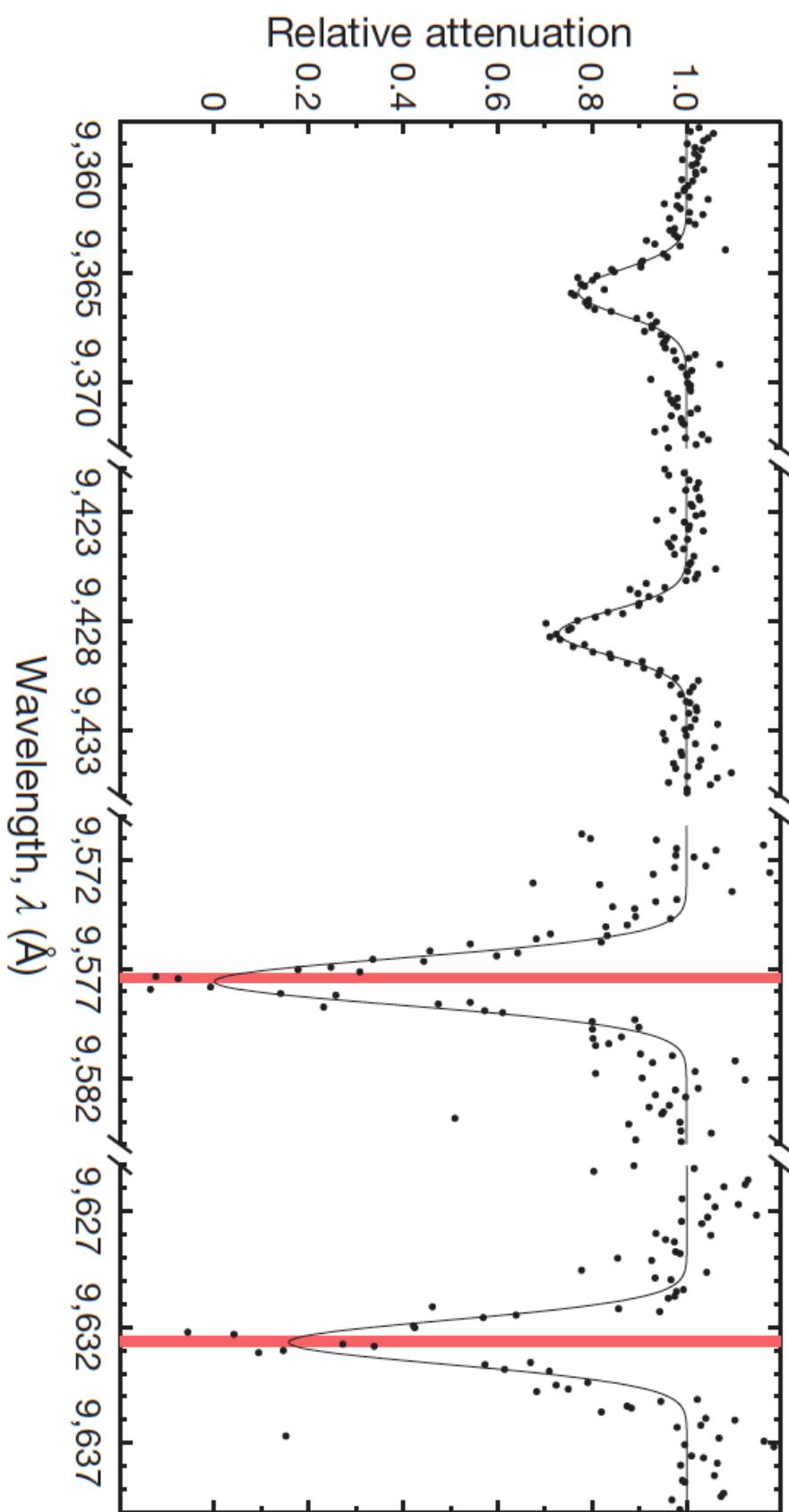
## Fullerene solves an interstellar puzzle



Laboratory confirmation of C<sub>60</sub><sup>+</sup> as the carrier of two DIBs discovered in 1994

Ehrenfreund and Foing, Nature 523, 2015  
E. K. Campbell, M. Holz, D. Gerlich & J. P. Maier, Nature, 523, 2015

## Laboratory confirmation of C<sub>60</sub><sup>+</sup> as the carrier of two DIBs



E. K. Campbell, M. Holz, D. Gerlich & J. P. Maier, Nature, 523, 2015

## Open Questions & Perspective

**Carbon molecules** are currently considered the most promising candidates for identifying the DIB carrier(s).

**Alternative candidate carriers** can not be dismissed, although the carriers are very likely **large carbonaceous gas phase molecules** that are **stable, UV resistant, but sensitive to the local cloud conditions**, in particular to the **UV radiation field**.

**Multi-object** line-of-sight high-resolution studies of **Local Group galaxies** are needed (EDIBLES).

**Spectroscopic signatures** in both the **UV** and the **NIR** are predicted for many (neutral/cation) **PAHs**.

Explore new environments other than diffuse/translucent ISM → **Circumstellar envelopes of evolved stars** ("PAH" factories)?

**Observational verification** of proposed candidates! e.g. **naphthalene+** detected in only 1 (peculiar) sightline.

**DIB correlations:** intrinsic scatter or measurement uncertainties?

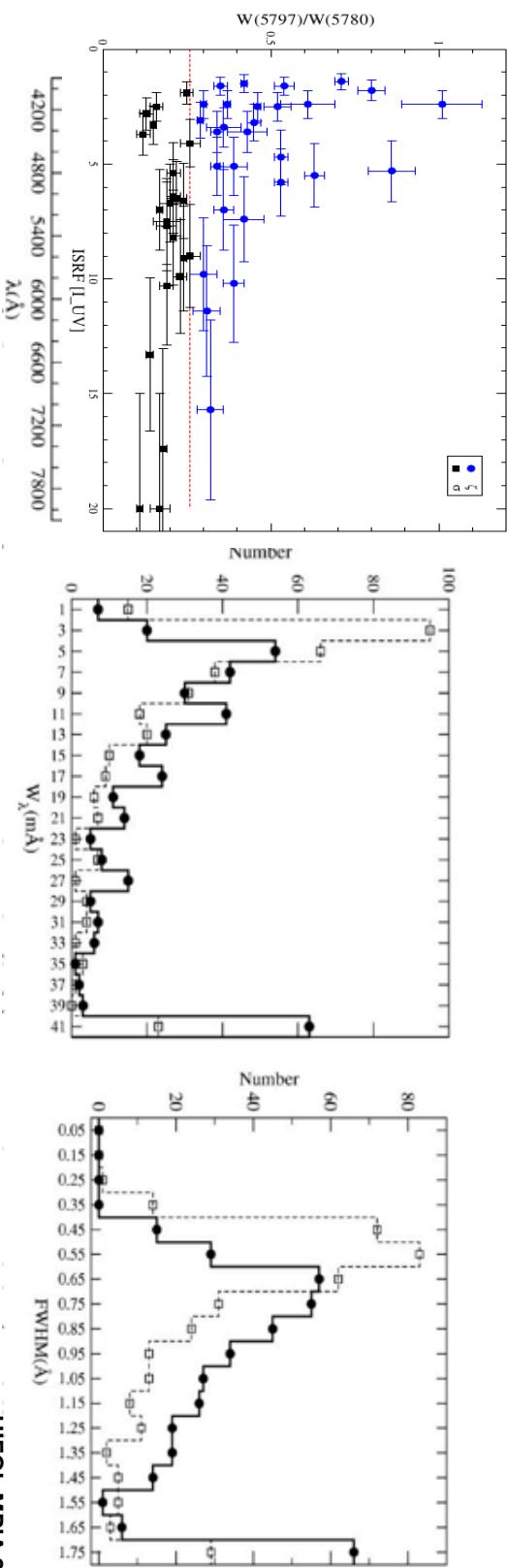
# EDIBLES: ESO DIB Large Exploration Survey

High-resolution, high-precision spectroscopic  
UV/optical survey (280 hours) of interstellar  
clouds with UVES@VLT.

## Goals:

- \* Chemical make up: DIB carriers – ISM elemental abundances: depletion.
- \* Relation weak-strong DIBs: sequencing of 100+ DIBs.
- \* Effective DIB measurements to probe physical parameters.
- \* Identify physical-chemical parameters that influence DIB properties (PDR chemistry models).

$R \sim 120.000$
$S/N \sim 500-1000$
# ~ 150
$\lambda \sim 3300-10000 \text{ \AA}$



Astrophysics:

Energy budget and signature of aromatic carbon molecules

**PAHs & Grain formation**

Planetary:

Titan's atmosphere (haze)

ISS:

Exposure experiments on complex organic molecules

## Sources of PAH Formation:

Outflows of carbon stars –

→ AGB stars are the dominant source of PAHs

- Lifetime of PAHs in ISM long enough ( $\sim 10^8$  years)
- PAH mixing into the ISM not complete

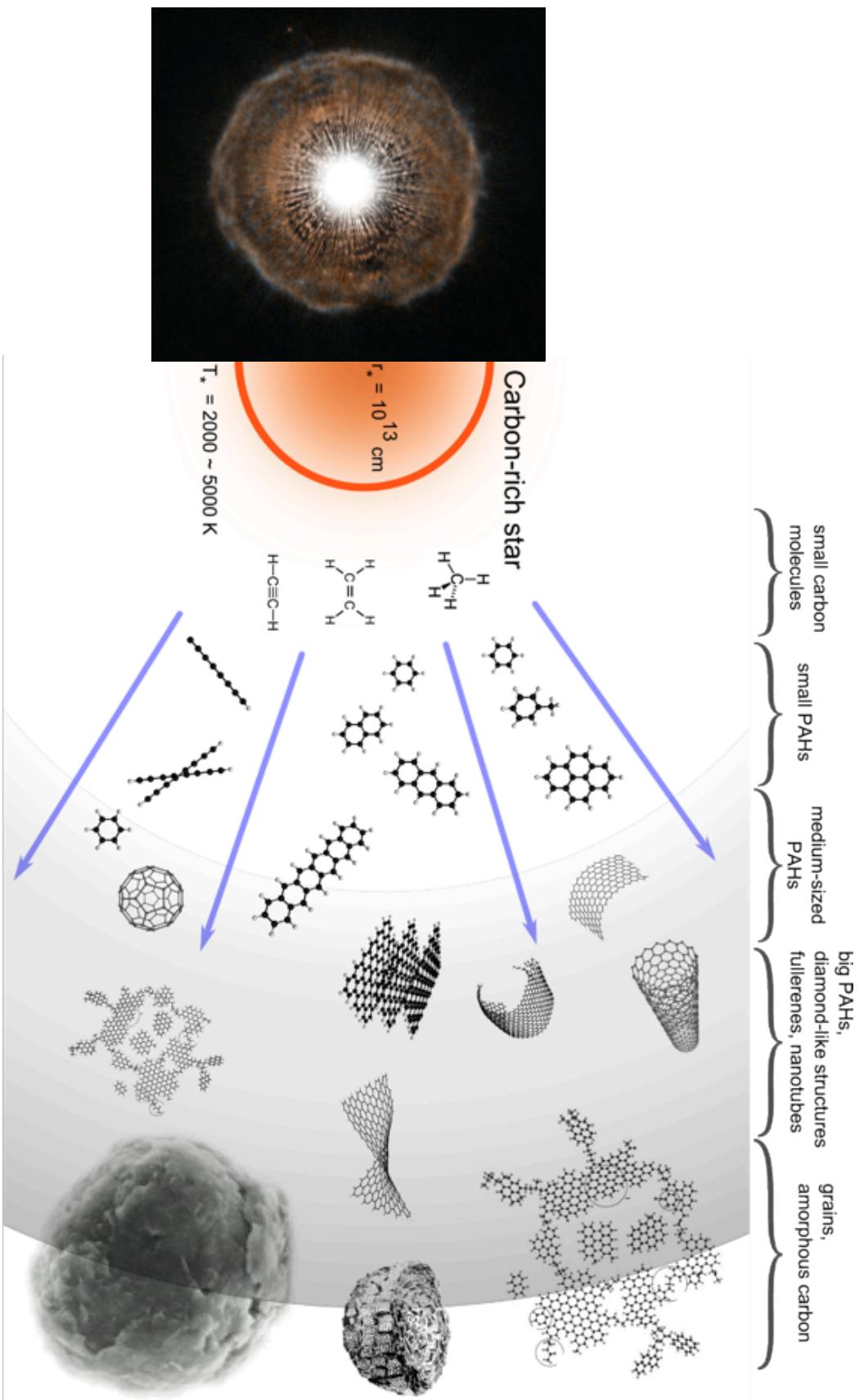
Other proposed mechanisms:

PAHs formed in UV photoprocessing of IS dust mantles

PAHs are the product of grain fracturing in shock waves

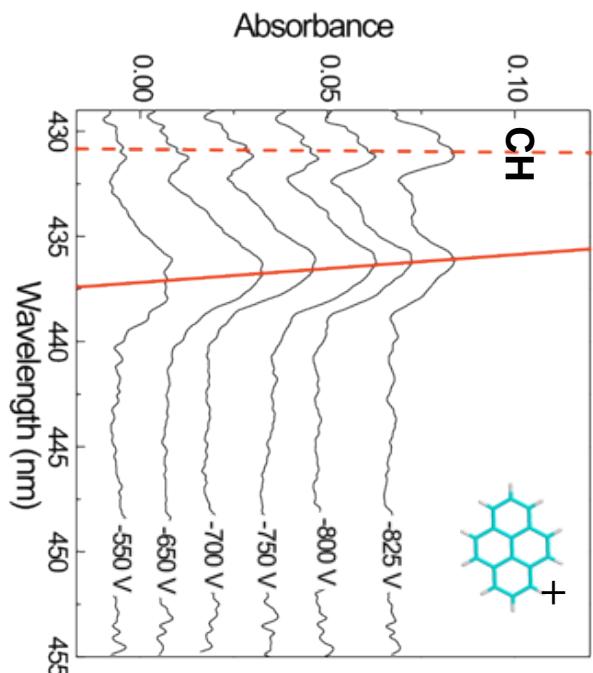
*In situ* formation of PAHs within dense IS clouds  
(ion-molecule reactions)

# Carbon in the Galaxy – Project 1 Investigations



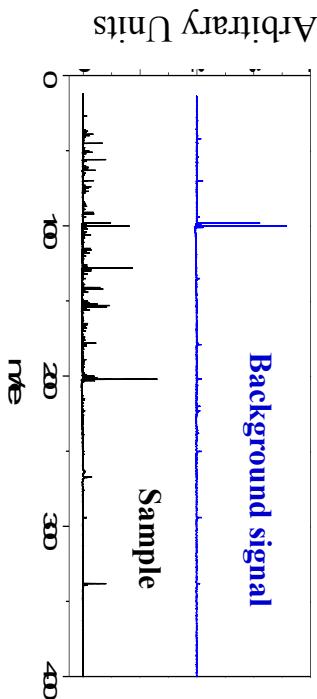
## Monitoring fragment formation & detection of carbon particles

### Spectrum of Pyrene ( $C_{16}H_{10}$ ) seeded plasma versus discharge energy



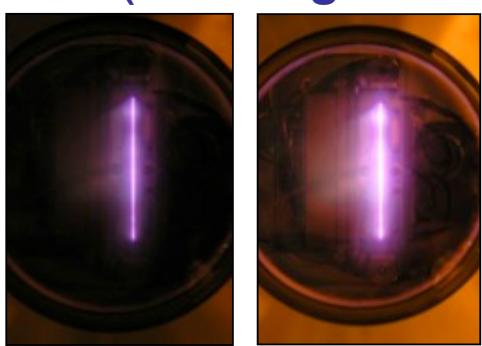
Mass Spectrometry studies confirm the formation of larger particles: LDMS of soot formed from  $C_{10}H_8$  (128 amu) precursor.

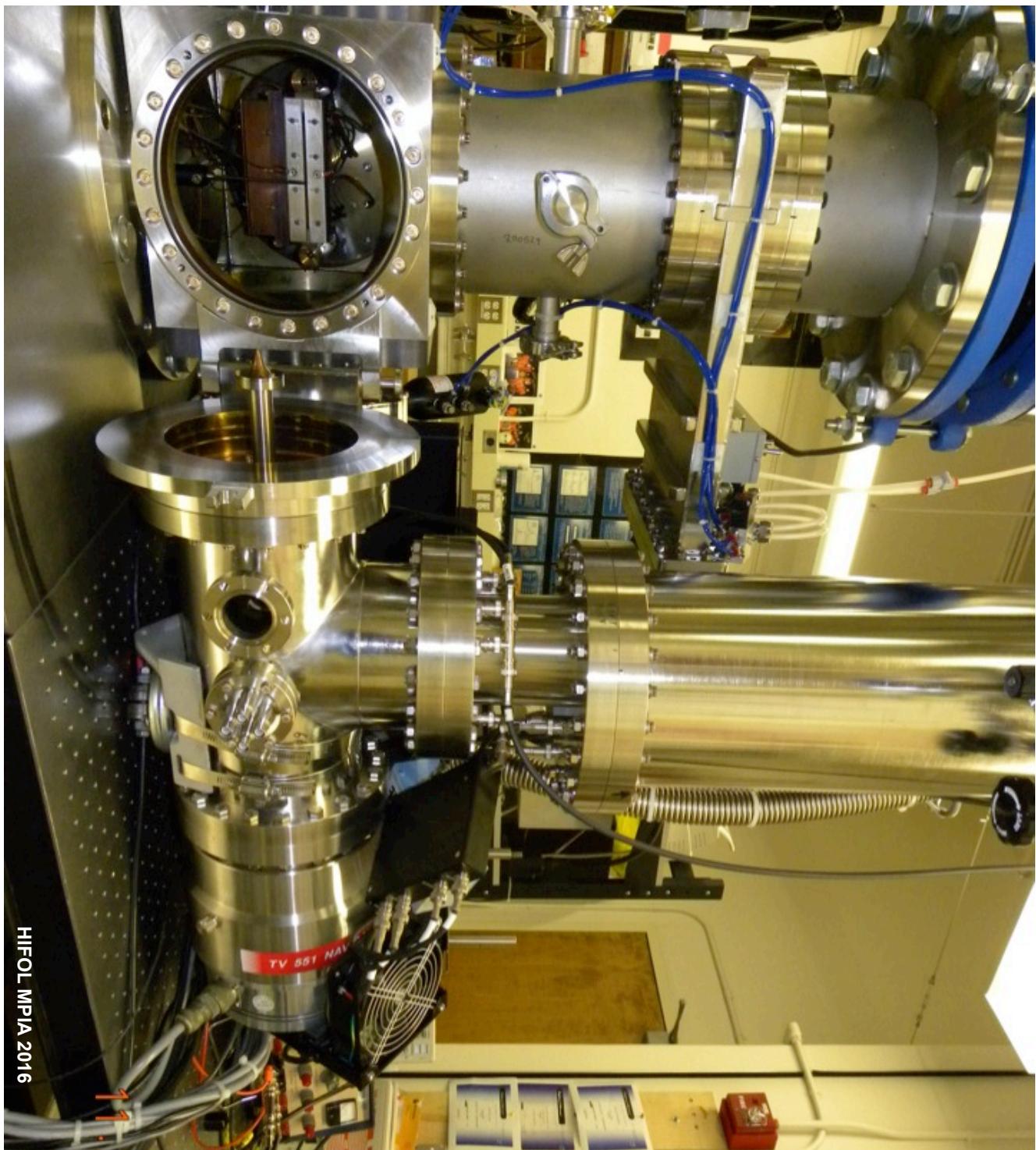
Observation of soot on the electrodes →



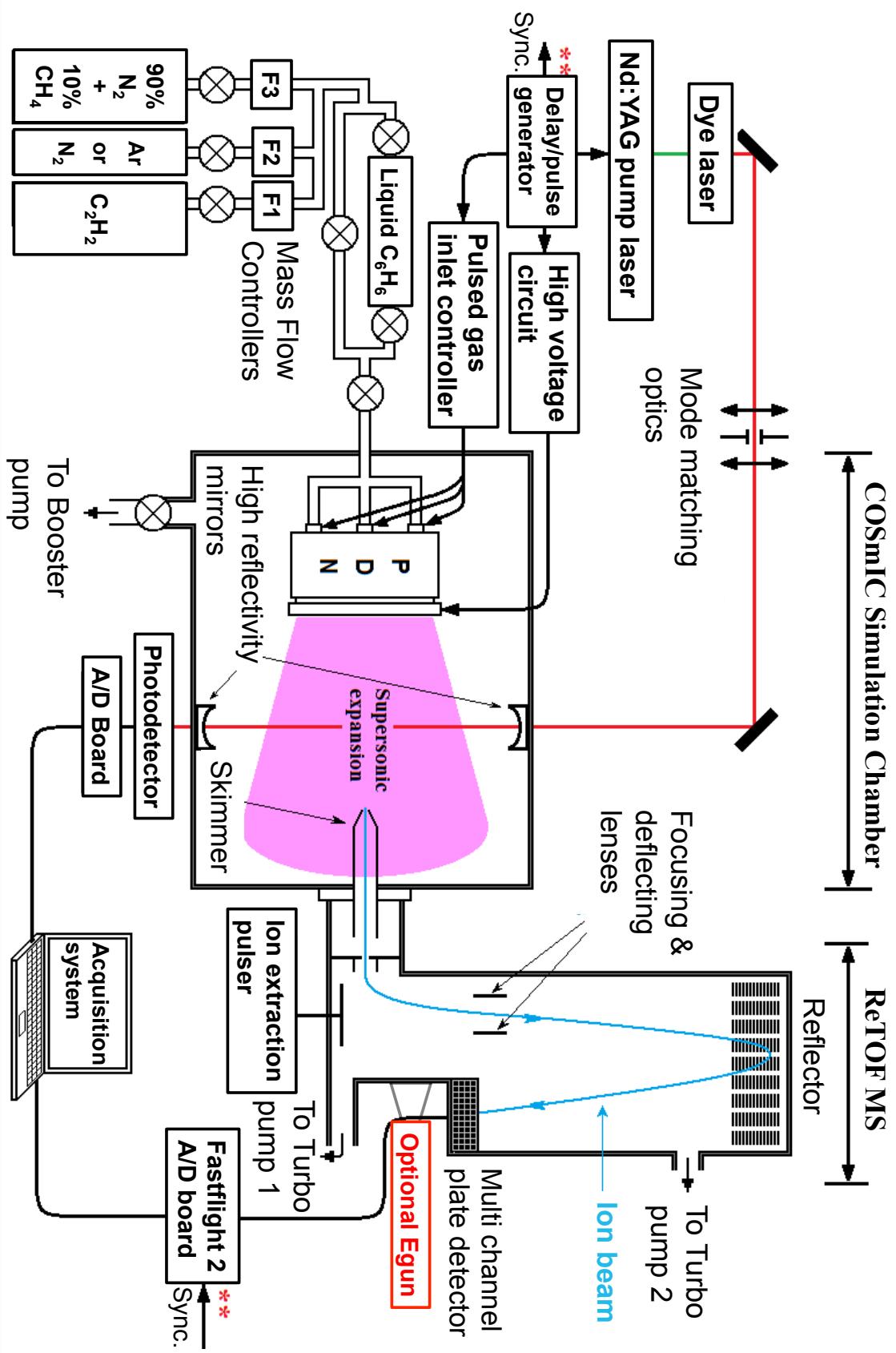
$\mu L^2 MS$  of soot formed from  $C_{12}H_{10}$  (154 amu) precursor

Plasma energy  
(discharge voltage)





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



Ricketts et al., 2011, Int. J. Mass Spectrom. Ion Processes, 300, 26

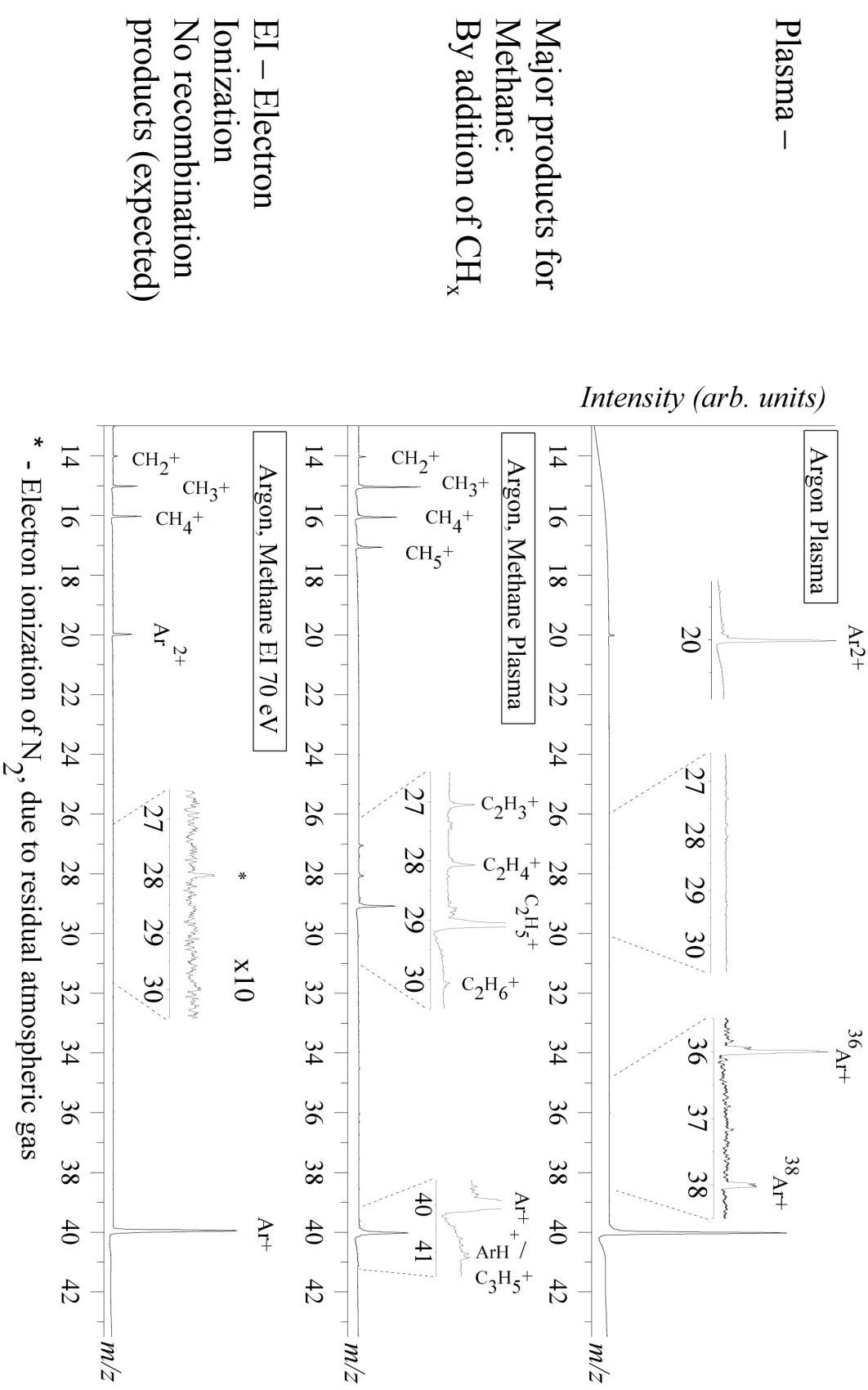
# ReTOF-MS Results - Summary of Experiments

## Precursor category and types

Hydrocarbons		Mixtures of Precursors
Alkanes		Benzene Analogs & Hydrocarbons
Methane (CH <sub>4</sub> )		PAH & Hydrocarbons
Ethane (C <sub>2</sub> H <sub>6</sub> )		Naphthalene (C <sub>10</sub> H <sub>8</sub> ) &
Alkenes		Methane (CH <sub>4</sub> )
Ethylene (C <sub>2</sub> H <sub>4</sub> )		Ethane (C <sub>2</sub> H <sub>6</sub> )
Alkynes		Ethylene (C <sub>2</sub> H <sub>4</sub> )
Acetylene (C <sub>2</sub> H <sub>2</sub> )		Acetylene (C <sub>2</sub> H <sub>2</sub> )
Aromatics		1-Methylnaphthalene (C <sub>10</sub> H <sub>7</sub> CH <sub>3</sub> )
Benzene (C <sub>6</sub> H <sub>6</sub> )		Methane (CH <sub>4</sub> )
Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )		Ethane (C <sub>2</sub> H <sub>6</sub> )
Pyridine (C <sub>5</sub> H <sub>5</sub> N)		Ethylene (C <sub>2</sub> H <sub>4</sub> )
<b>Polycyclic Aromatic Hydrocarbons</b>		Acetylene (C <sub>2</sub> H <sub>2</sub> )
Homogenous PAHs		Acenaphthene (C <sub>12</sub> H <sub>10</sub> ) &
Naphthalene (C <sub>10</sub> H <sub>8</sub> )		Methane (CH <sub>4</sub> )
1-Methylnaphthalene (C <sub>10</sub> H <sub>7</sub> CH <sub>3</sub> )		Ethane (C <sub>2</sub> H <sub>6</sub> )
Acenaphthene (C <sub>12</sub> H <sub>10</sub> )		Ethylene (C <sub>2</sub> H <sub>4</sub> )
Heterogeneous PAHs		Acetylene (C <sub>2</sub> H <sub>2</sub> )
Quinoline (C <sub>9</sub> H <sub>7</sub> N)		Quinoline (C <sub>9</sub> H <sub>7</sub> N) &
2,3-Benzofuran (C <sub>8</sub> H <sub>6</sub> O)		Acetylene (C <sub>2</sub> H <sub>2</sub> )
Thianaphthene (C <sub>8</sub> H <sub>6</sub> S)		2,3-Benzofuran (C <sub>8</sub> H <sub>6</sub> O) &
		Acetylene (C <sub>2</sub> H <sub>2</sub> )
		Thianaphthene (C <sub>8</sub> H <sub>6</sub> S) &
		Acetylene (C <sub>2</sub> H <sub>2</sub> )

# ReTOF-MS Results – Hydrocarbons: Methane

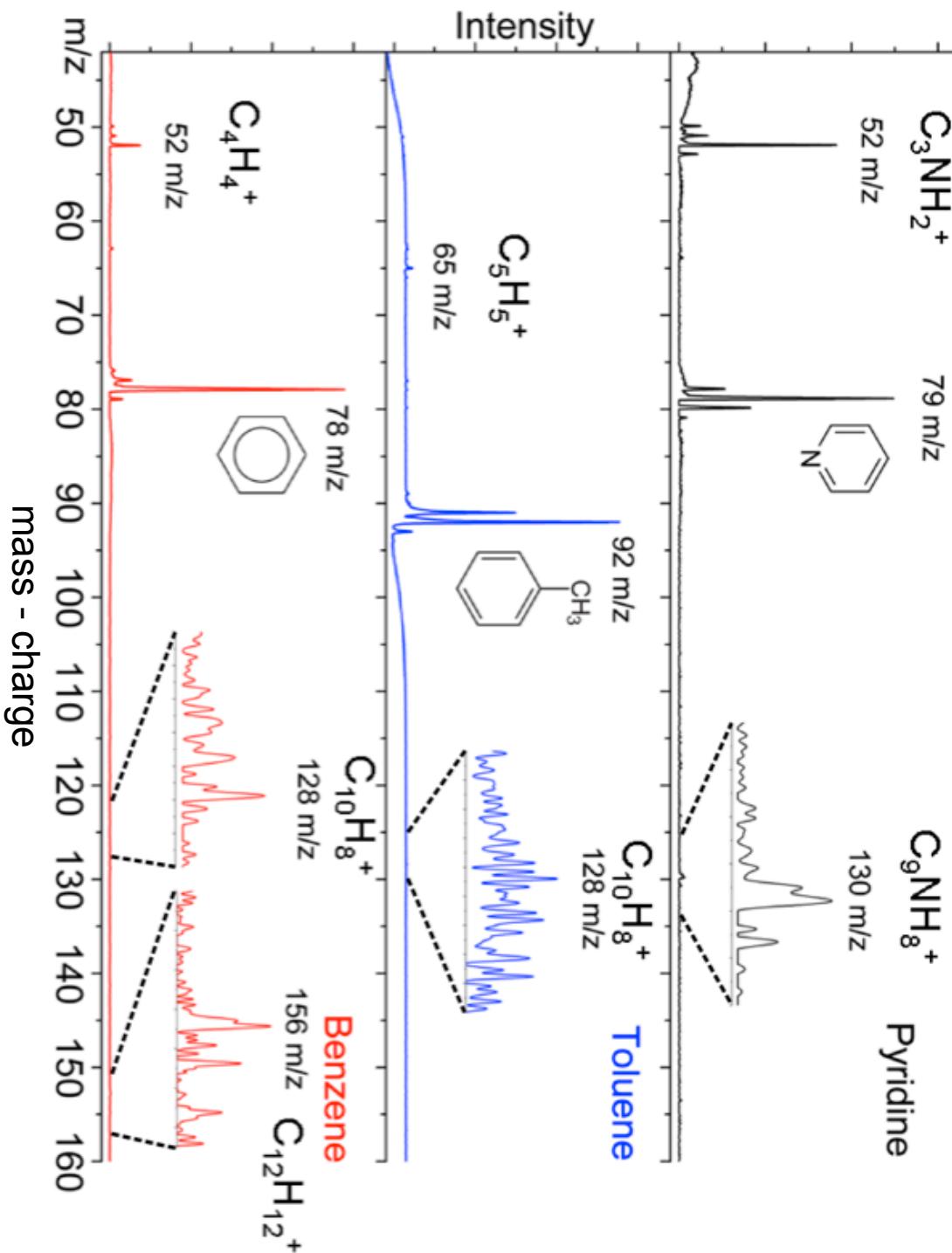
## *Comparison of Mass Spectra between ionization types*



\* - Electron ionization of  $\text{N}_2$ , due to residual atmospheric gas

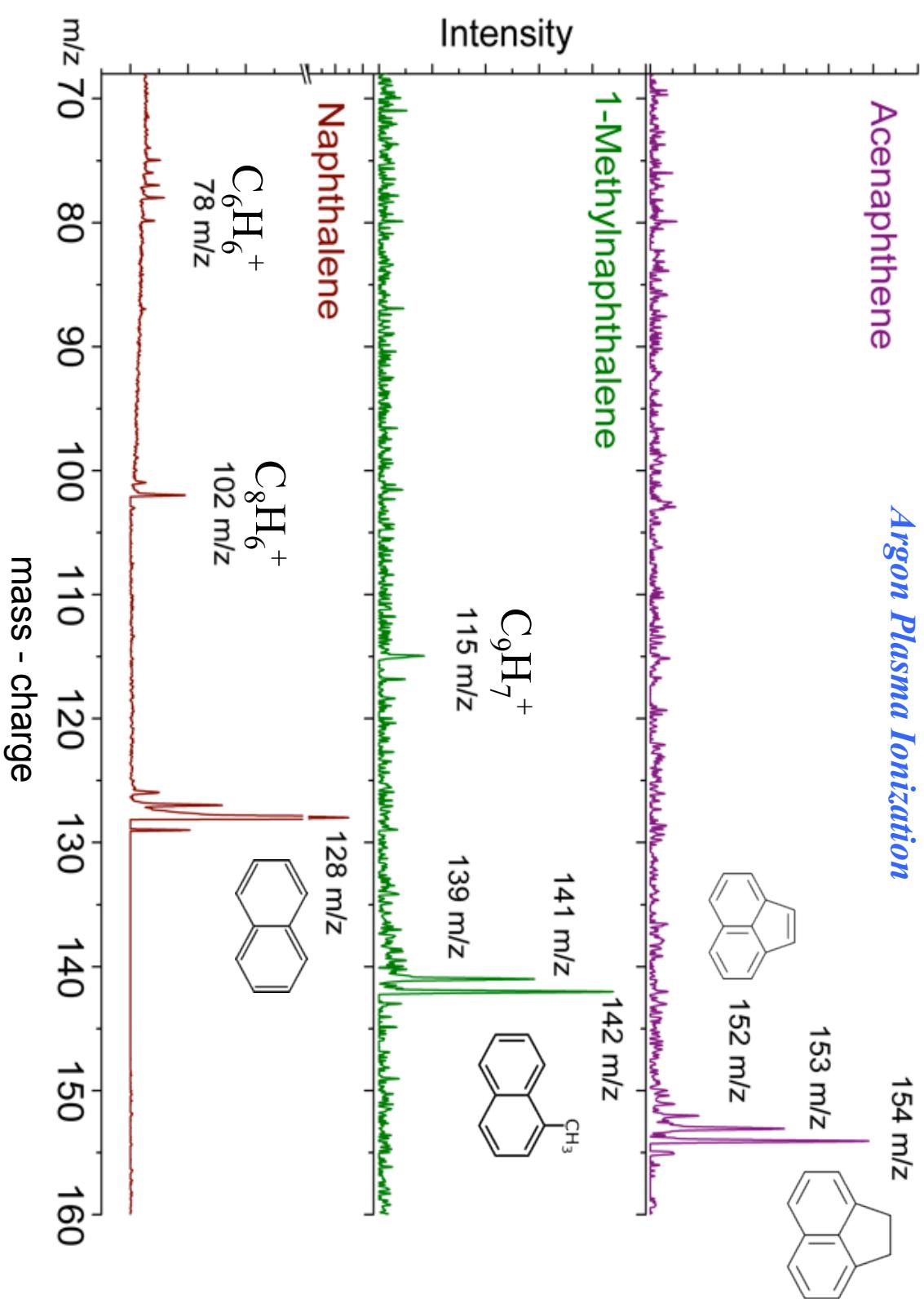
# ReTOF-MS Results – Single Ring Aromatics

*Argon Plasma Ionization*



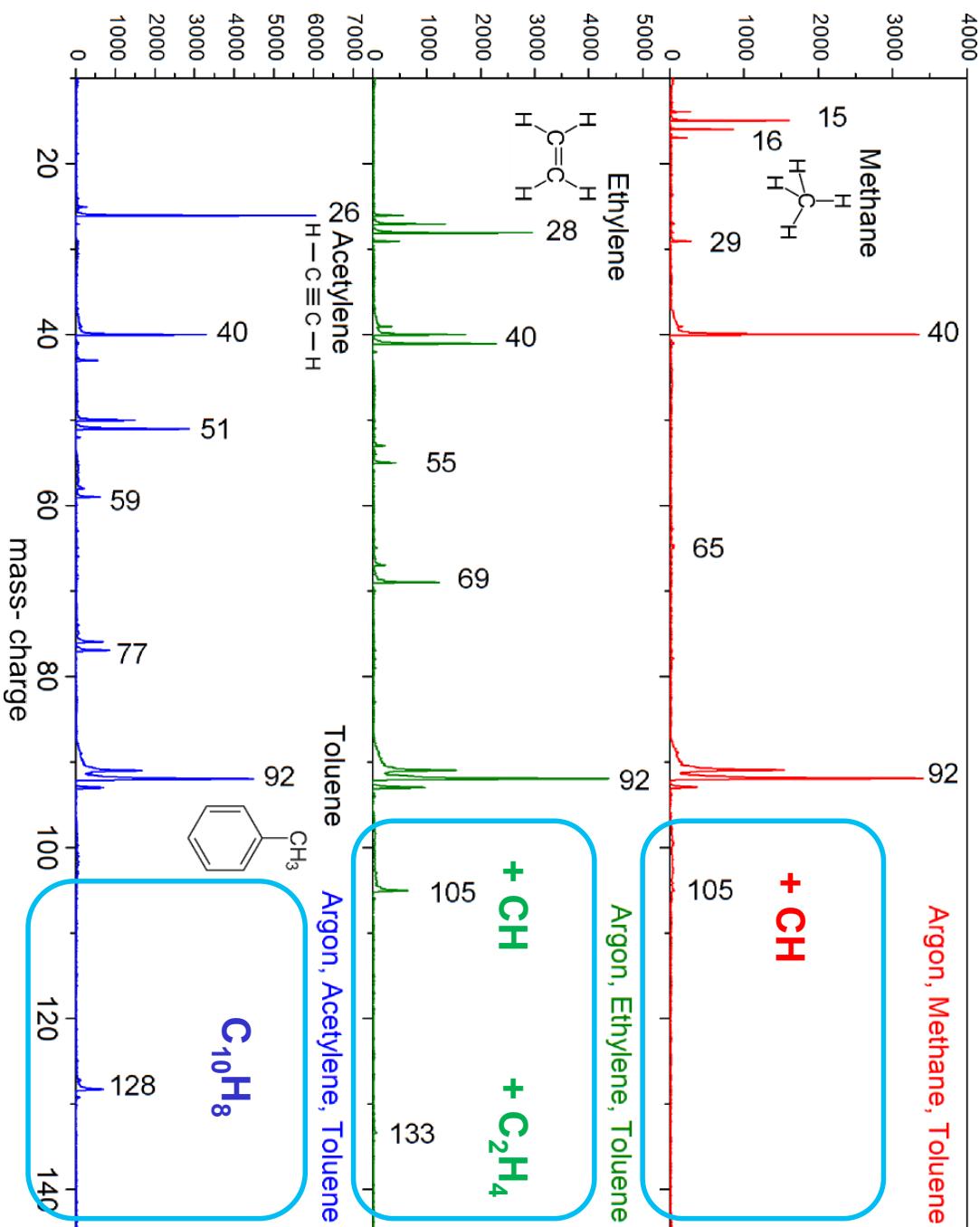
# ReTOF-MS Results – Homogeneous PAHs

*Argon Plasma Ionization*



# ReTOF-MS Results – Mixtures: Toluene/Hydrocarbons

*Distinct chemistry occurs with each different hydrocarbon starting compound*



# ReTOF-MS Summary

## *Hydrocarbons*

- Methane, Ethane, Ethylene show sequential  $\text{CH}_x$  growth
- Acetylene major growth involves  $\text{C}_2$  groups
- Acetylene experiments show growth up to  $\text{C}_6\text{H}_5$  ions

## *Single-ring aromatics*

- Benzene, toluene, pyridine all show recombination product ions
- Benzene forms ions  $\text{C}_{10}\text{H}_8^+$  (128 m/z) and  $\text{C}_{12}\text{H}_{12}^+$  (156 m/z)
- Toluene also forms  $\text{C}_{10}\text{H}_8^+$  (128 m/z)
- Pyridine has an analogous ion at 130 m/z,  $\text{C}_9\text{H}_8\text{N}^+$

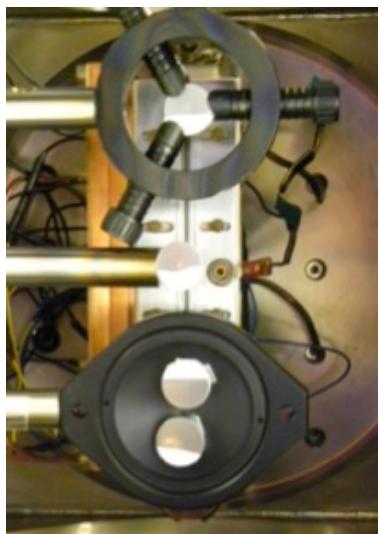
## *PAHs*

- 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.

# Formation of carbon grain analogs in CO SmIC



Characterization of soot nanoparticles and micrograins from the plasma experiments with SEM (Hitachi S4800), x80k – 200k magnification.

Precursors:

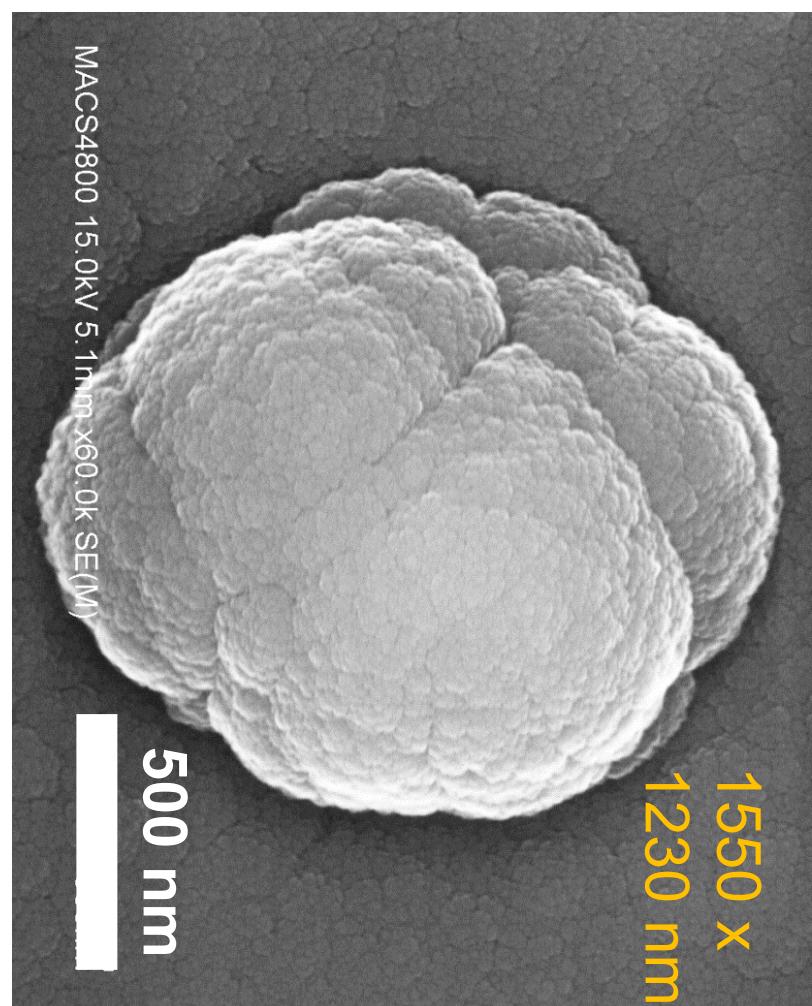
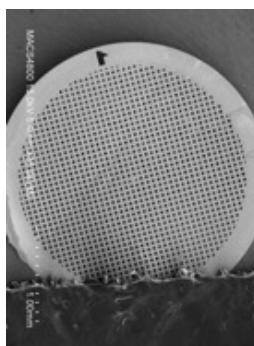
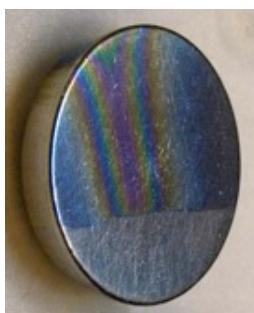
Ar-Methane ( $\text{CH}_4$ )

Ar-Acetylene ( $\text{C}_2\text{H}_2$ )

Ar-Methane-Acetylene

Substrates:

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



~ 1.5  $\mu\text{m}$  aggregate of nanograins produced from HC precursors

### Astrophysics:

- Energy budget and signature of aromatic carbon molecules
- Grain formation

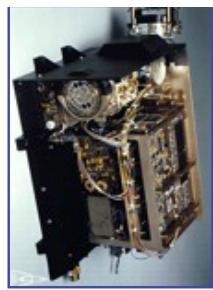
### Planetary:

- **Titan's atmosphere (haze)**

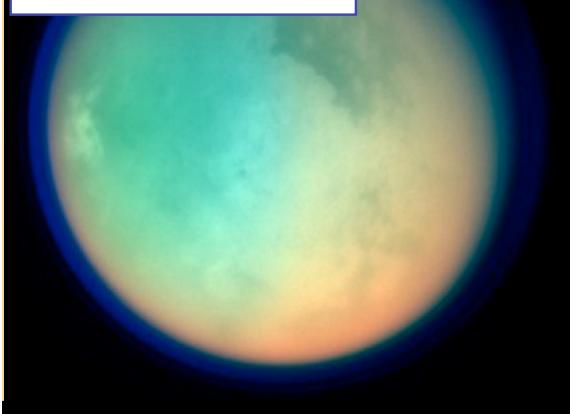
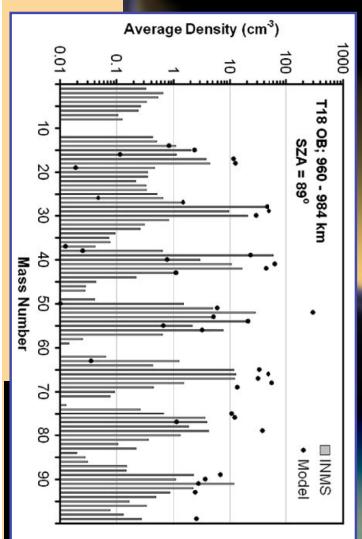
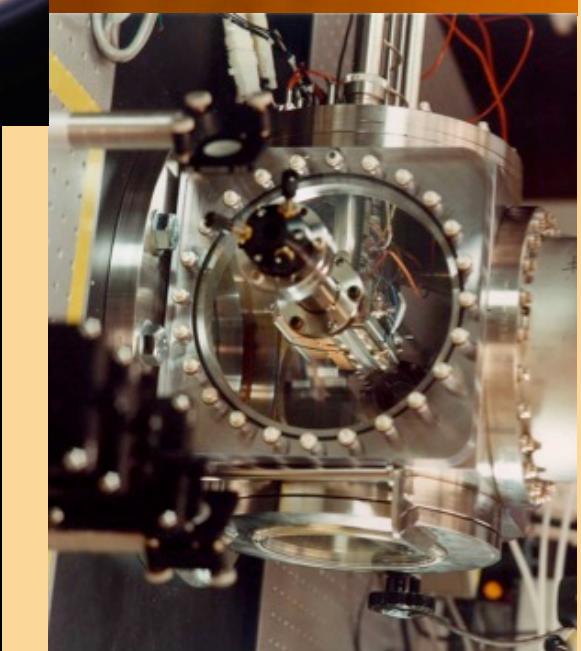
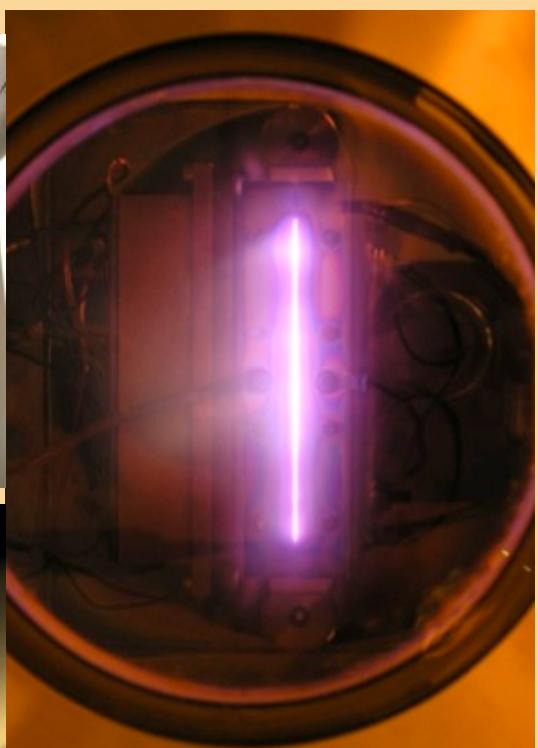
### ISS:

- Exposure experiments on complex organic molecules

# Formation of Carbon Aerosols on Titan



Ion Neutral Mass  
Spectrometer  
(INMS) - Cassini.



# Motivation: Titan's atmospheric chemistry

Major components:

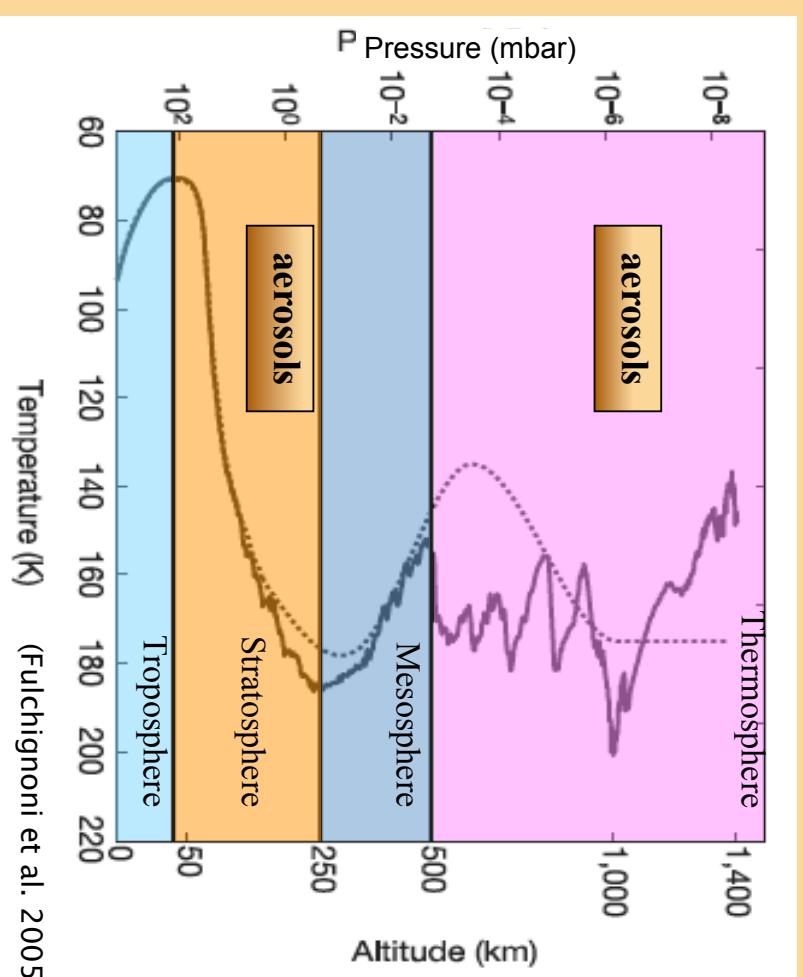
$\text{N}_2$  (95-99%)

$\text{CH}_4$  (2-5%)



**Complex organic chemistry**

Atmospheric temperatures: **70 K < T < 180 K**



Complex molecules??



Haze/Condensates

Titan's Surface

# Motivation: Titan's atmospheric chemistry

Major components:  $\text{N}_2$  (94-98%)  
 $\text{CH}_4$  (1.8-6%)



Complex organic chemistry



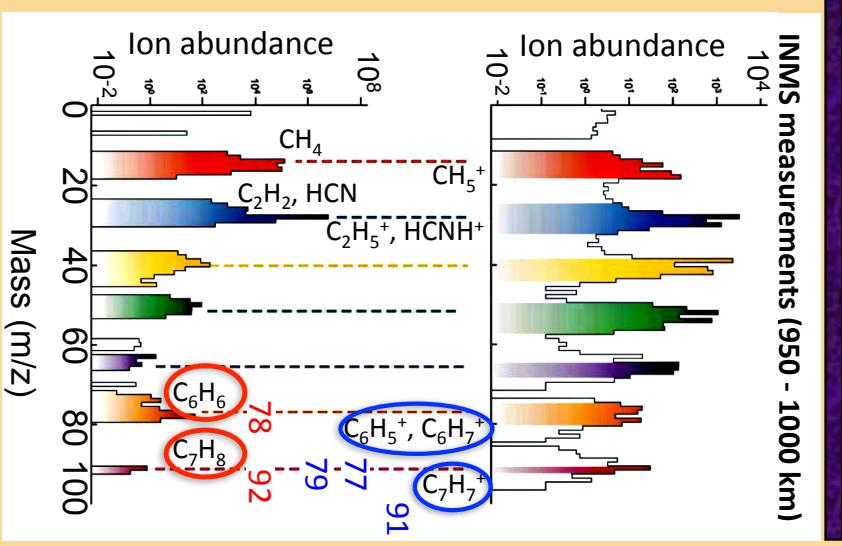
Atmospheric temperatures:  $70 \text{ K} < T < 180 \text{ K}$

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)

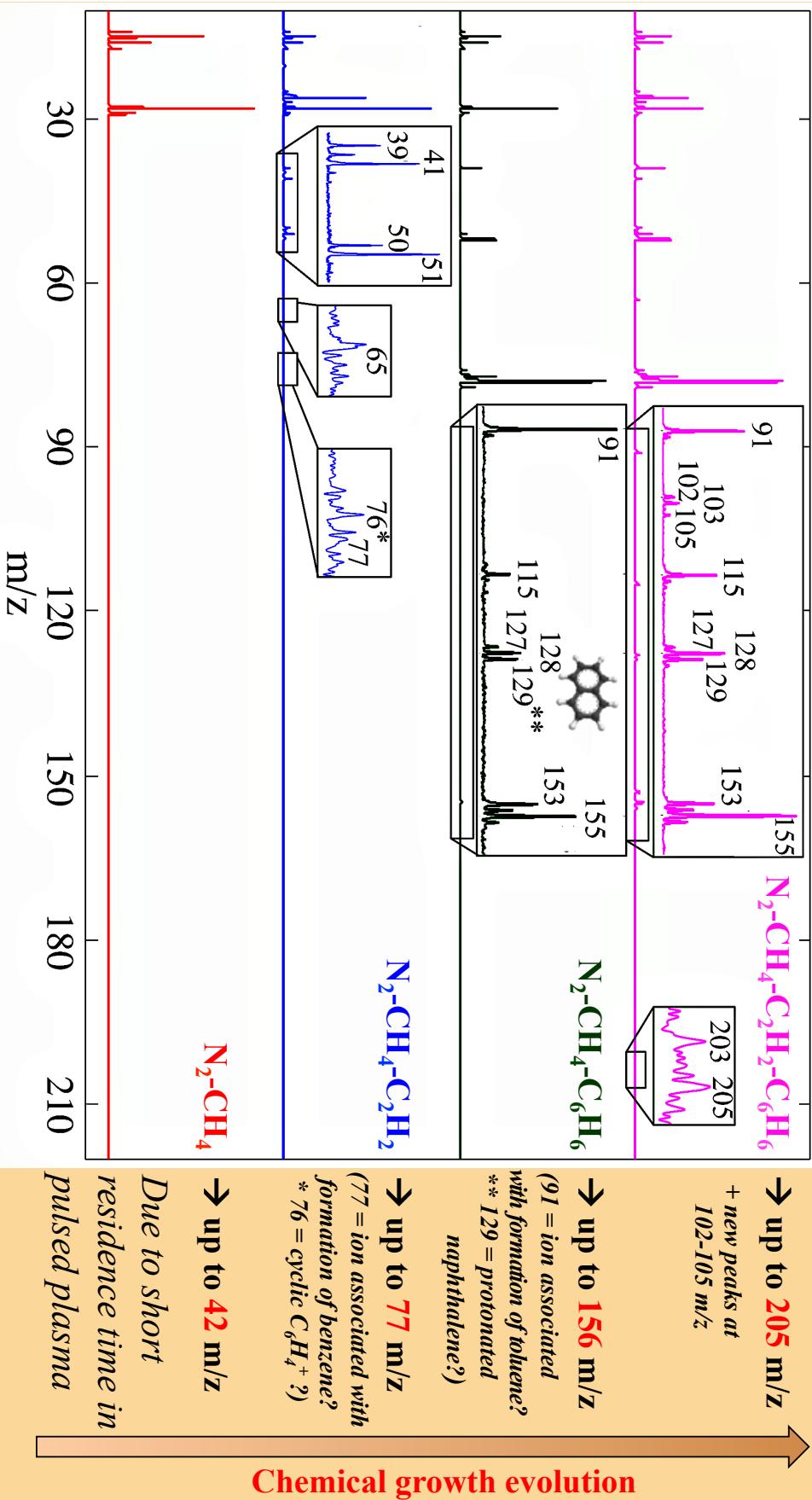
+ Results from experimental simulation (Khare et al 2002, Imanaka et al. 2004, Trainer et al. 2004, Gautier et al. 2011)

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



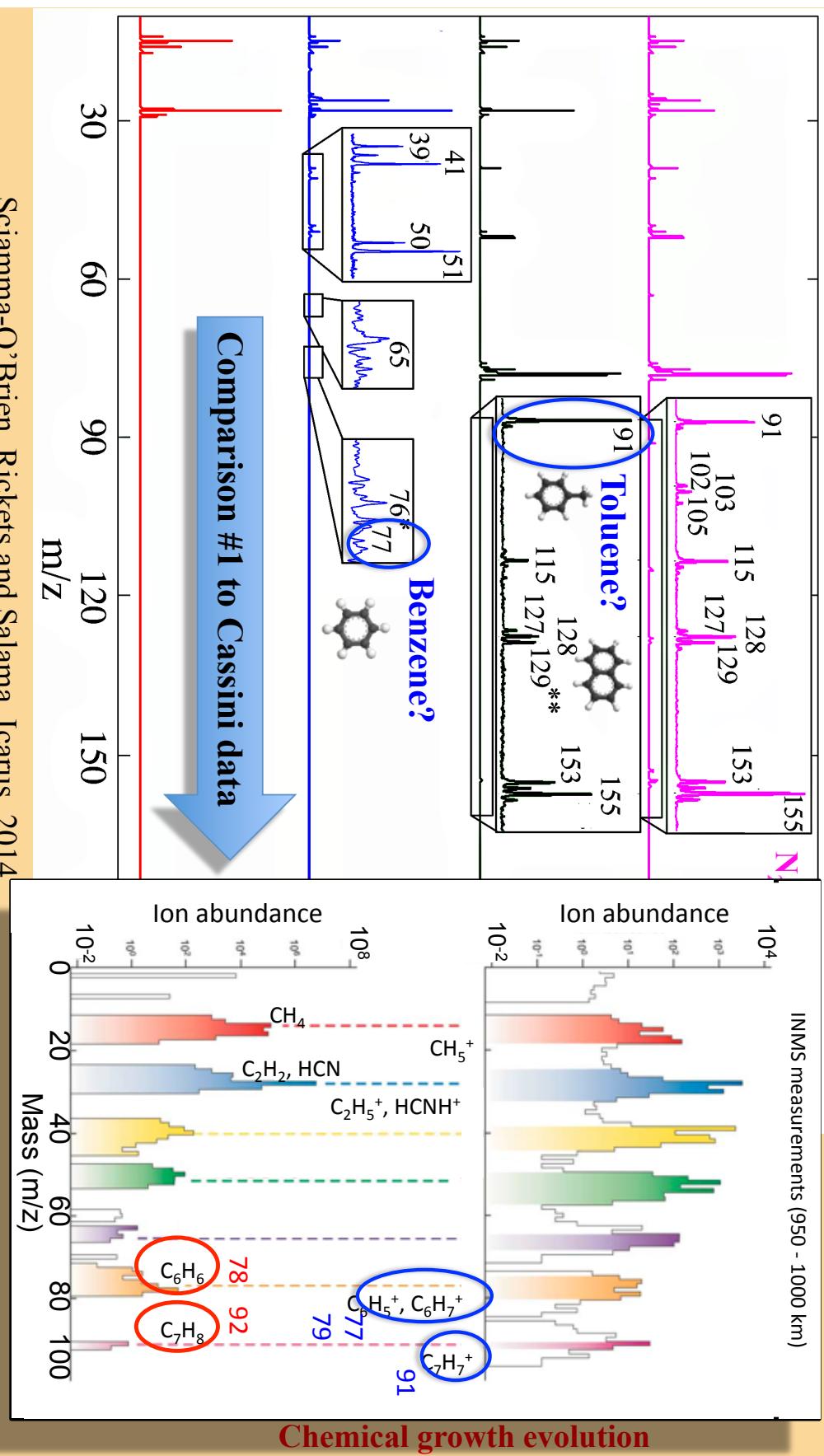
# GAS PHASE: ReTOF-MS analysis

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



# GAS PHASE: ReTOF-MS analysis

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



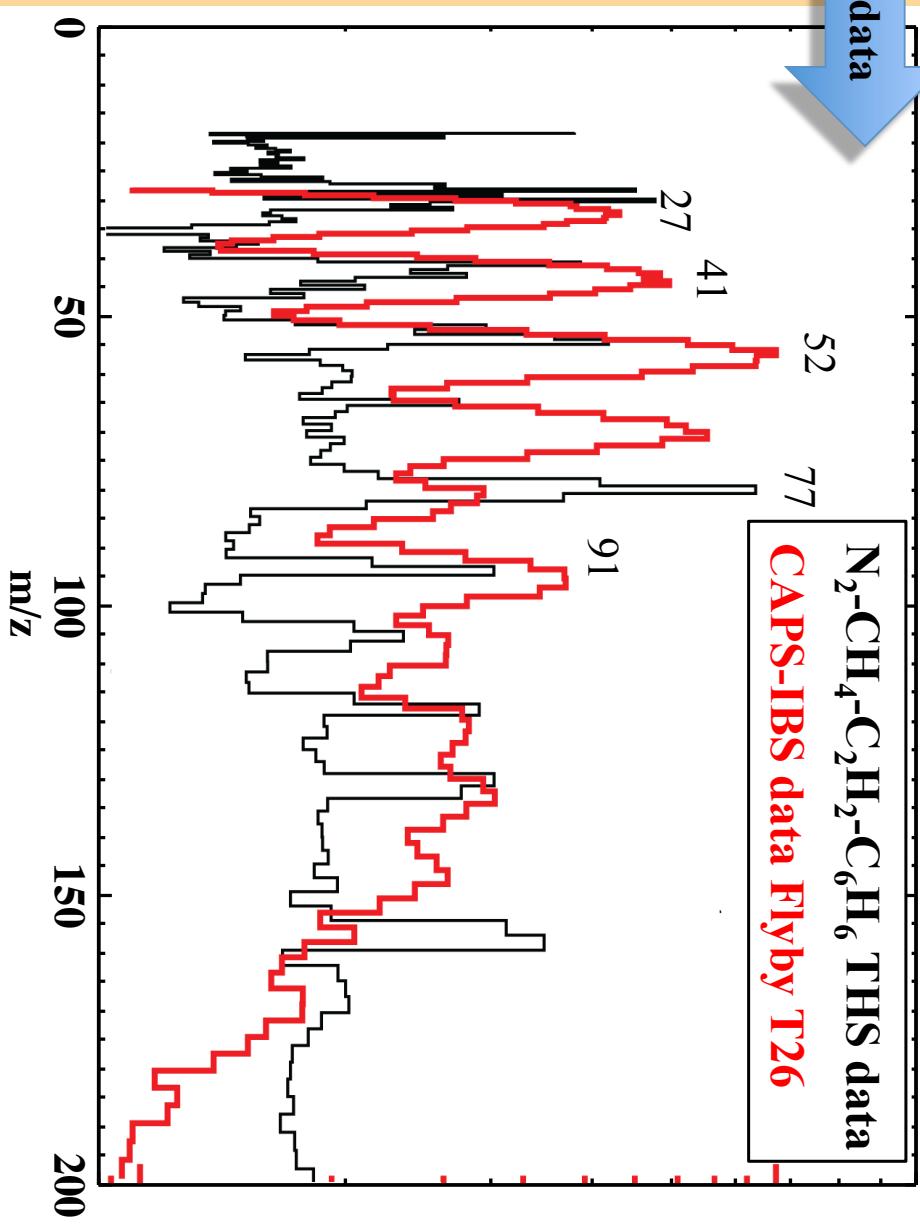
# GAS PHASE: ReTOF-MS analysis

## 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-O'Brien, Ricketts and Salama, Icarus, 2014

HIFOL MPIA 2016

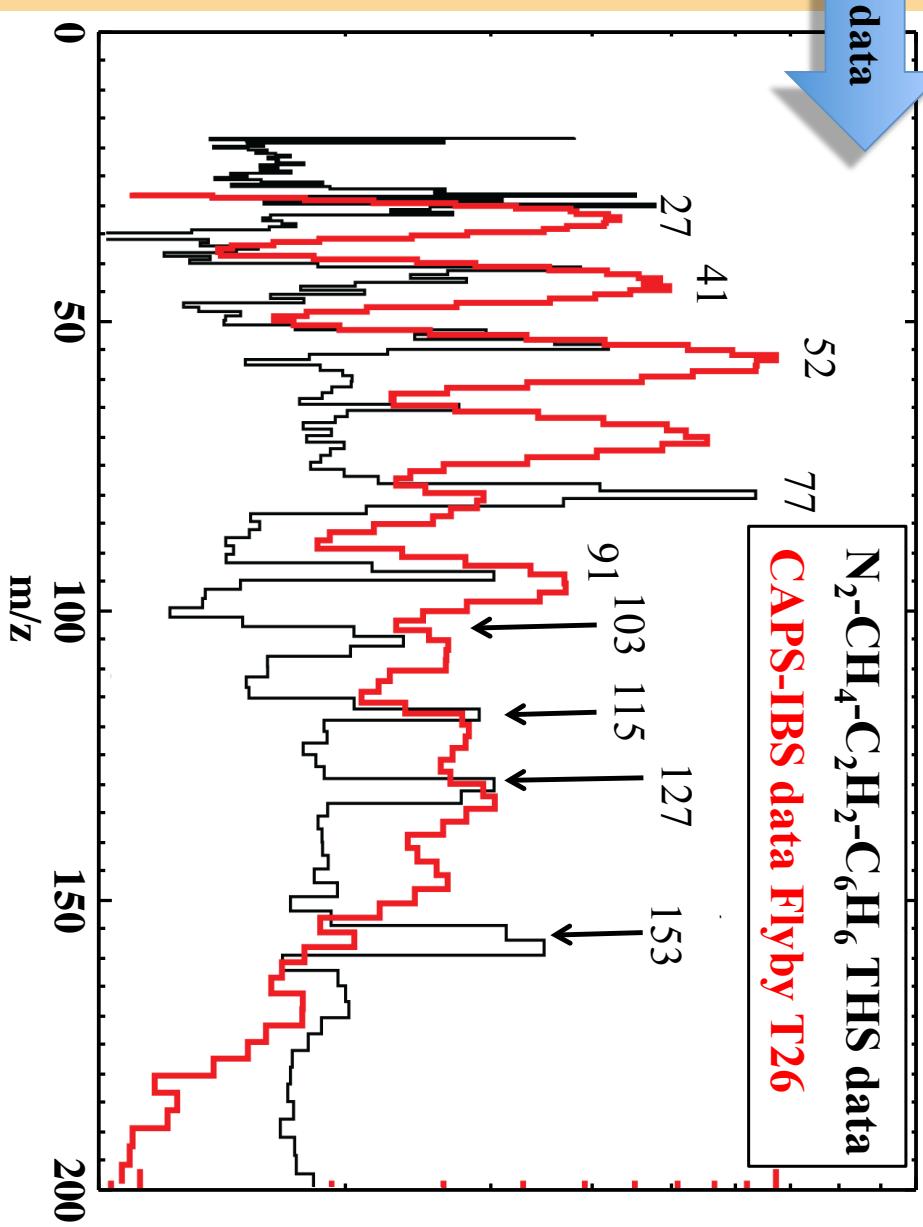
# GAS PHASE: ReTOF-MS analysis

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- above 100 m/z (not achieved in gas phase experiments at low temperature before),  
→ most probably due to aromatic compounds



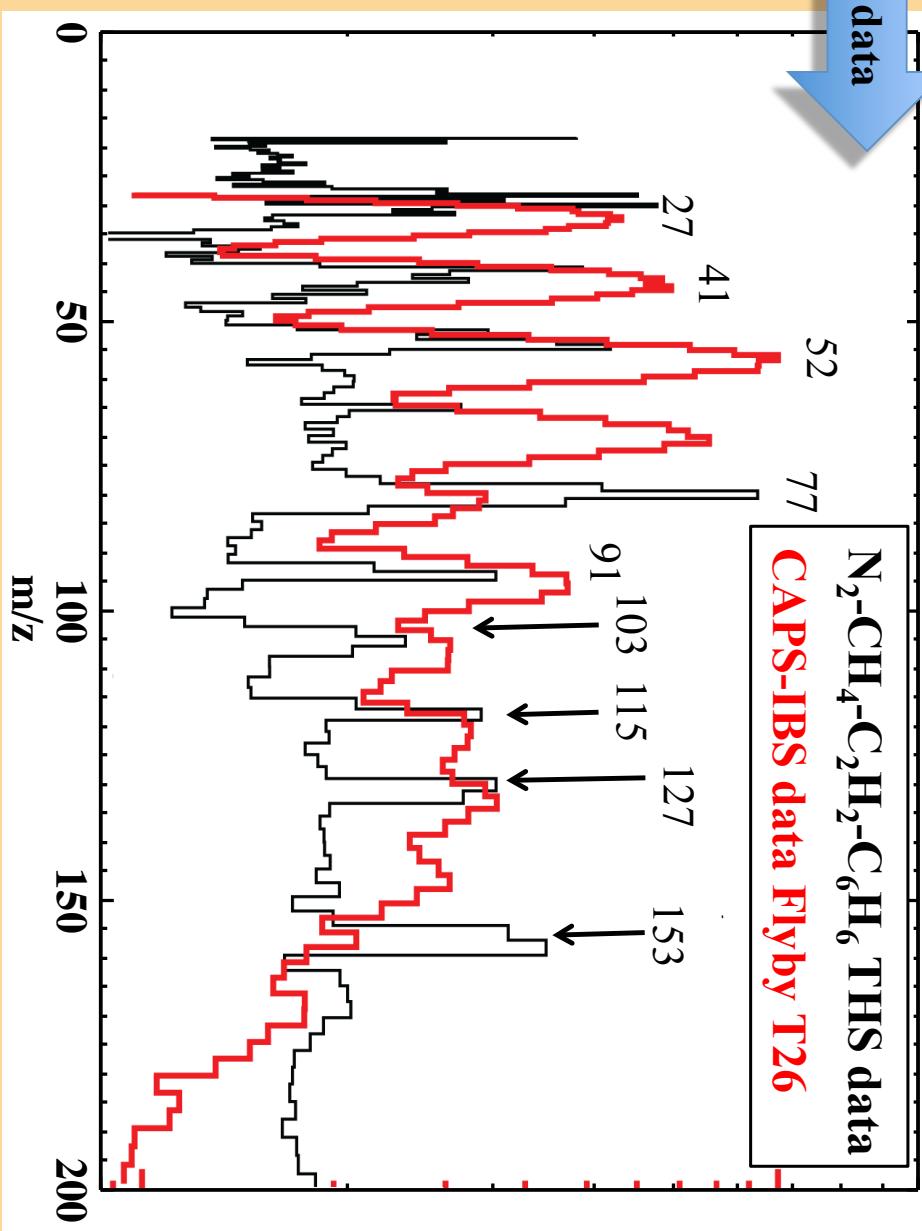
# GAS PHASE: ReTOF-MS analysis

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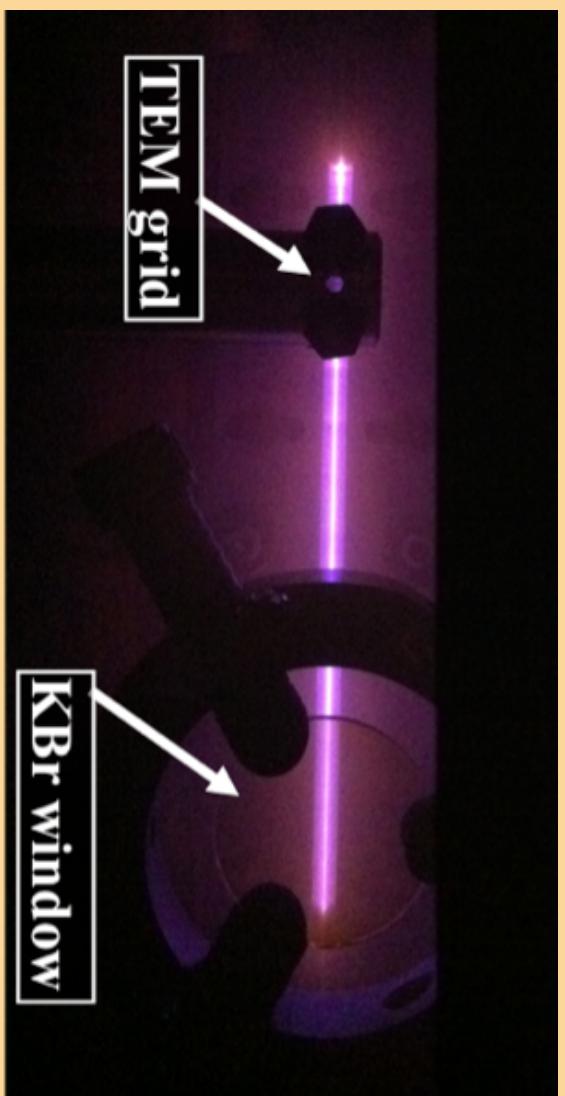
- below 100 m/z (also in agreement with INMS)
- above 100 m/z (not achieved in gas phase experiments at low temperature before),  
→ most probably due to aromatic compounds



NEXT:  
- Missing regions: due to aliphatic compounds?

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

# SOLID PHASE: Tholin deposition



## Substrates:

KBr window

Ex situ analyses:

IR spectroscopy

NMR spectroscopy

Mass Spectrometry



TEM grid

# SOLID PHASE: Tholin ex situ analysis

## Mass Spectrometry (UHV Al foil)

### Direct Analysis in Real Time (DART)



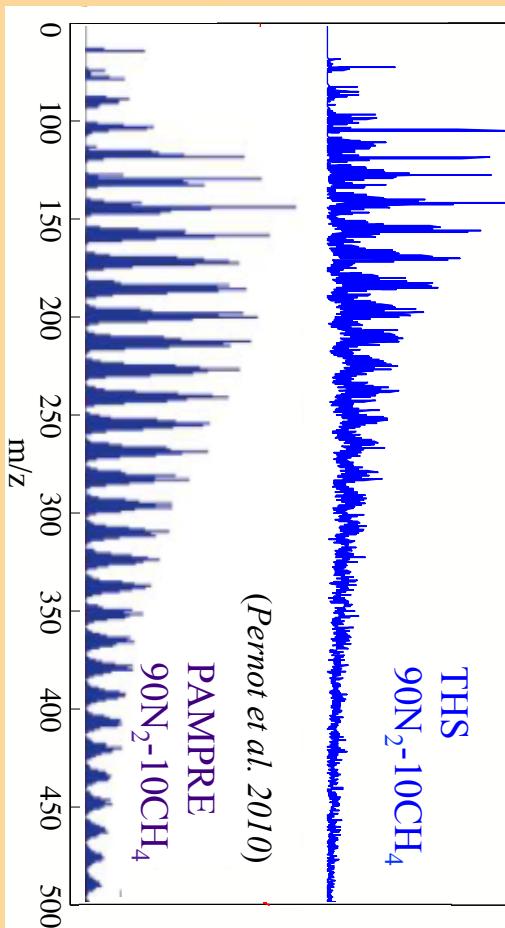
Soft ionization method (no fragmentation) operating at atmospheric pressure and ambient conditions.



Common Tholin mass spectra  
→ forest of peaks with periodicity

**Early chemistry:** made of  
**less complex molecules**  
**than other Titan simulants**

(PAMPRE)



⇒ CONSISTENT WITH  
GAS PHASE RESULTS

Upton, Beauchamp et al. 2014

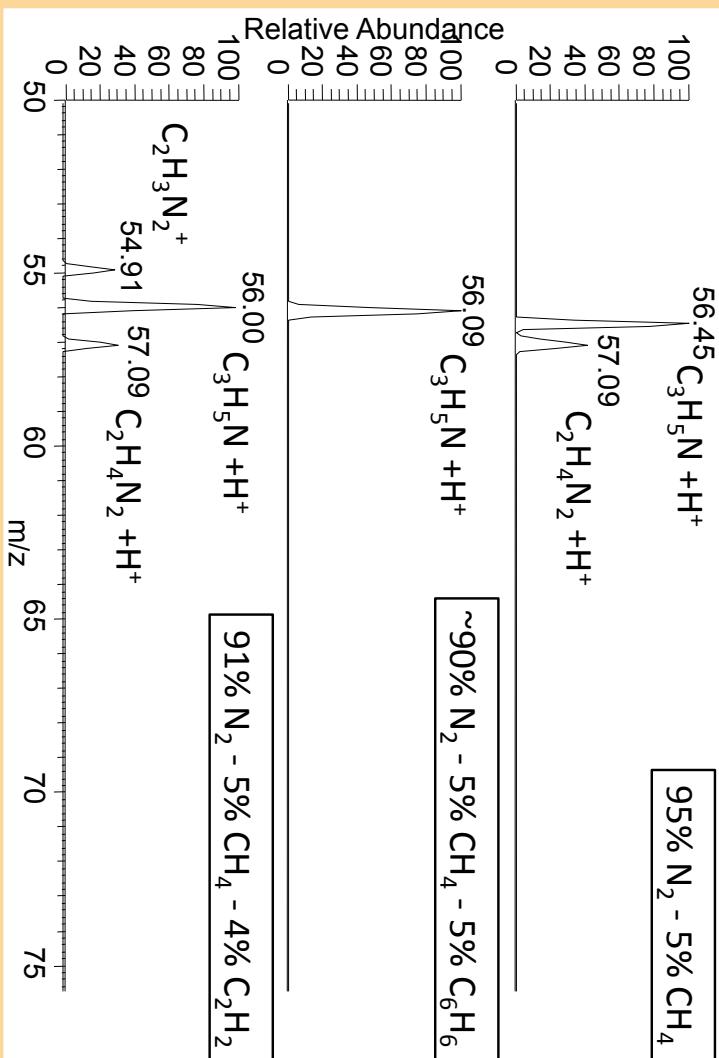
# SOLID PHASE: Tholin ex situ analysis

Mass Spectrometry (UHV Al foil)

## Direct Analysis in Real Time (DART)



Soft ionization method (no fragmentation) operating at atmospheric pressure and ambient conditions.



MS/MS data of peak at 77 m/z

→ shows production of aminoacetonitrile ( $\text{C}_2\text{H}_4\text{N}_2$ )

Upton, Beauchamp et al. 2014

# SOLID PHASE: Tholin ex situ analysis

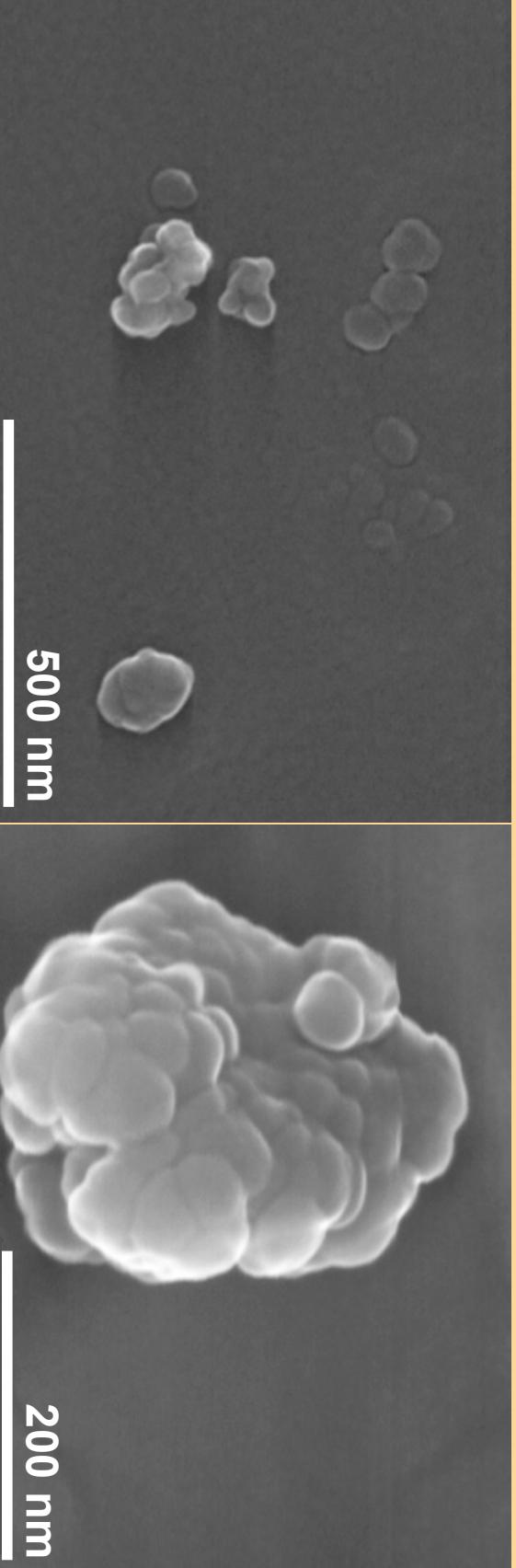
Scanning Electron Microscopy (TEM grid)

→ Can look at growth structure / morphology

N<sub>2</sub>-CH<sub>4</sub>(95:5)

Substrate covered with impacted 10-50 nm nanoparticles

Grains: 100-300 nm in diameter made of ~10-50 nm sized nanoparticles



# SOLID PHASE: Tholin ex situ analysis

Scanning Electron Microscopy (TEM grid)

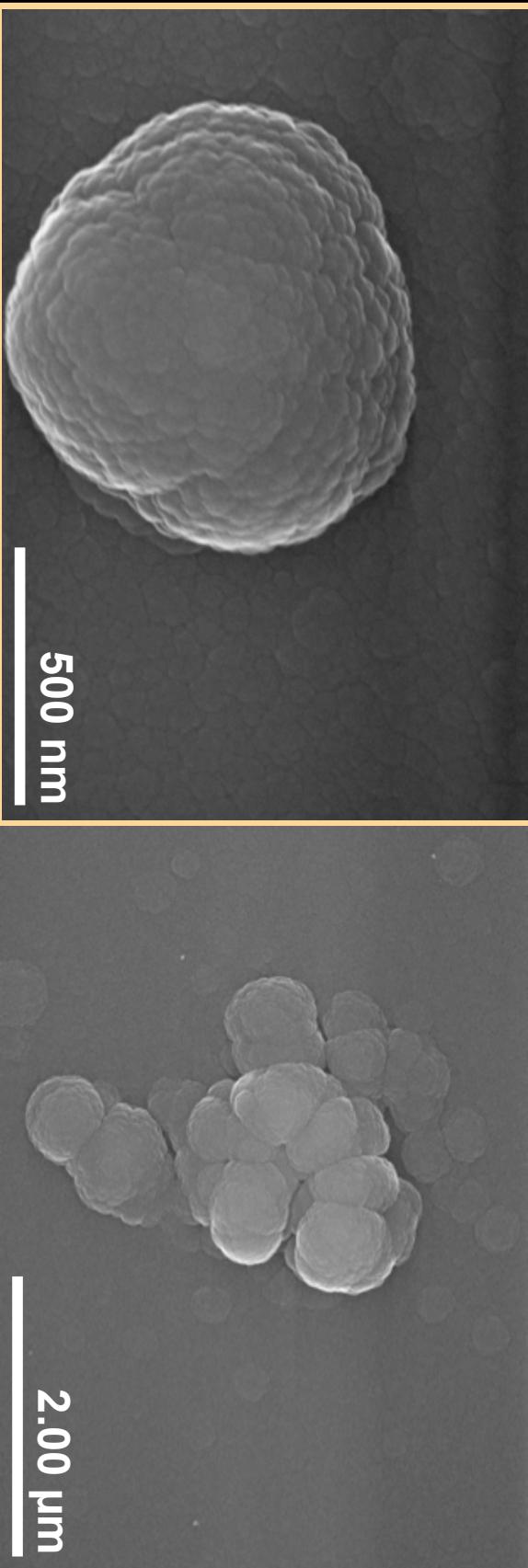
→ Can look at growth structure / morphology



Substrate covered with impacted 10-50 nm nanoparticles

Grains: 300 to 500 nm in diameter made of ~10-50 nm sized nanoparticles

Aggregates: up to 3000 nm in diameter made of 500 nm sized grains



# SOLID PHASE: Tholin ex situ analysis

Scanning Electron Microscopy (TEM grid)

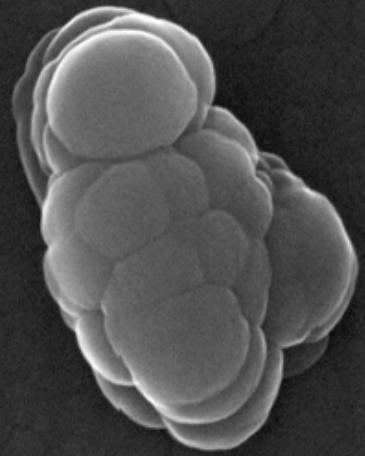
→ Can look at growth structure / morphology



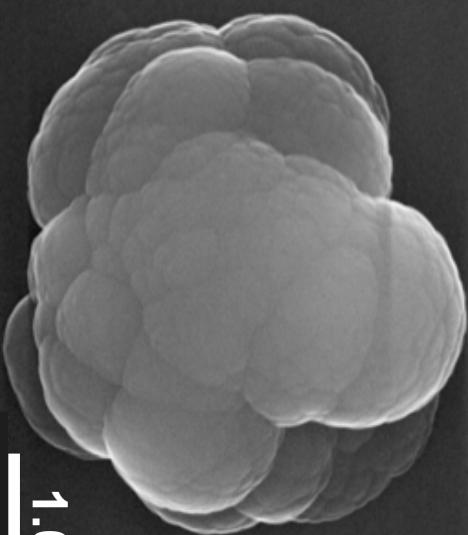
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Aggregates: up to 3000 nm in diameter made of 500 nm sized grains



500 nm



1.00 μm

# SOLID PHASE: Tholin ex situ analysis

Scanning Electron Microscopy (TEM grid)

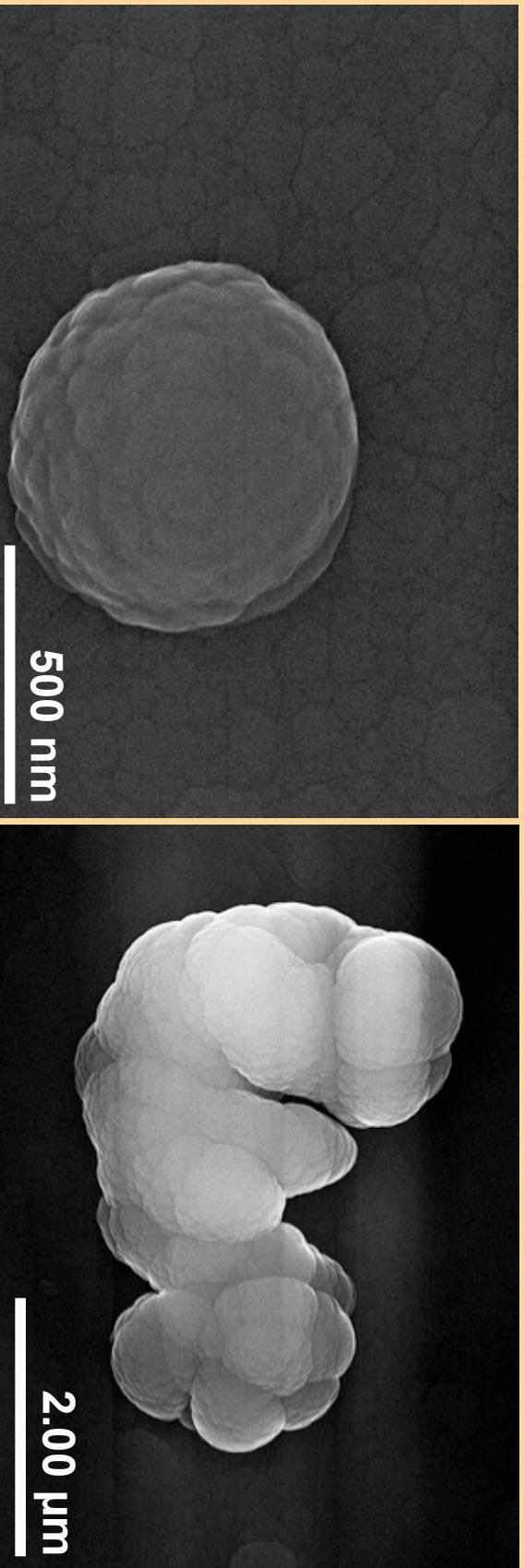
→ Can look at growth structure / morphology



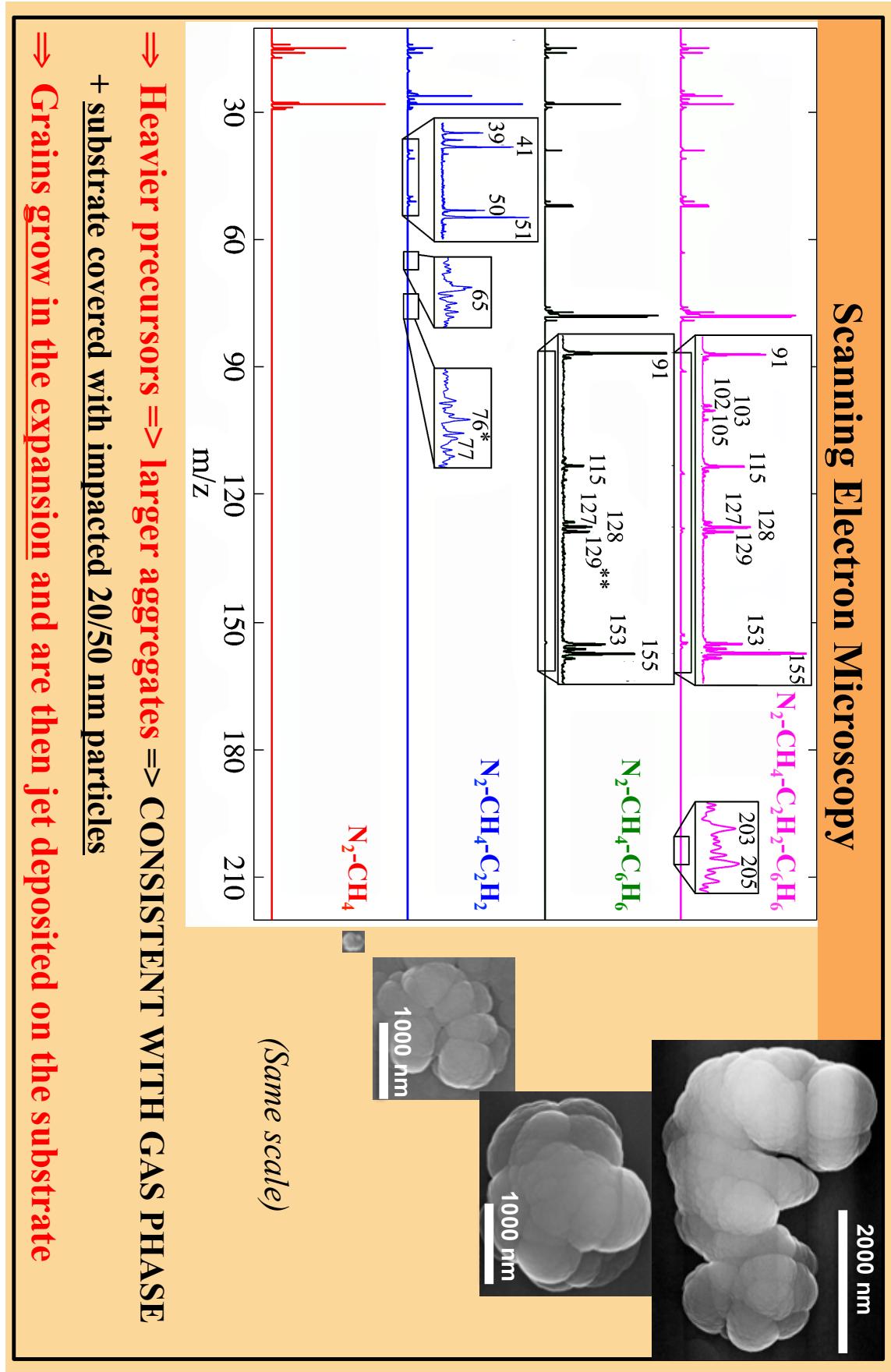
Substrate covered with impacted 10-50 nm nanoparticles

Grains: 300 to 500 nm in diameter made of ~10-50 nm sized nanoparticles

Aggregates: up to 5000 nm in diameter made of 500 nm sized grains



# SOLID PHASE coherent with GAS PHASE



# 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

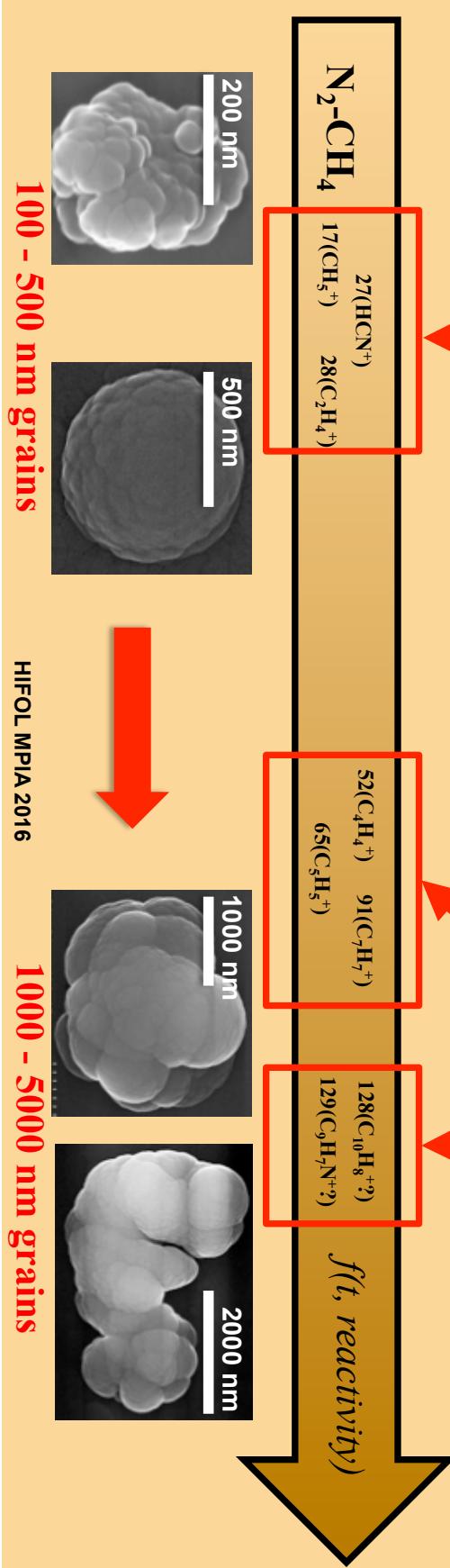
Short plasma + N<sub>2</sub> - CH<sub>4</sub> mixture:

⇒ Probing the initial products of the N<sub>2</sub> - CH<sub>4</sub> chemistry  
and specific chemical pathways

### Intermediary steps

N<sub>2</sub> - CH<sub>4</sub> - C<sub>6</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>2</sub> (and other) mixtures:

⇒ probing next steps of chemistry  
and specific chemical pathways



### Astrophysics:

- Energy budget and signature of aromatic carbon molecules
- Grain formation

### Planetary:

- Titan's atmosphere (haze)

### ISS:

- **Exposure experiments** on complex organic molecules

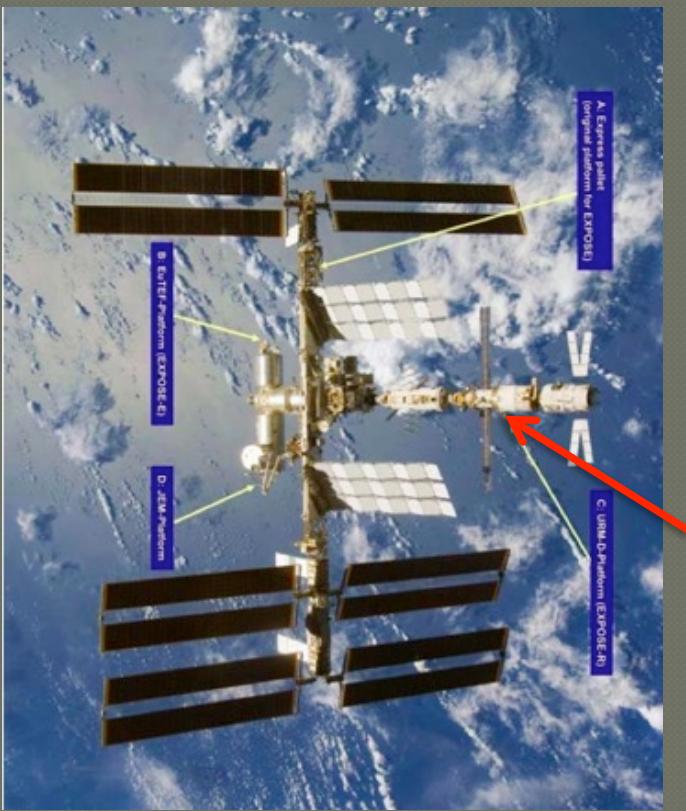
# EXPOSE-R Facility

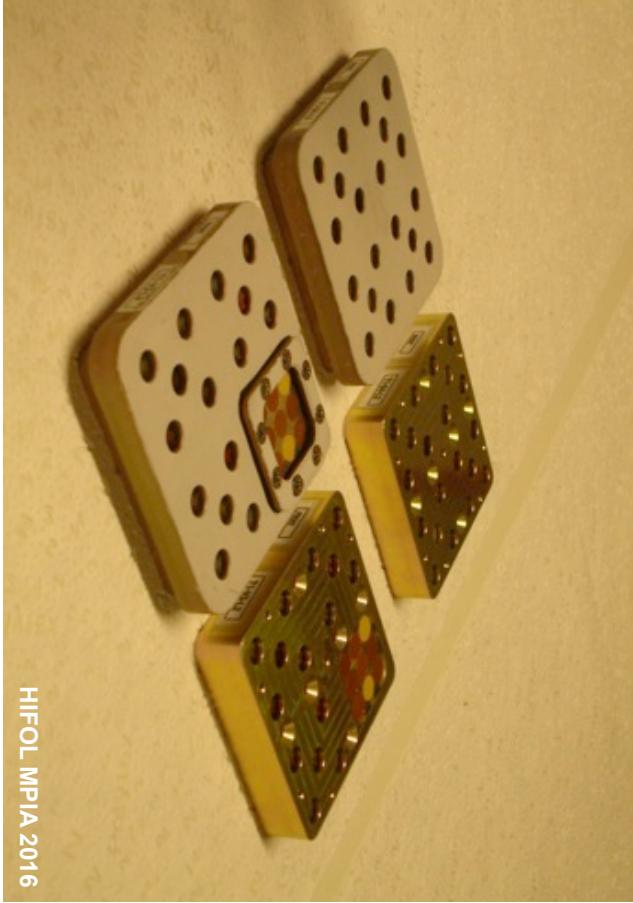
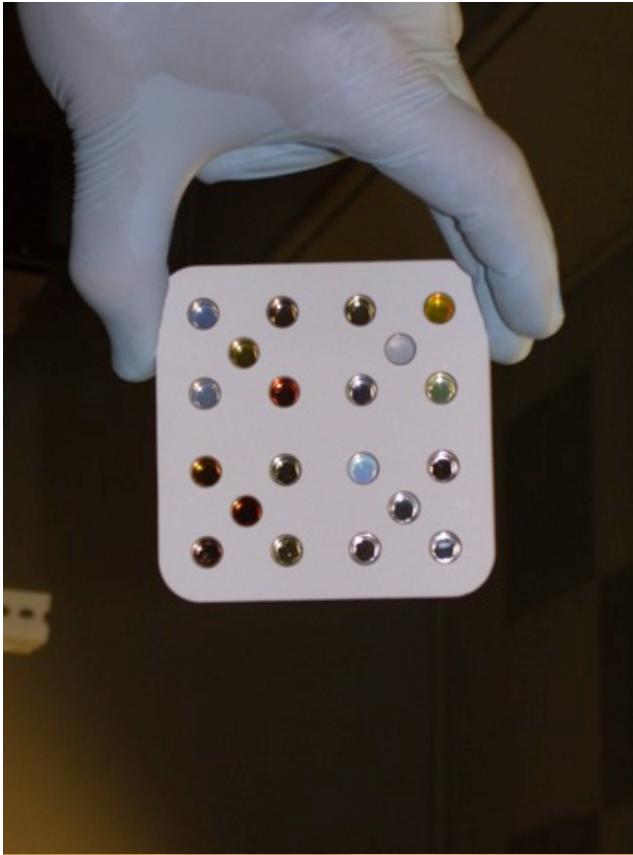
- Second mission of the EXPOSE family

- Adapted on Universal Workplace D (URM-D platform), one of the four external platforms of the Russian Zvezda-Module of the ISS

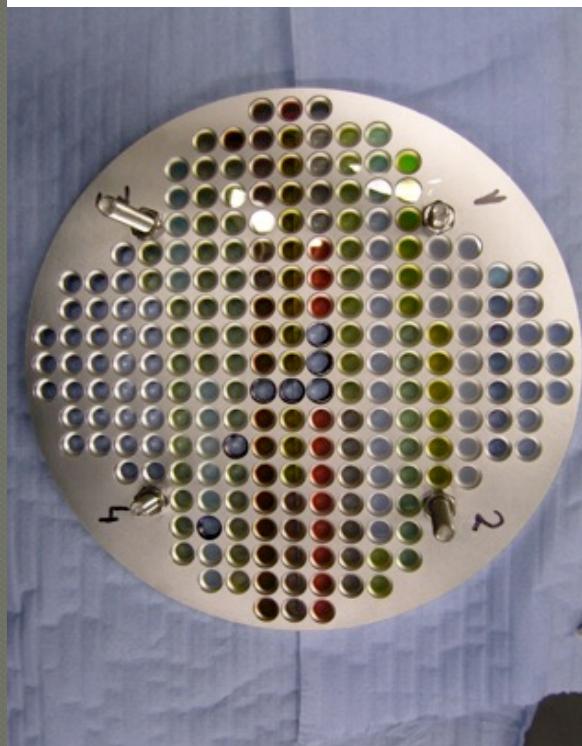
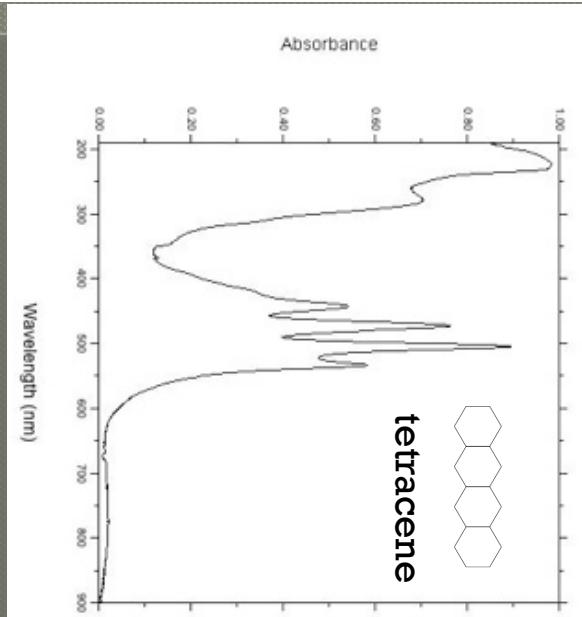
- Provides space for astrobiology samples, sensors, heating systems, electronics for data collection, storage, telemetry and telecommand, and mechanical and electronic interfaces to the ISS platform
- Hosts 10 international astrobiology experiments

EXPOSE-R





## PAH samples Cells and Carriers



**EXPOSE-R**

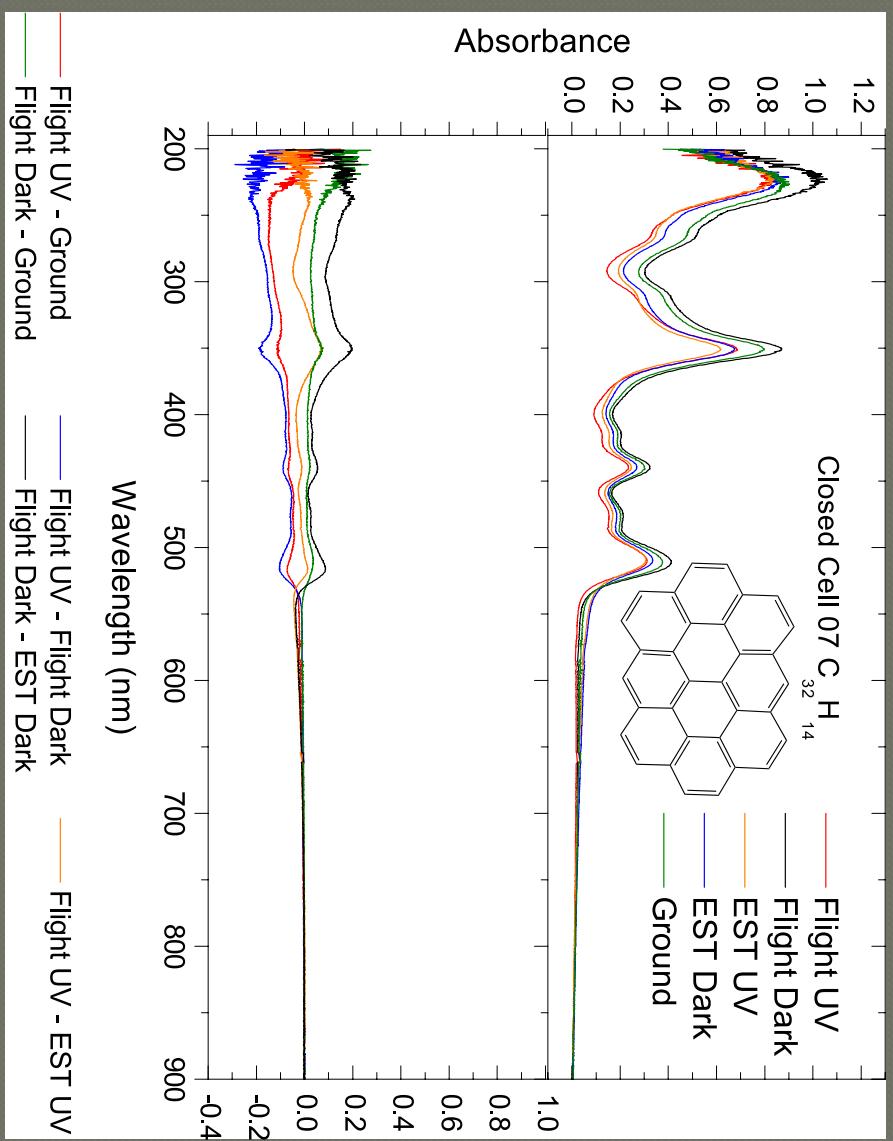
# Space Exposure

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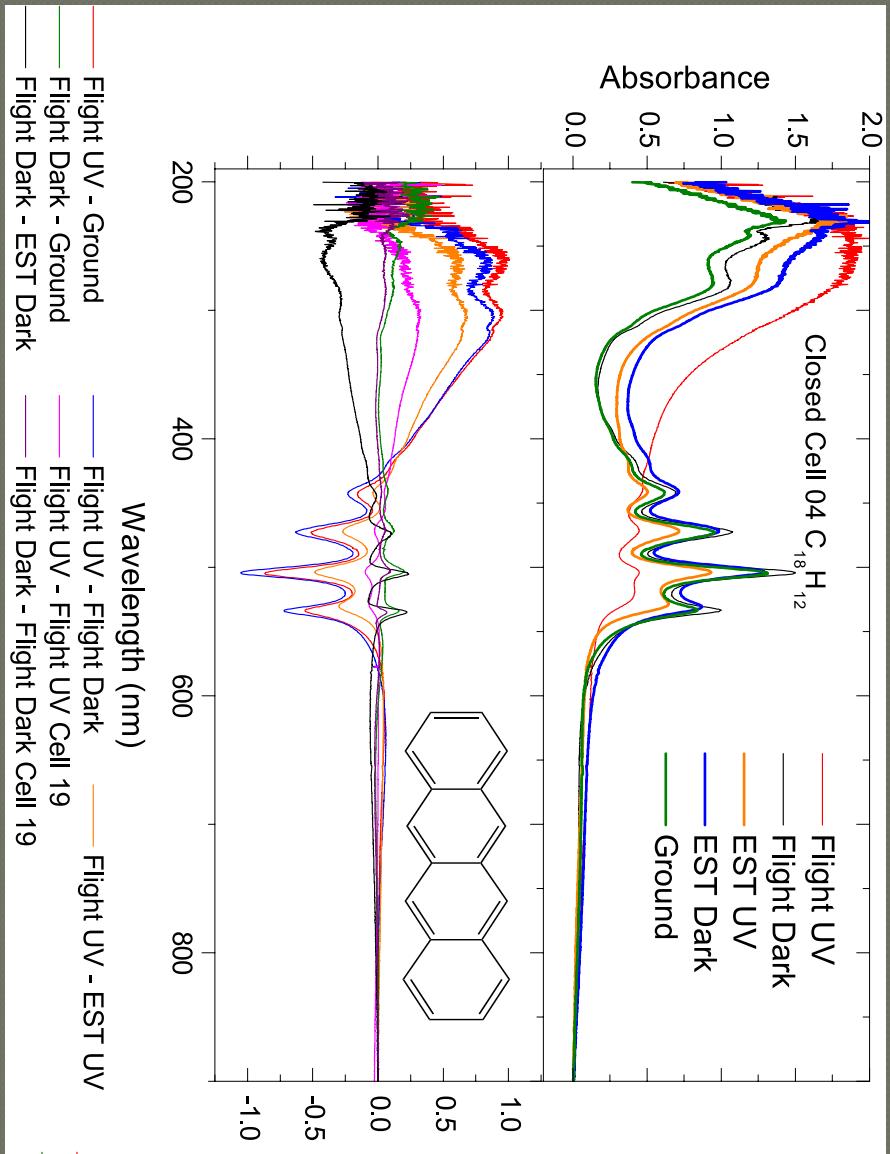
- ORGANIC on Biopan exposed
  - 58 h effective over 380 h flight
  - total fluence of 602.45 kJ m<sup>-2</sup> for photons in the range 170-280 nm
- ORGANIC on EXPOSE-R exposed
  - irradiation dose of the order of 14000 MJ m<sup>-2</sup> over 2900 h of unshadowed solar illumination

# Compact PAH



Bryson et al., Int. J. Astrobiol., 2015

# Non-Compact PAH



Bryson et al. 2015

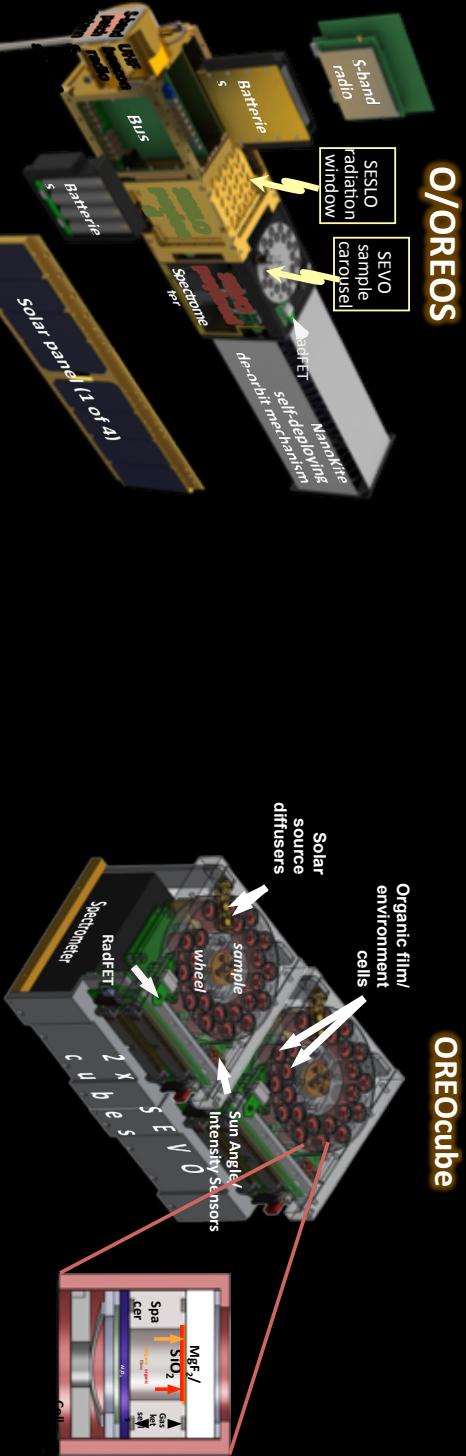
# ORGANIC on EXPOSE-R RESULTS

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- Limited spectral changes
- Known trend in the stability of PAH species according to molecular structure
  - Compact PAHs most stable (below 10% depletion)
  - Then non-compact PAHs
  - Least stable PAHs containing heteroatoms, the last category being the most prone to degradation in the space environment
- Extreme case – tetracene (smallest, non-compact PAH sample)
  - Estimated depletion rate of the order of  $85 \pm 5\%$  over the 17 equivalent weeks of continuous unshaded solar exposure
- Future Experiments
  - Interactions with inorganic substrates
  - OREOcube: ORganics Exposure in Orbit Experiment

# EXOcube - EXposure of Organisms/Organics cube

## EXOcube heritage



- O/OREOS (NASA Astrobiology Small Payloads (ASP)):
  - Develop and fly small astrobiology payloads, from single-cube free flyers to suitcase-sized payloads, to address fundamental astrobiology objectives, using a variety of launch opportunities
  - selected for Definition Phase by the European Space Agency (ESA) to be installed on the ISS.
  - designed to perform *in situ* UV-Vis spectroscopy to study the chemistry of biomolecules in Low Earth Orbit.
  - sample cell gas compositions and relative humidity can be controlled to create space and planetary "micro-environments".
- O/OREOS (Organism/Organics Exposure to Orbital Stresses) is the first technology demonstration mission for ASP
  - Launched: November 19, 2010
  - Nominal performance in orbit, 146 days
  - <http://ooreos.engr.scu.edu/dashboard.htm>

# Acknowledgments



## NASA Ames COSMIC Lab

Cesar Contreras (Astrophysics)

Ella Sciamma-O'Brien (Planetary)

Claire Ricketts (Planetary)

Kathryn Bryson (Exposure)

Salma Bejaoui (Astrophysics)

Robert Walker (Eng. support)

NASA SMD APRA and Solar System R&A Programs.

ASL, a NASA ARC-UCSC Consortium

