

# Dust nucleation in very-low pressure plasmas

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X. Glad, H. Sabbah, C. Joblin

M. Rojo, S. Dap

A. Perdrau, J. Philbrick

# Outline

**I** **CONTEXT**

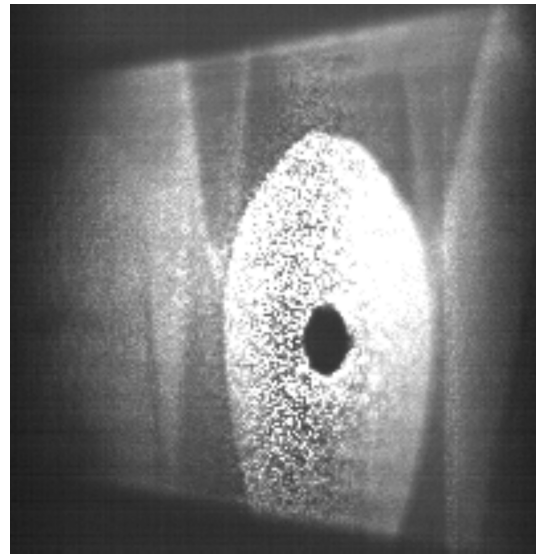
II MATERIALS & METHODS

III DUST PARTICLES FORMED IN C<sub>2</sub>H<sub>2</sub> PLASMAS

IV DUST PARTICLES FORMED FROM PAHs

V CONCLUSION AND PERSPECTIVE

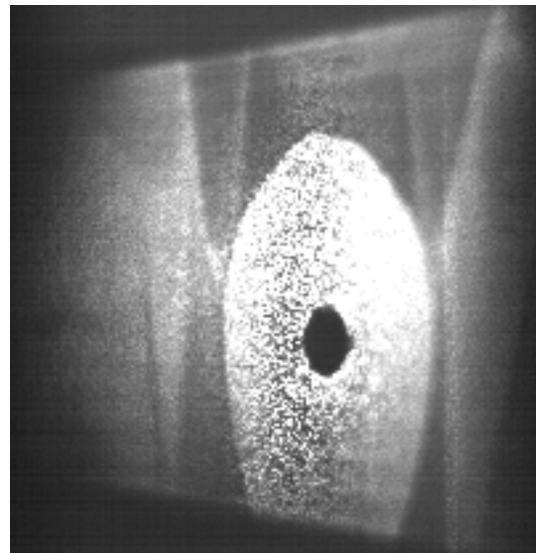




Couedel et al., *Self-excited void instability during dust particle growth in a dusty plasma*, PoP (2010)

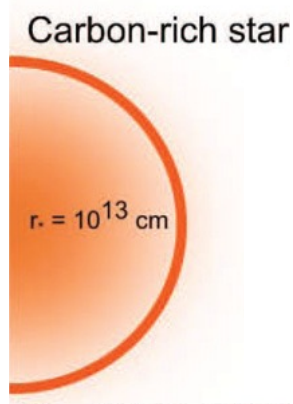


Shaddix et al., *Soot: Giver and Taker of Light*,  
Am.Sci (2007)

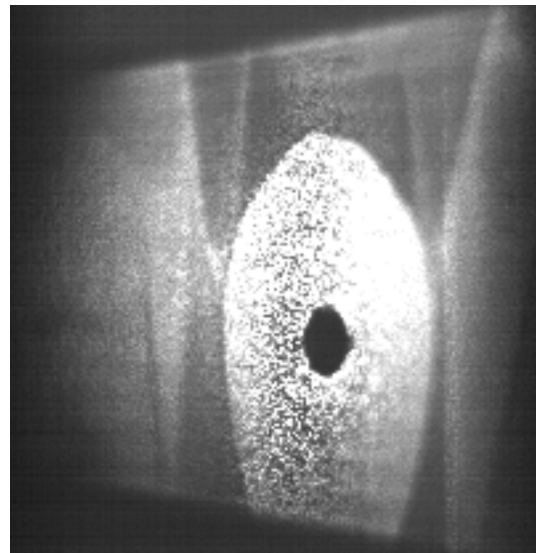


Couedel et al., *Self-excited void instability  
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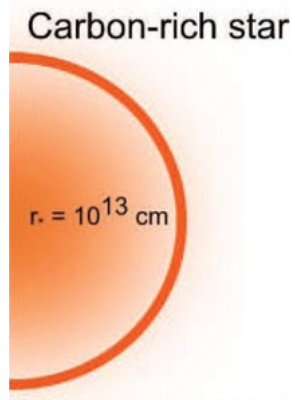
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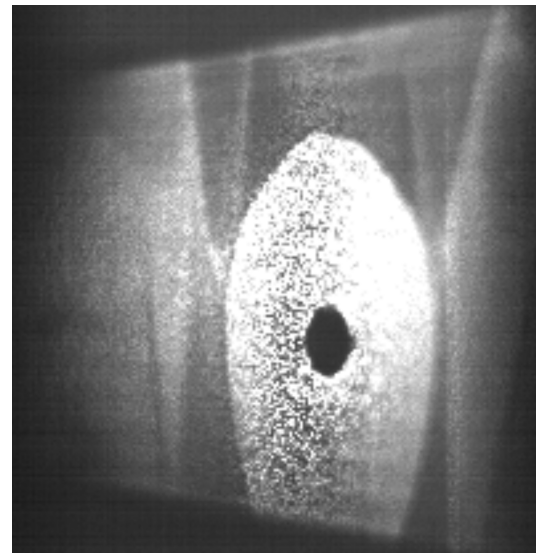
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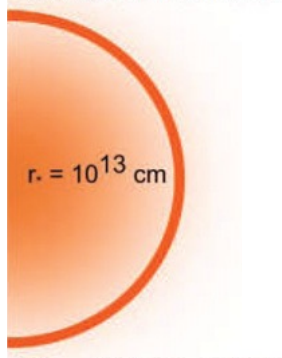
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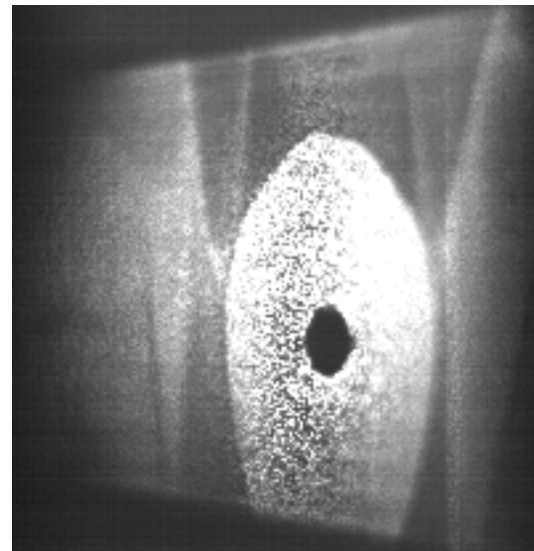
NUCLEATION → COAGULATION → ACCRETION

Contreras et al., *Laboratory investigations of polycyclic aromatic hydrocarbon formation and destruction in the circumstellar outflows of carbon stars*, ApJS (2013)

Carbon-rich star



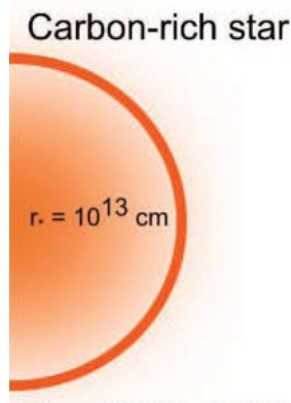
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# Cosmic dusts

Contreras et al., *Laboratory investigations of polycyclic aromatic hydrocarbon formation and destruction in the circumstellar outflows of carbon stars*, ApJS (2013)



$$d = 10^{18} \text{ cm}^{-3}$$

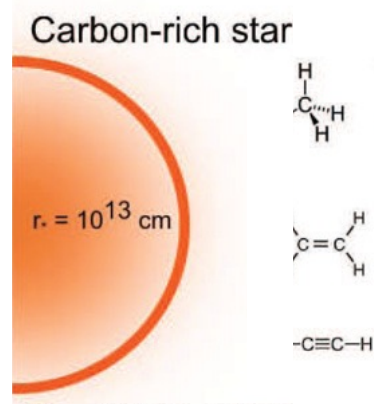
$$d = 10^9 \text{ cm}^{-3}$$

$$d = 10^5 - 10^3 \text{ cm}^{-3}$$



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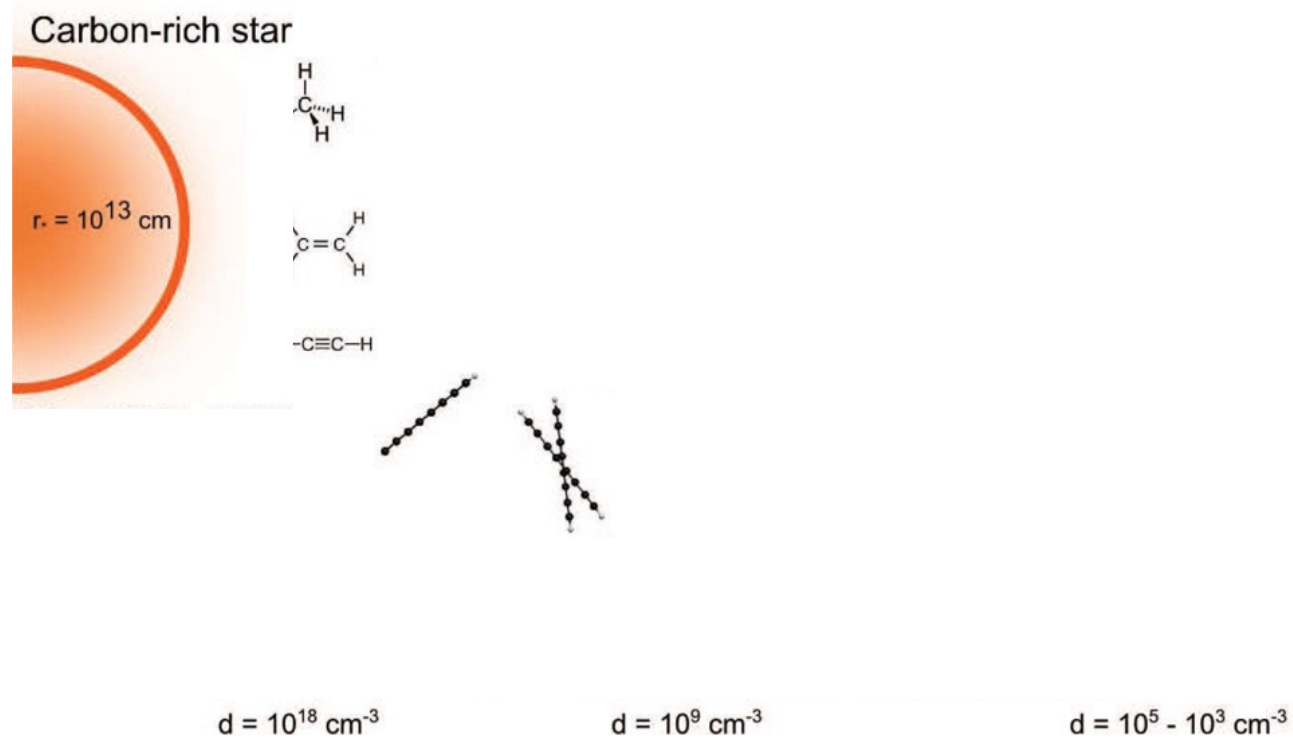
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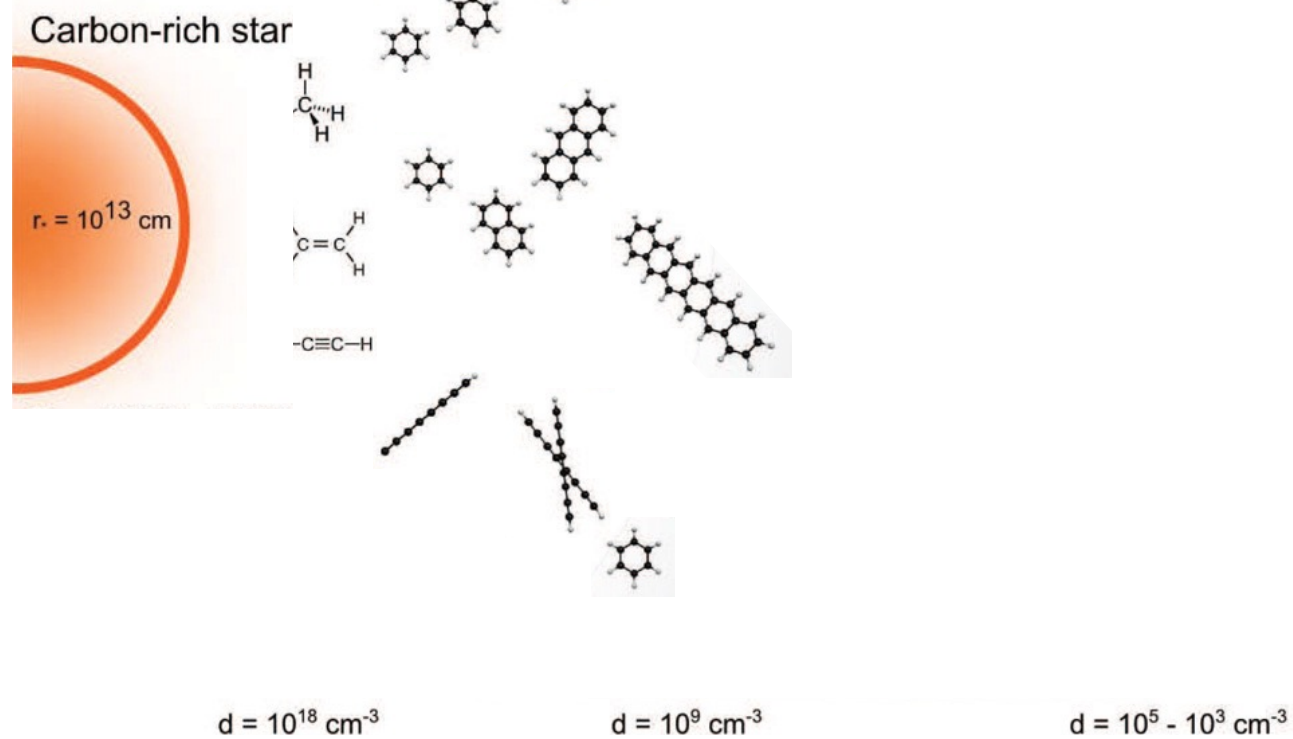
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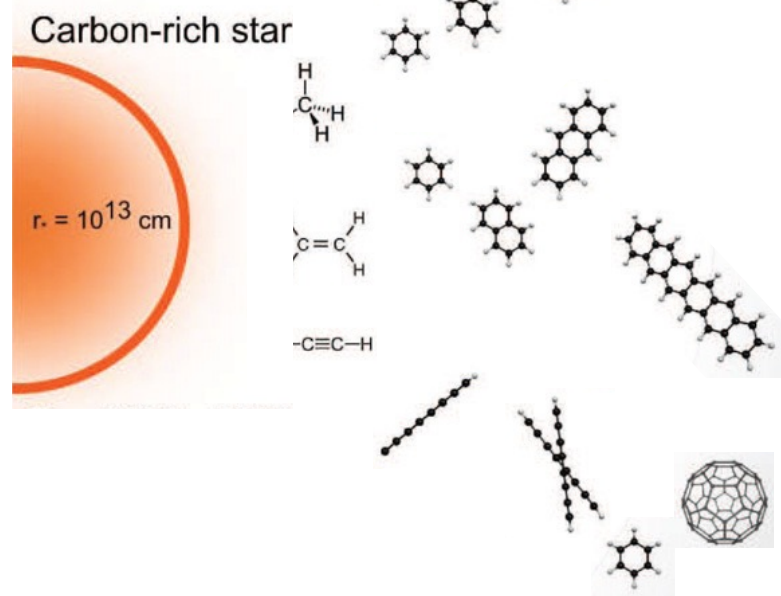
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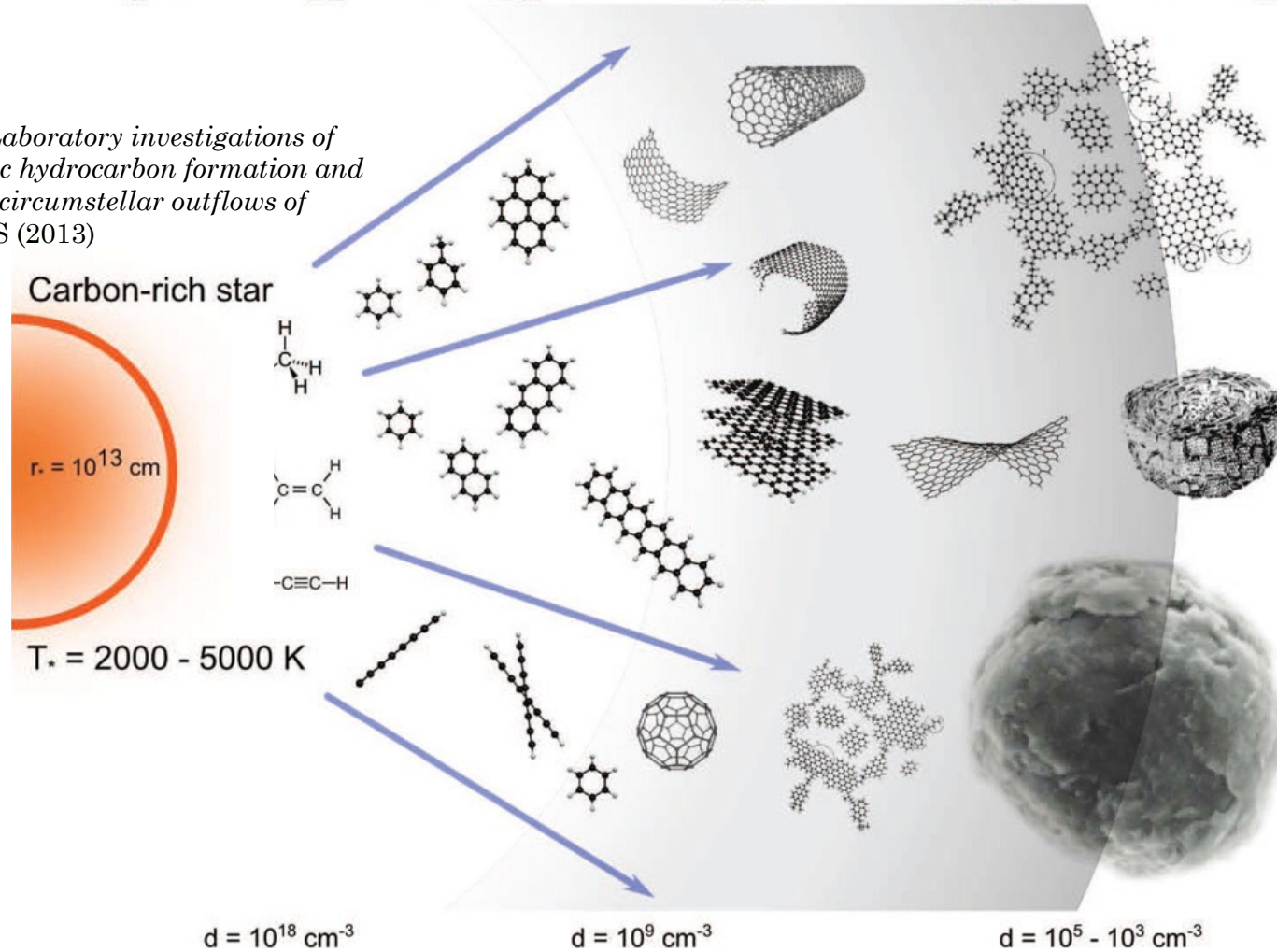
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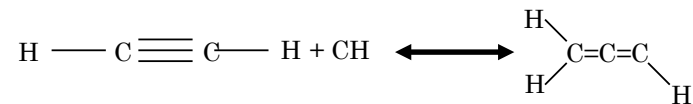
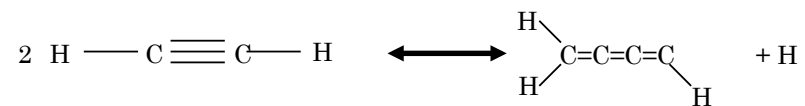
small carbon molecules      small PAHs      medium-sized PAHs      big PAHs, diamond-like structures, fullerenes, nanotubes      grains, amorphous carbon

Contreras et al., *Laboratory investigations of polycyclic aromatic hydrocarbon formation and destruction in the circumstellar outflows of carbon stars*, ApJS (2013)



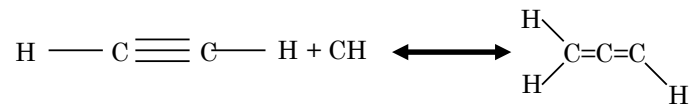
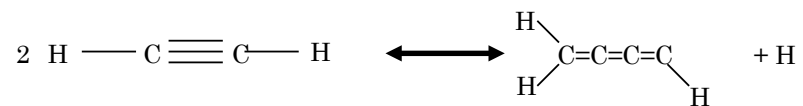


## Formation of linear polyalkyne

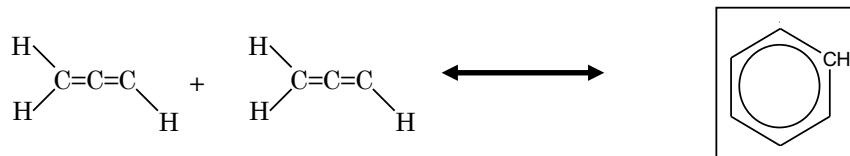
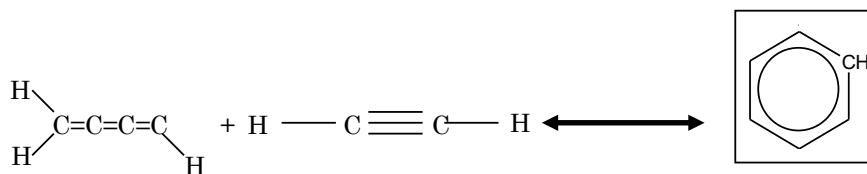


Wang and Frenklach., *A detailed kinetic modeling study of aromatics formation in laminar premixed acetylene and ethylene flames*, Comb. Flame (1997)

## Formation of linear polyalkyne

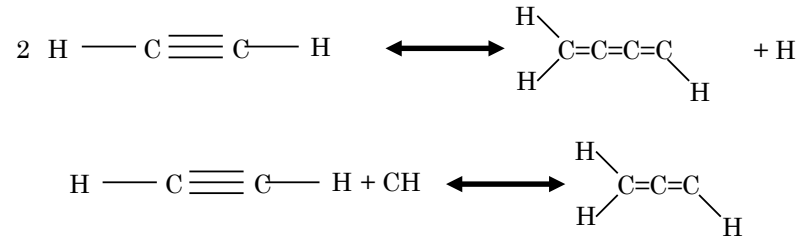


## Formation of aromatic rings

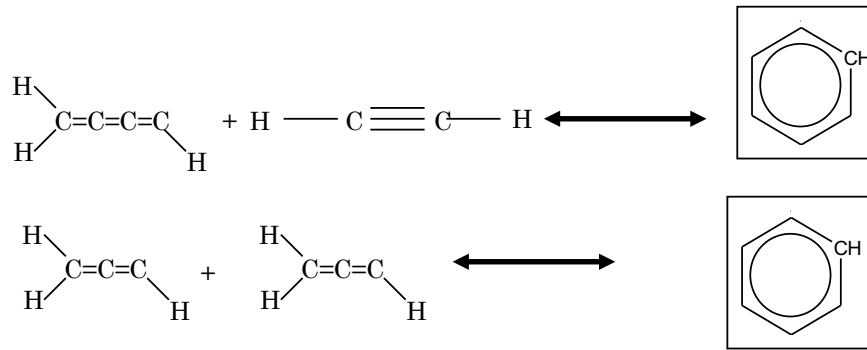


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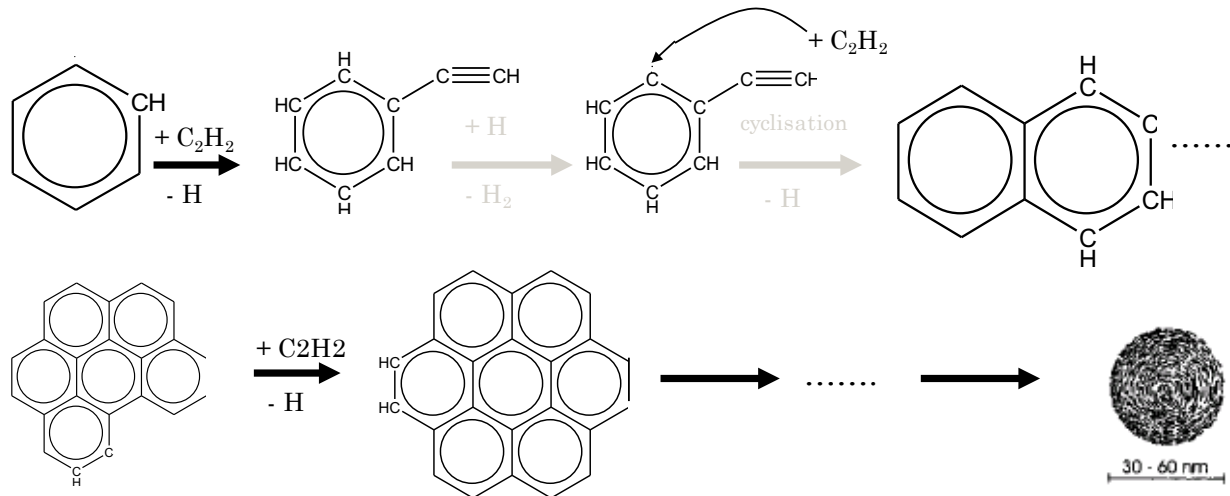
## Formation of linear polyalkyne



## Formation of aromatic rings



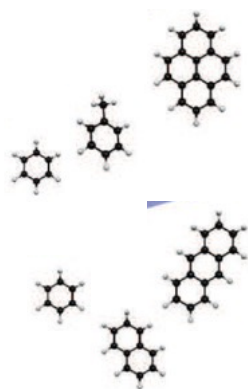
## Hydrogen Abstraction Carbon Addition (HACA)



Wang and Frenklach., *A detailed kinetic modeling study of aromatics formation in laminar premixed acetylene and ethylene flames*, Comb. Flame (1997)

# Nucleation?

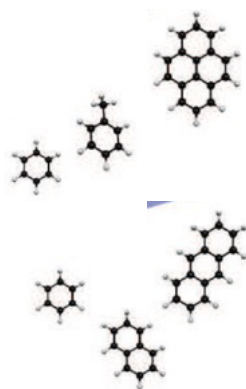
PAHs formation / HACA shown in SOOTY FLAMES





# Nucleation?

PAHs formation / HACA shown in SOOTY FLAMES



often used

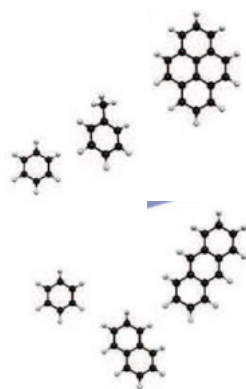
CARBON-RICH STARS

DUSTY PLASMAS

# Nucleation?

PAHs formation / HACA shown in SOOTY FLAMES

$$N_n = 5 \cdot 10^{18} \text{ cm}^{-3} / T = 1000\text{-}2000 \text{ K}$$
$$N_e > 10^{11} \text{ cm}^{-3} / T_e = 0.2 \text{ eV}$$



often used

**CARBON-RICH STARS**

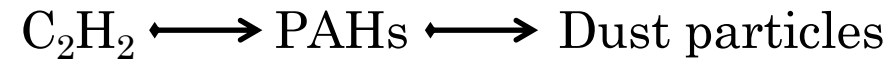
$$N_n = 5 \cdot 10^8 \text{ cm}^{-3} / T = 2000\text{-}5000 \text{ K}$$
$$N_e \approx 2 \cdot 10^2 \text{ cm}^{-3} / T_e = 0.1 \text{ eV}$$

**DUSTY PLASMAS**

$$N_n = 10^{14}\text{-}10^{15} \text{ cm}^{-3} / T = 300 \text{ K}$$
$$N_e = 10^8\text{-}10^9 \text{ cm}^{-3} / T_e = 2\text{-}4 \text{ eV}$$

# Dust particle growth in plasmas

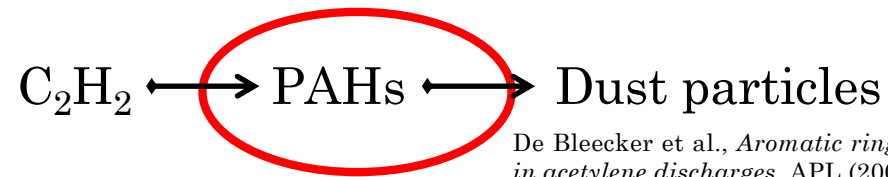
- In C<sub>2</sub>H<sub>2</sub> dusty plasmas:



De Bleecker et al., *Aromatic ring generation as a dust precursor in acetylene discharges*, APL (2006)

# Dust particle growth in plasmas

- In  $C_2H_2$  dusty plasmas:

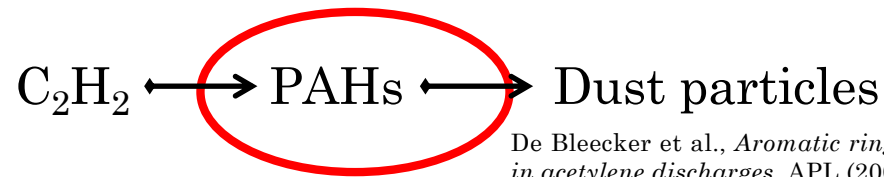


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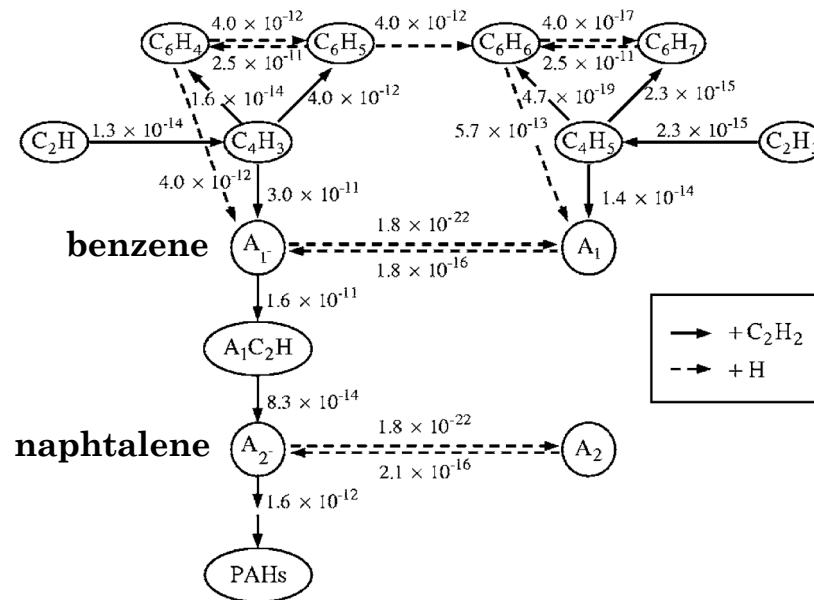
MODELLING

# Dust particle growth in plasmas

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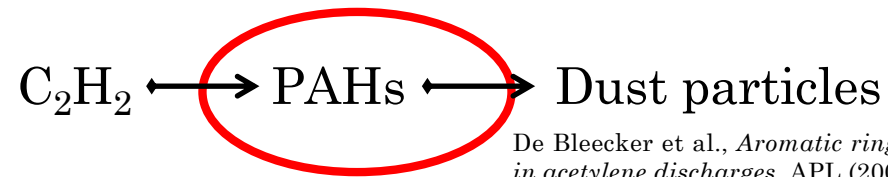


## MODELLING



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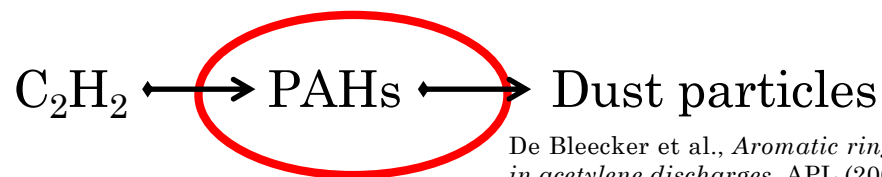


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EXPERIMENTS

# Dust particle growth in plasmas

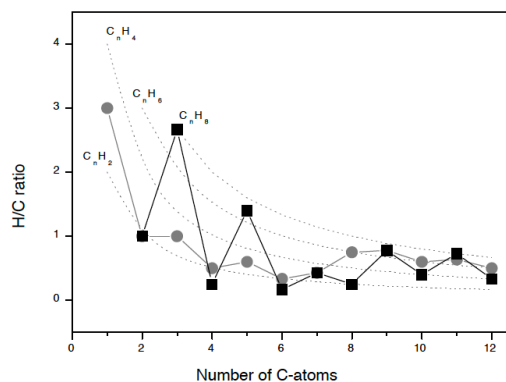
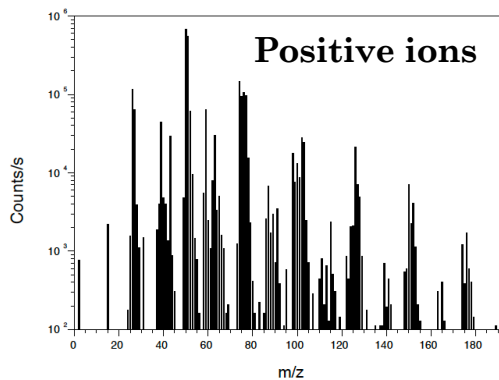
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## EXPERIMENTS

### Mass spectrometry

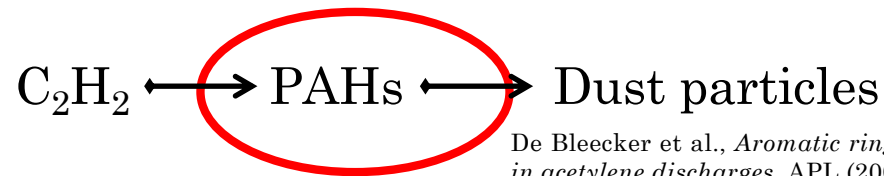


Linear polyalkynes  $\rightarrow$  Aromatic rings

Descheneaux et al., *Investigations of  $CH_4$ ,  $C_2H_2$  and  $C_3H_4$  dusty RF plasmas by means of FTIR absorption spectroscopy and mass spectrometry*, JPD (1999)

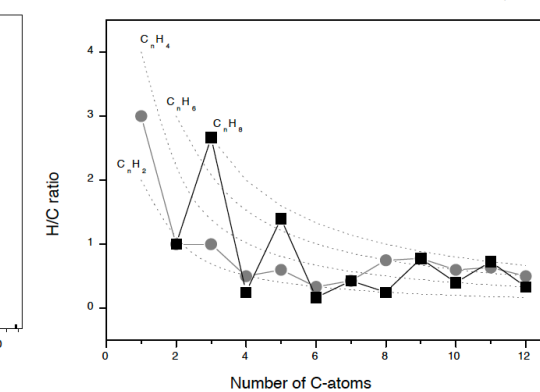
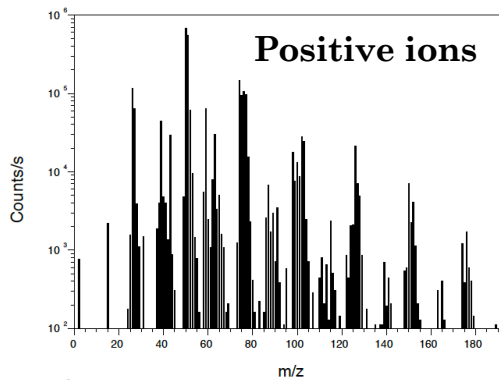
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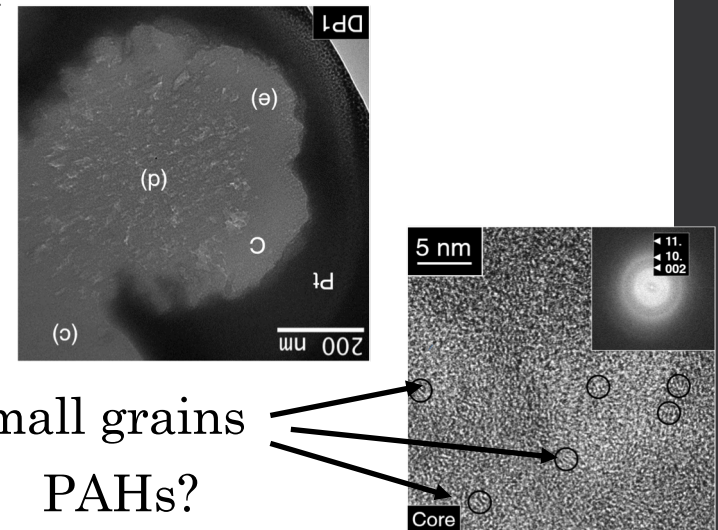


## EXPERIMENTS

### Mass spectrometry



### Microscopy



Very small grains  
PAHs?

Descheneaux et al., *Investigations of  $CH_4$ ,  $C_2H_2$  and  $C_3H_4$  dusty RF plasmas by means of FTIR absorption spectroscopy and mass spectrometry*, JPD (1999)

Al Makdessi et al., *Influence of a magnetic field on the formation of carbon dust particles in very low-pressure high-density plasmas*, JPD (2016)



No real evidence of PAHs

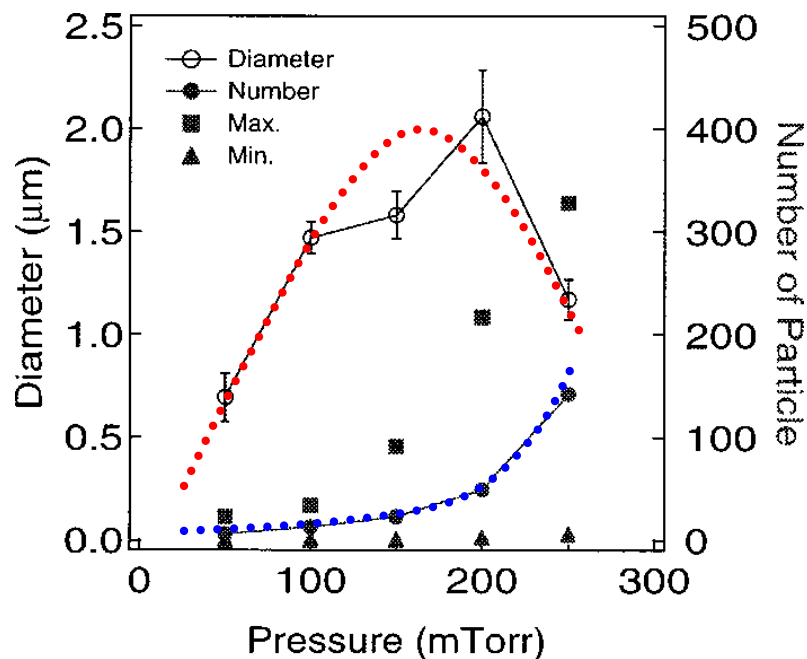
# Dust particle growth in plasmas

- tricky under specific experimental conditions  
for example, with the working pressure

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At low-pressure

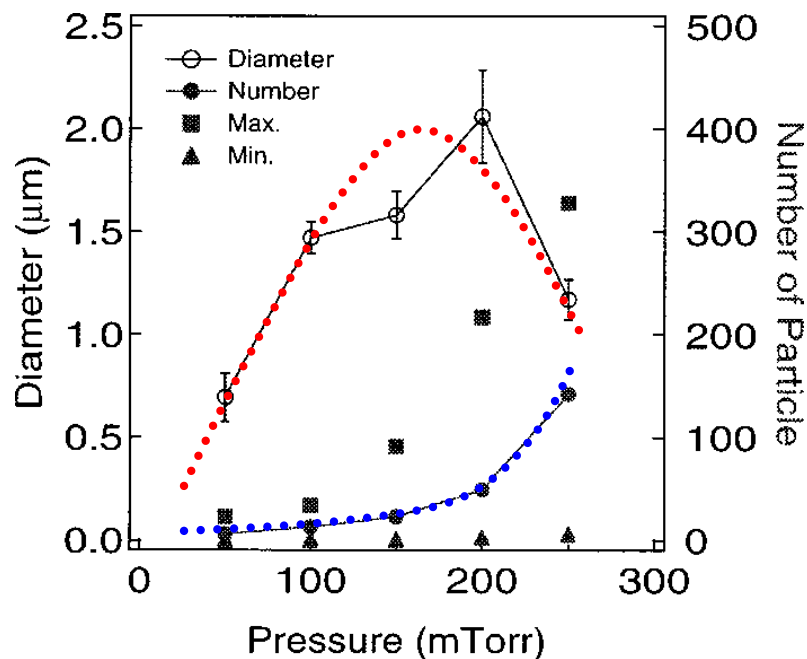
→ probability of recombination  $\ll$

Takahashi et al., *Solid particle production in fluorocarbon plasmas. I. Correlation with polymer film deposition*, JVSTA (2001)

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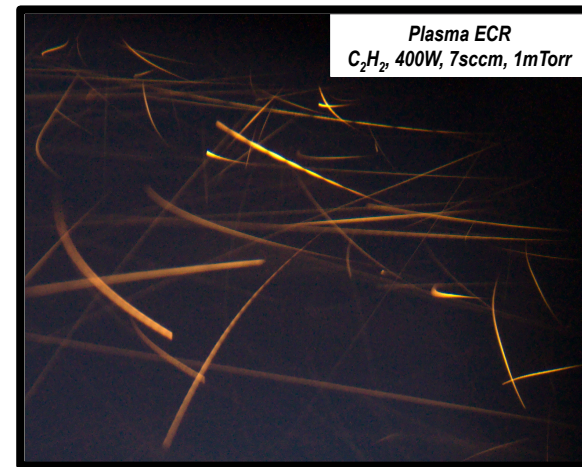


Takahashi et al., *Solid particle production in fluorocarbon plasmas. I. Correlation with polymer film deposition*, JVSTA (2001)

At low-pressure

→ probability of recombination  $\ll$

However...



Drenik et al., *Trajectories of dust particles in low-pressure magnetized plasma*, IEEEETPS (2011)

No real evidence of PAHs

What's happening at really low-pressure?

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III DUST PARTICLES FORMED IN C<sub>2</sub>H<sub>2</sub> PLASMAS

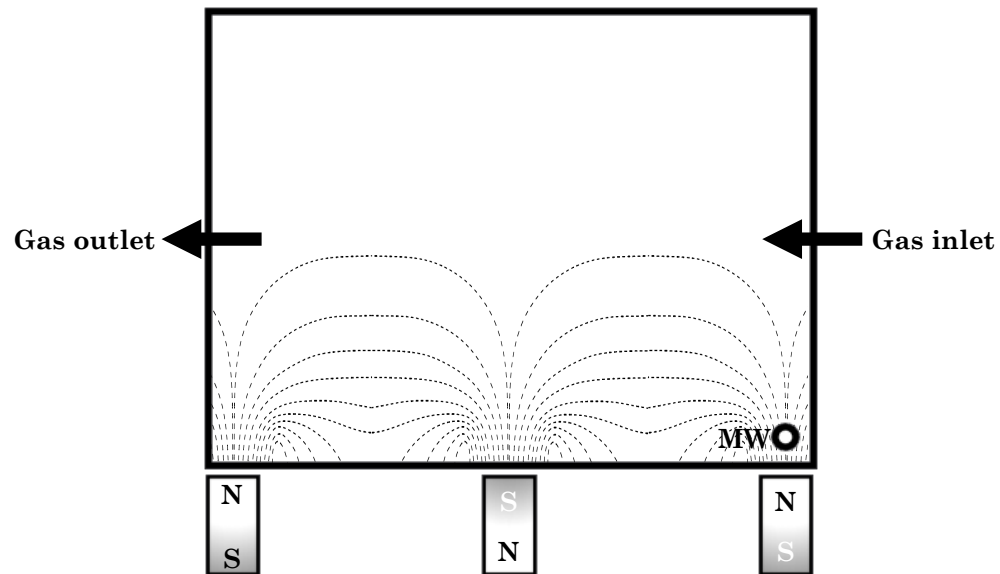
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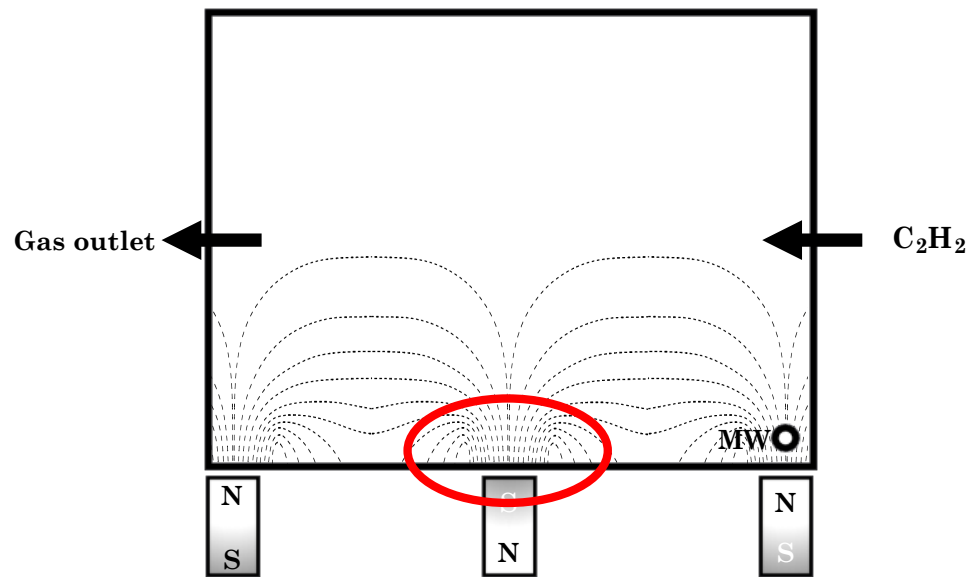
# ECR plasmas

- static magnetic field
  - electron confinement
  - electron heating
  - $B=875$  Gauss  $\Leftrightarrow$  microwave (2.45 GHz)

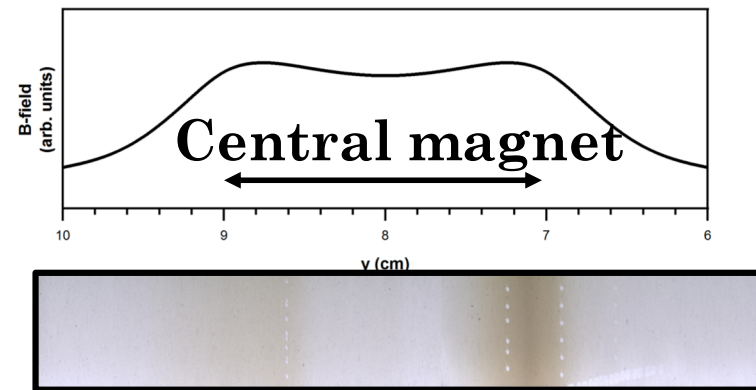
- really-low pressure regime – 0.1 Pa



# ECR plasmas / $C_2H_2$



Deposition above the magnets / edges





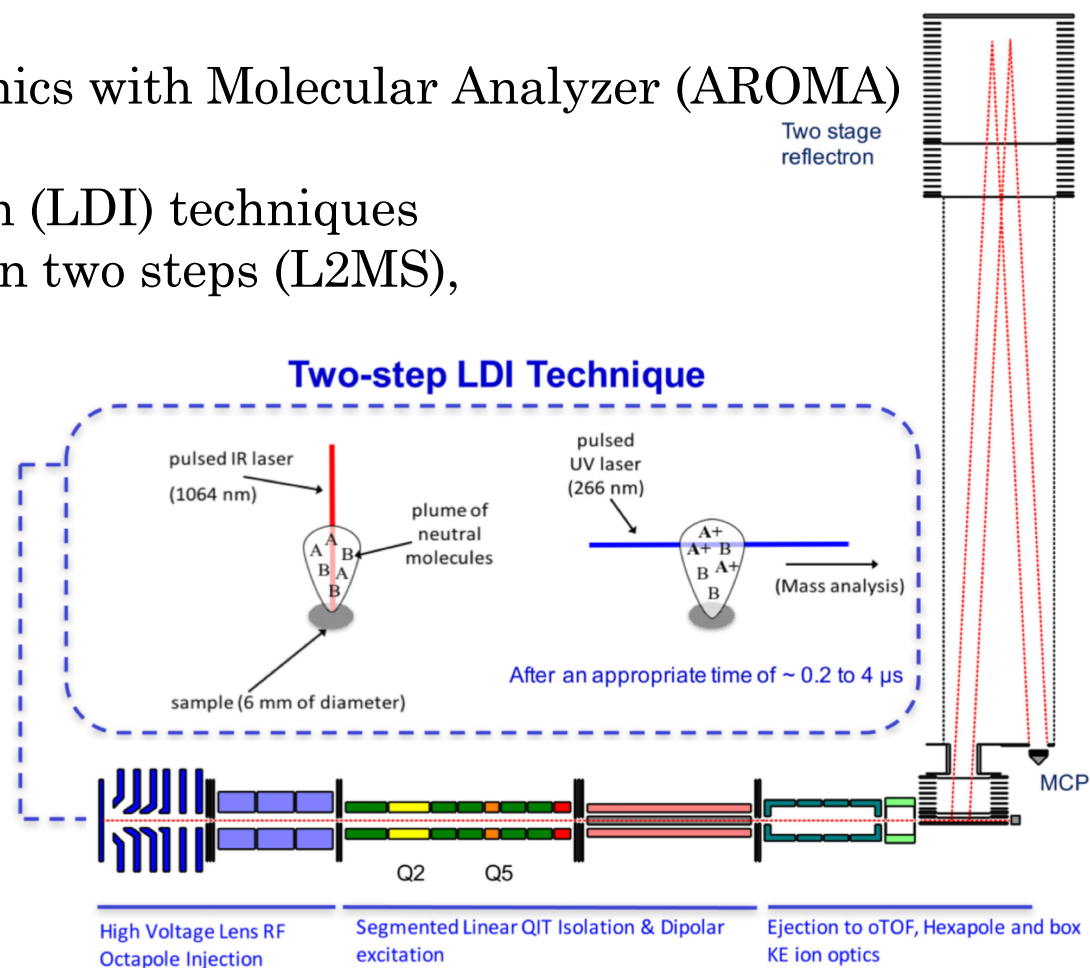
# Ex-situ measurements

Microscopies (SEM / TEM)

Spectroscopies

Astrochemistry Research of Organics with Molecular Analyzer (AROMA)

couples laser desorption/ionization (LDI) techniques  
with ion trap mass spectrometry in two steps (L2MS),

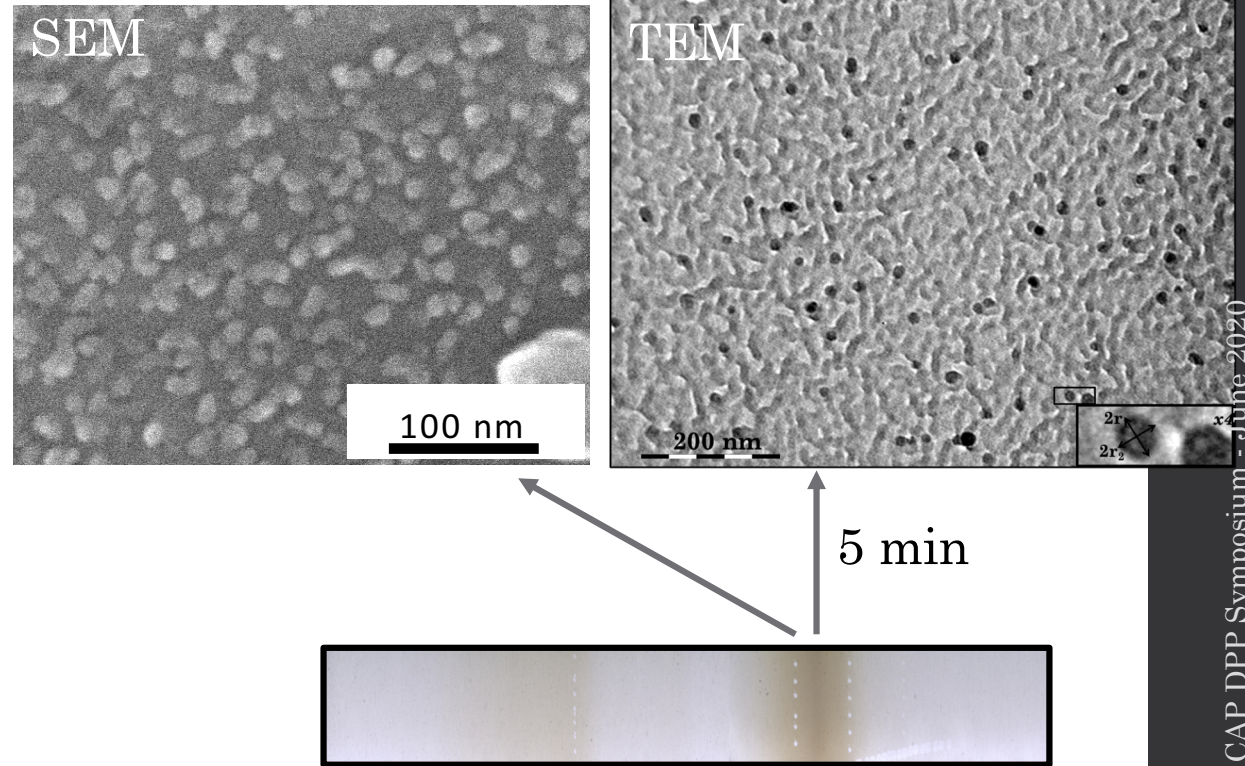


Sabbah et al., *Identification of PAH Isomeric Structure in Cosmic Dust Analogues: the AROMA setup*, ApJ (2017)

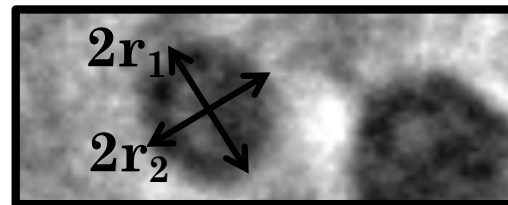
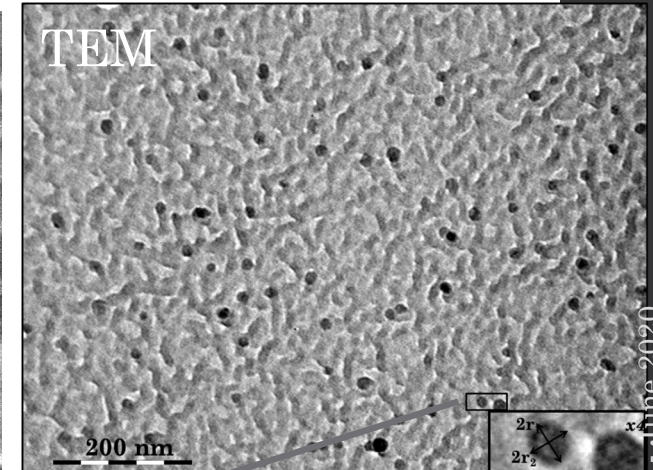
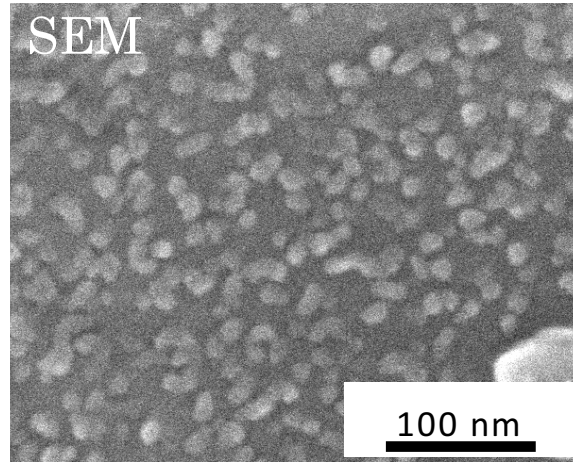
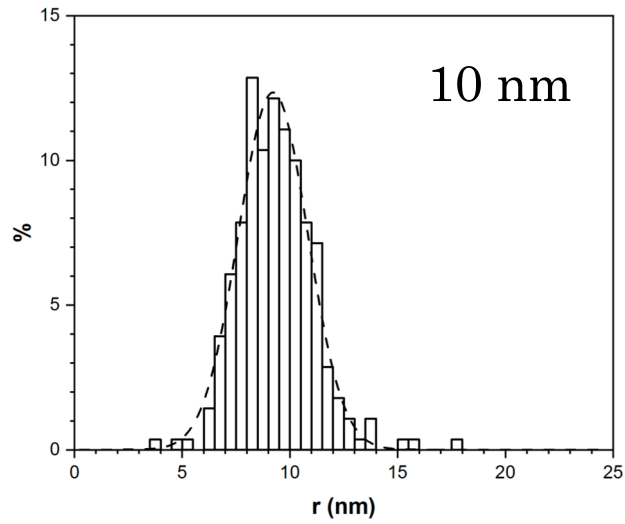
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# ECR plasmas / $C_2H_2$

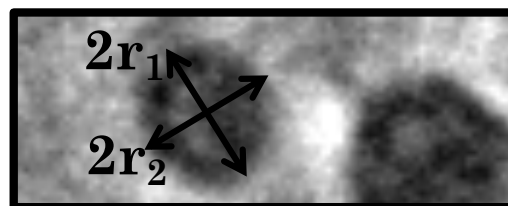
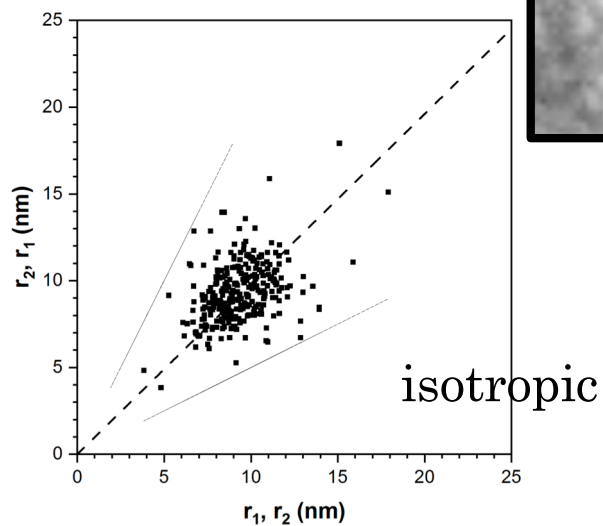
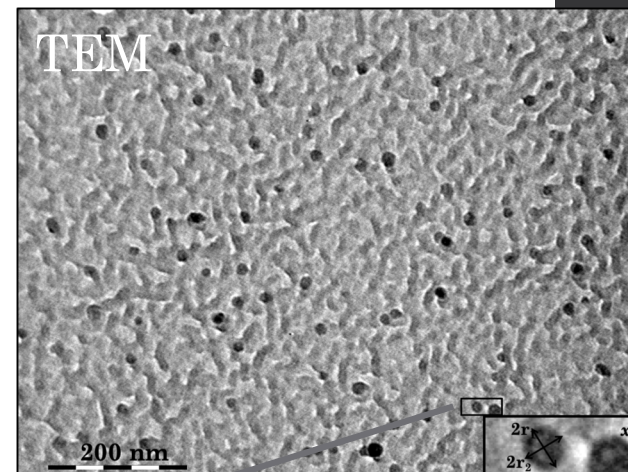
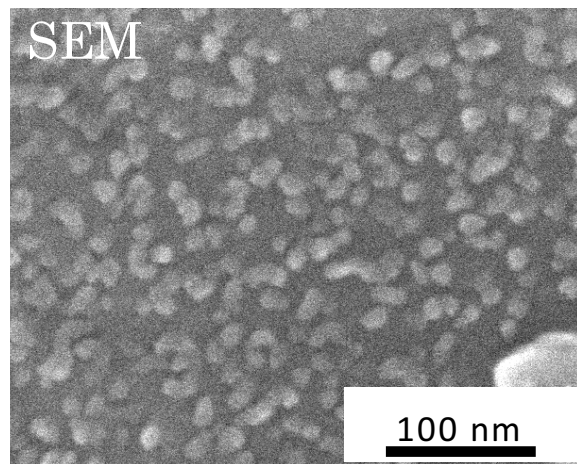
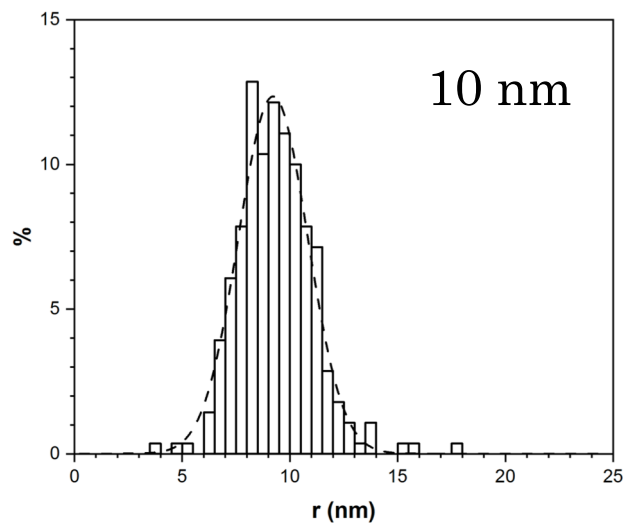


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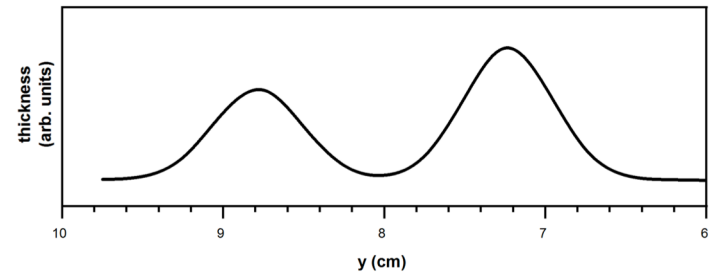
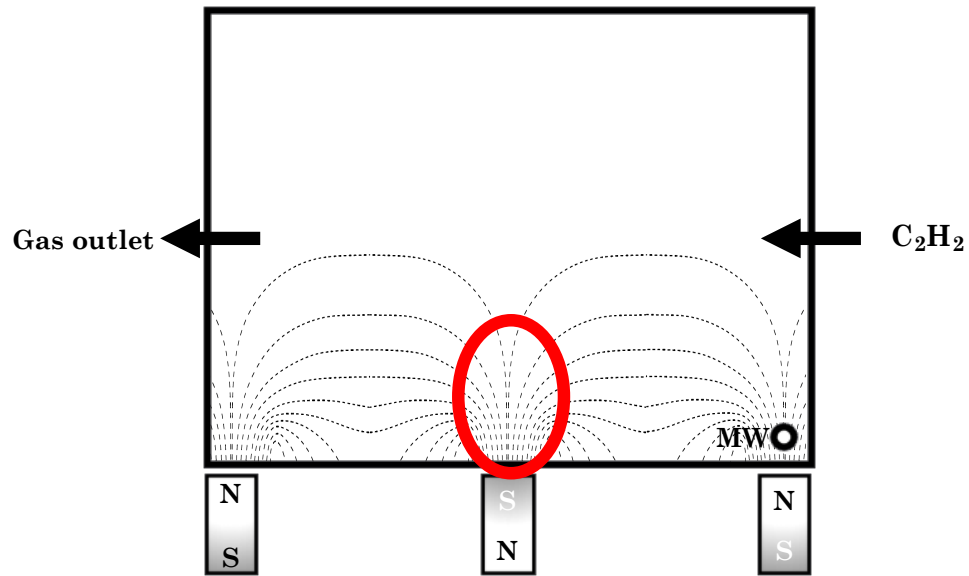




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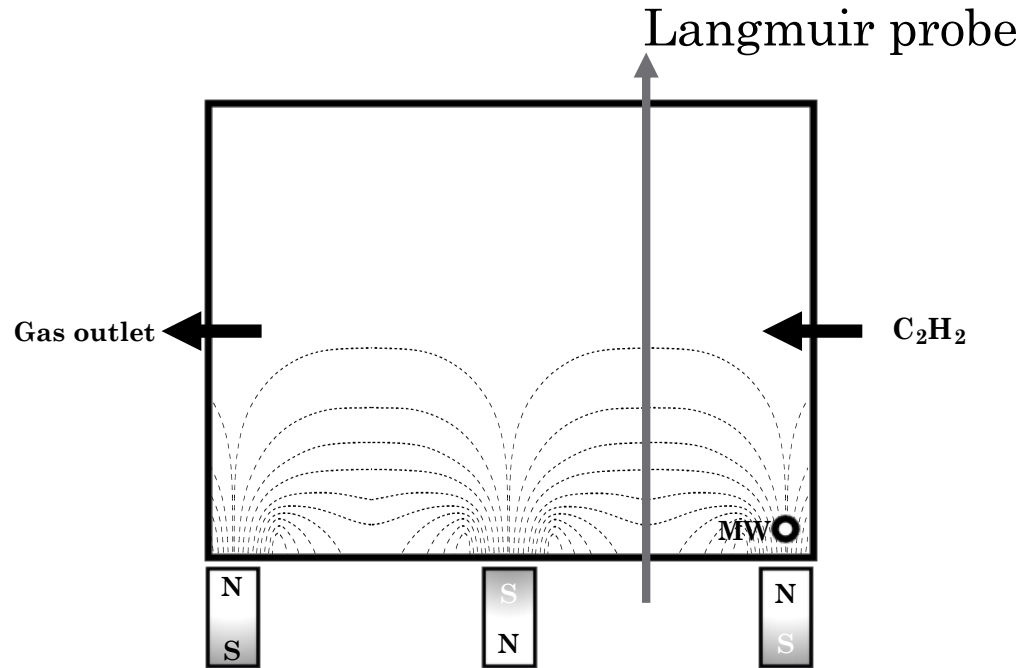


5 min

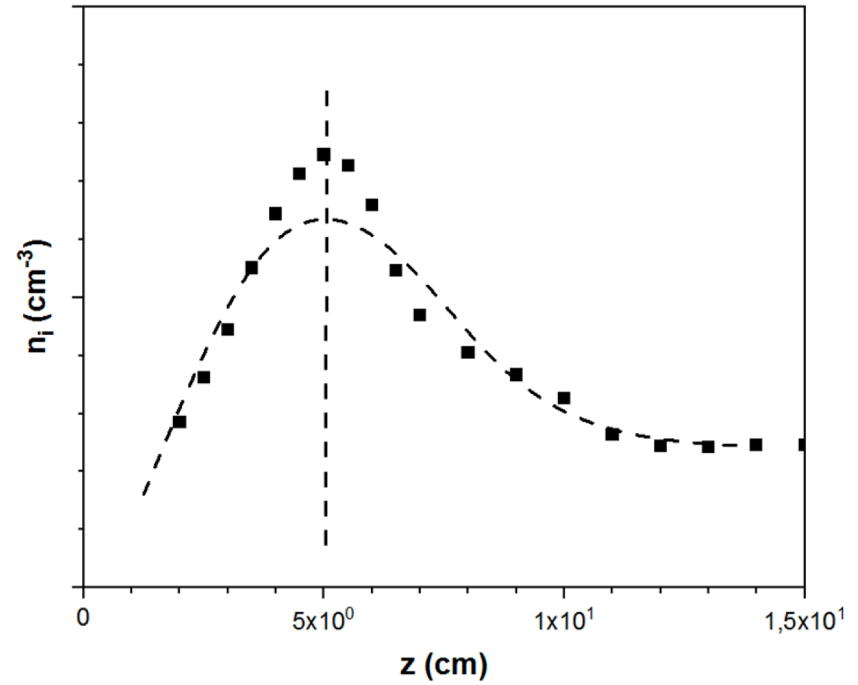
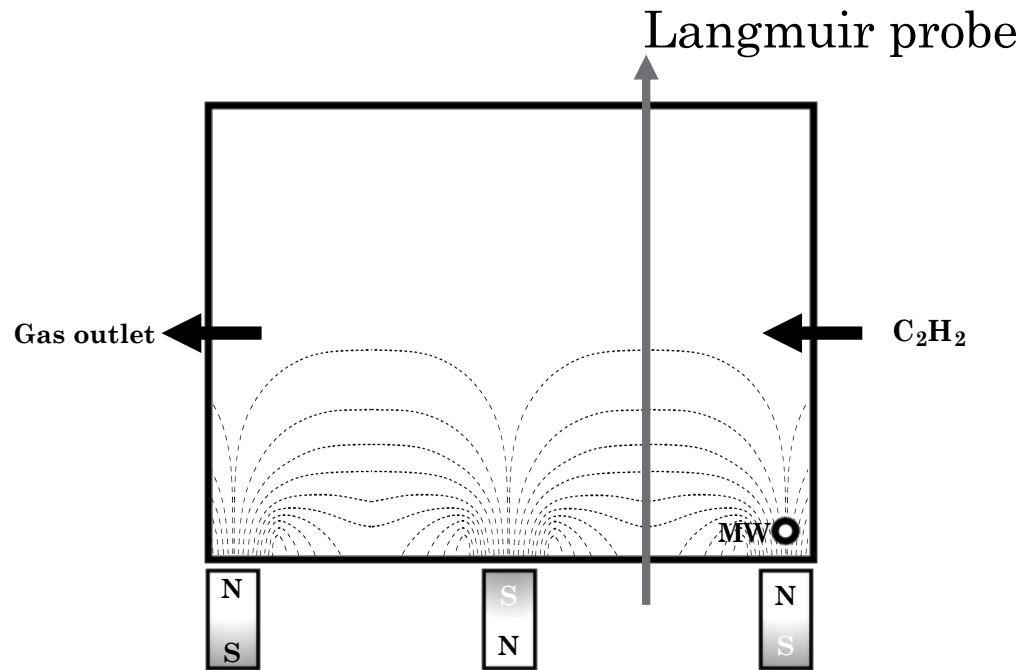


➔ Growth in the plasma volume

# Growth processes?

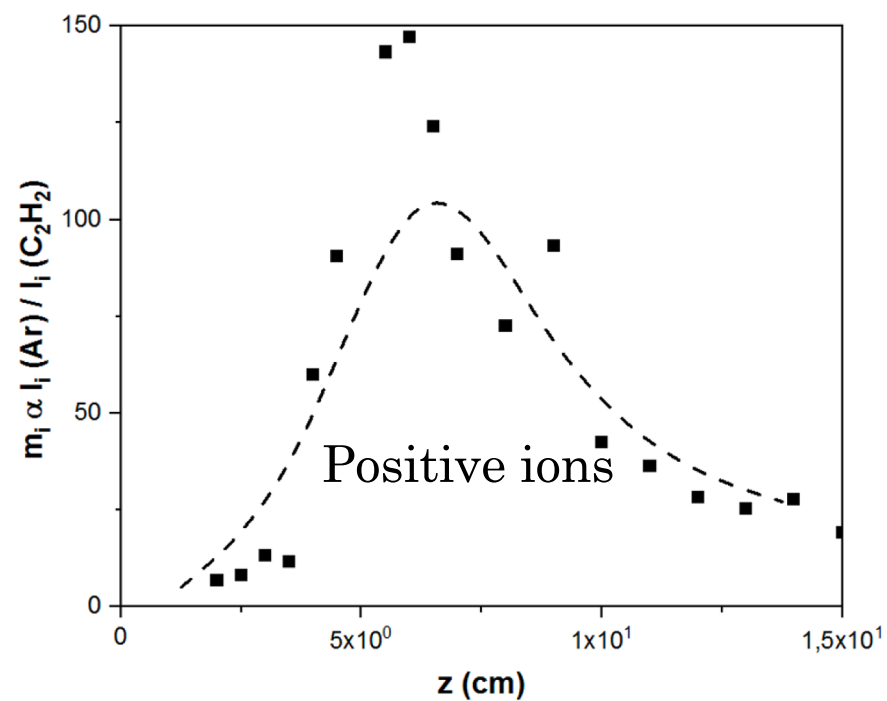
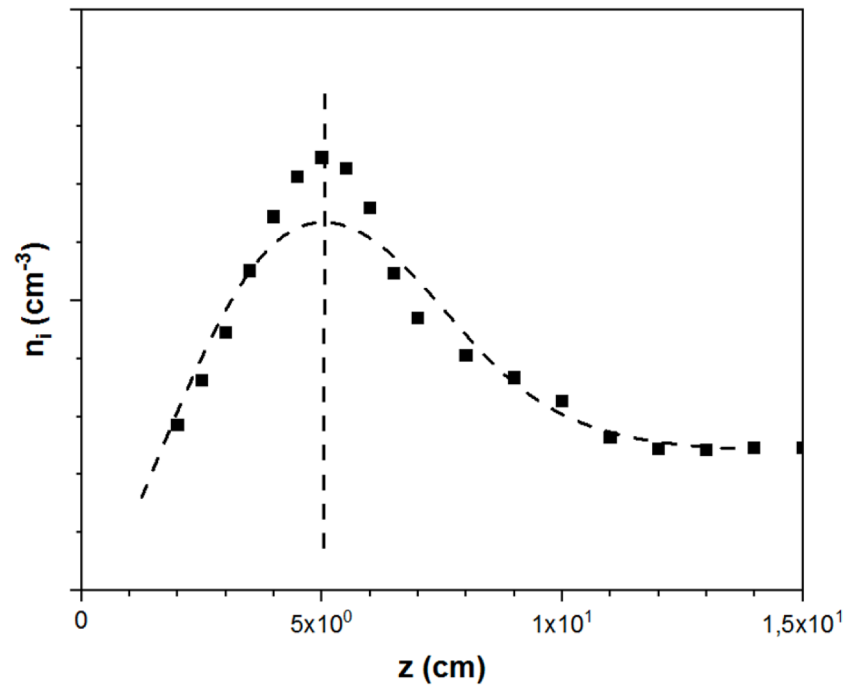
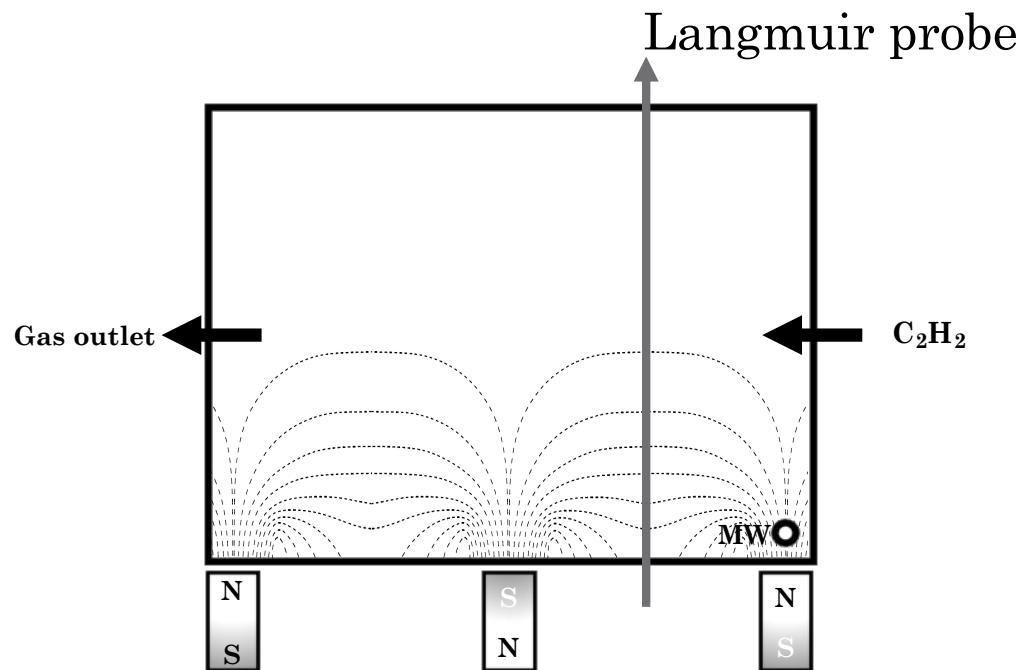


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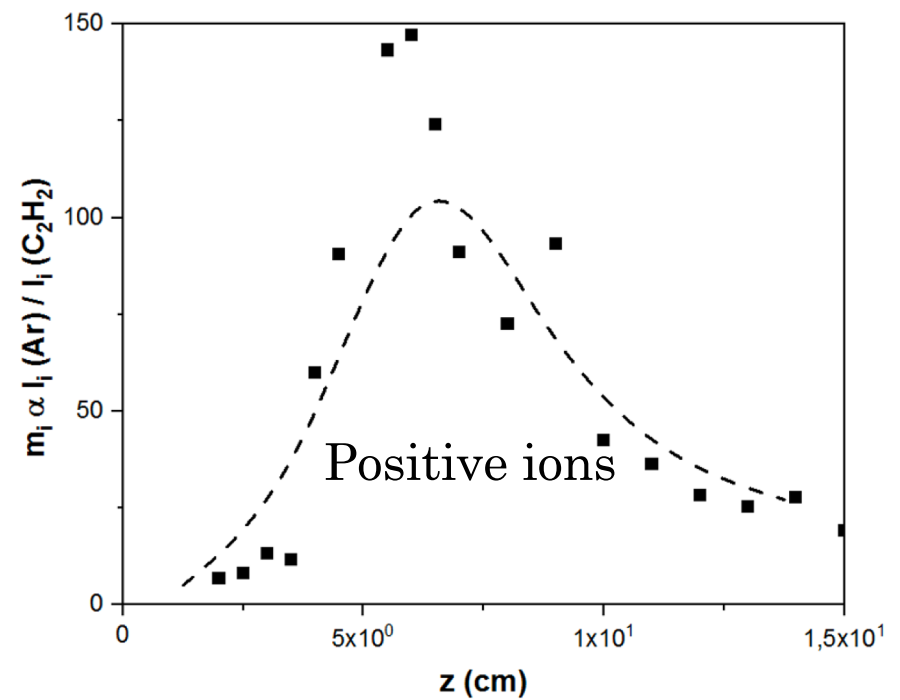
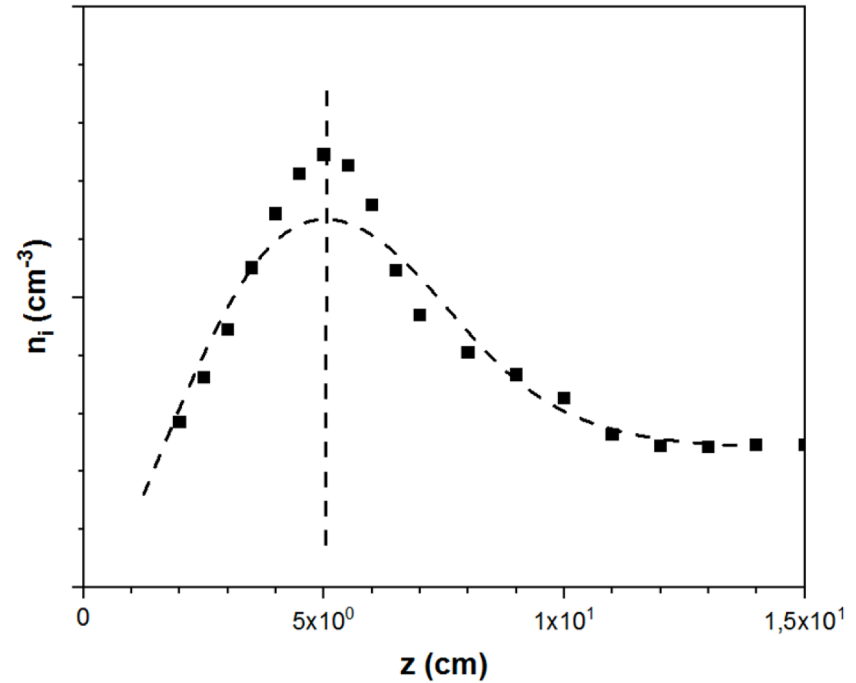
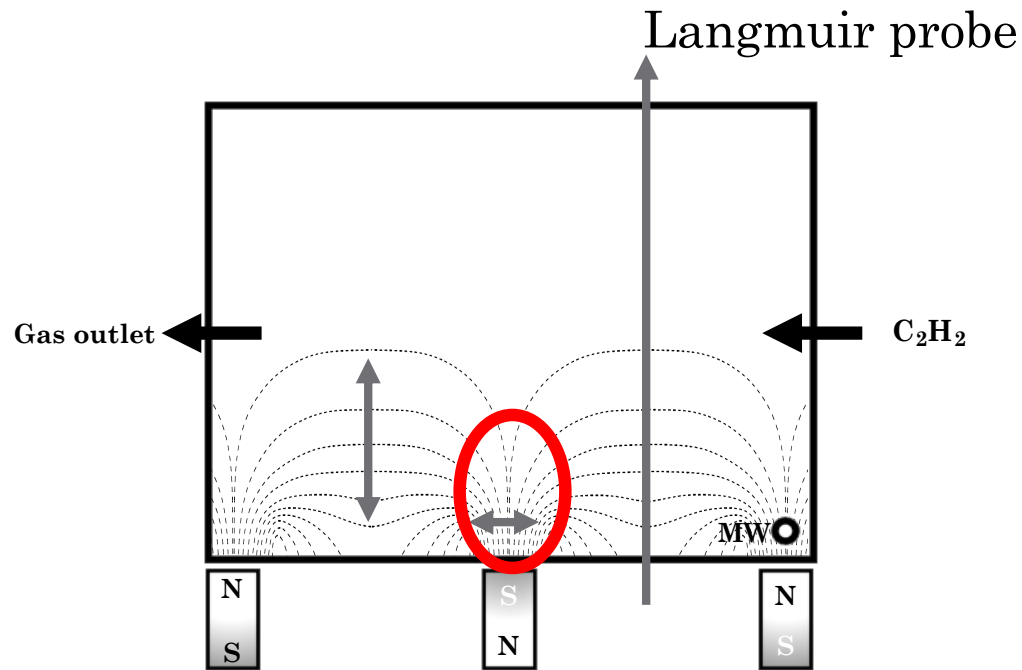


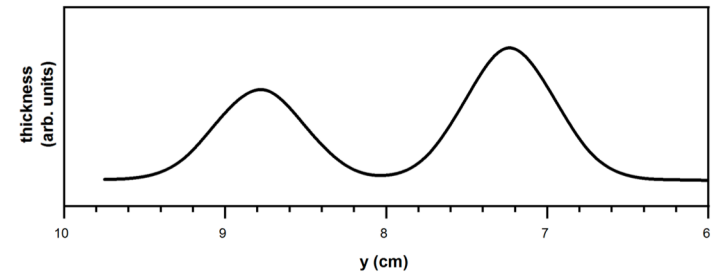
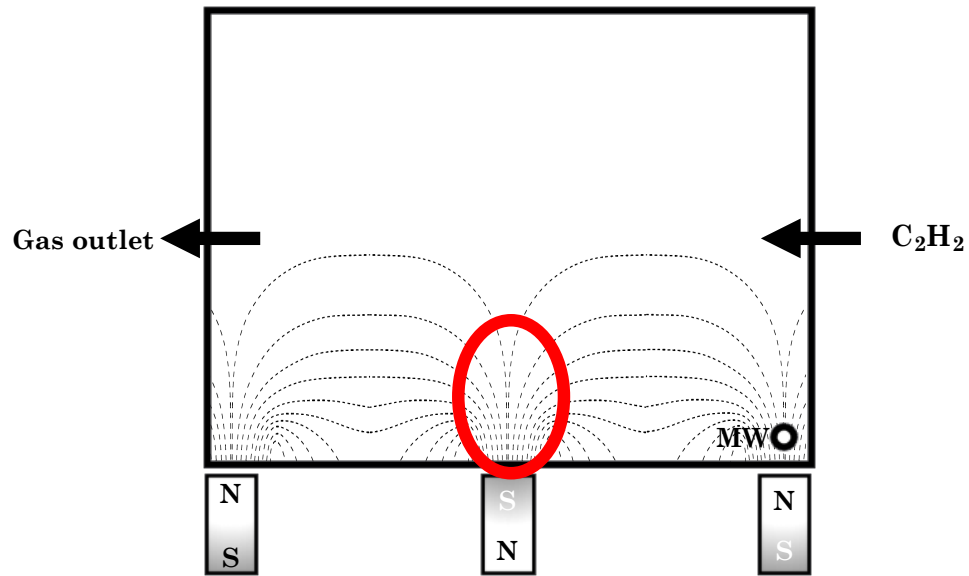


# Growth processes?

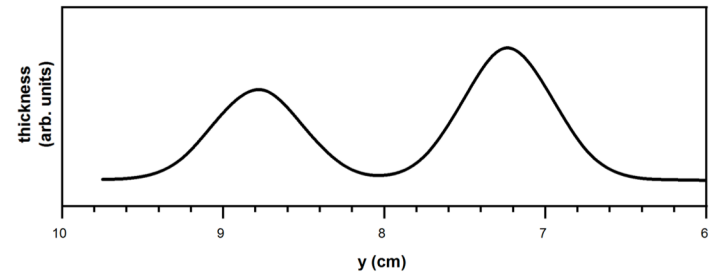
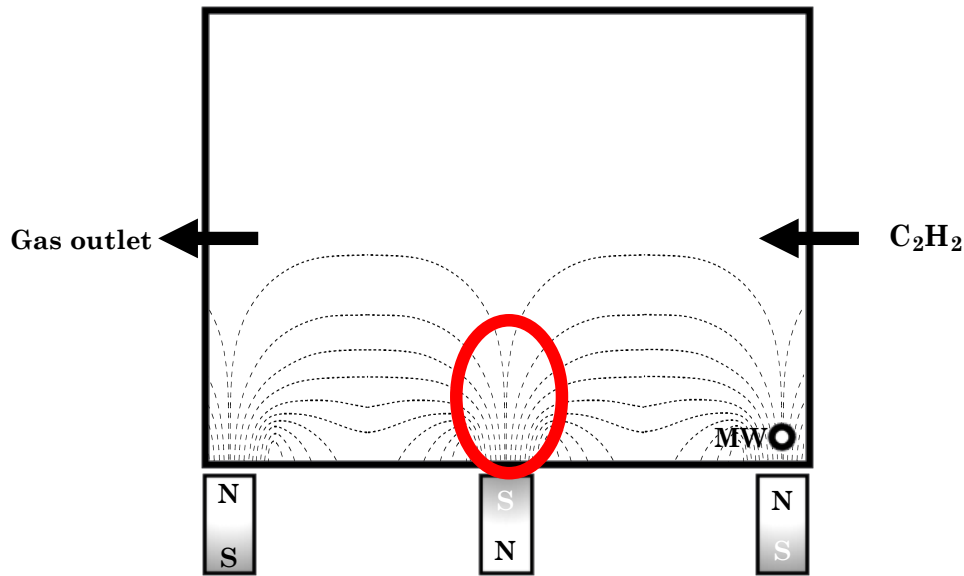


# Growth processes?



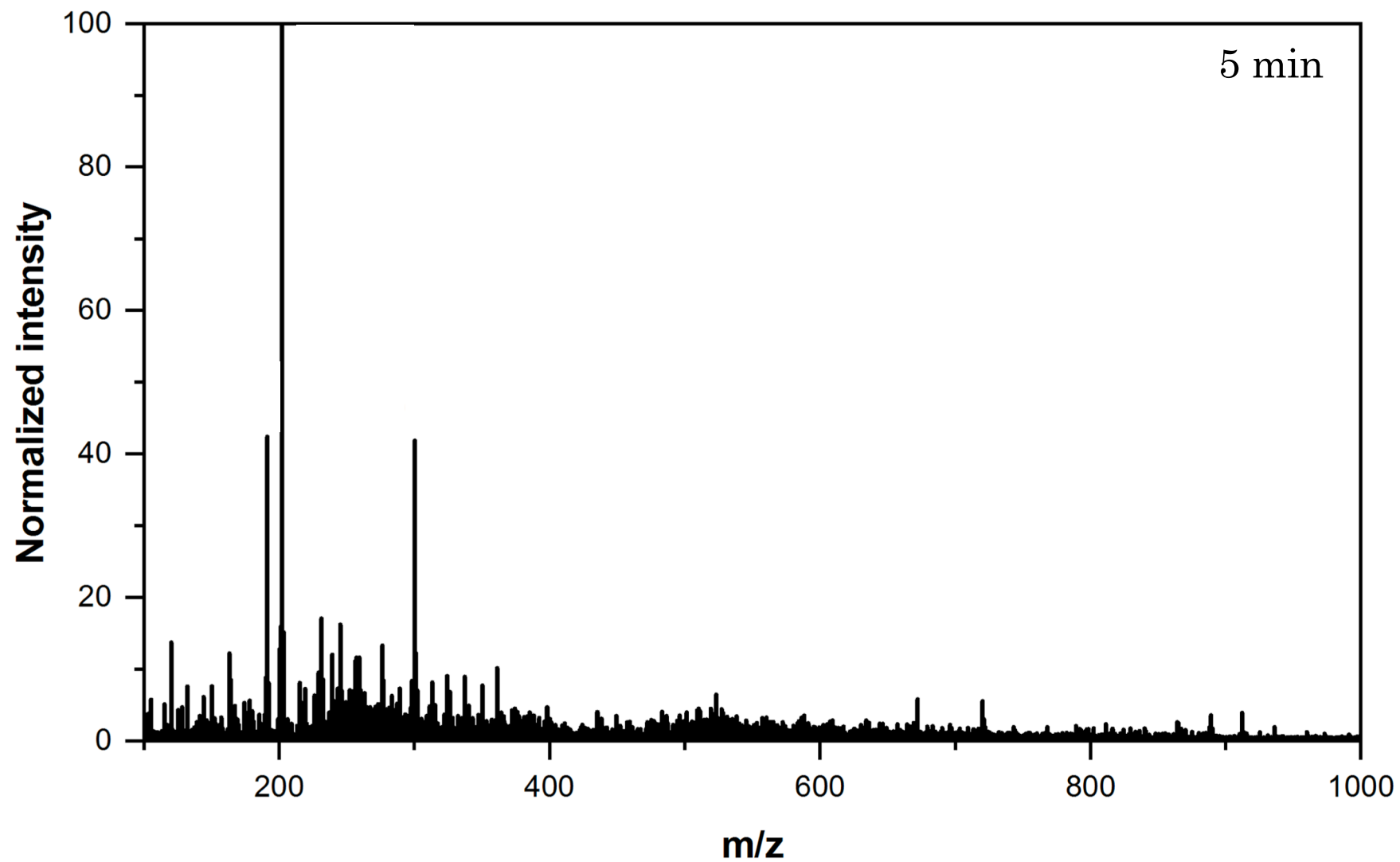


- ➔ Growth in the plasma volume
- ➔ Local growth

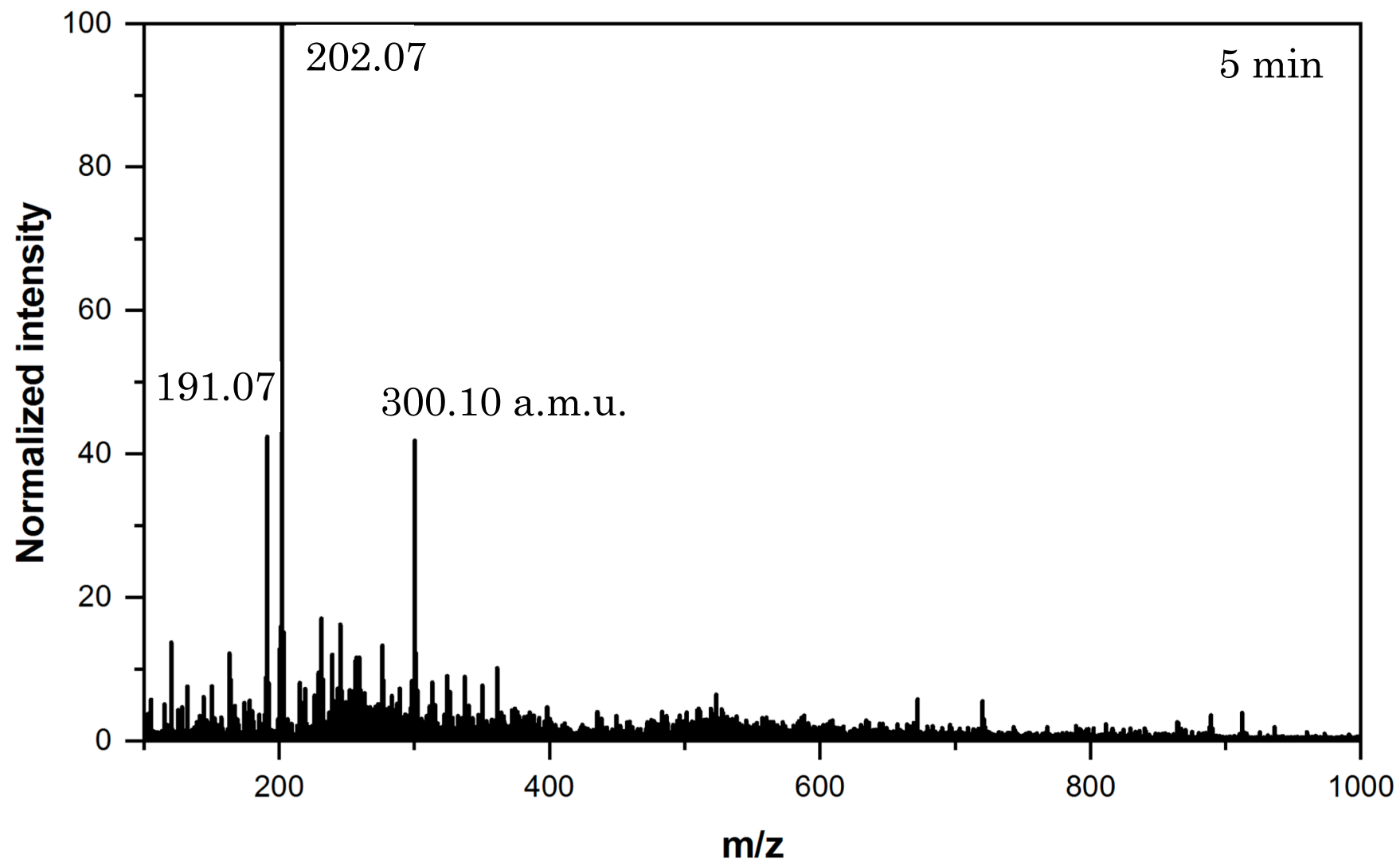


- ➔ Growth in the plasma volume
- ➔ Local growth
- ➔ Molecular composition?

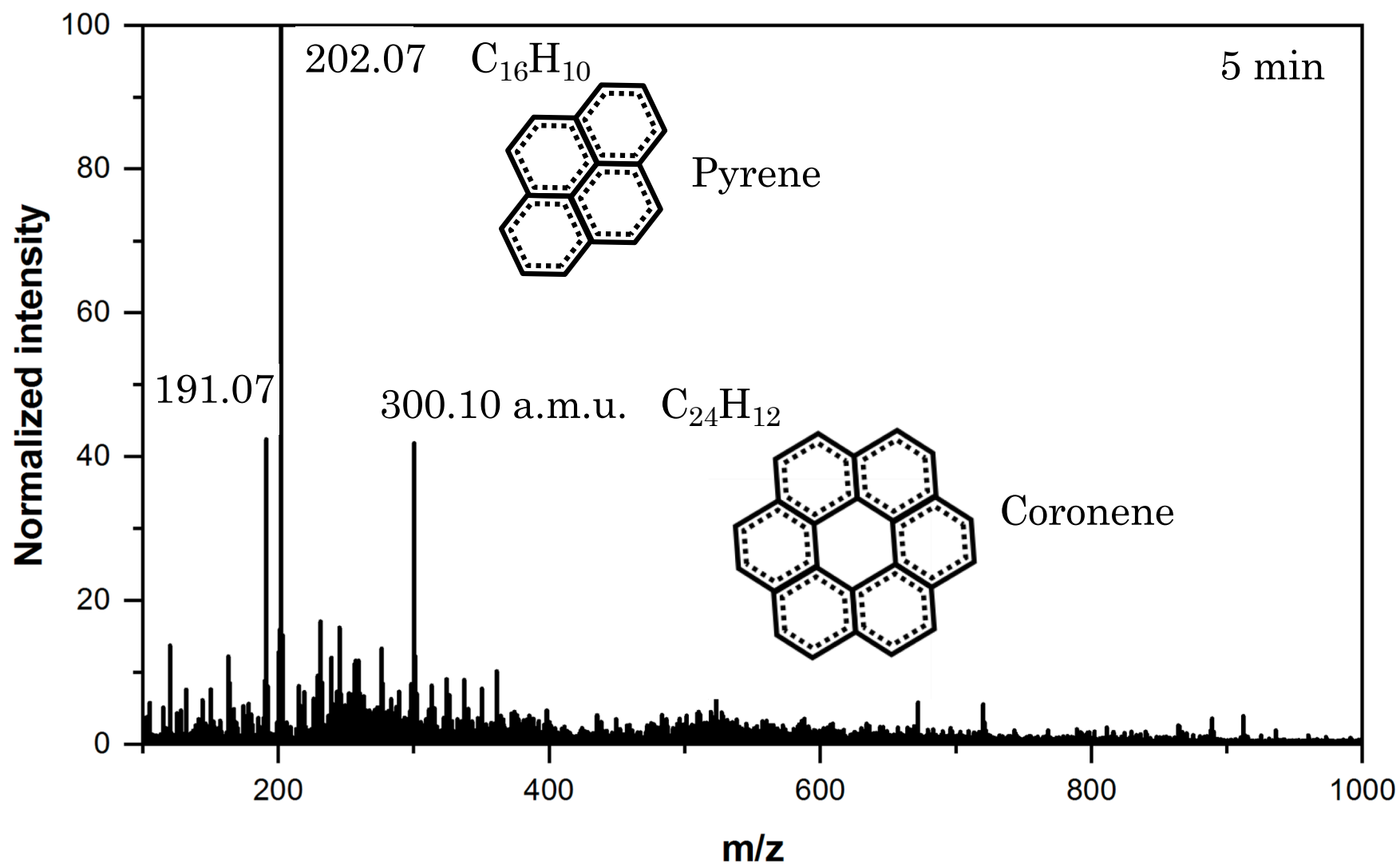
# AROMA analyses



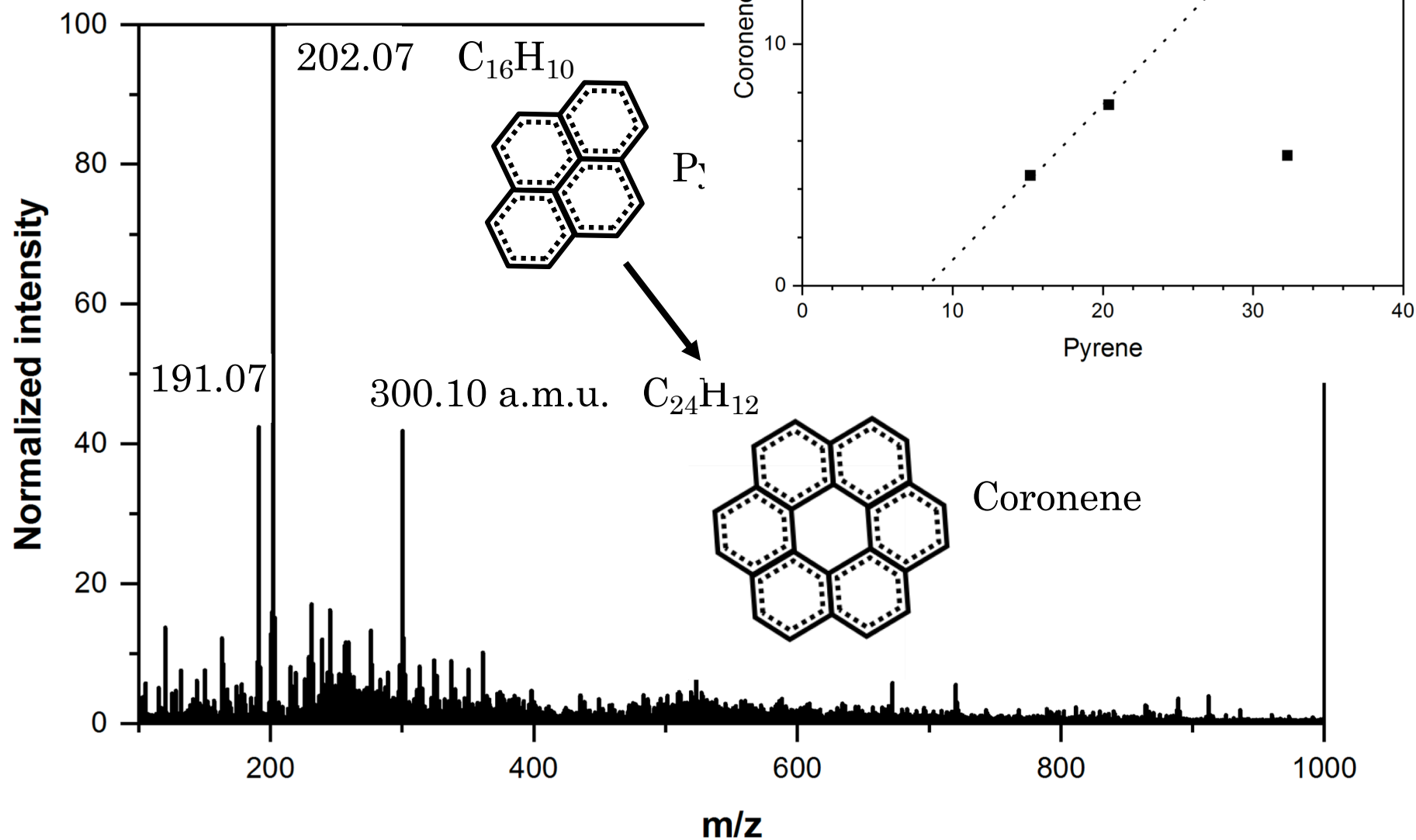
# AROMA analyses



# AROMA analyses

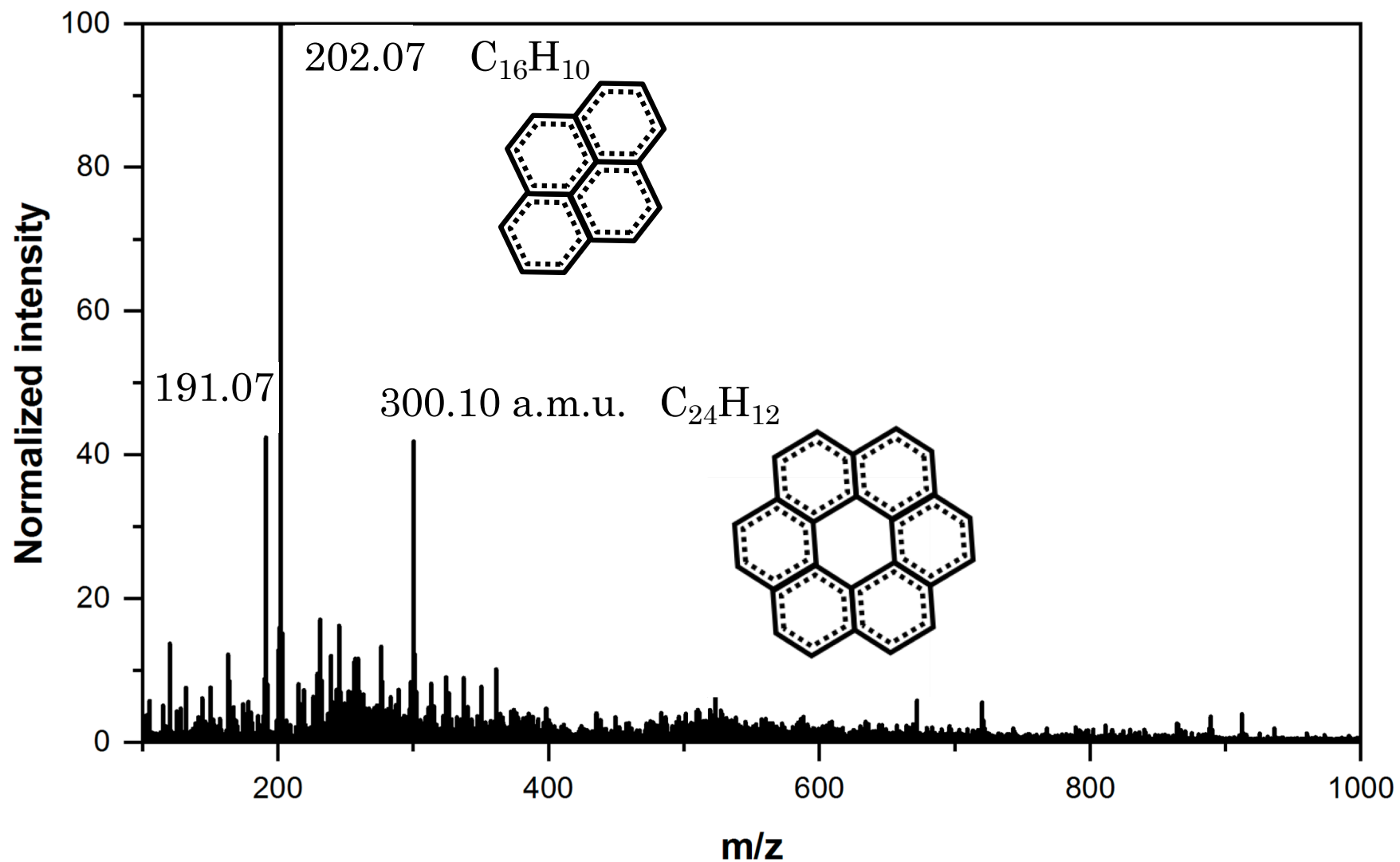


# AROMA analyses

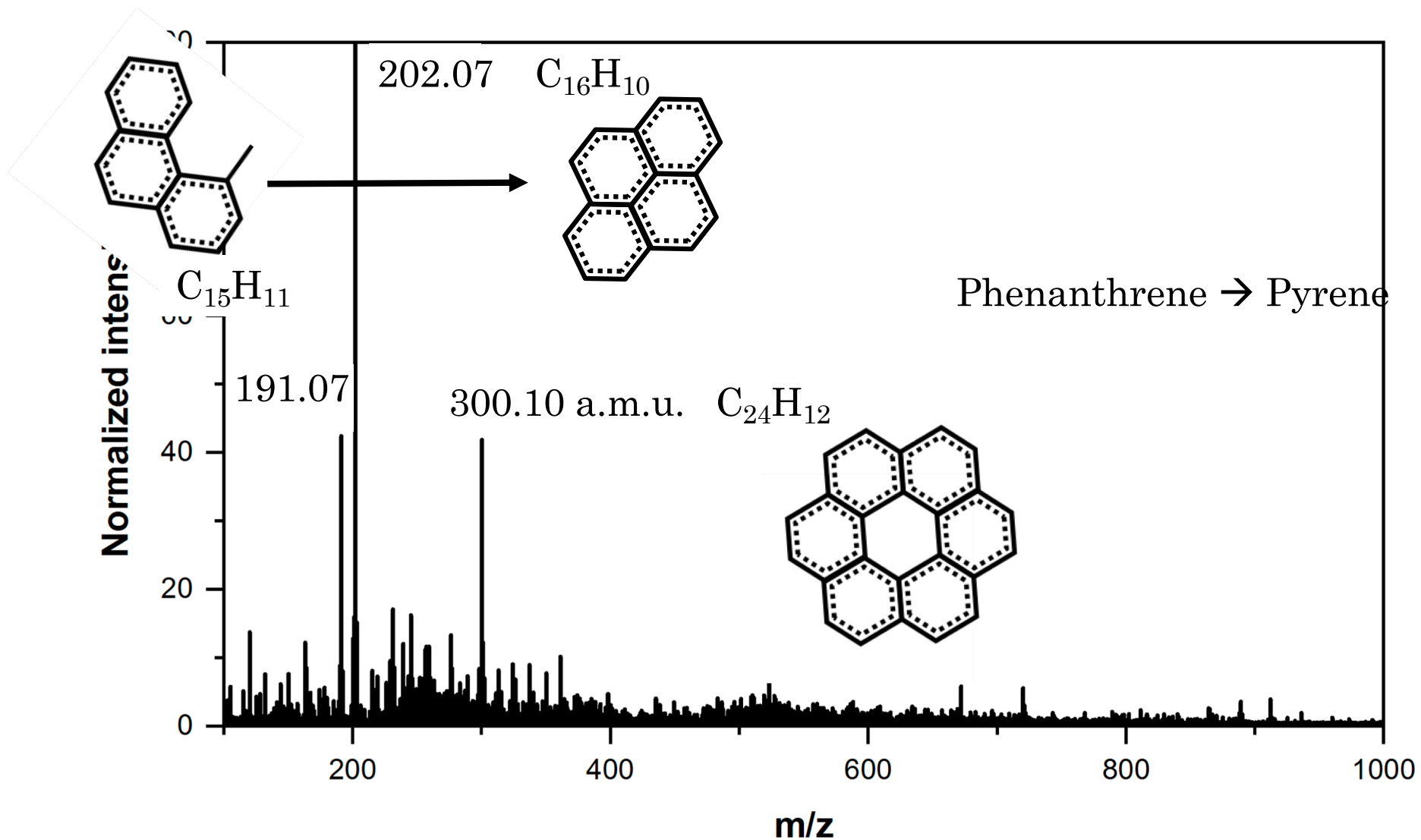




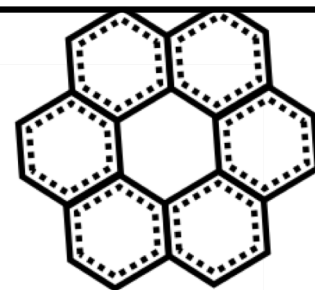
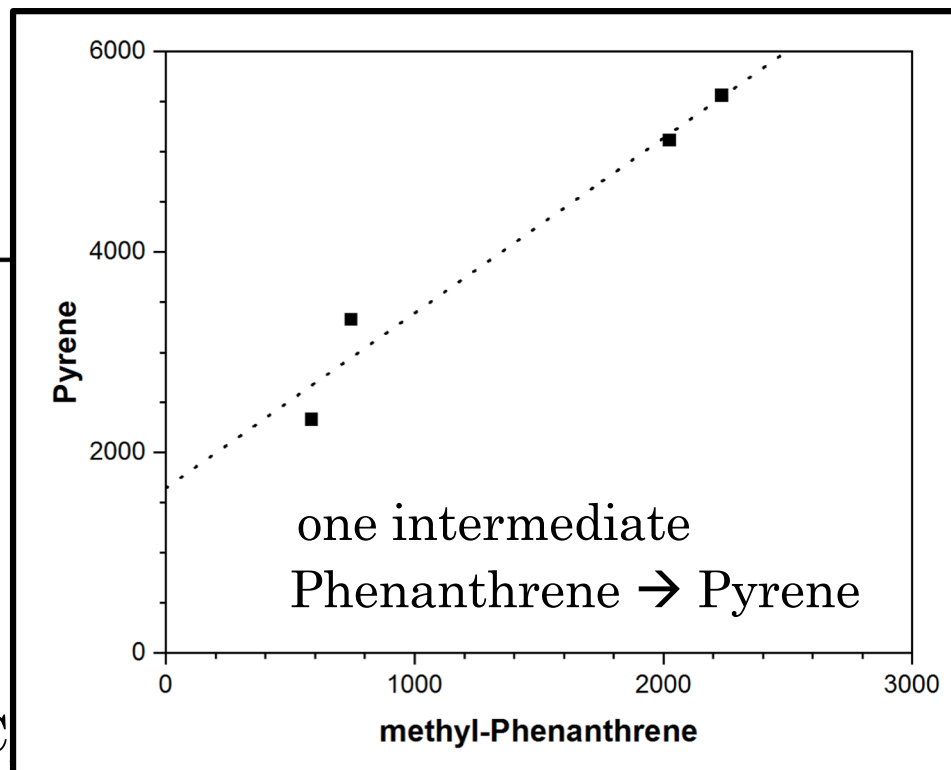
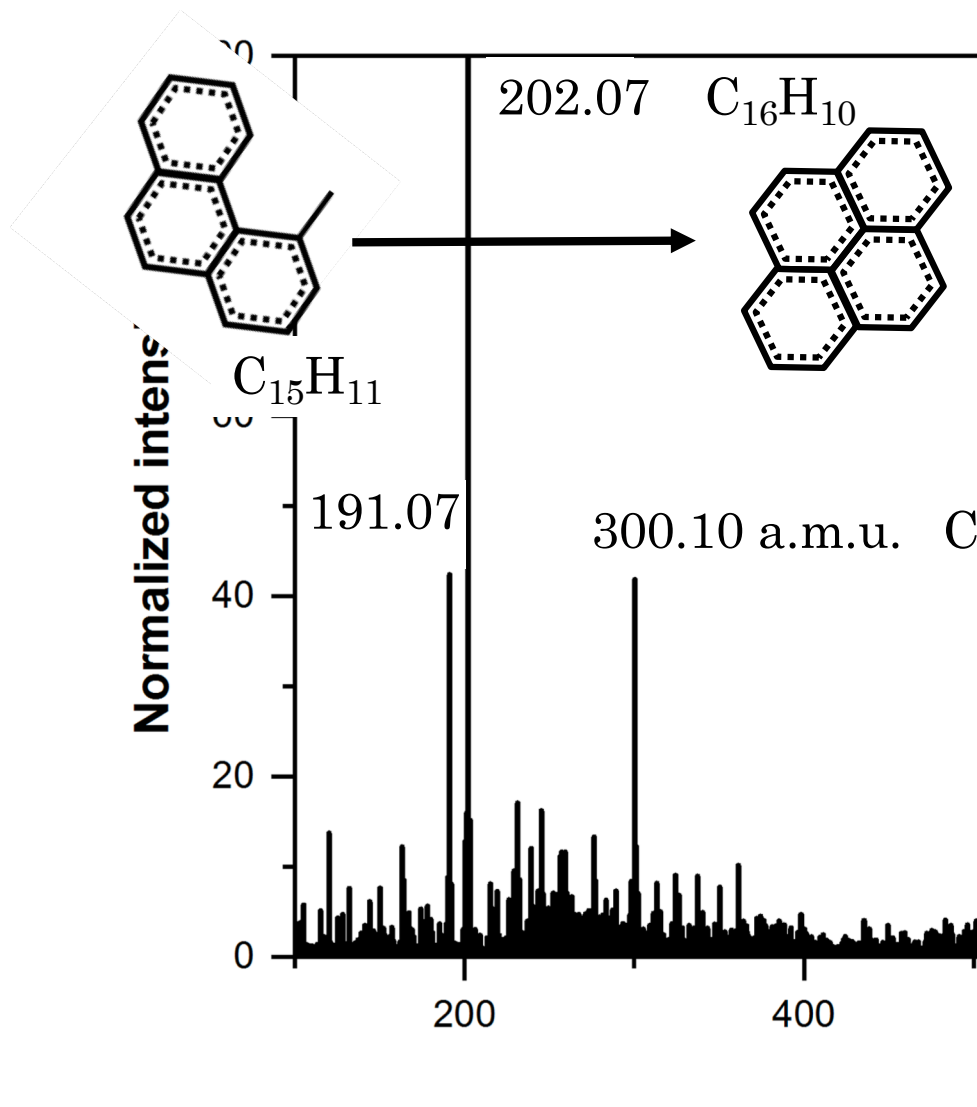
# AROMA analyses



# AROMA analyses

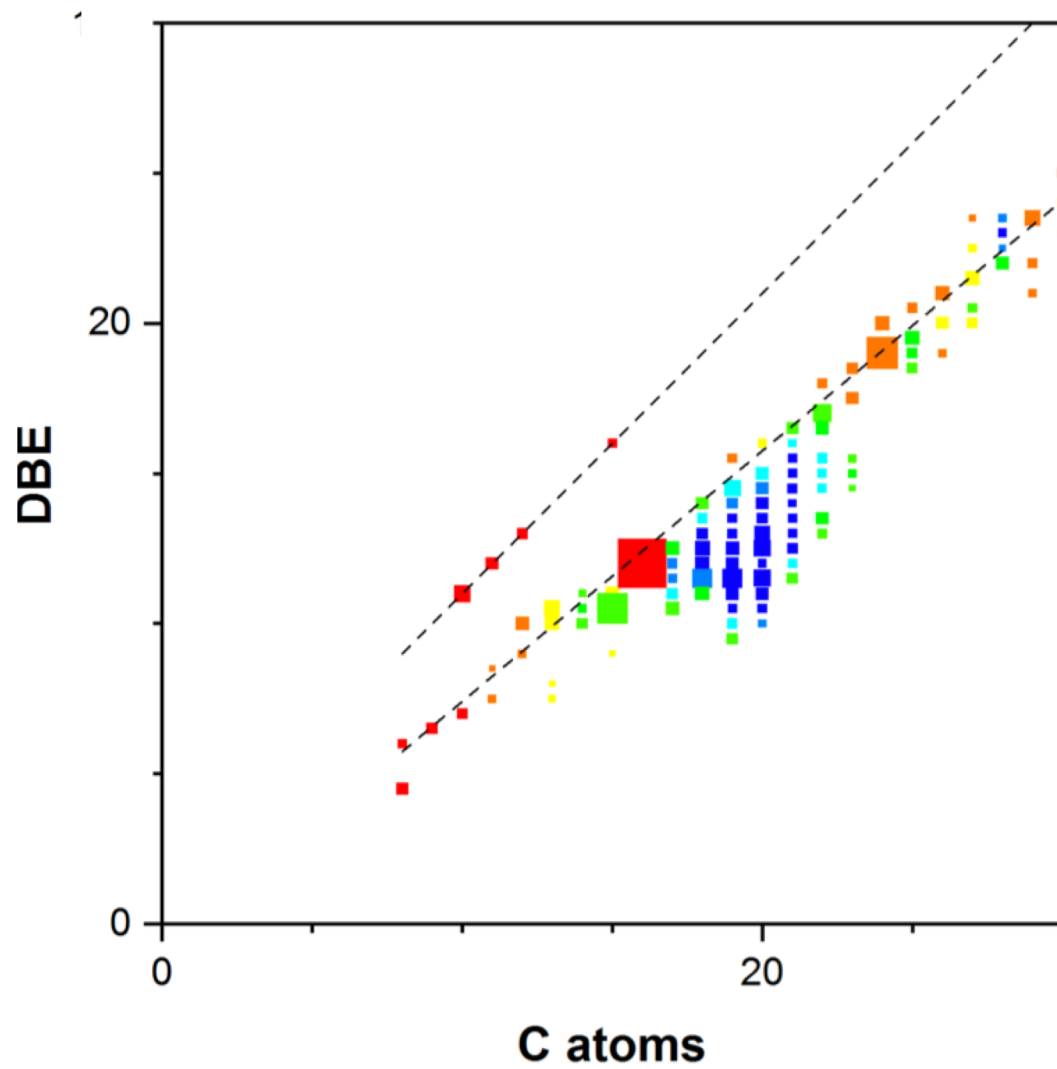


# AROMA analyses



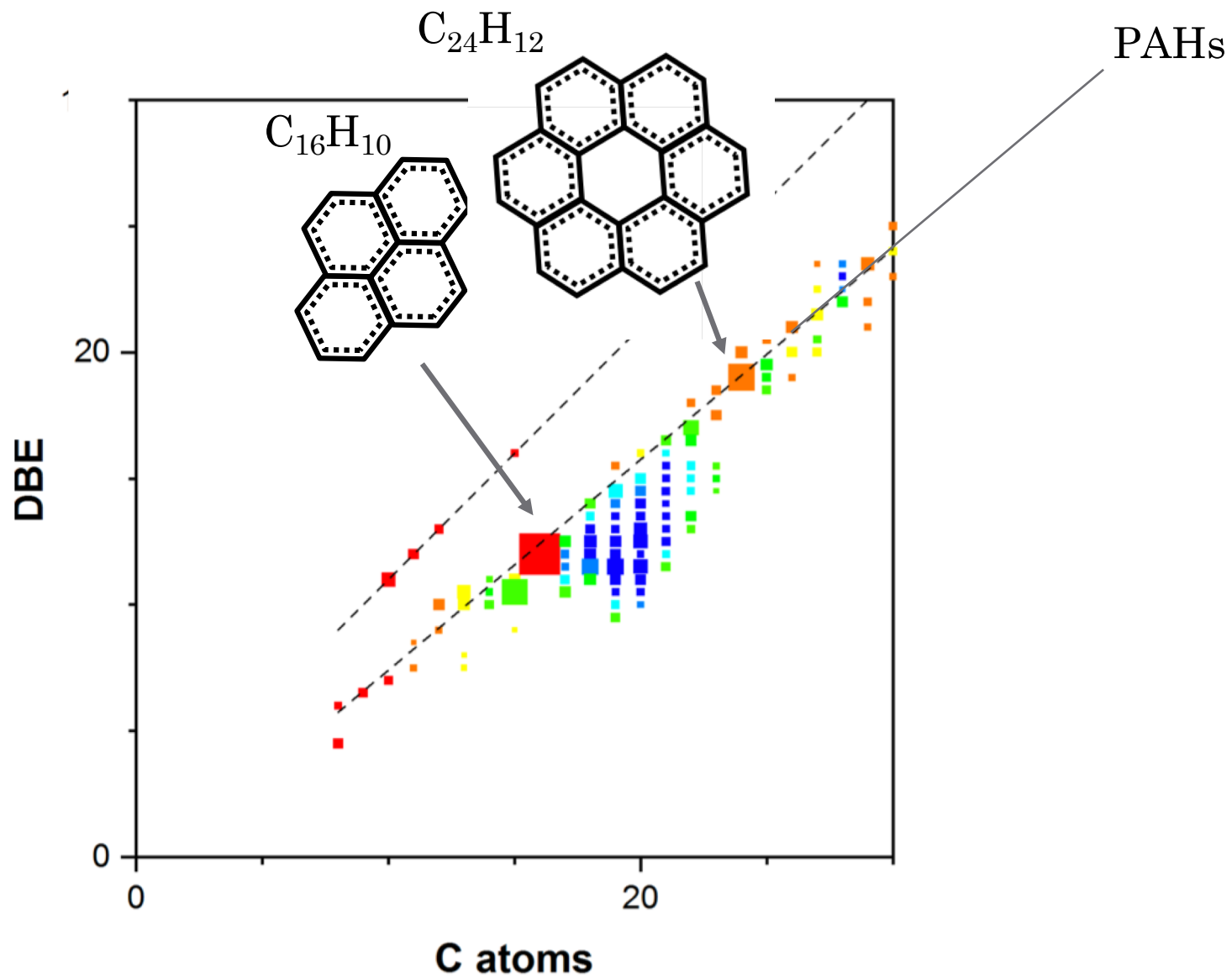
$C_xH_y \rightarrow$  Double Bond Equivalent (DBE)

$$DBE(C_xH_y) = x - y/2 + 1$$



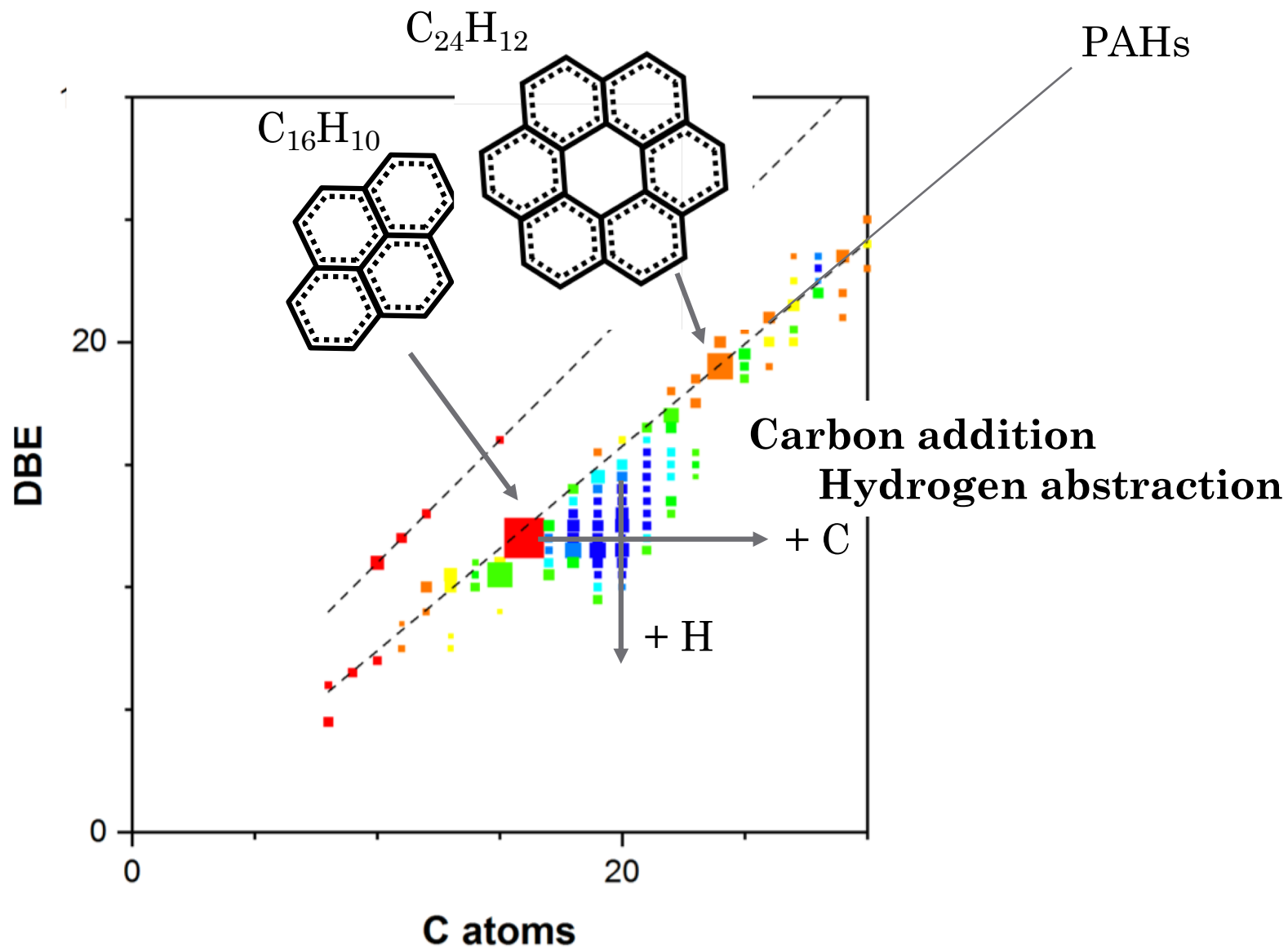
$C_xH_y \rightarrow$  Double Band Equivalent (DBE)

$$DBE(C_xH_y) = x - y/2 + 1$$

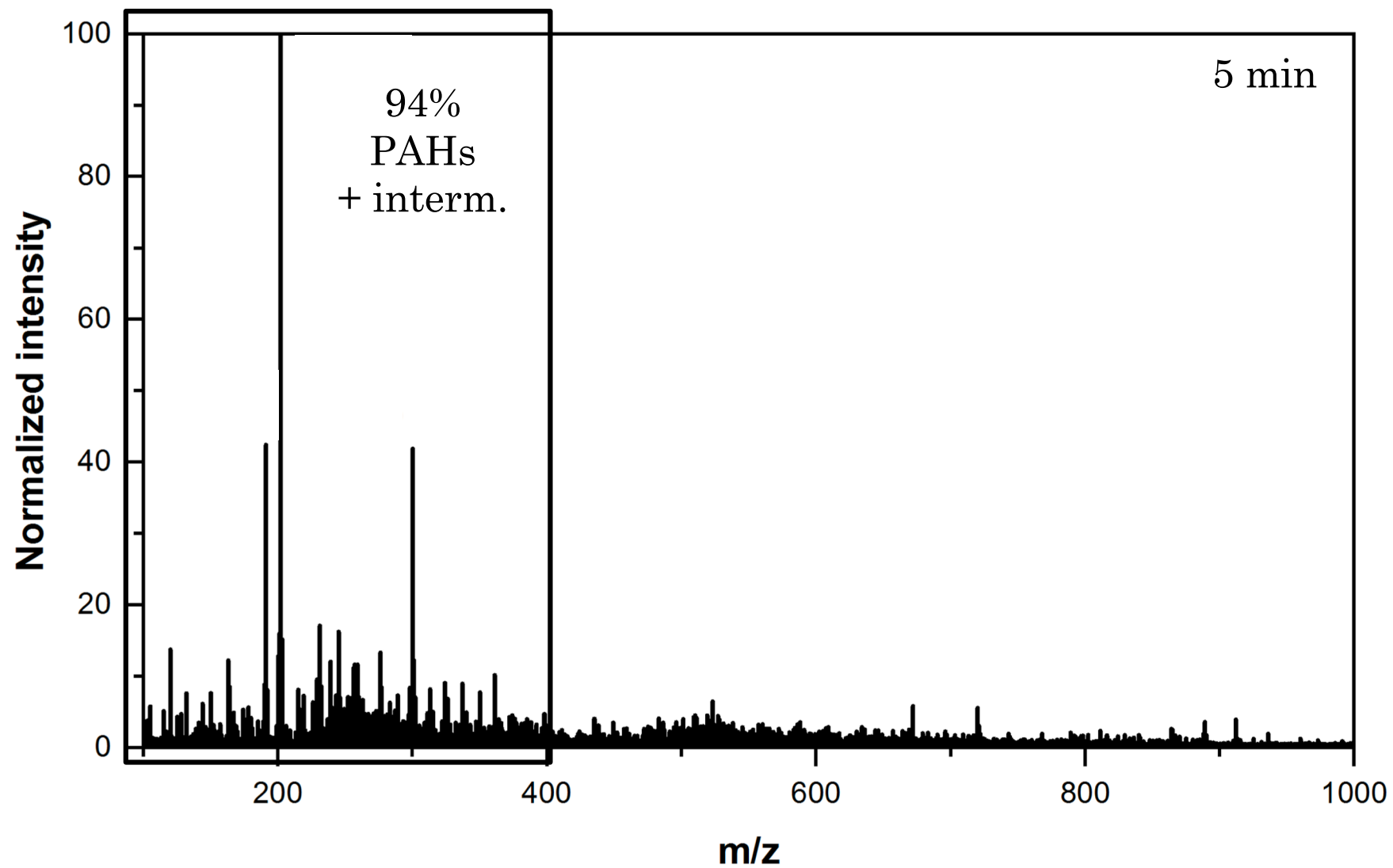


$C_xH_y \rightarrow$  Double Band Equivalent (DBE)

$$DBE(C_xH_y) = x - y/2 + 1$$



# AROMA analyses



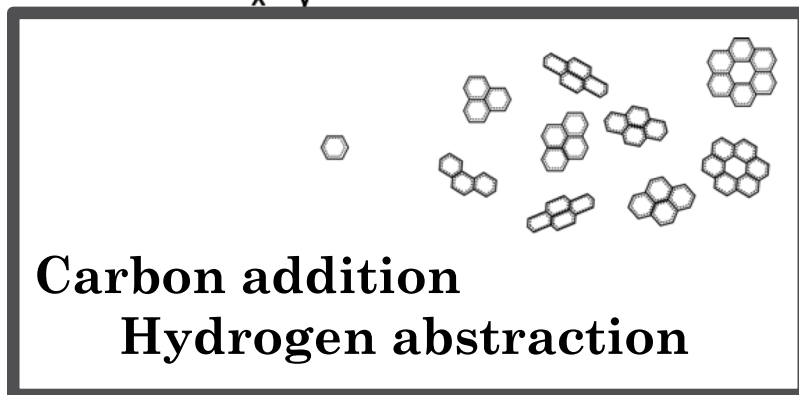
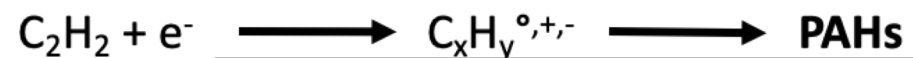
***Above the magnets***



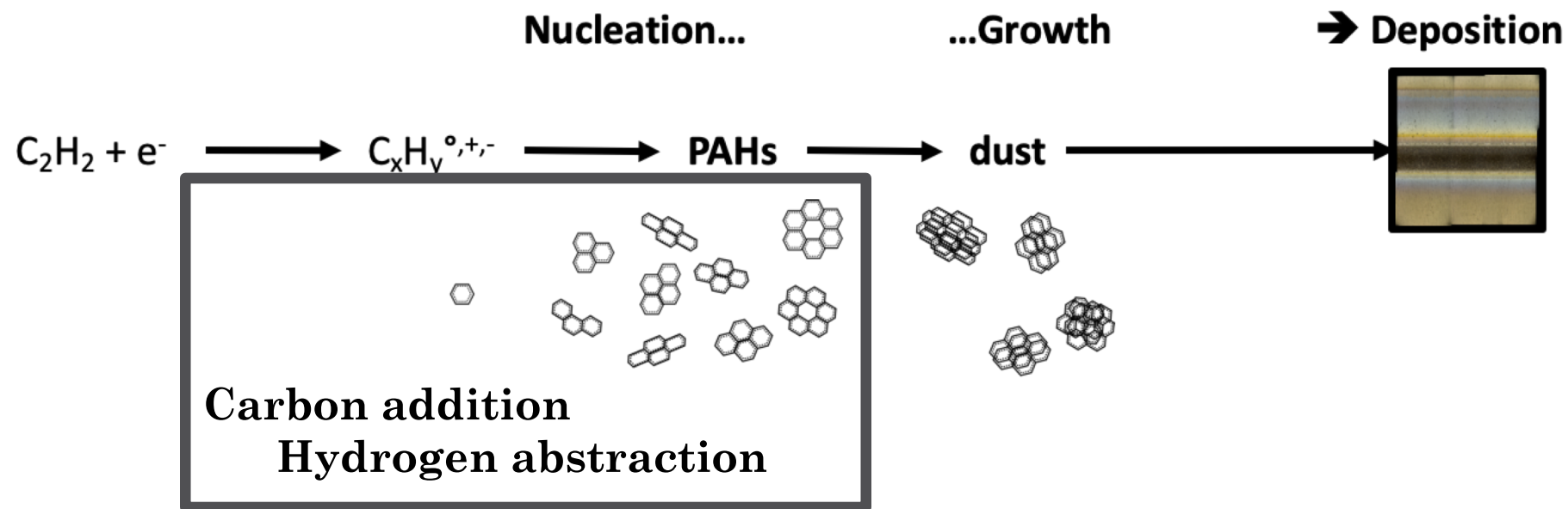


***Above the magnets***

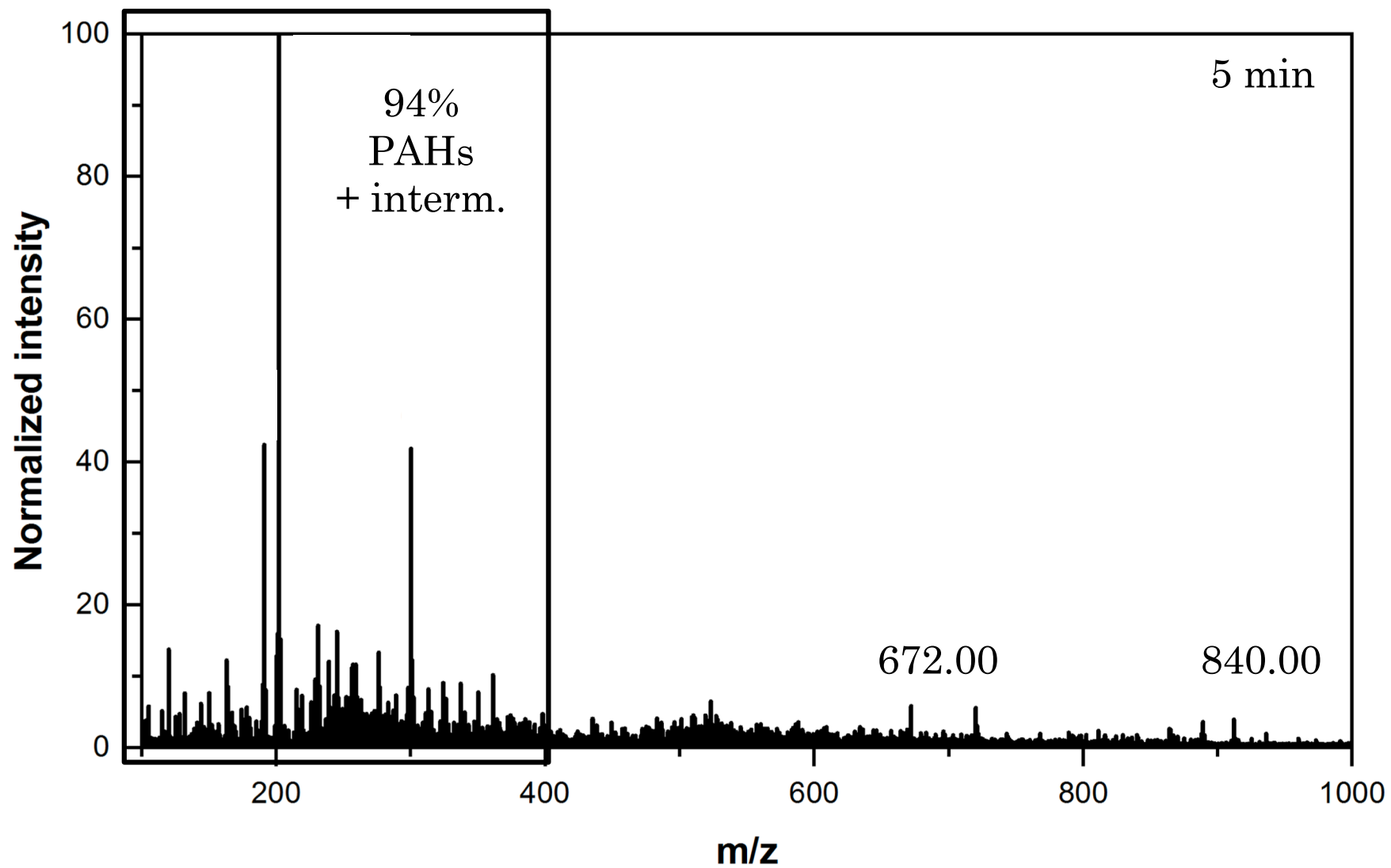
**Nucleation...**



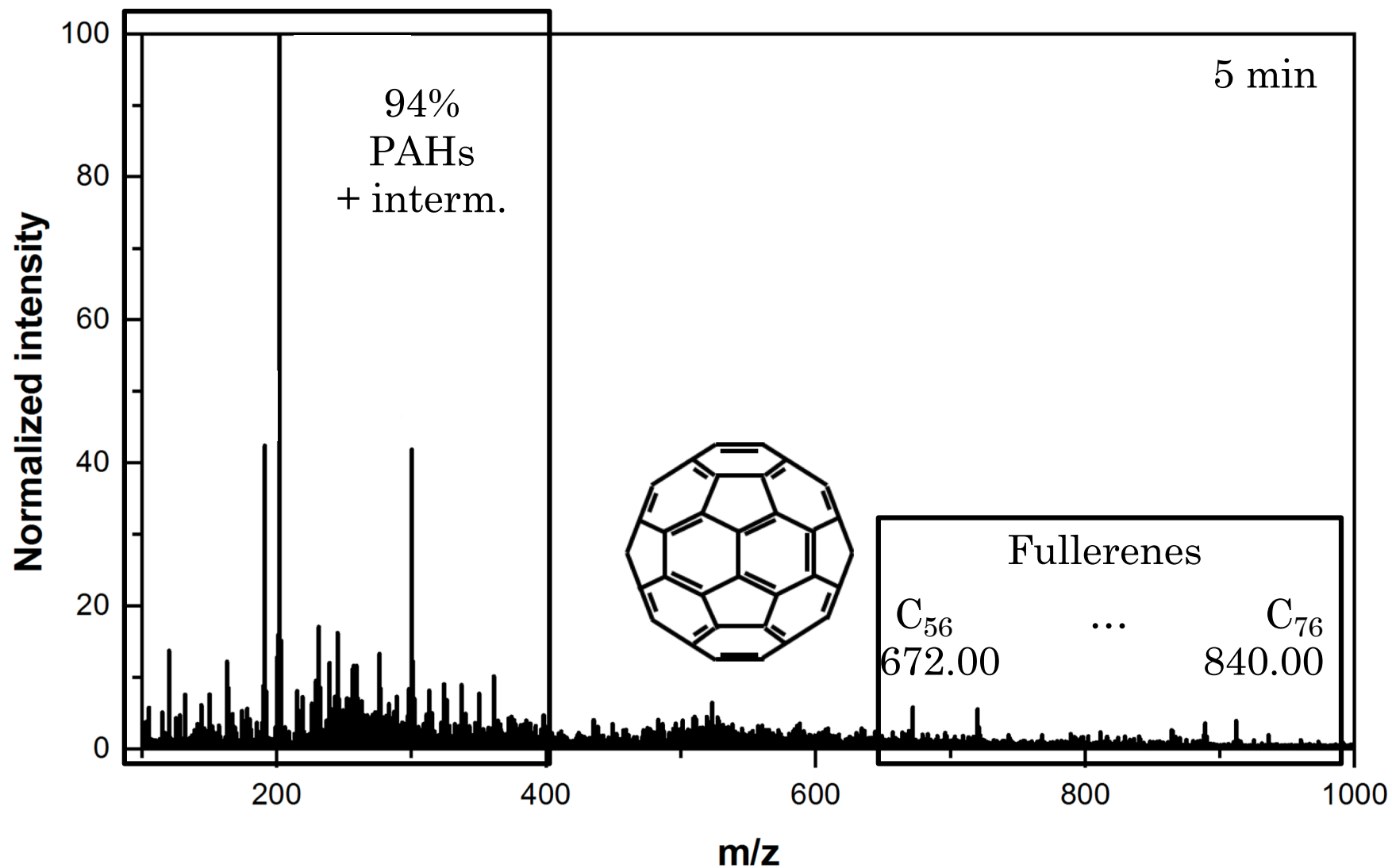
*Above the magnets*



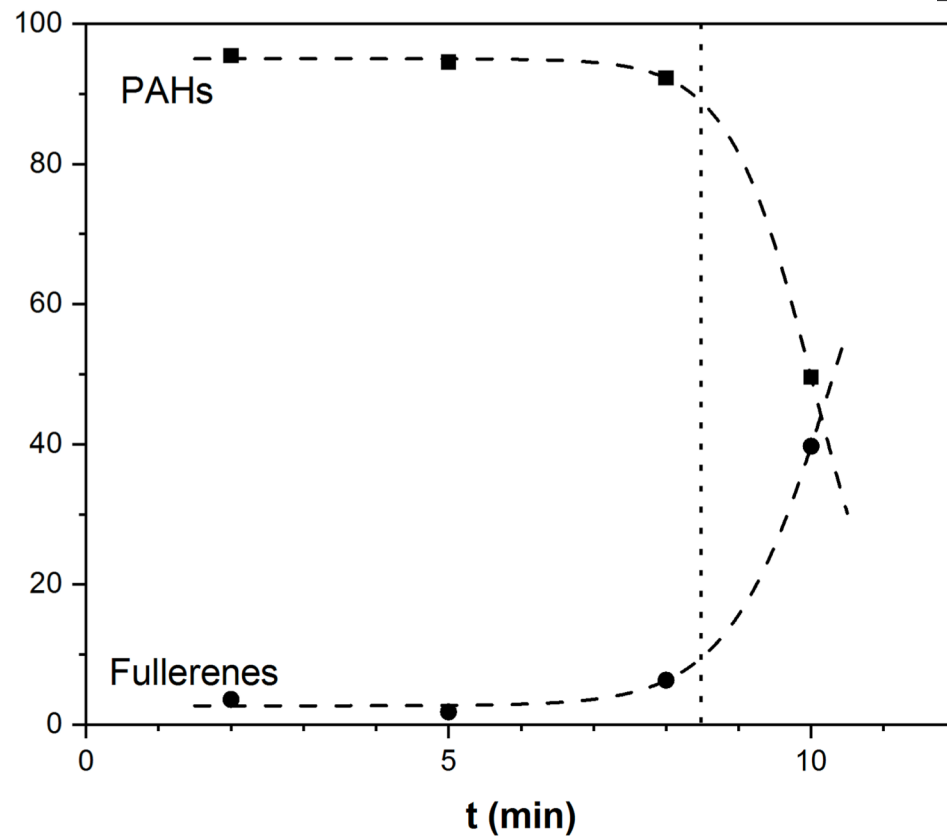
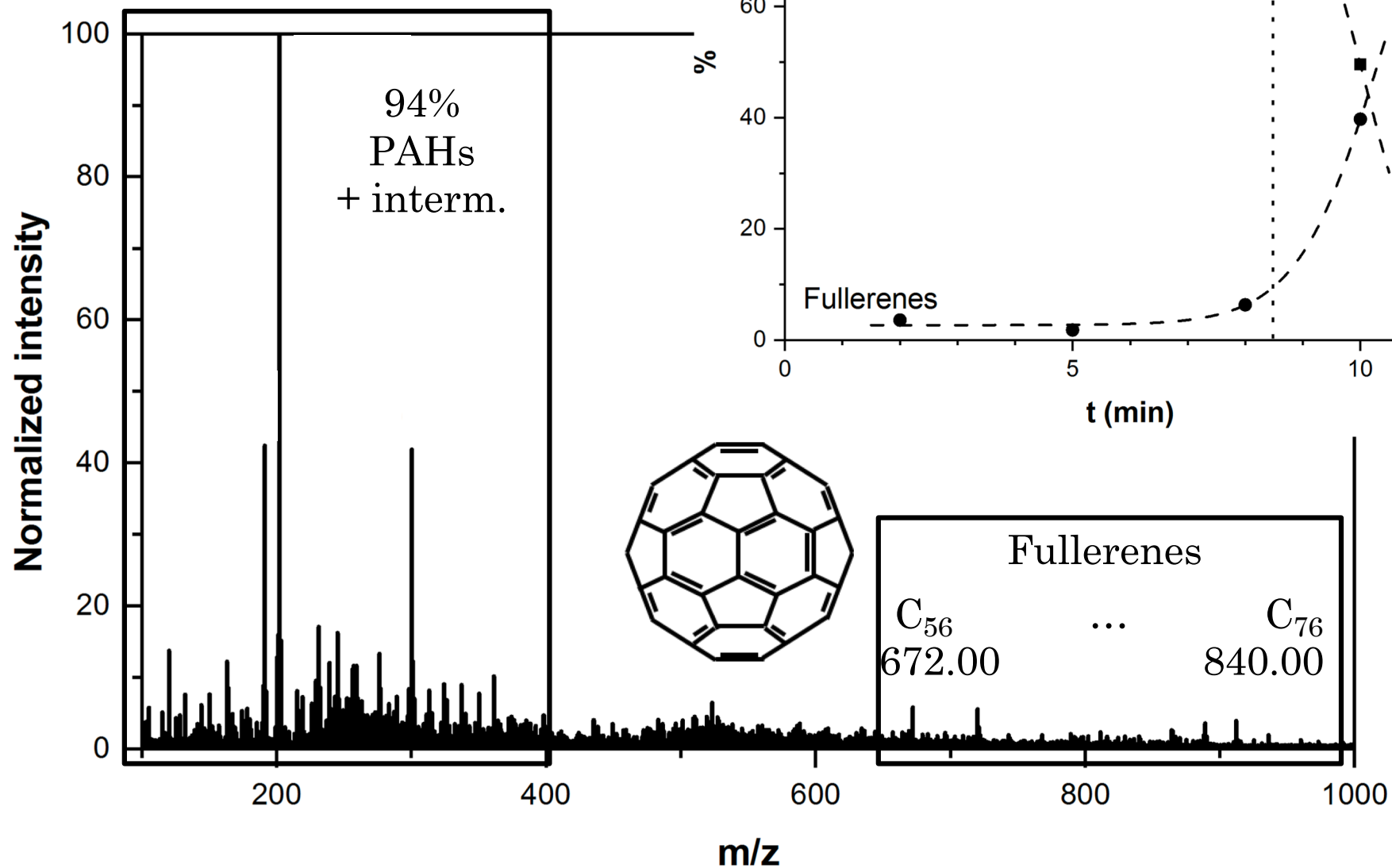
# AROMA analyses



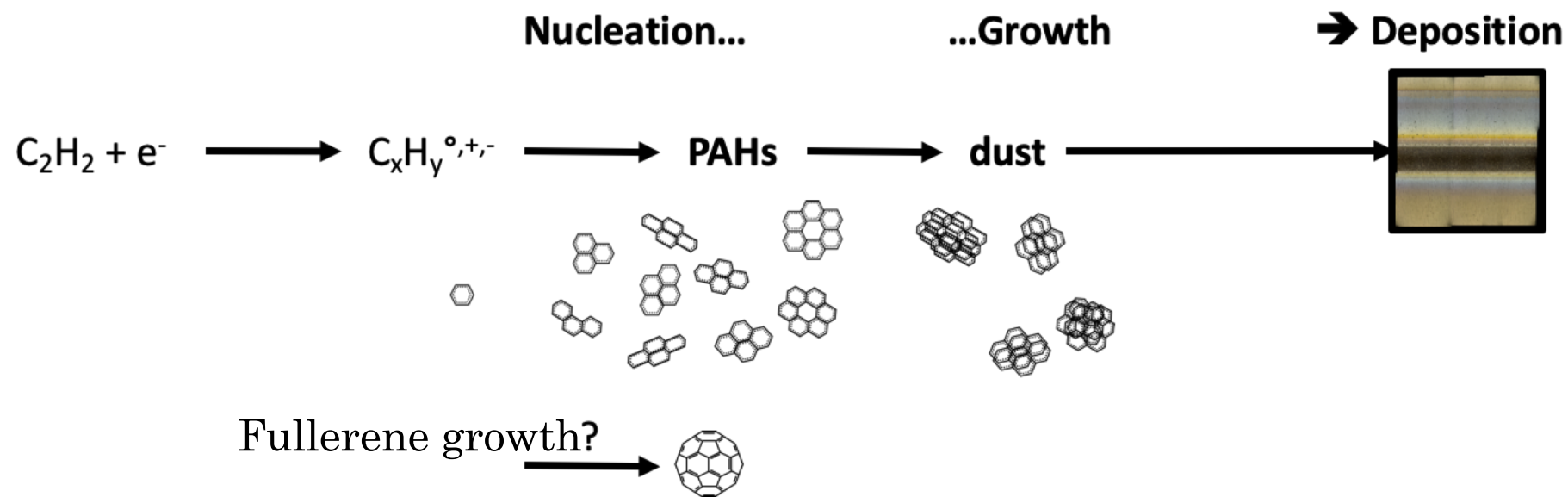
# AROMA analyses



# AROMA analyses



*Above the magnets*



# Nucleation of Fullerenes?

# Nucleation of Fullerenes?

Arc discharges



Ablation plume





# Nucleation of Fullerenes?

Arc discharges



Ablation plume



- High electron density /  $n_e > 10^{19} \text{ m}^{-3}$
- High pressure /  $n_{\text{radicals}} > 10^{22} \text{ m}^{-3}$
- High temperature /  $T > 4000\text{K}$

# Nucleation of Fullerenes?

Arc discharges



Ablation plume

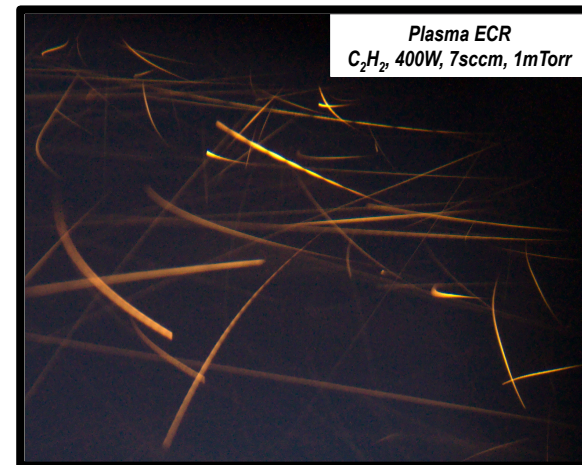


- High electron density /  $n_e > 10^{19} \text{ m}^{-3}$
- High pressure /  $n_{\text{radicals}} > 10^{22} \text{ m}^{-3}$
- High temperature /  $T > 4000\text{K}$

**Obviously far from our conditions...**

# Formation of Fullerenes?

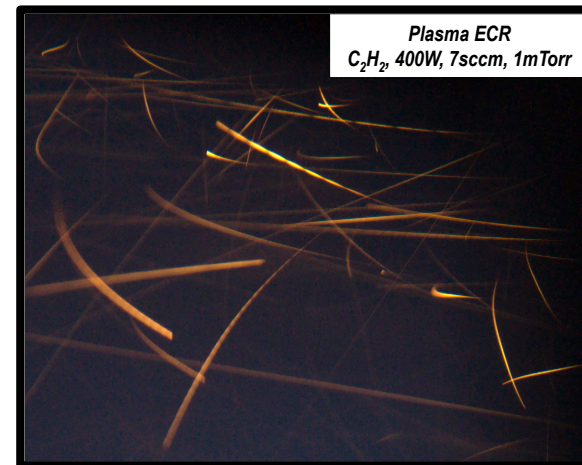
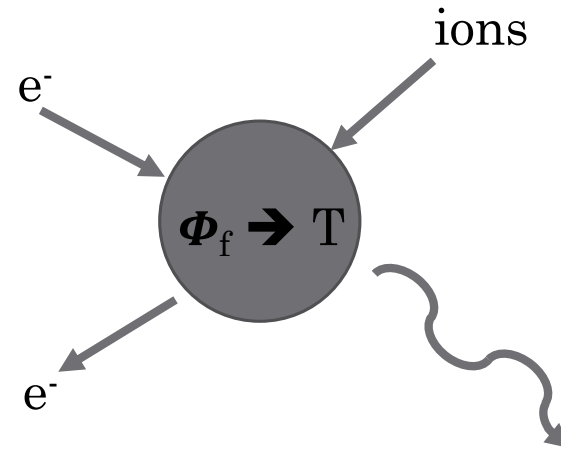
→ Heating ?



Drenik et al., *Trajectories of dust particles in low-pressure magnetized plasma*, IEEEETPS (2011)

# Formation of Fullerenes?

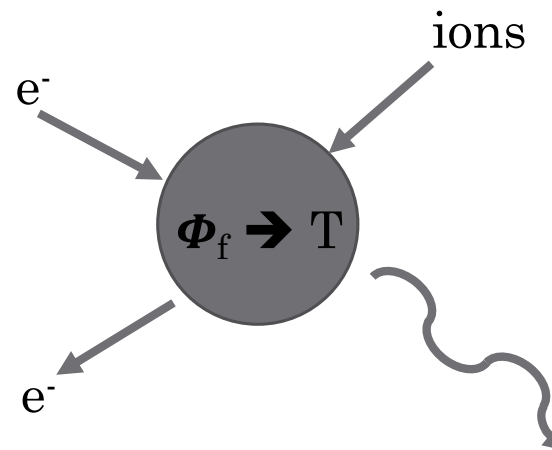
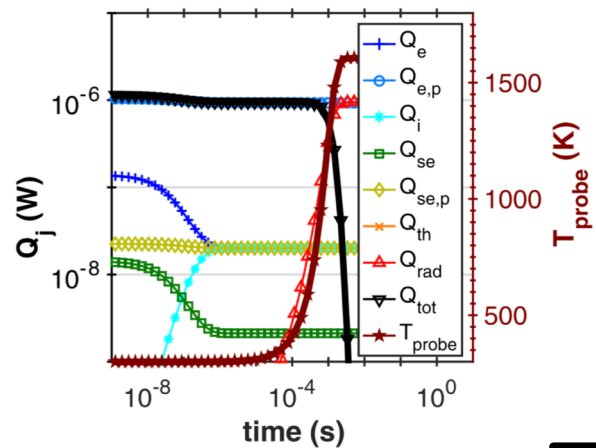
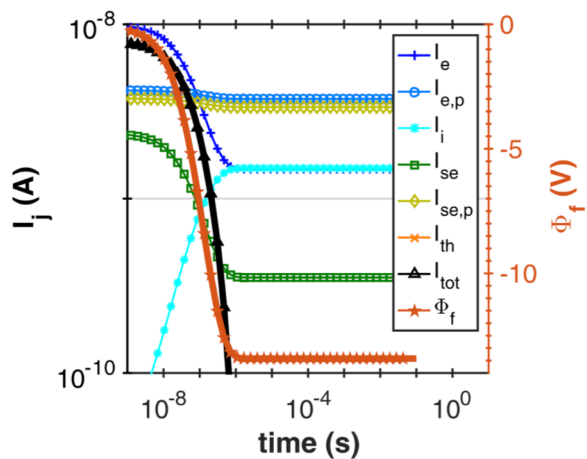
→ Heating ?



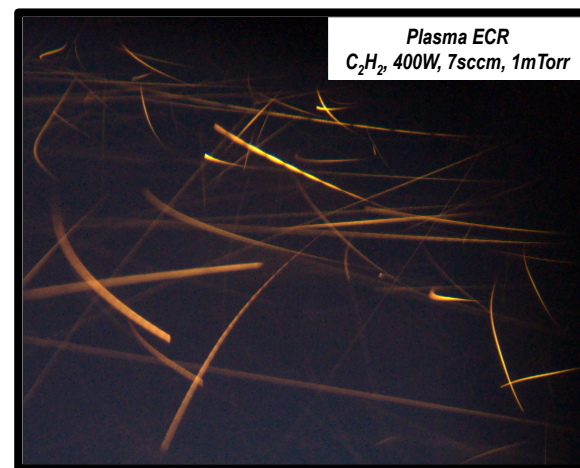
Drenik et al., *Trajectories of dust particles in low-pressure magnetized plasma*, IEEEETPS (2011)

# Formation of Fullerenes?

→ Heating ?



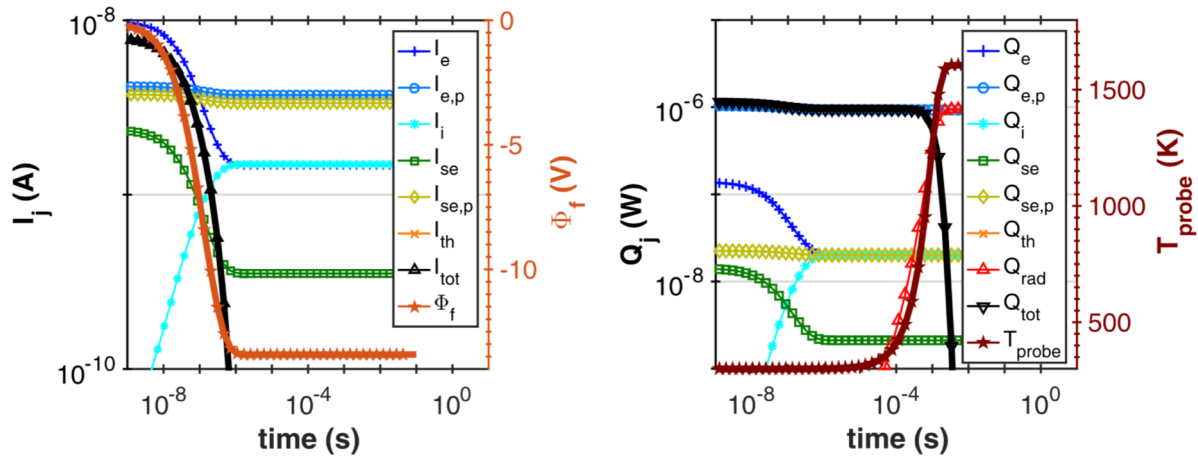
Rojo et al., *Charging and heating processes of dust particles in an electron cyclotron resonance plasma*, PSST (2019)



Drenik et al., *Trajectories of dust particles in low-pressure magnetized plasma*, IEEEETPS (2011)

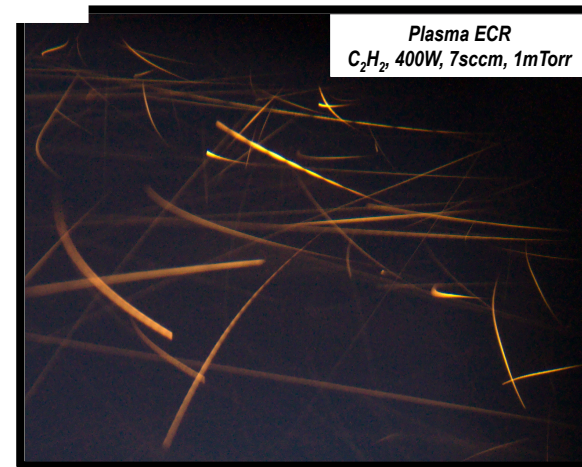
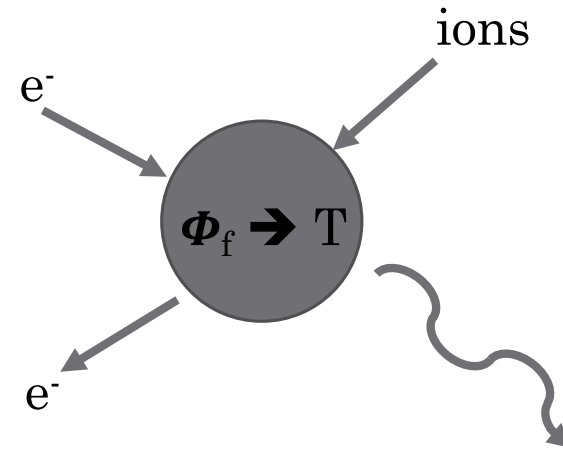
# Formation of Fullerenes?

→ Heating ?



Rojo et al., *Charging and heating processes of dust particles in an electron cyclotron resonance plasma*, PSST (2019)

→  $T \ll$  to transform PAHs into fullerenes

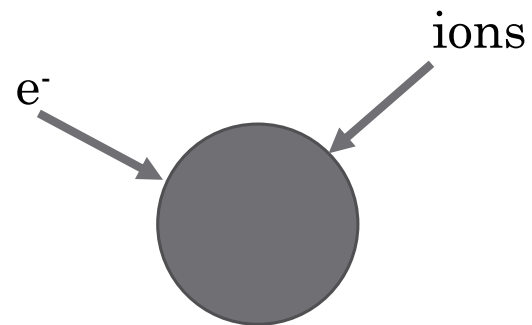


Drenik et al., *Trajectories of dust particles in low-pressure magnetized plasma*, IEEE TPS (2011)

# Formation of Fullerenes?

→ Heating ?

→ Processing of PAHs on dust particles ?



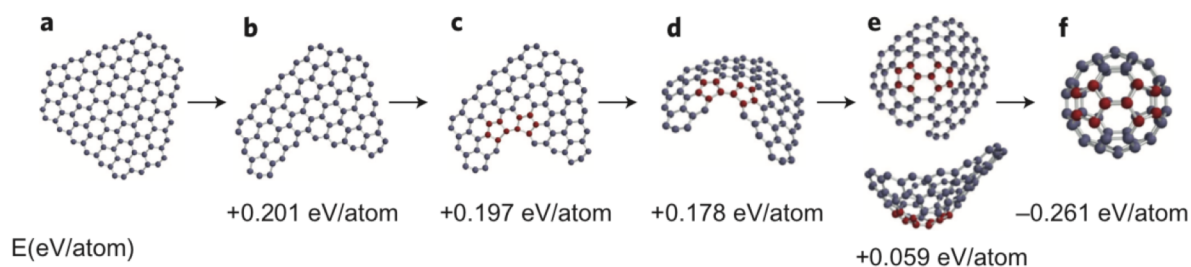
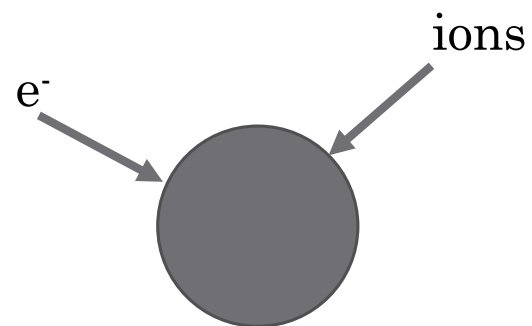
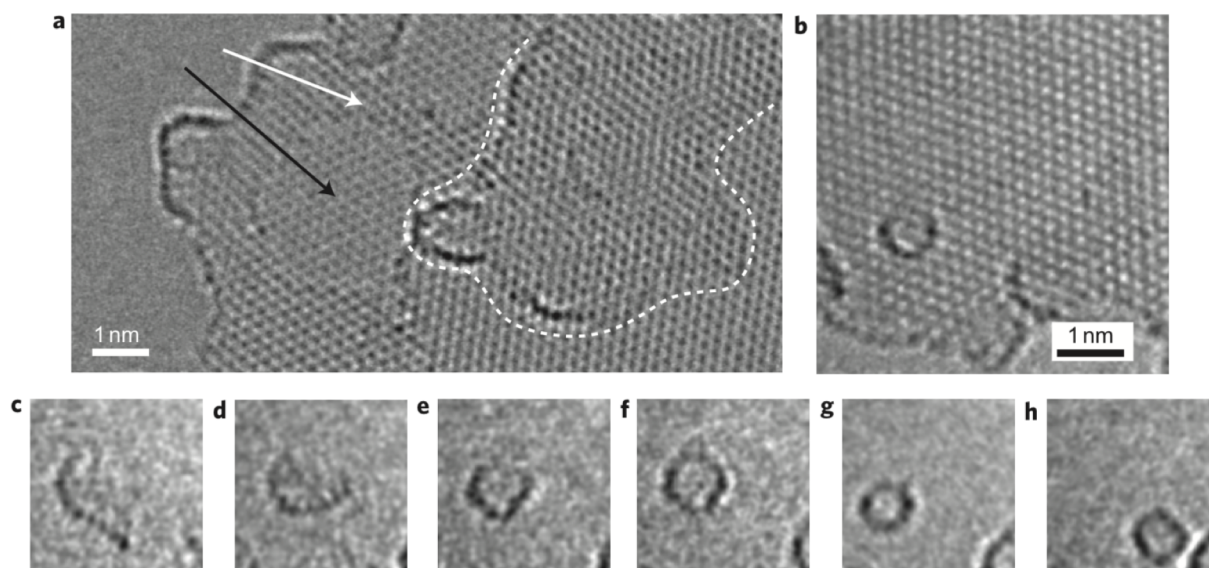


# Formation of Fullerenes?

→ Heating ?

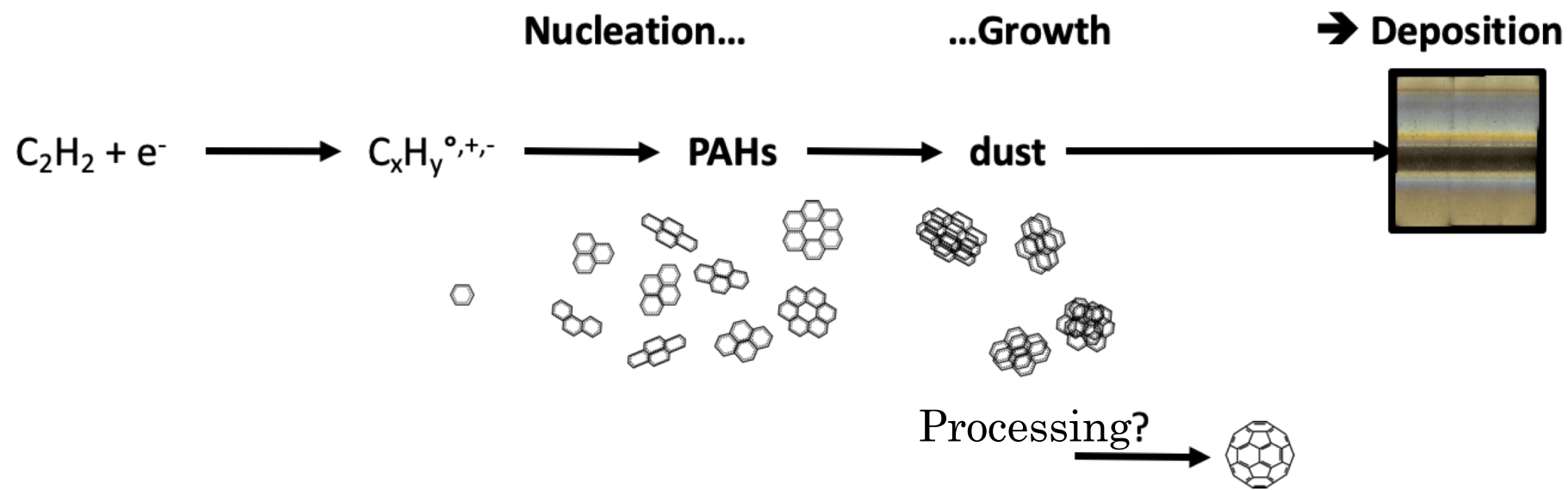
→ Processing of PAHs on dust particles ?

In TEM



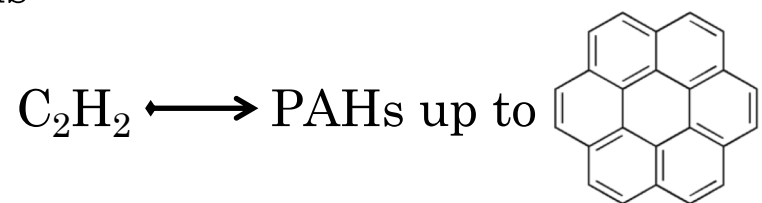


*Above the magnets*



# Nucleation in ECR plasmas

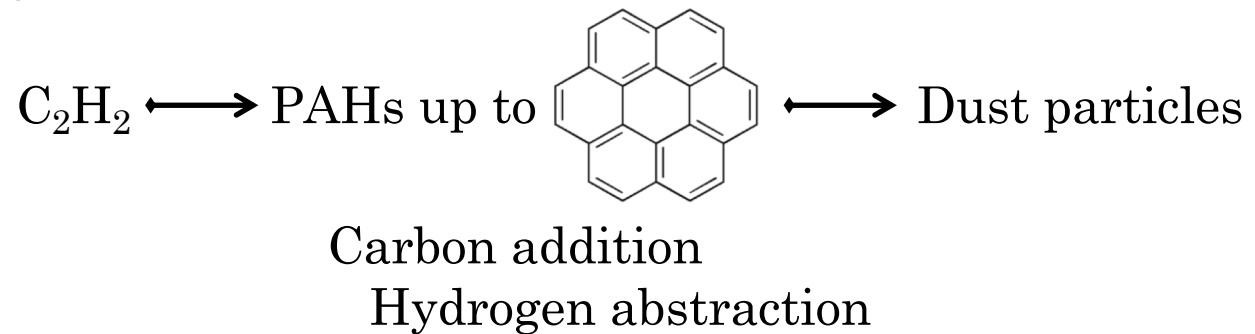
- in our conditions



Carbon addition  
Hydrogen abstraction

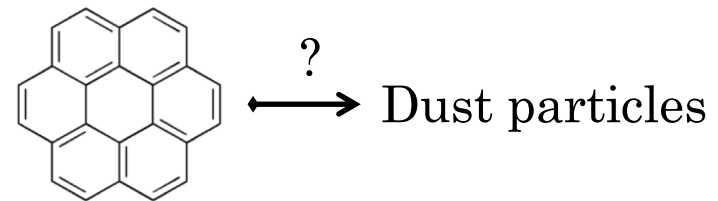
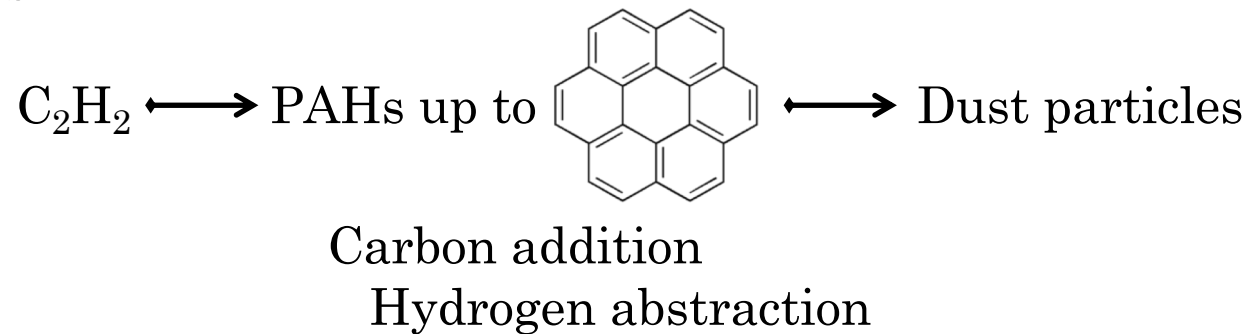
# Nucleation in ECR plasmas

- in our conditions



# Nucleation in ECR plasmas

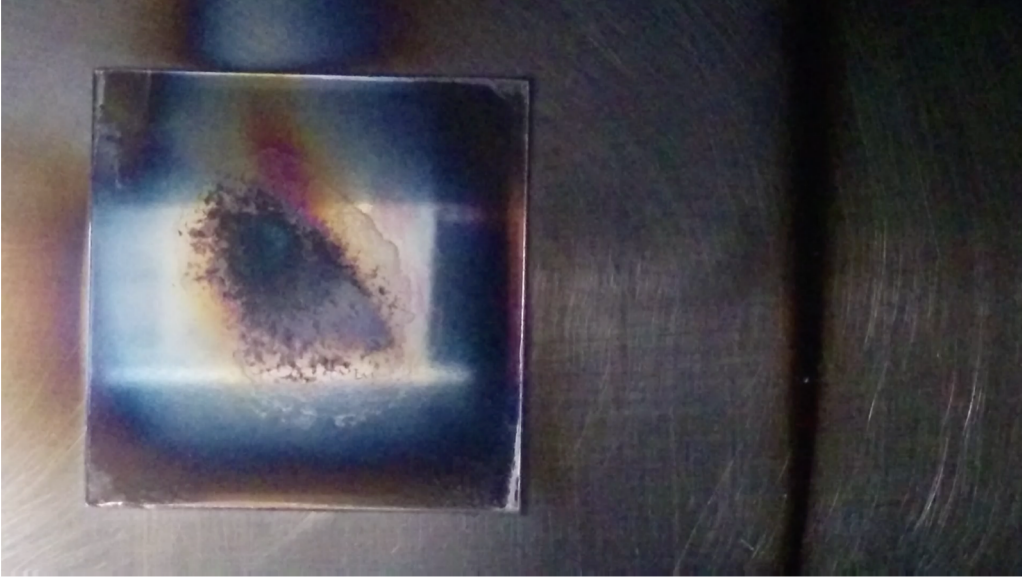
- in our conditions



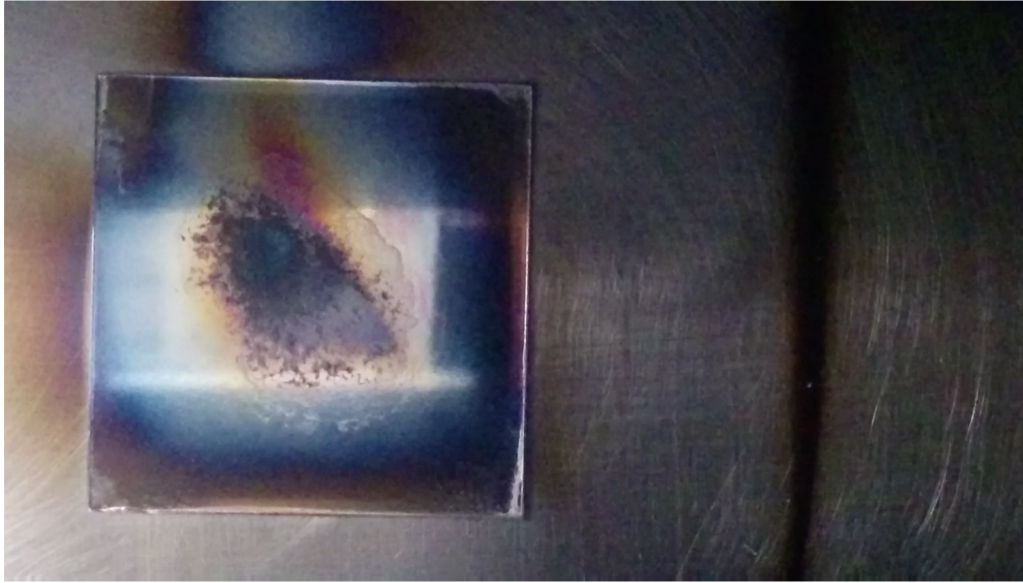
# Outline

- I CONTEXT
- II MATERIALS & METHODS
- III DUST PARTICLES FORMED IN C<sub>2</sub>H<sub>2</sub> PLASMAS
- IV DUST PARTICLES FORMED FROM PAHs**
- V CONCLUSION AND PERSPECTIVE

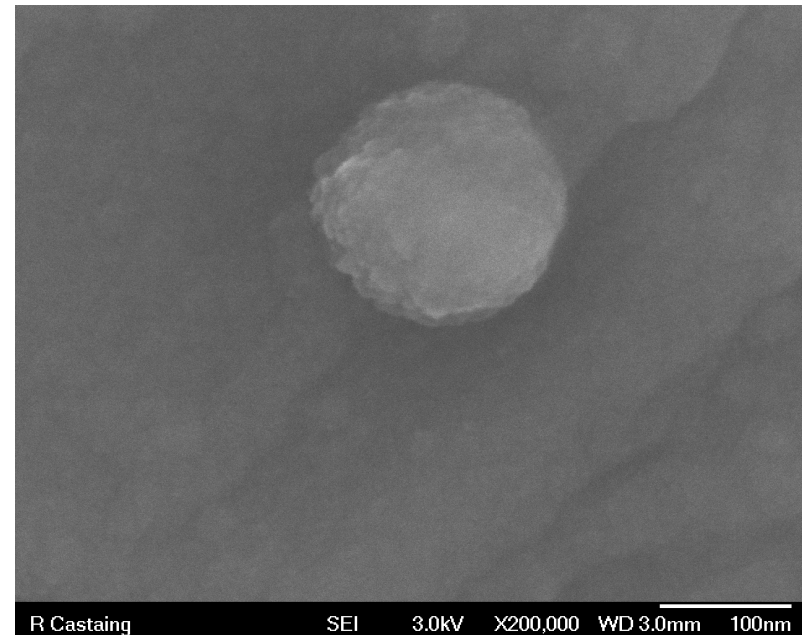
# Plasmas seeded with PAHs



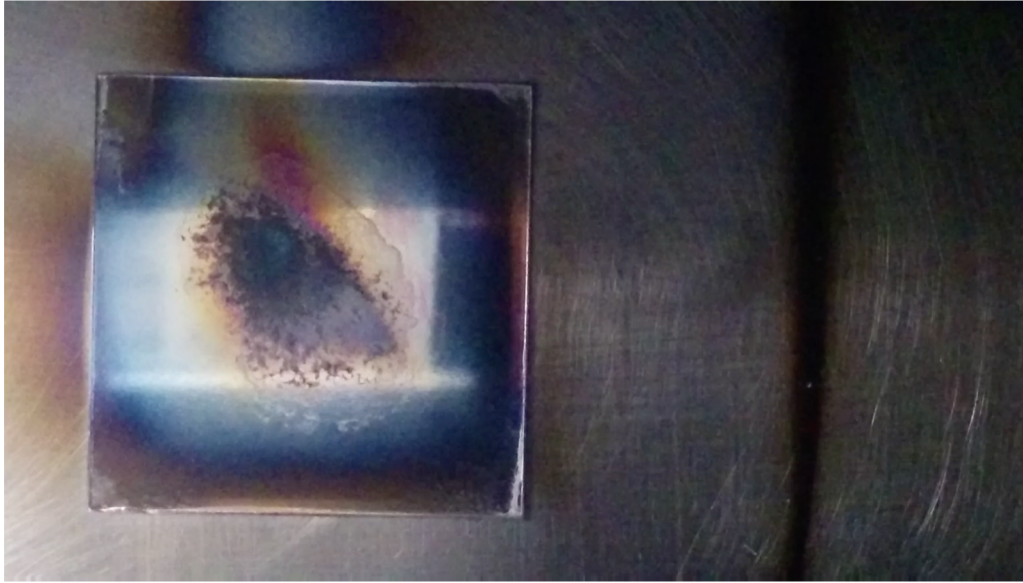
# Plasmas seeded with PAHs



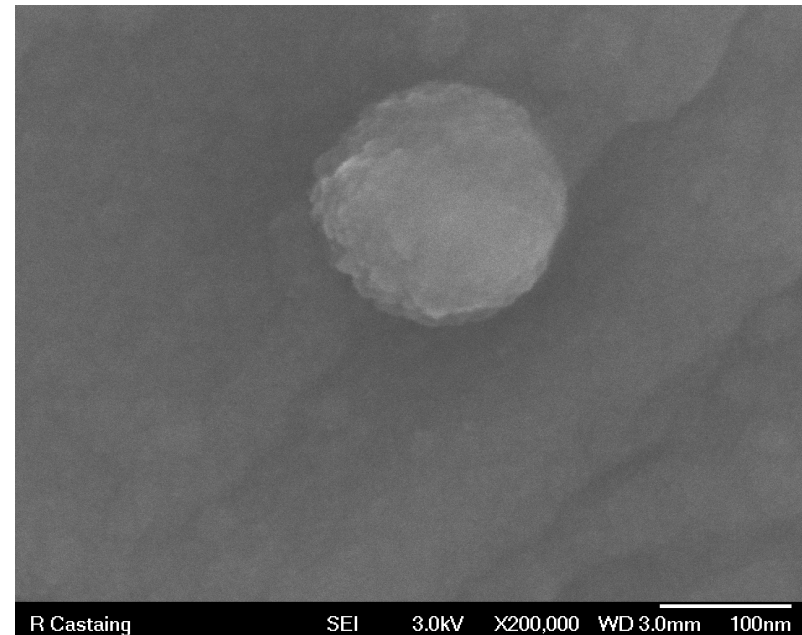
Anthracene  
Perylene  
Benzoperylene  
Coronene



# Plasmas seeded with PAHs



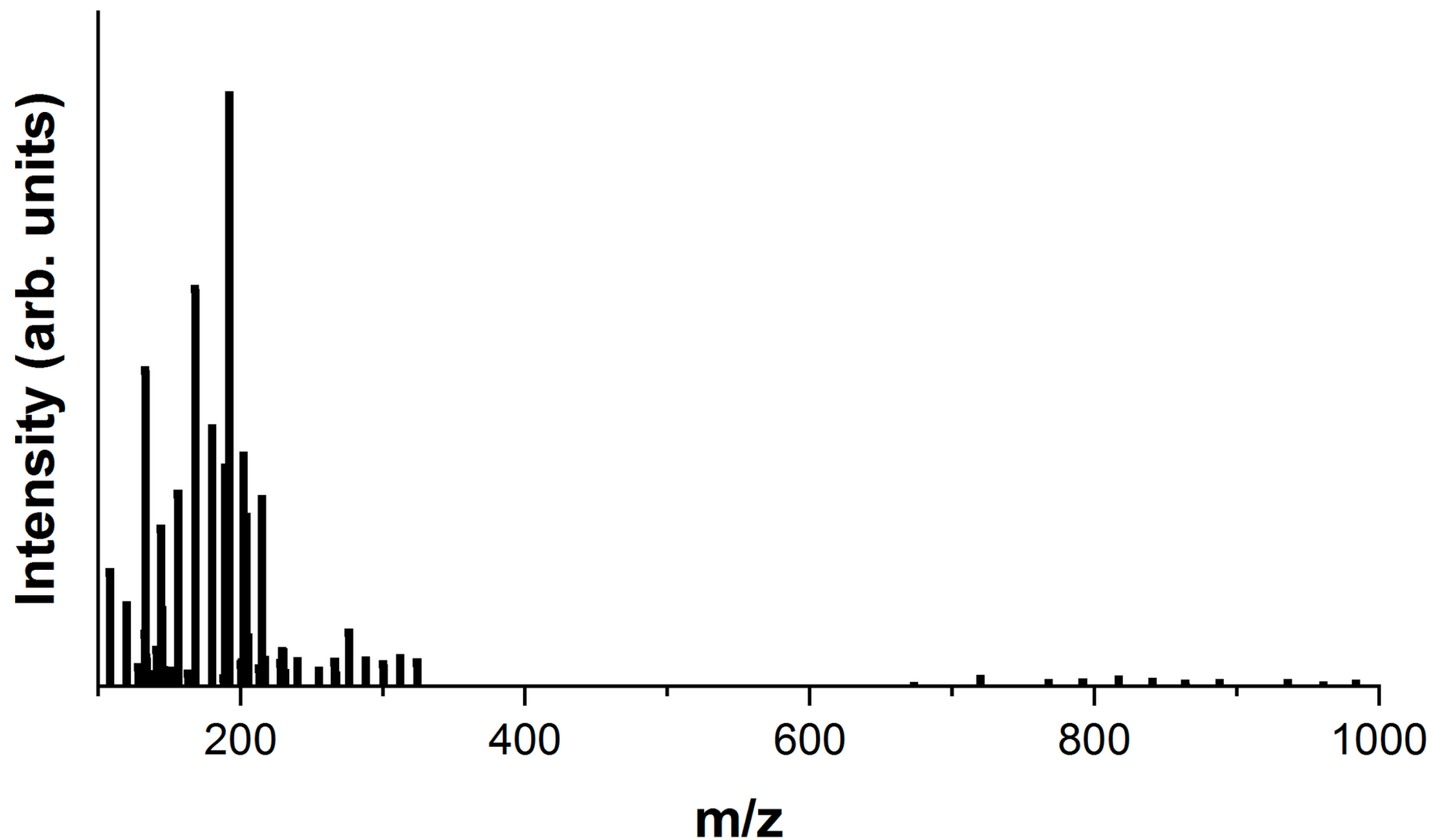
Anthracene  
Perylene  
Benzoperylene  
Coronene



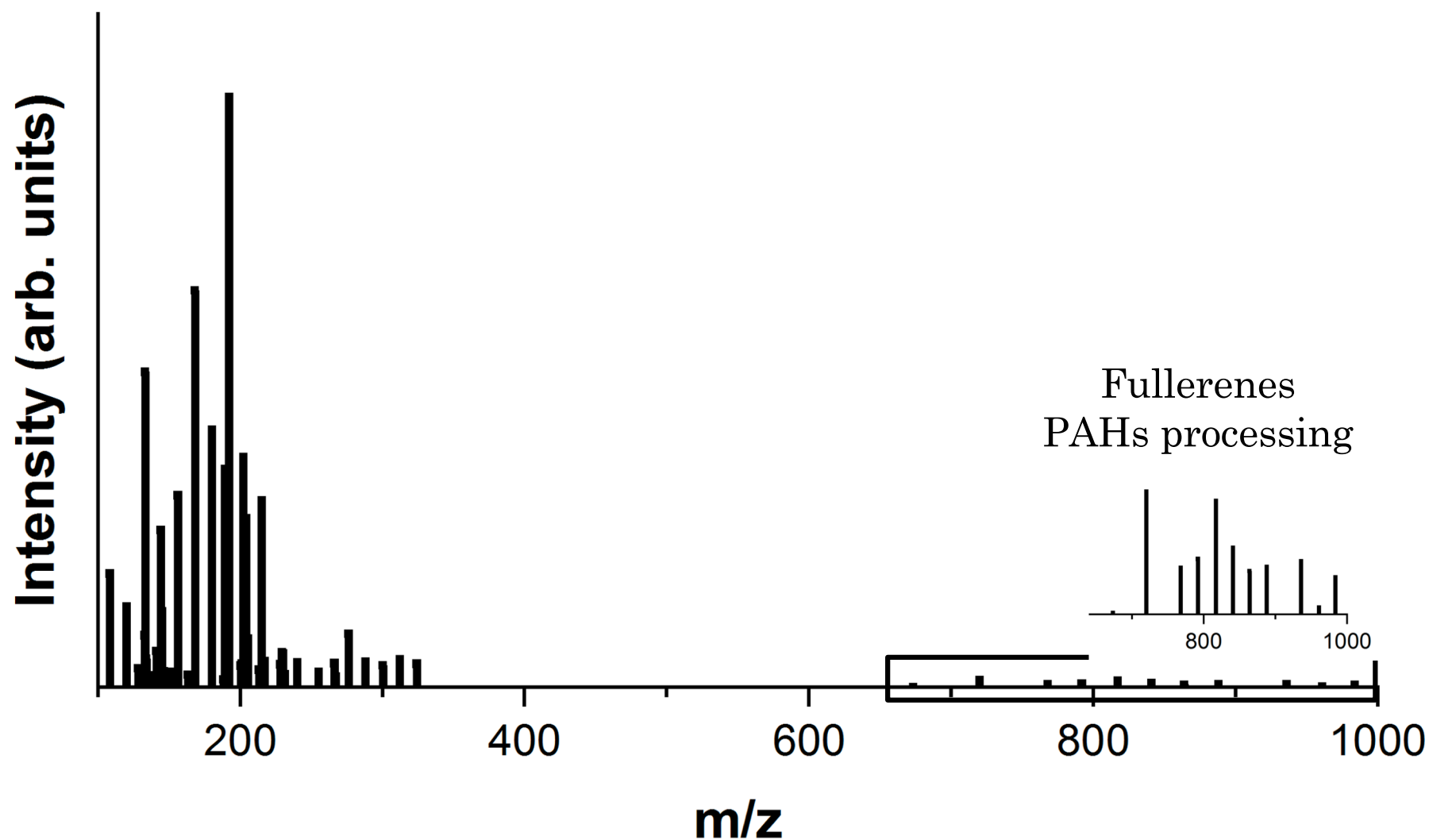
really larger than in  $C_2H_2$  ECR plasmas



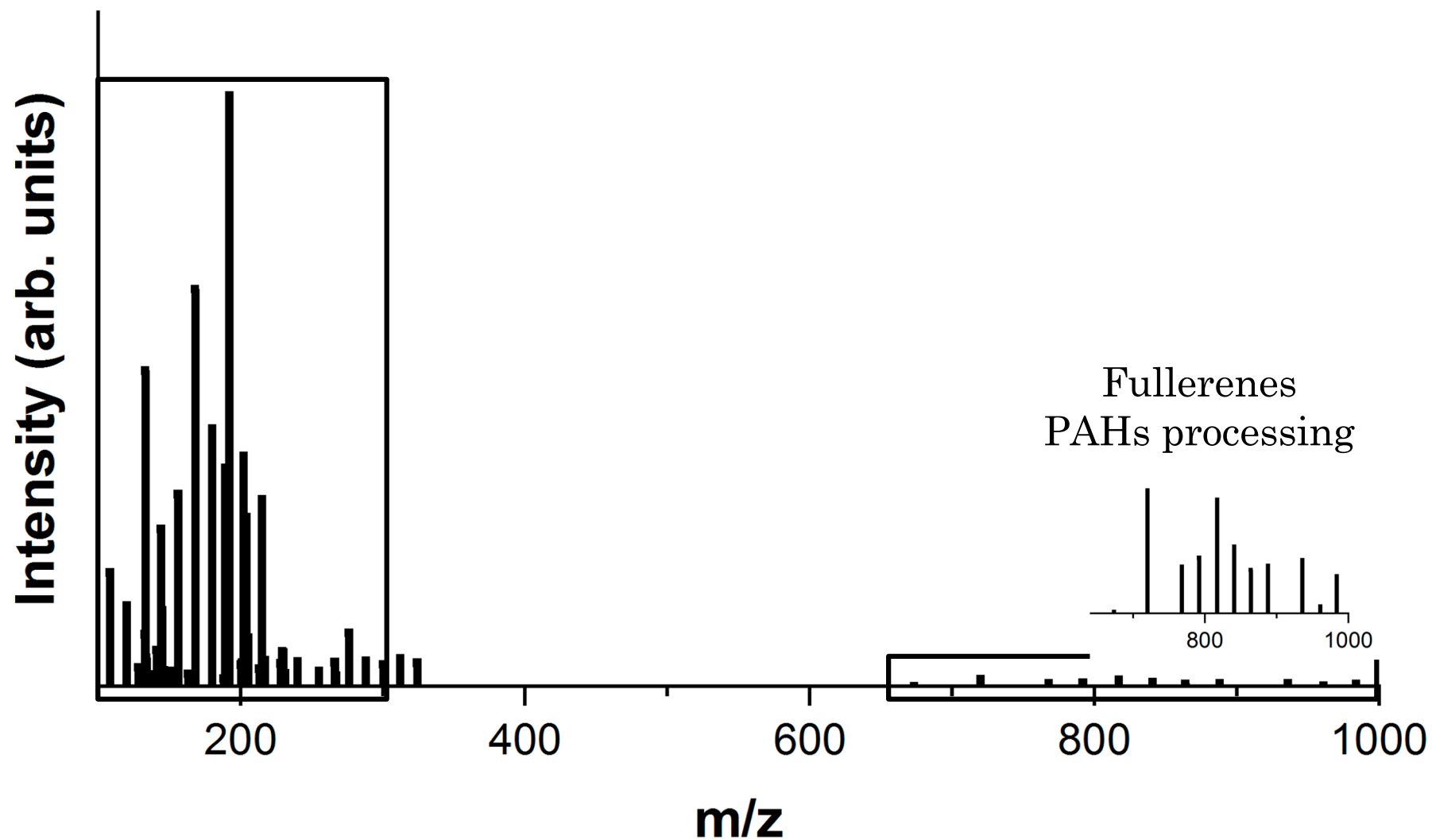
# AROMA analyses



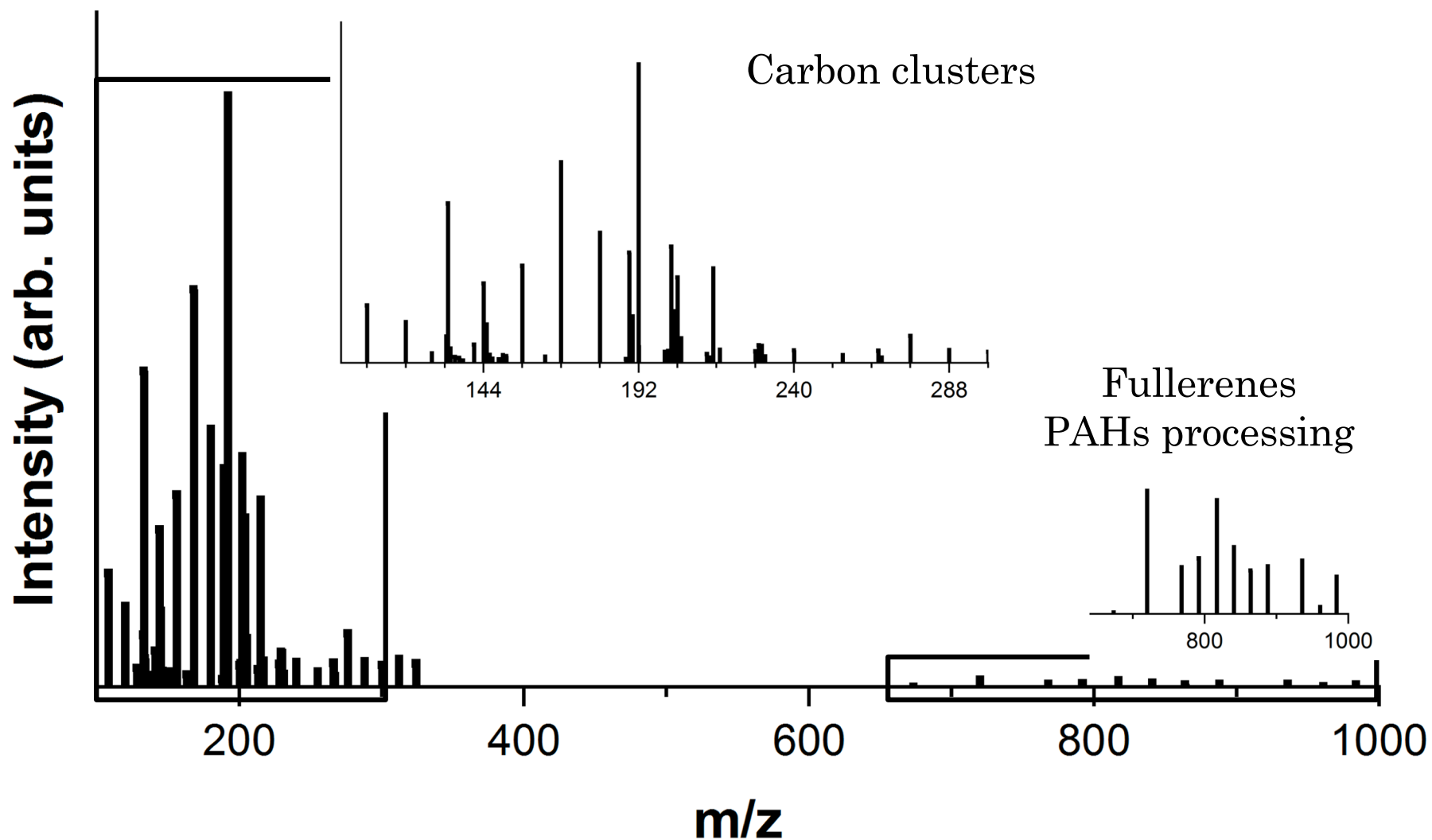
# AROMA analyses

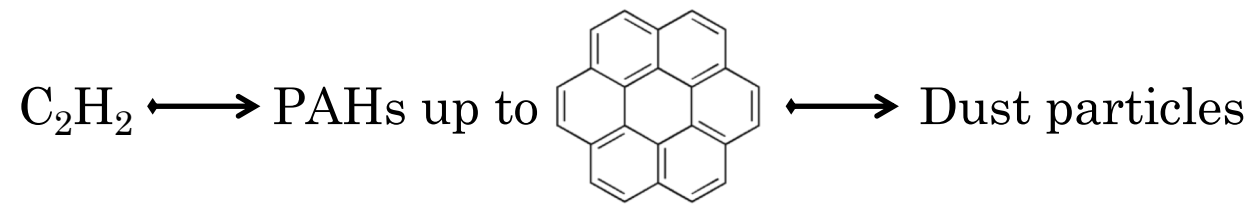


# AROMA analyses

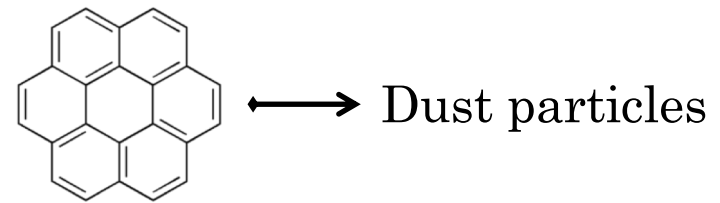


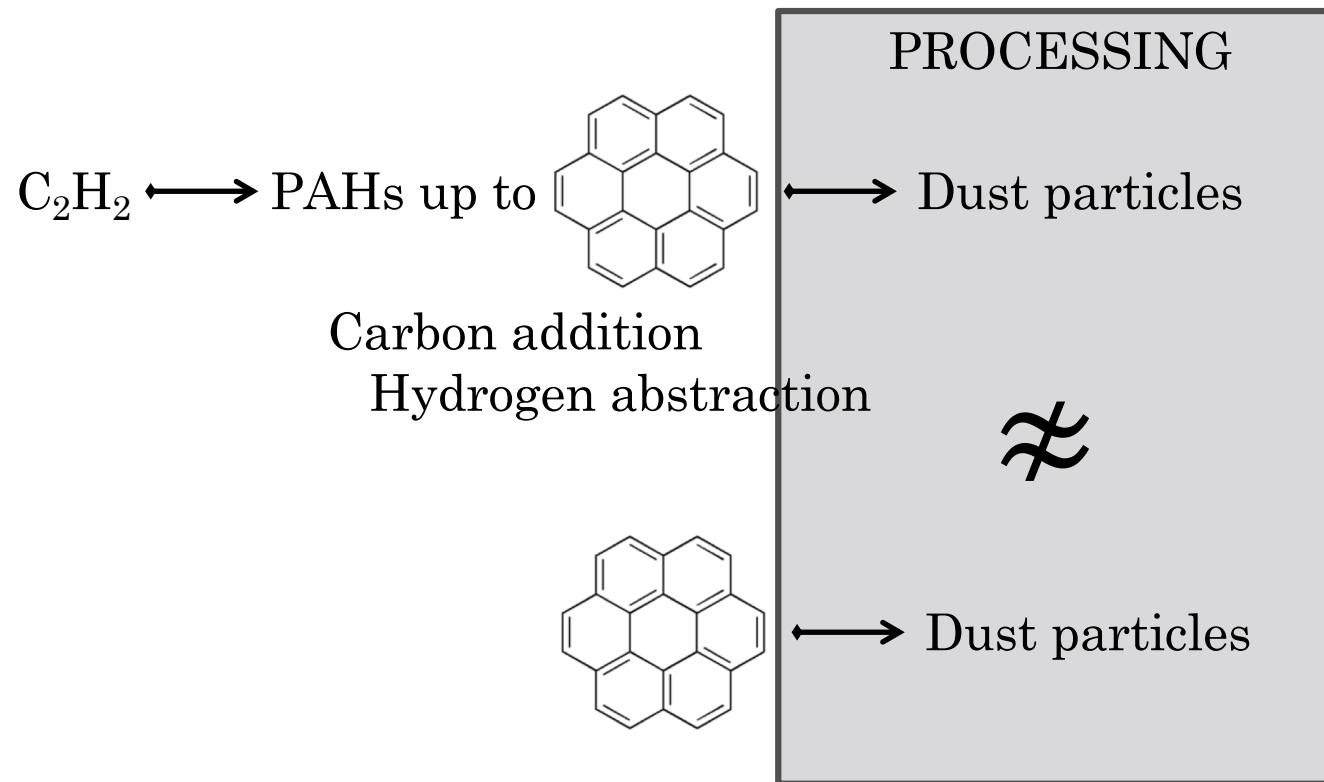
# AROMA analyses





Carbon addition  
Hydrogen abstraction





# Outline

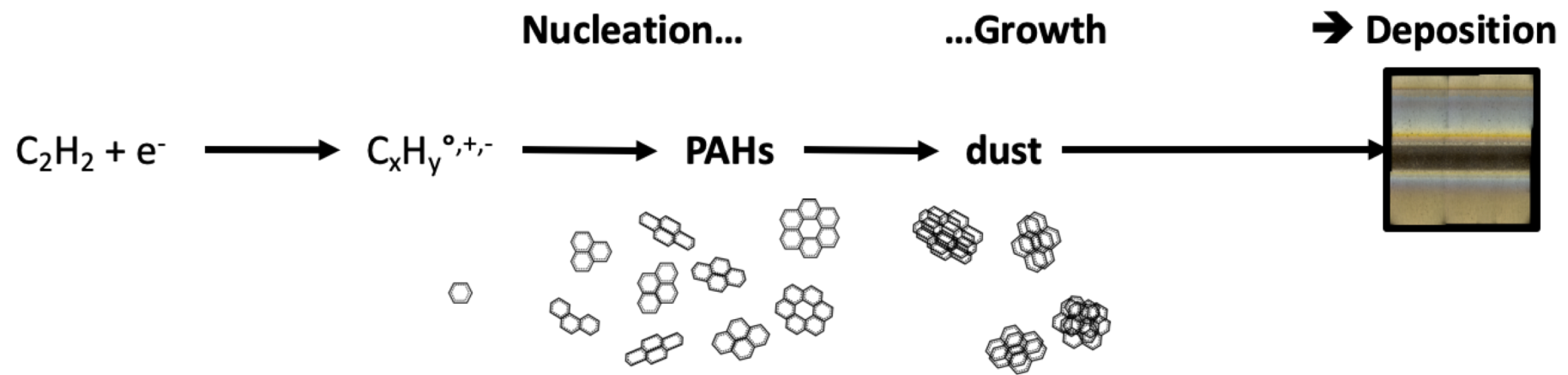
I CONTEXT

II MATERIALS & METHODS

III DUST PARTICLES FORMED IN C<sub>2</sub>H<sub>2</sub> PLASMAS

IV DUST PARTICLES FORMED FROM PAHs

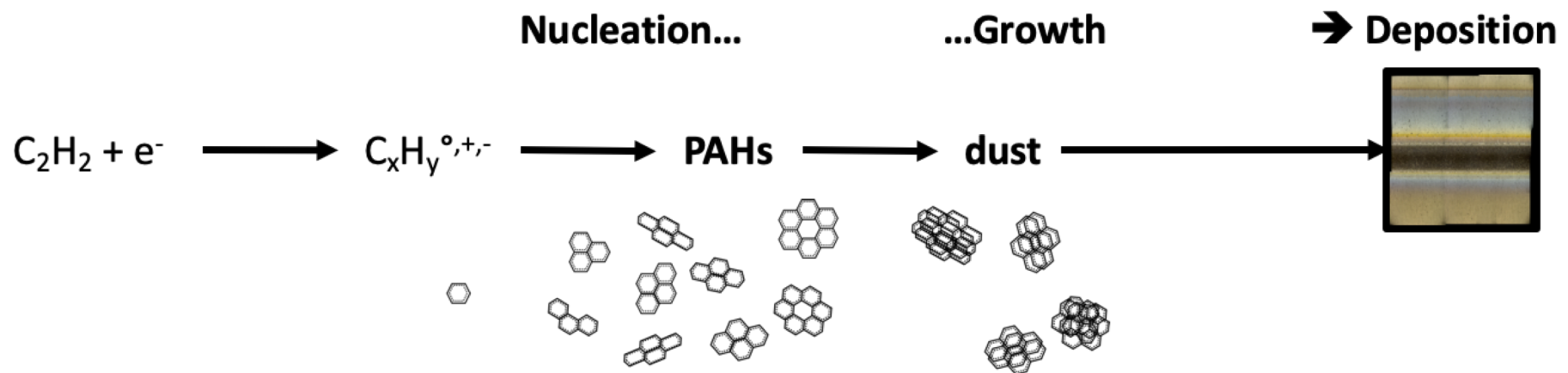
V CONCLUSION





Nucleation in  $C_2H_2$  ECR plasmas involve the formation of PAHs

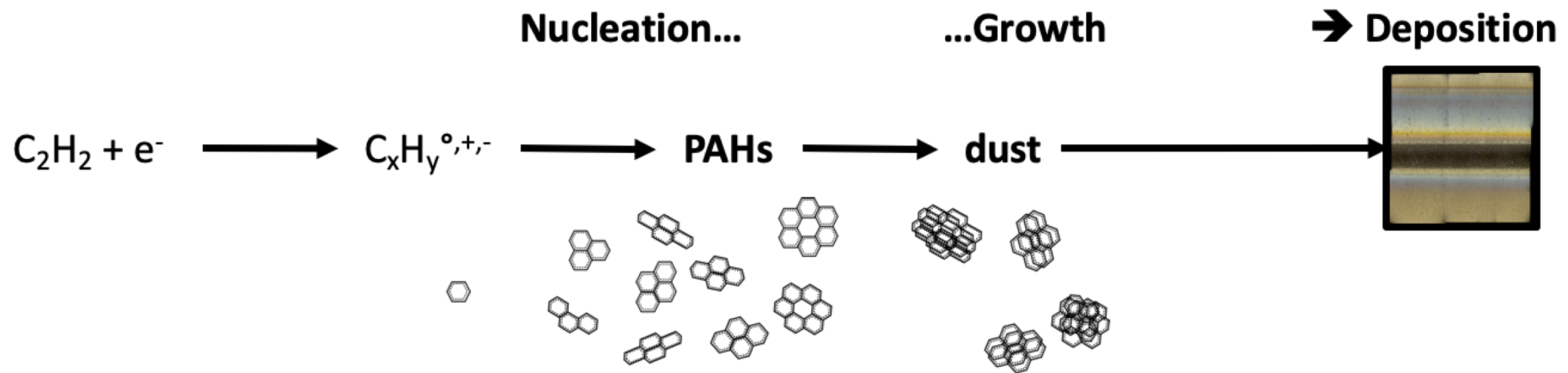
Through similar Hydrogen abstraction Carbon addition pathways as described in combustion



Nucleation in  $C_2H_2$  ECR plasmas involve the formation of PAHs

Through similar Hydrogen abstraction Carbon addition pathways as described in combustion

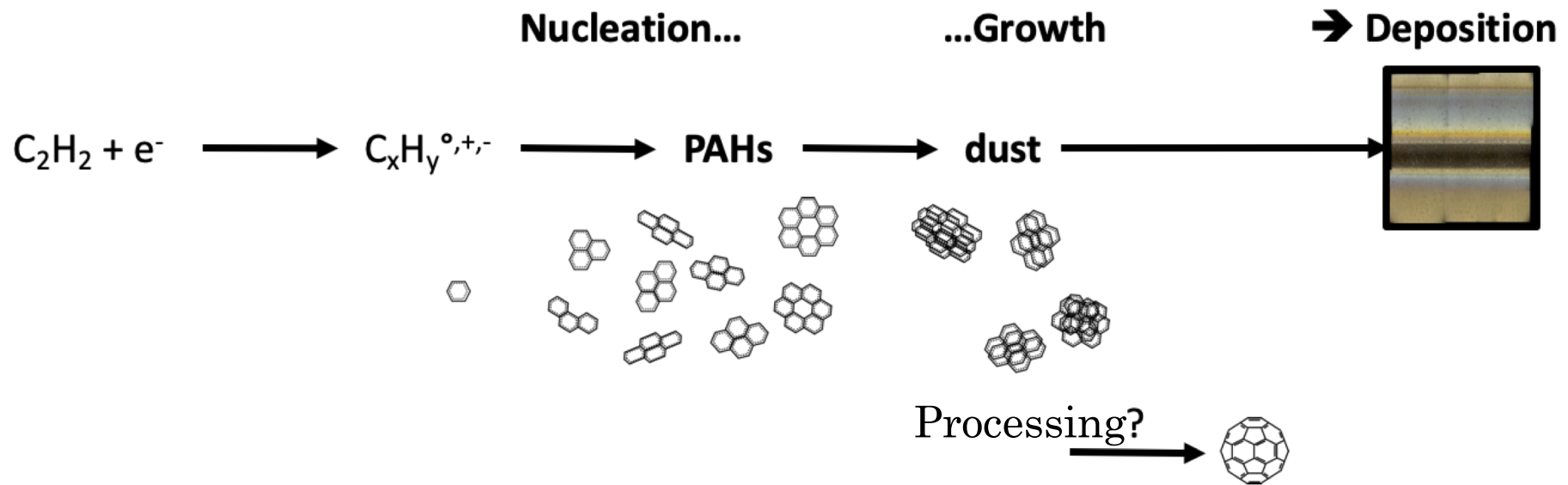
PAHs further stack into dust particles



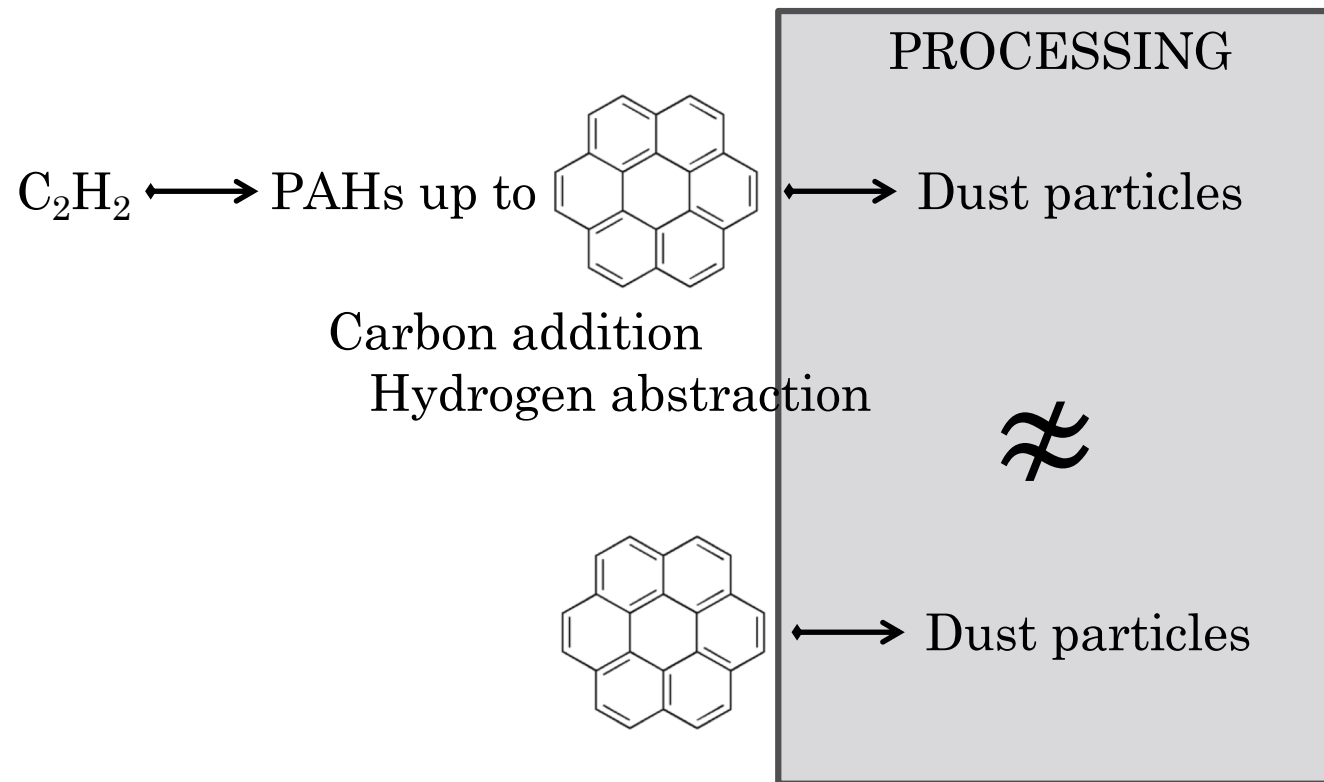
Nucleation in  $C_2H_2$  ECR plasmas involve the formation of PAHs

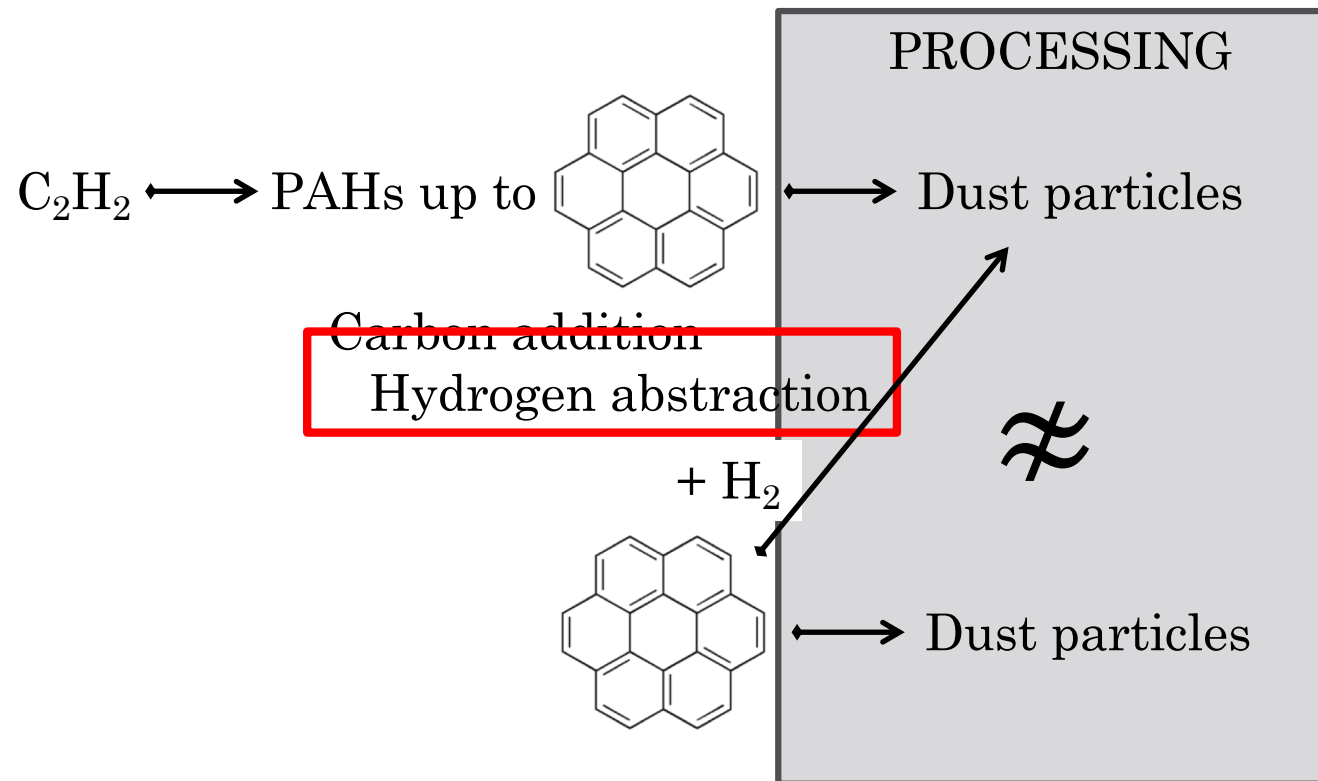
Through similar Hydrogen abstraction Carbon addition pathways as described in combustion

PAHs further stack into dust particles



However, a lot of other mechanisms are also involved (thermal heating, electron bombardment, etc.)









X. Glad



H. Sabbah



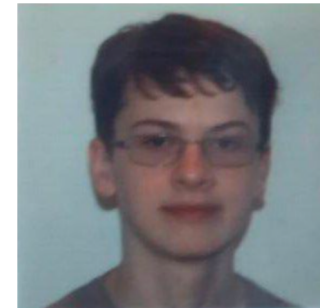
M. Rojo



C. Joblin



A. Perdrau



J. Philbrick