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KAUST

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Dynamic chemical evolution of incipient soot: An FT-ICR MS-based investigation

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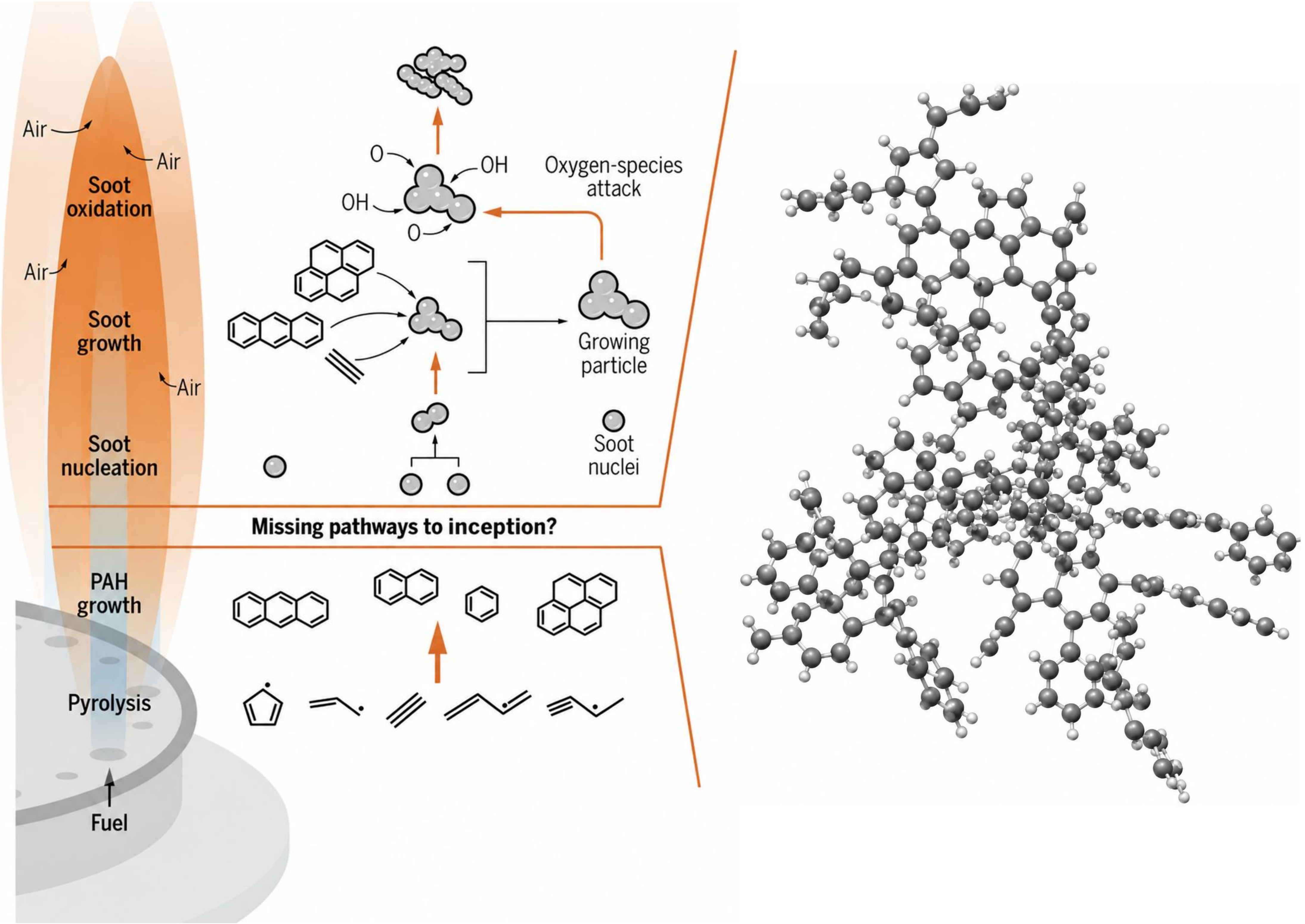
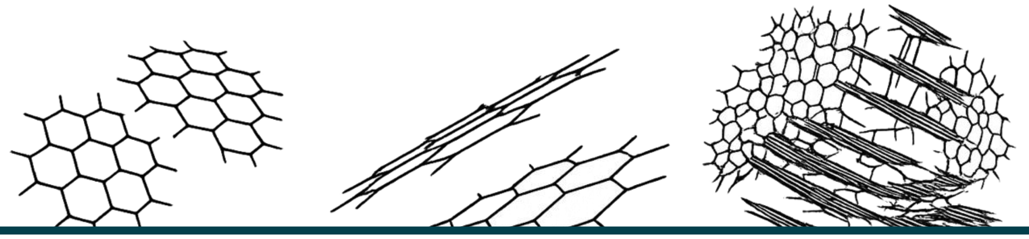
Inception: the key missing puzzle in flame chemistry



Thomson and Mitra, Science, 2018
Johansson et al., Science, 2018

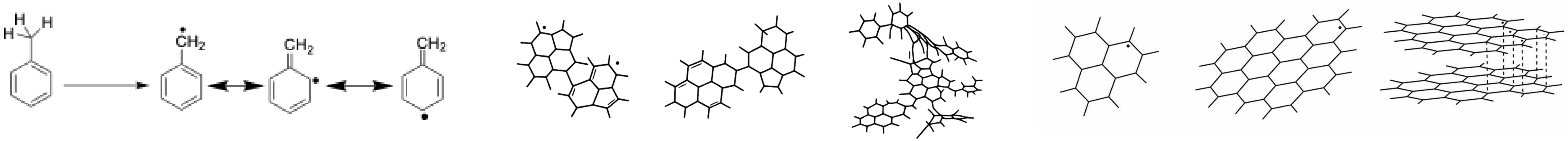
Multiple pathways have been proposed, but each has its own limitations

- Clustering by dispersion interactions



Analyze the chemical composition of early formed soot particles in ethylene/oxygen premixed flame by accurately tracking different types of species to get deeper insights into the underlying clustering mechanism

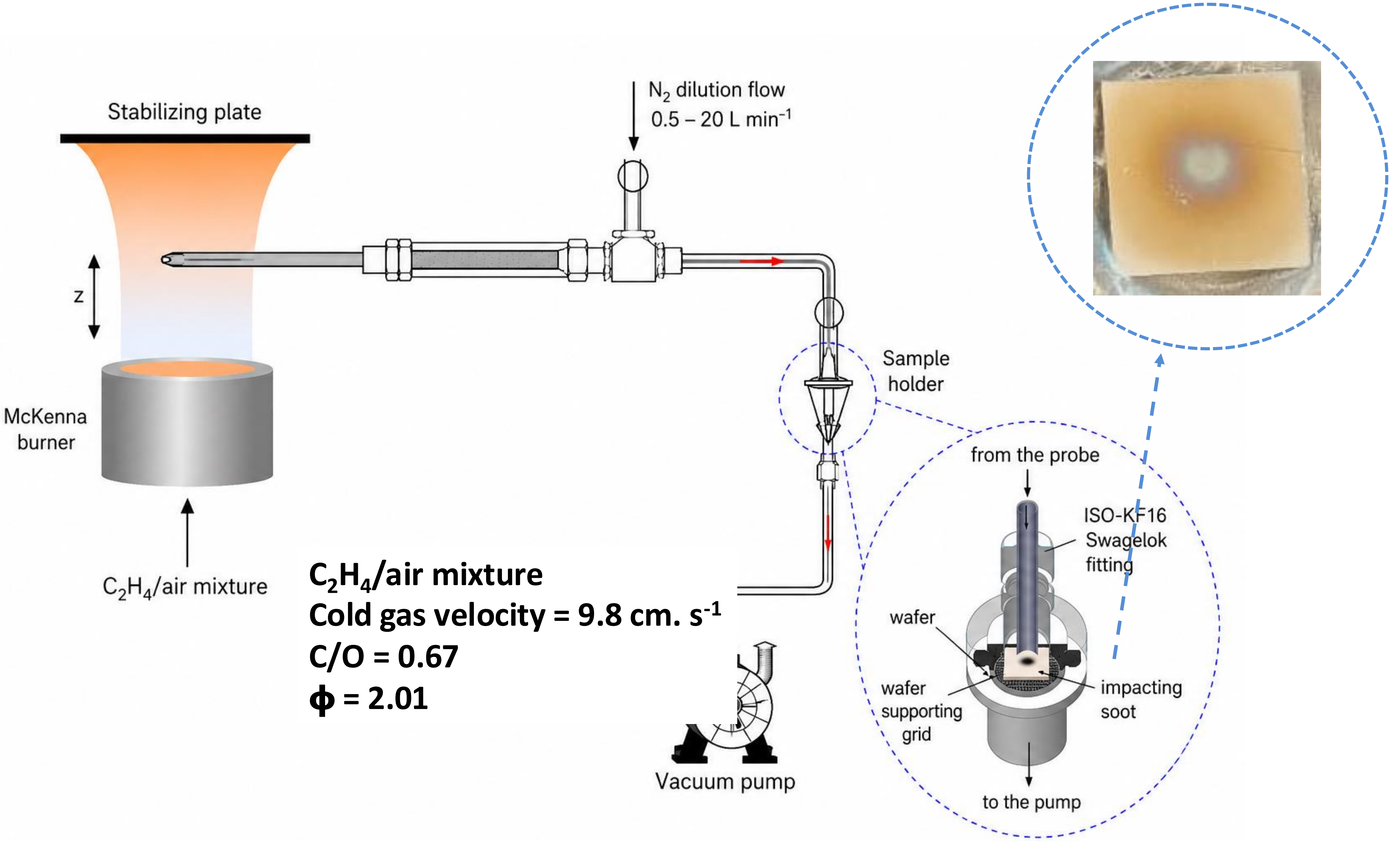
- Clustering by reaction with ***π*** radicals (RSRs)



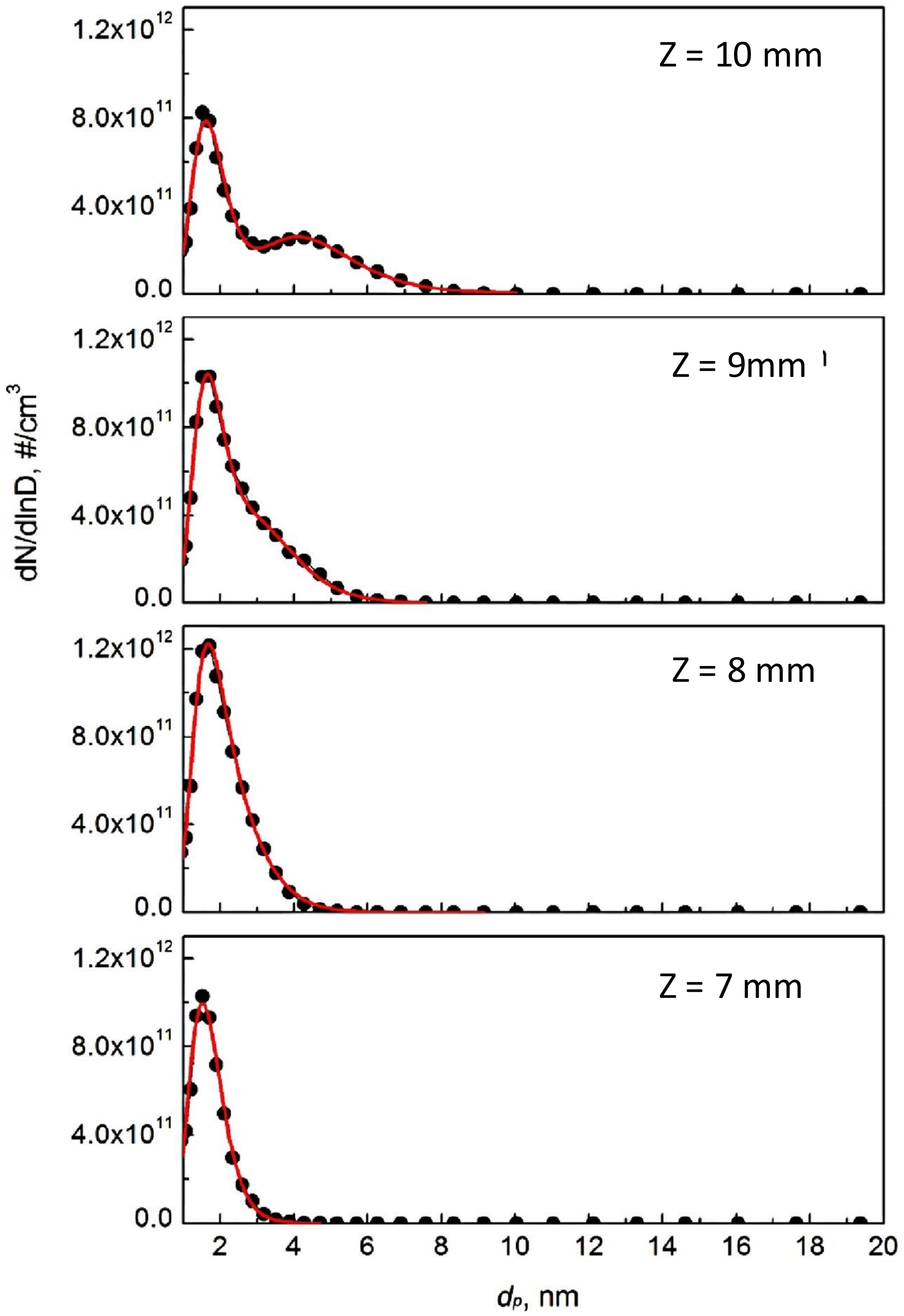
  - Tracking π radicals remains challenging; empirically odd mass peaks have been considered as π radicals, but this may not be true
    - Example C26H15, 13CC25H14, and C25H11O all have same nominal mass = 327 u

Martin et al., PECS, 2022

Sample collection

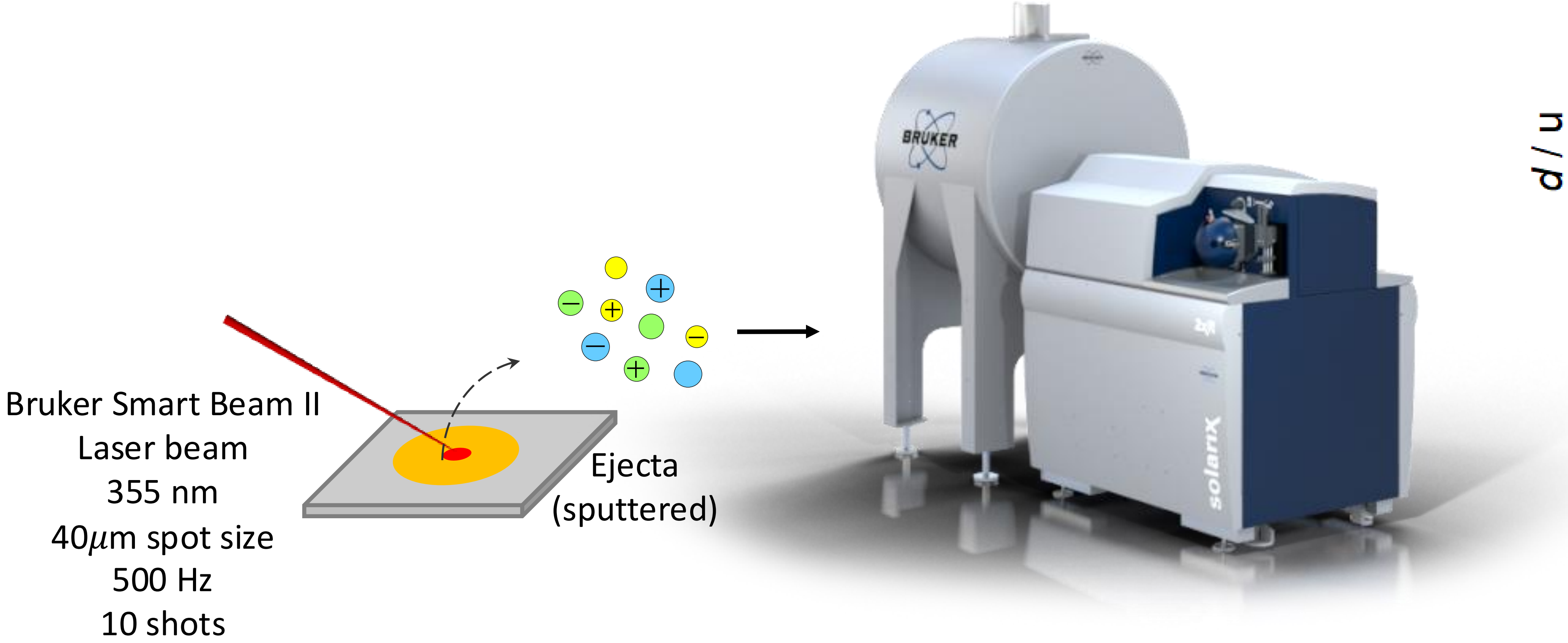


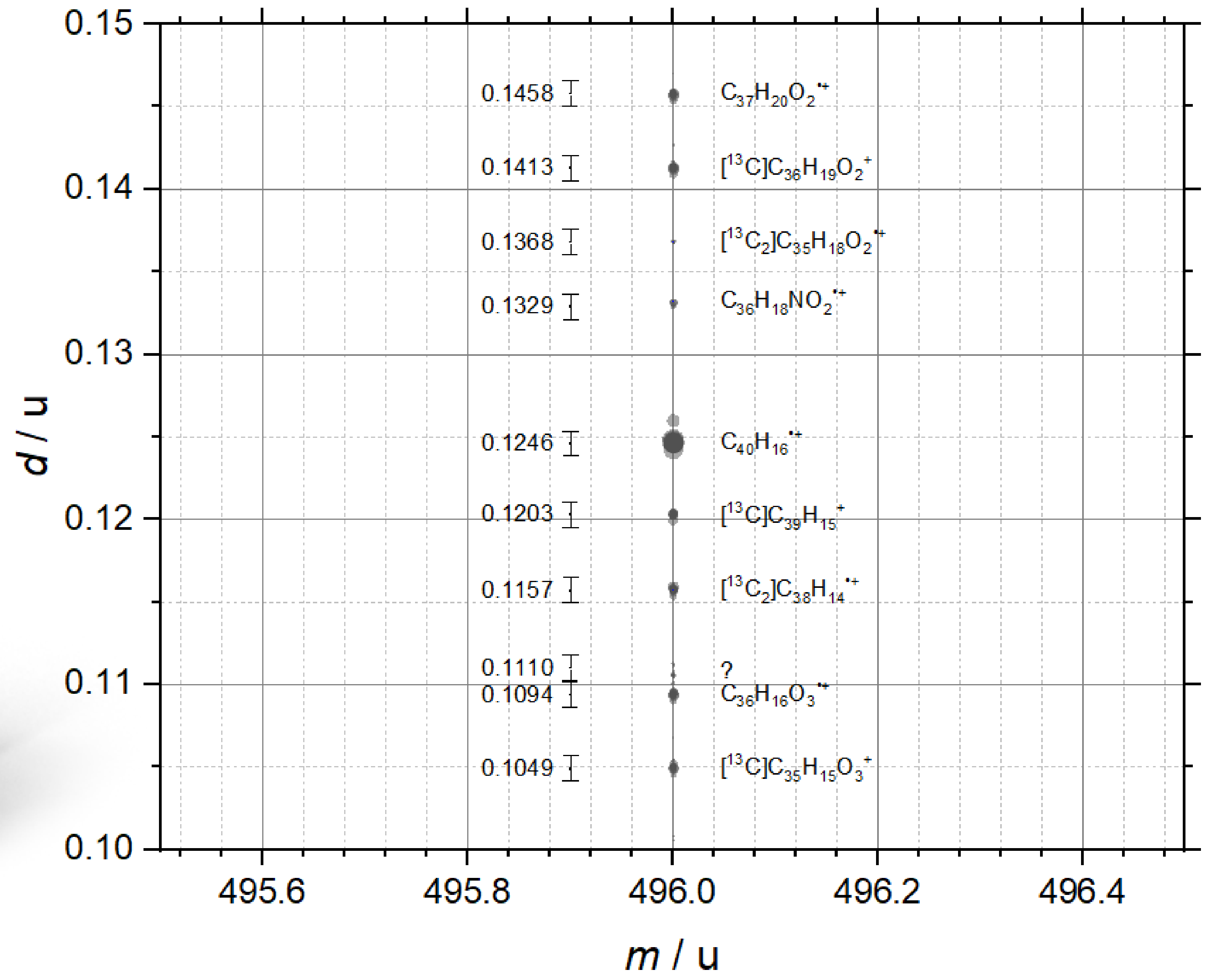
C_2H_4/air mixture
Cold gas velocity = 9.8 cm. s^{-1}
C/O = 0.67
ϕ = 2.01



Particle Size Distribution from Commodo et al., CnF, 2015

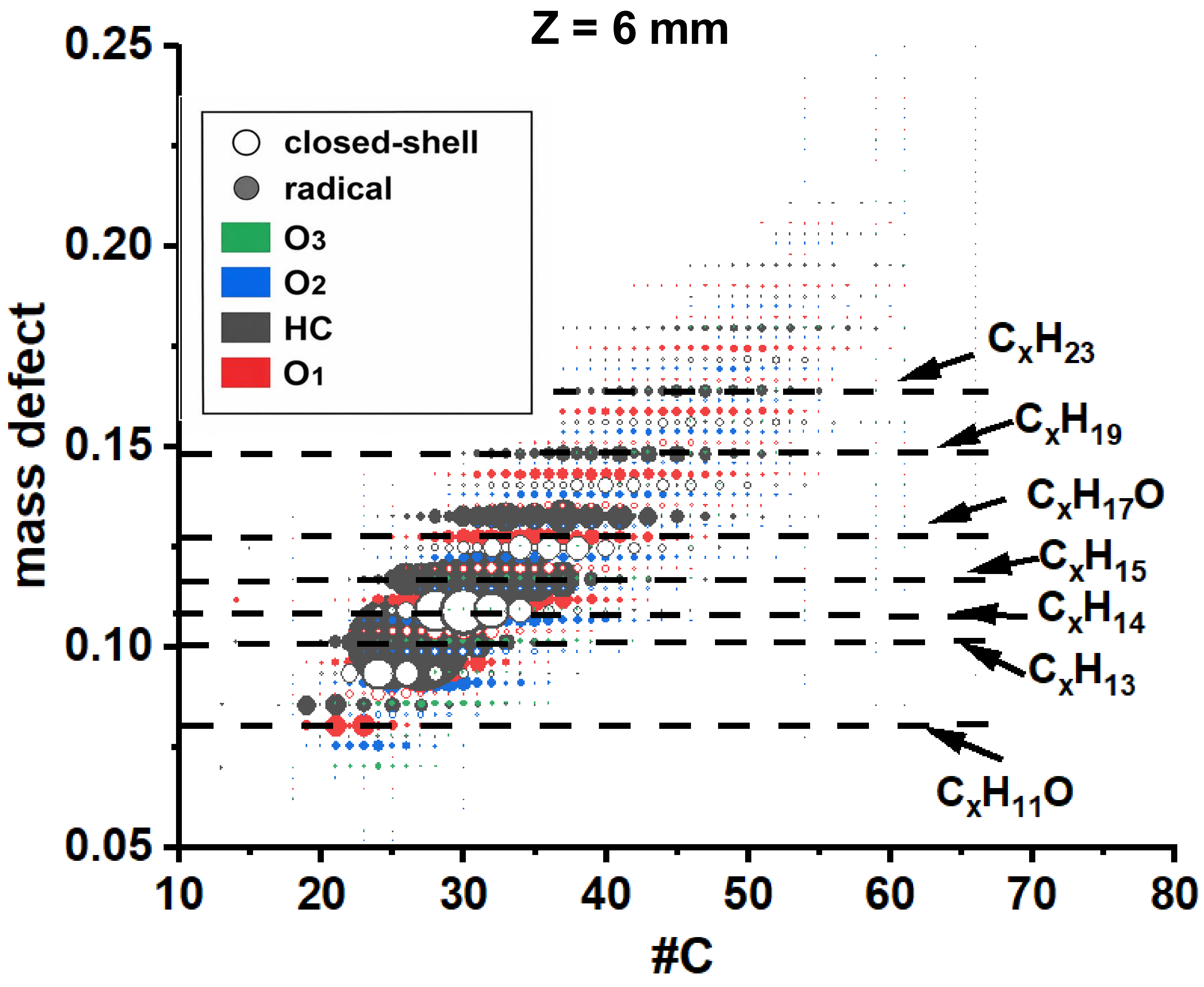
Chemical analysis

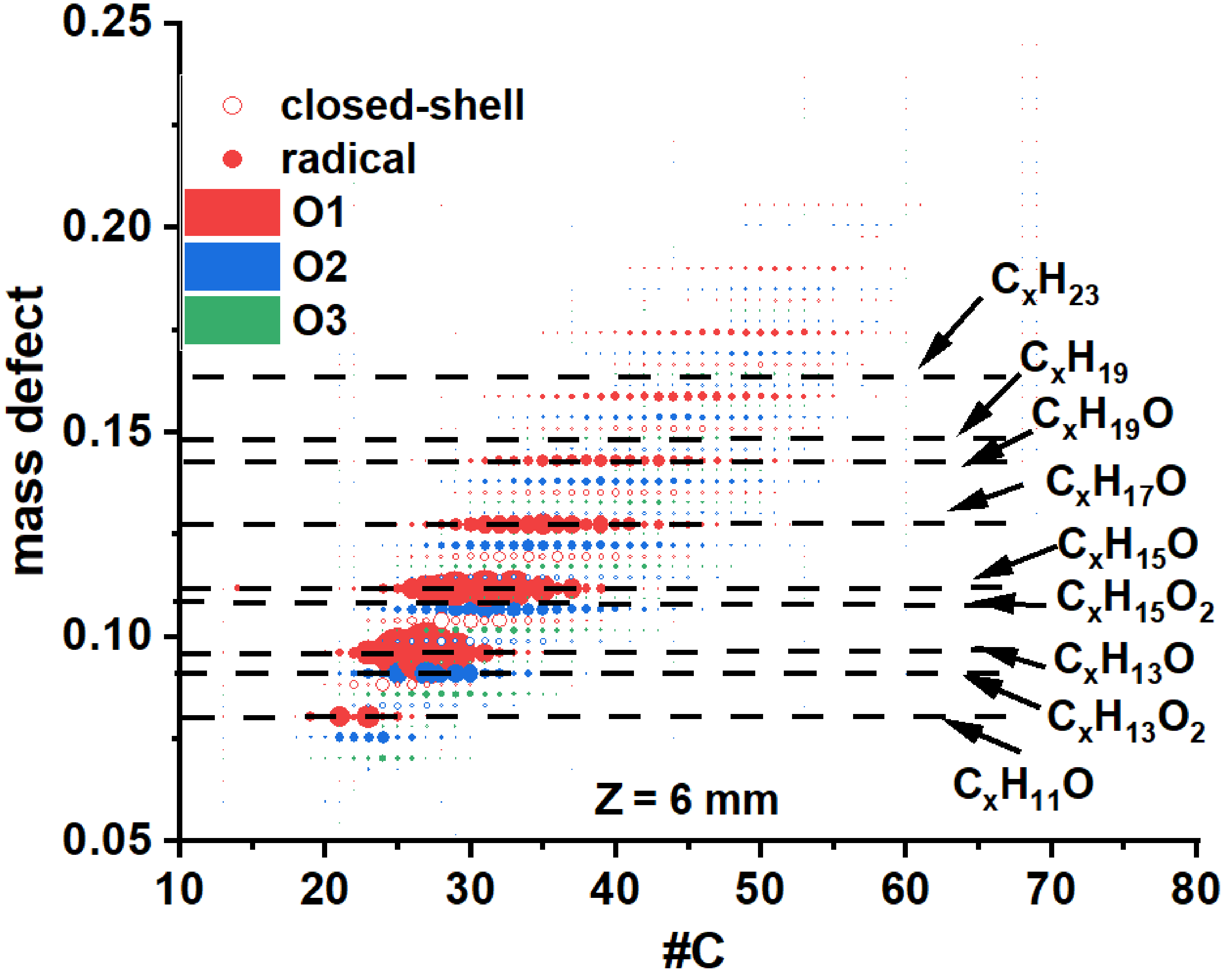




Mass resolution = 5 x 10^5 at m/z = 496
Mass accuracy better than 0.5 ppm

Chemical evolution of particles (Z=6mm)

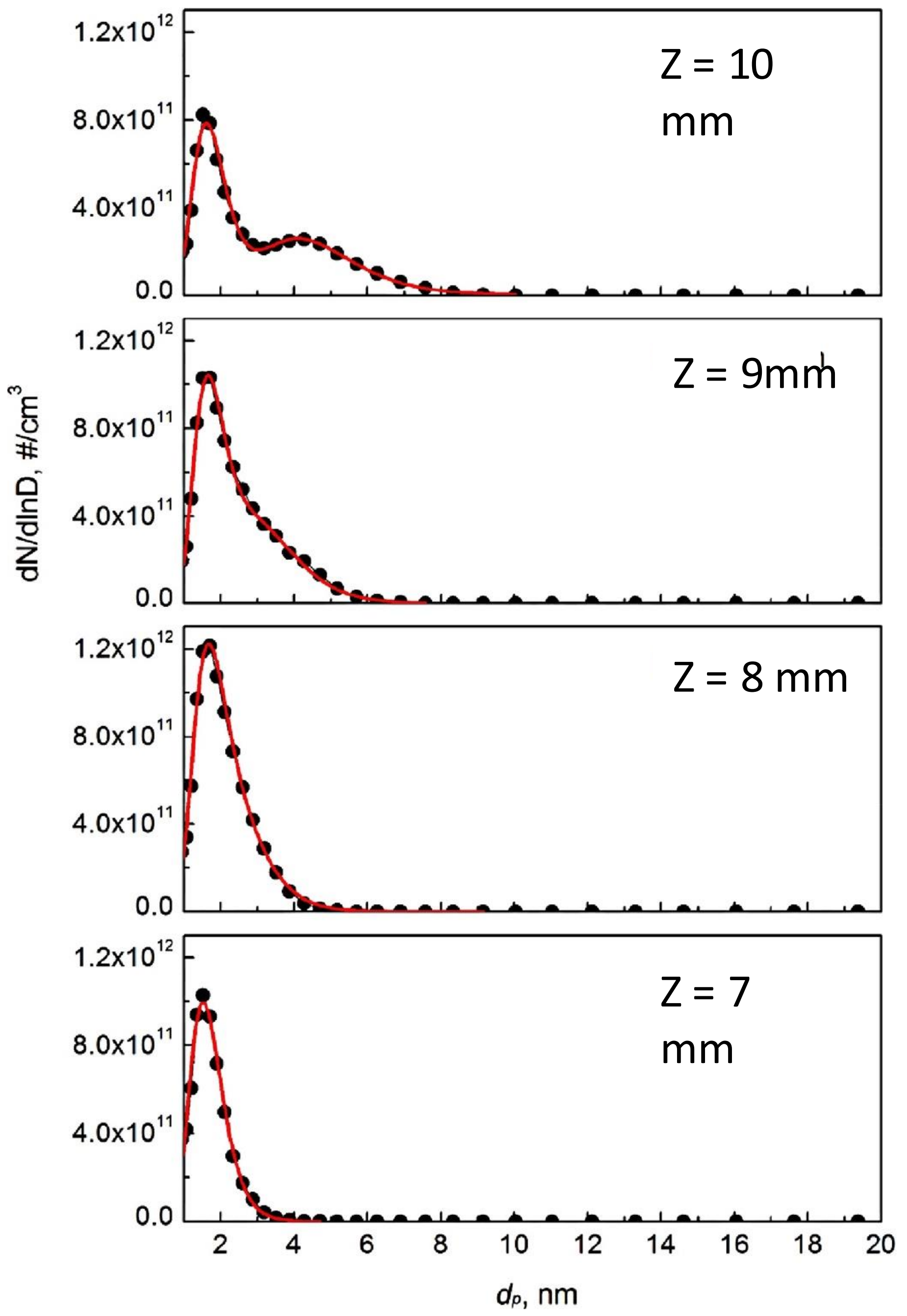


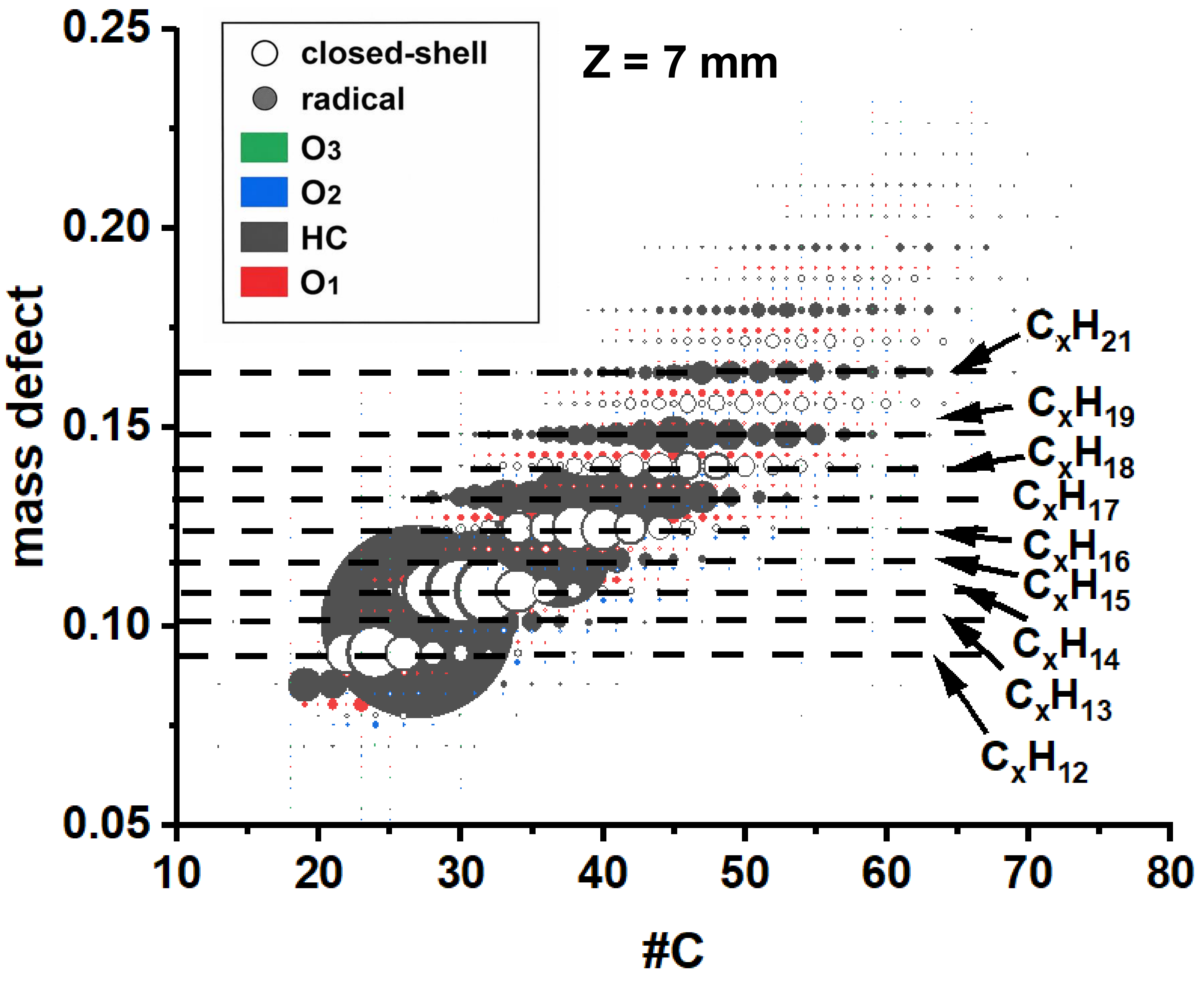


Mass defect = Exact mass – nominal mass

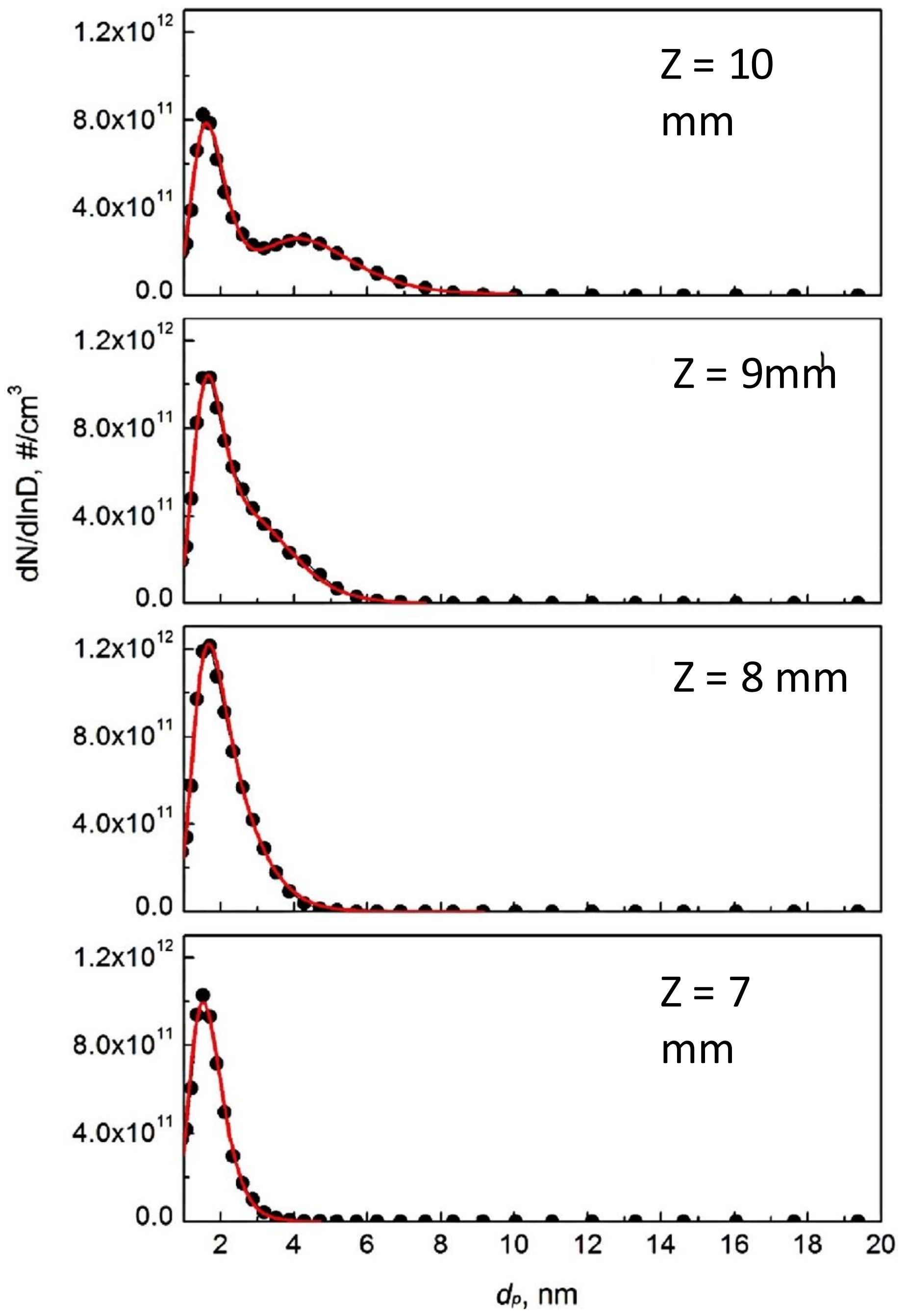
E.g. Mass defect of CH_3=exact mass (15.02347) – nominal mass (15)=0.02347

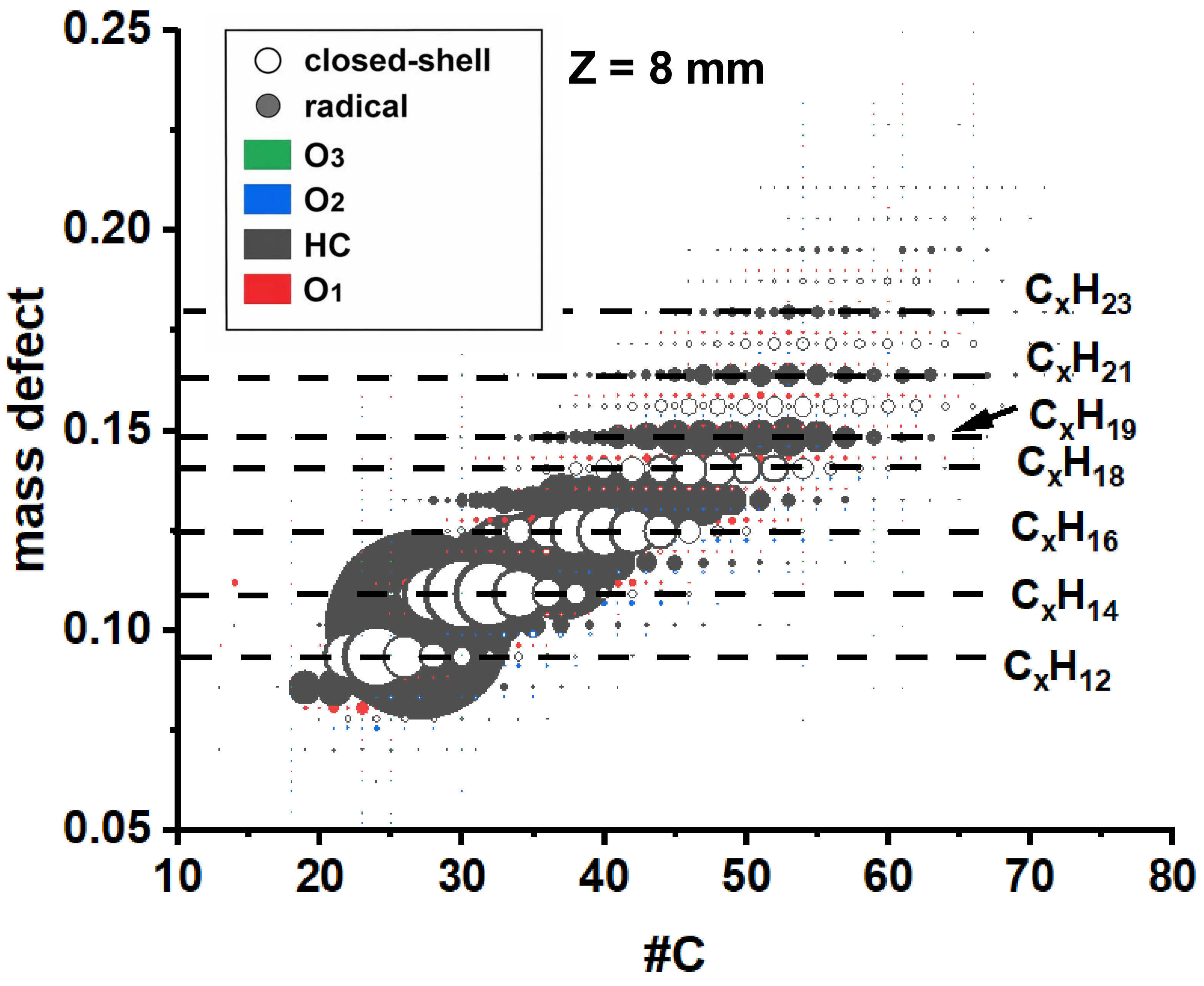
Chemical and morphological evolution of particles (Z = 7 mm)



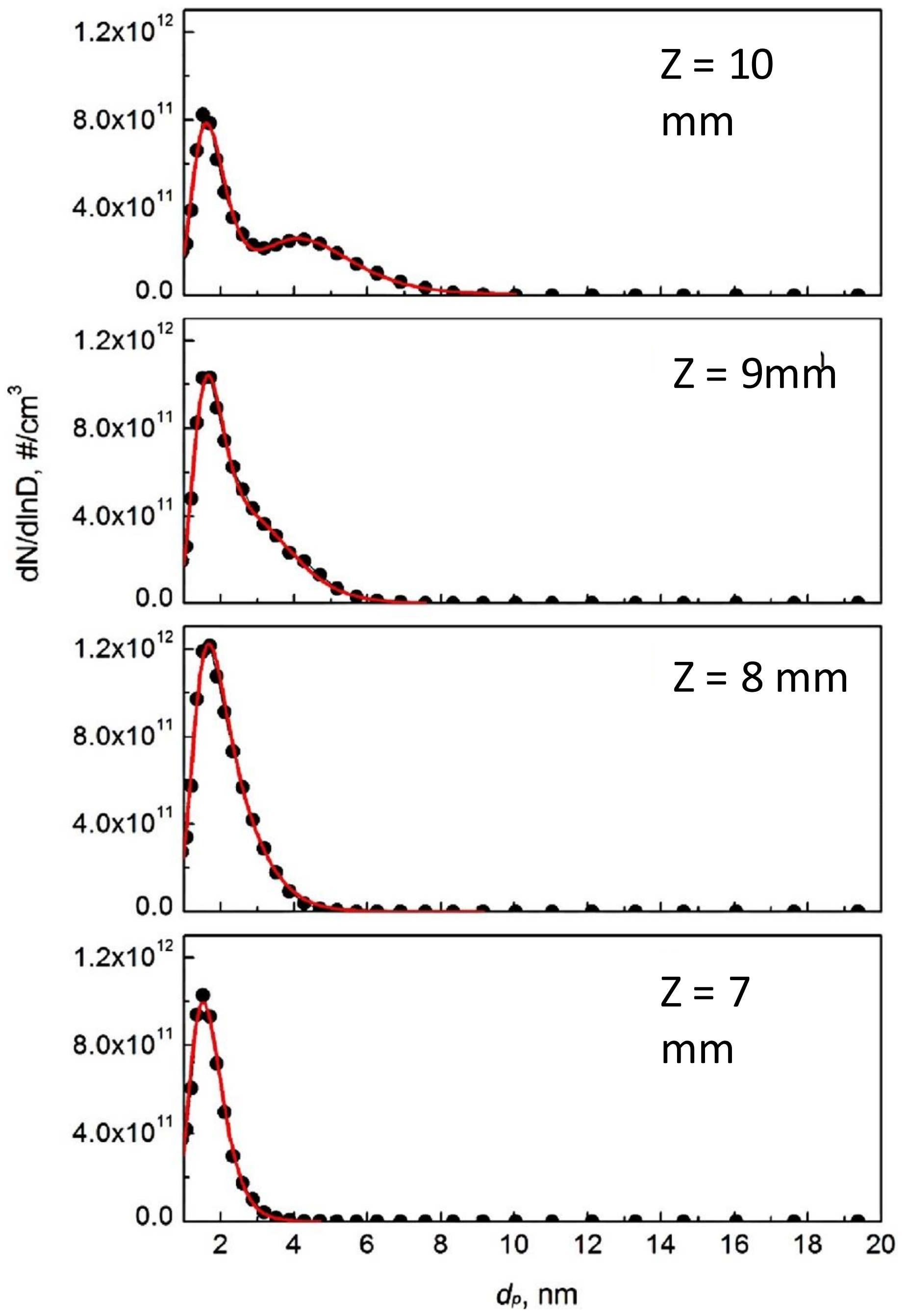


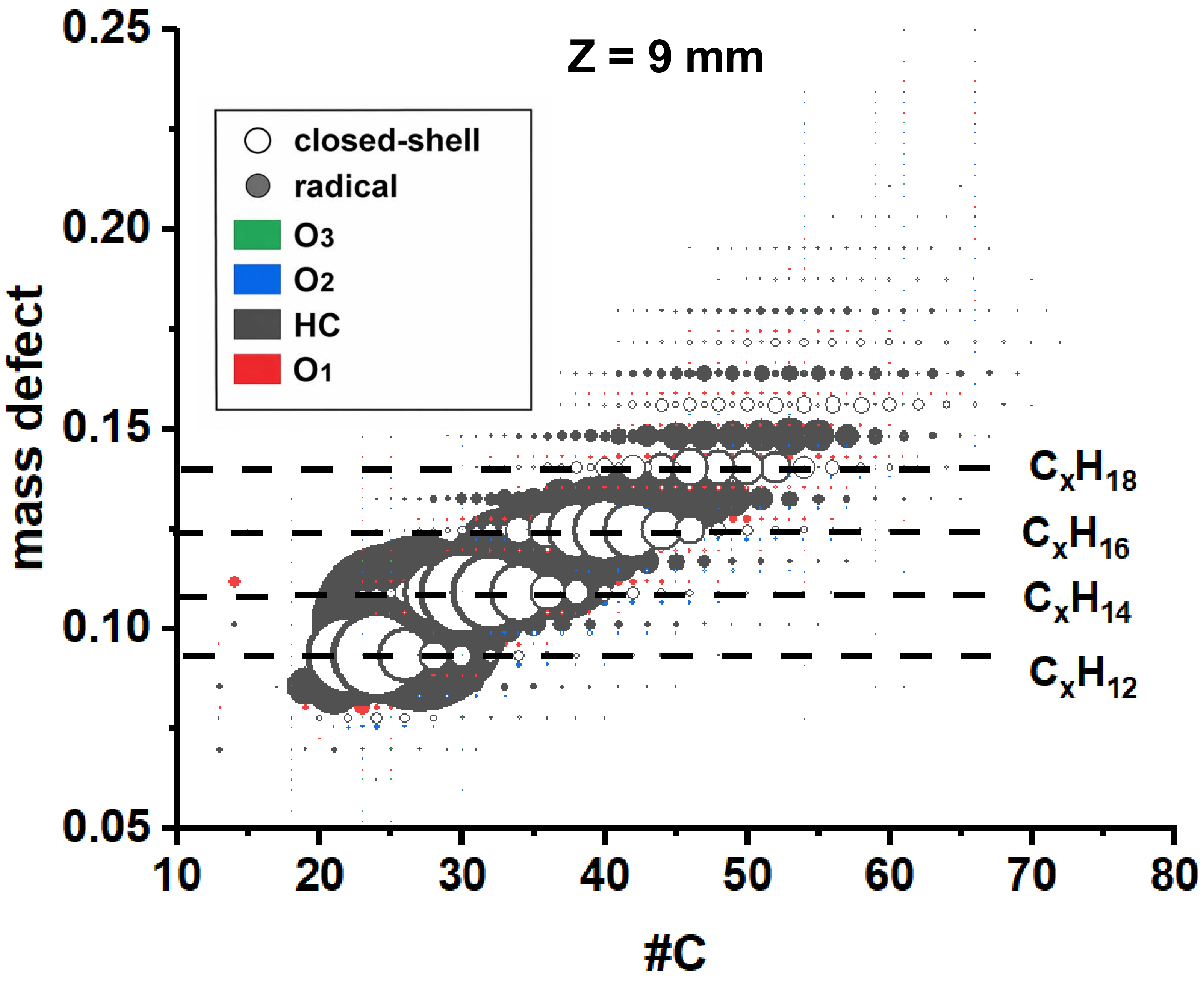
Chemical and morphological evolution of particles (Z = 8 mm)



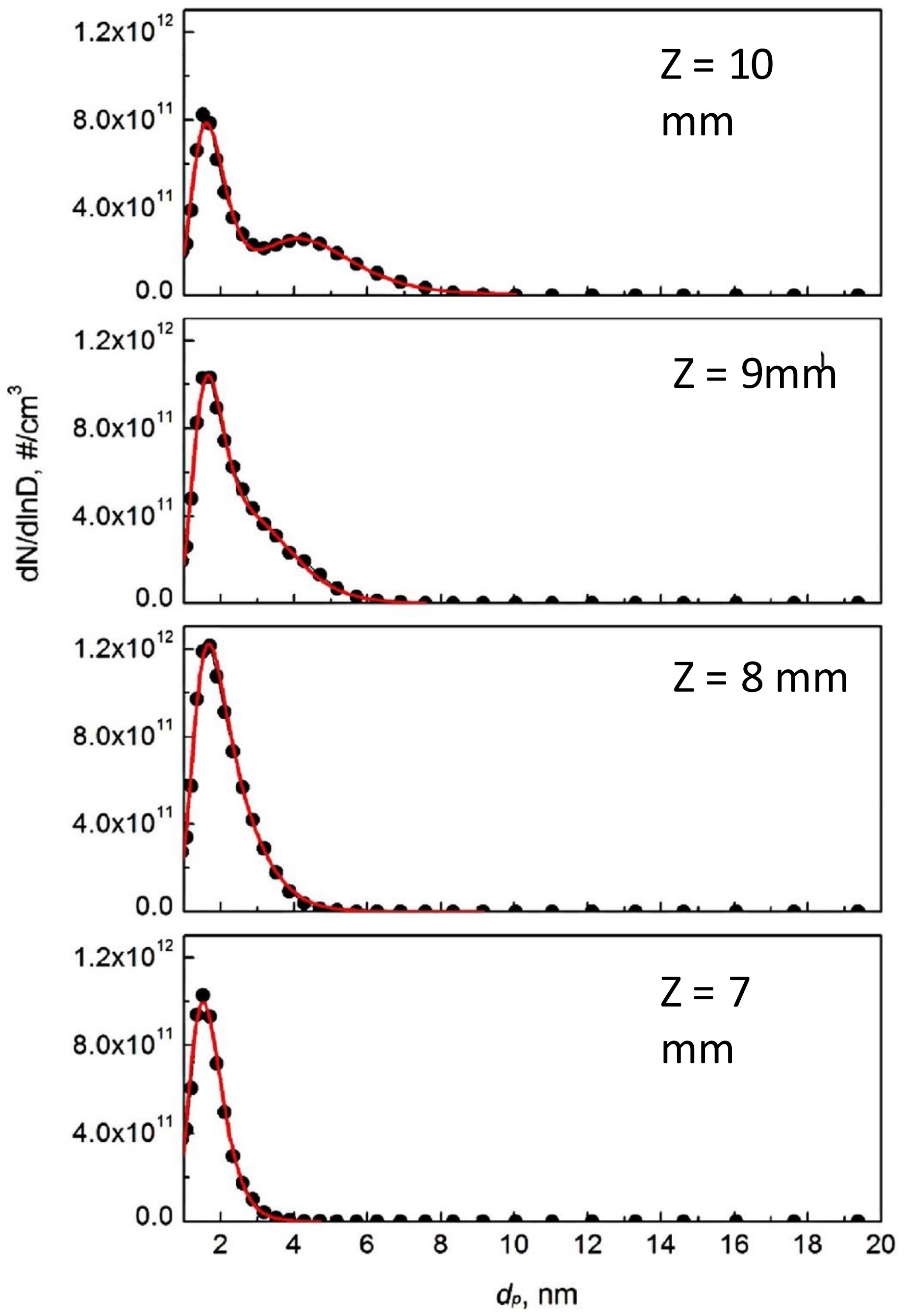


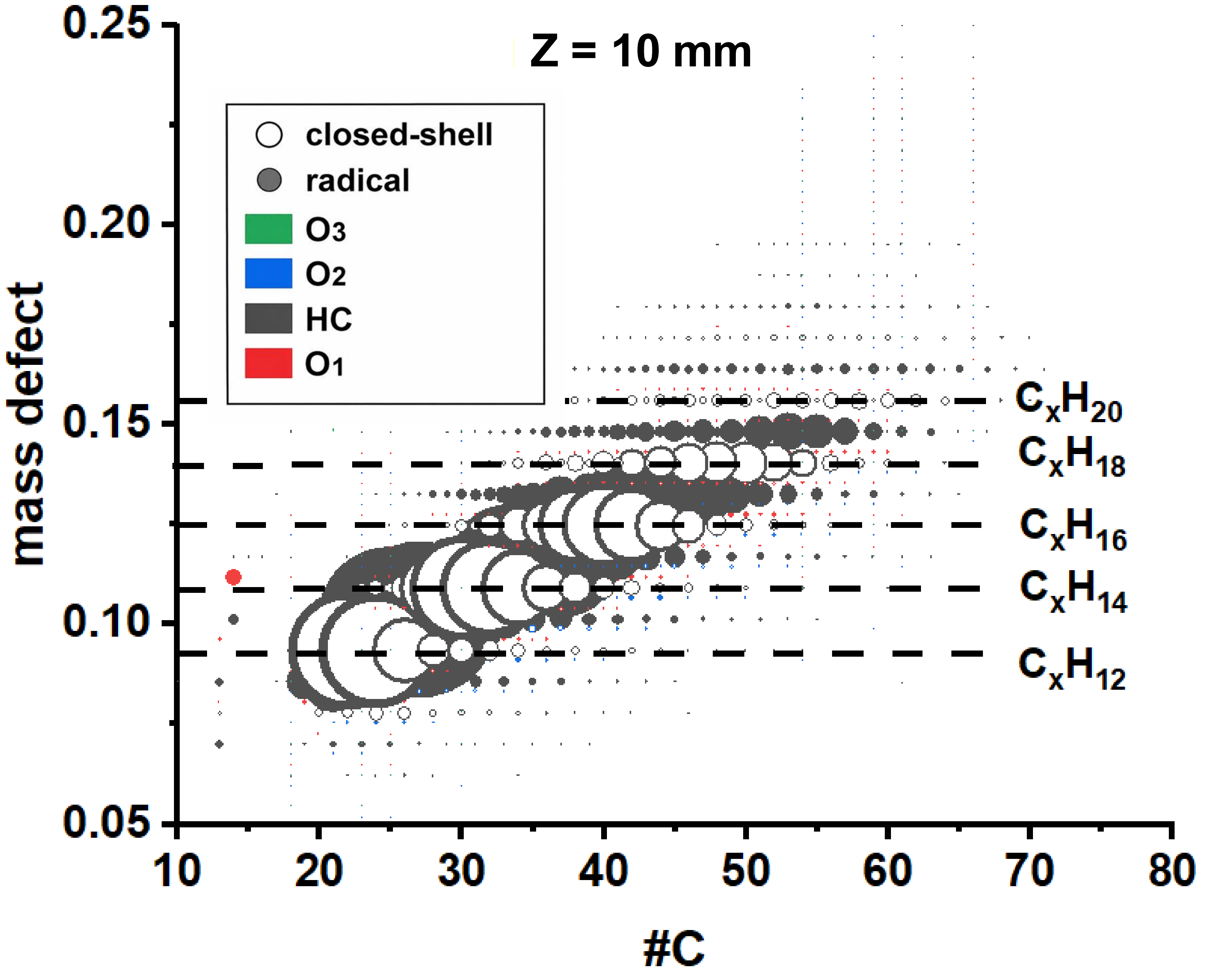
Chemical and morphological evolution of particles (Z = 9 mm)





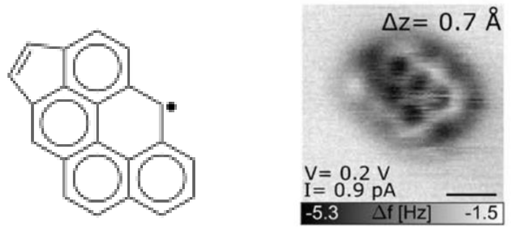
Chemical and morphological evolution of particles (Z = 10 mm)



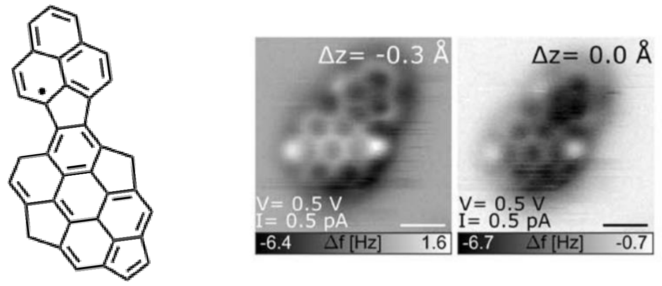


Correlation with HR-AFM images

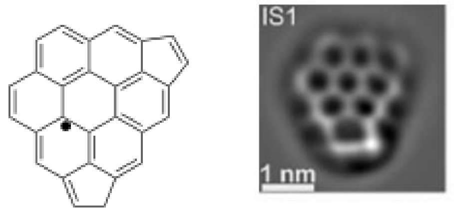
$C_{21}H_{11}$



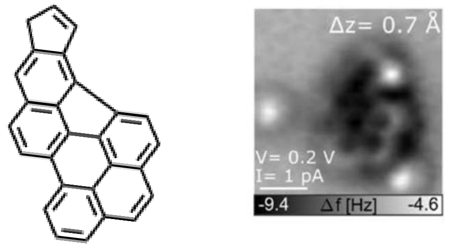
$C_{39}H_{17}$



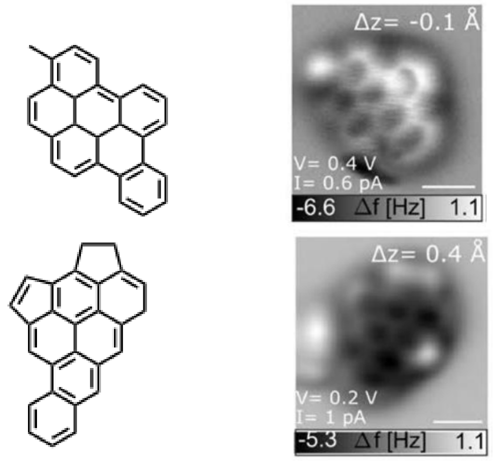
$C_{25}H_{13}$



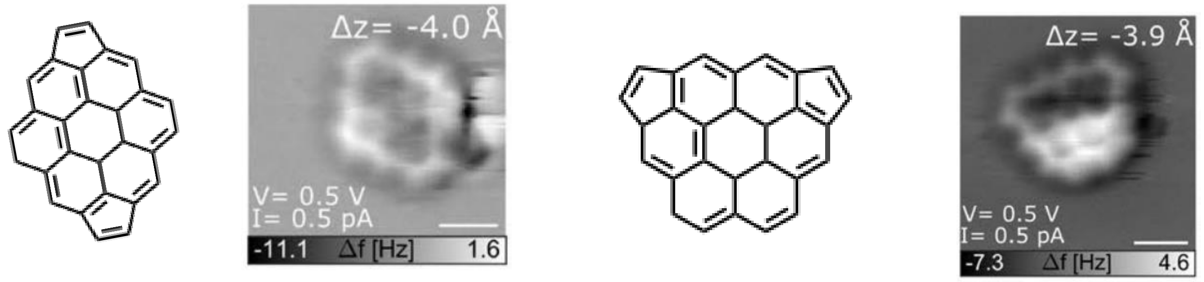
$C_{27}H_{14}$



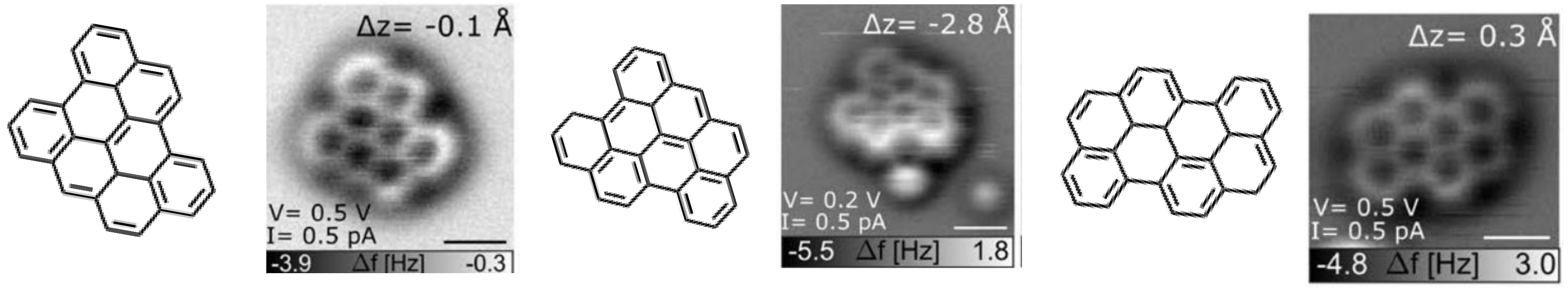
$C_{27}H_{16}$



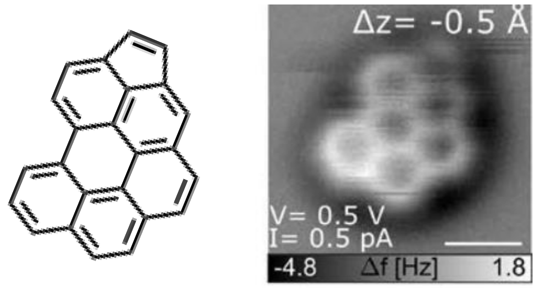
$C_{28}H_{12}$



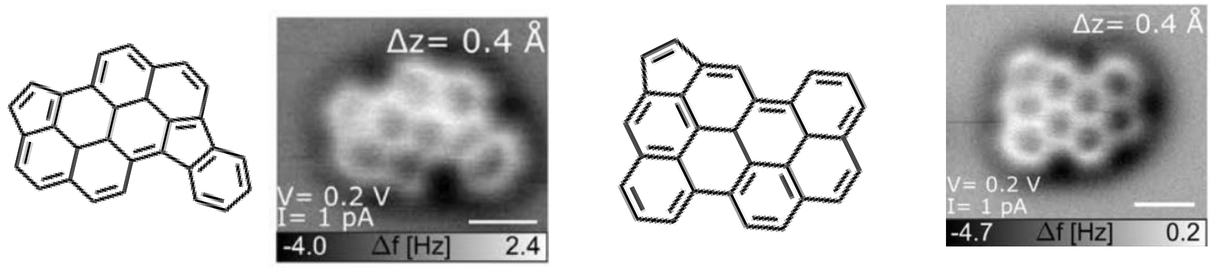
$C_{28}H_{14}$



$C_{24}H_{12}$



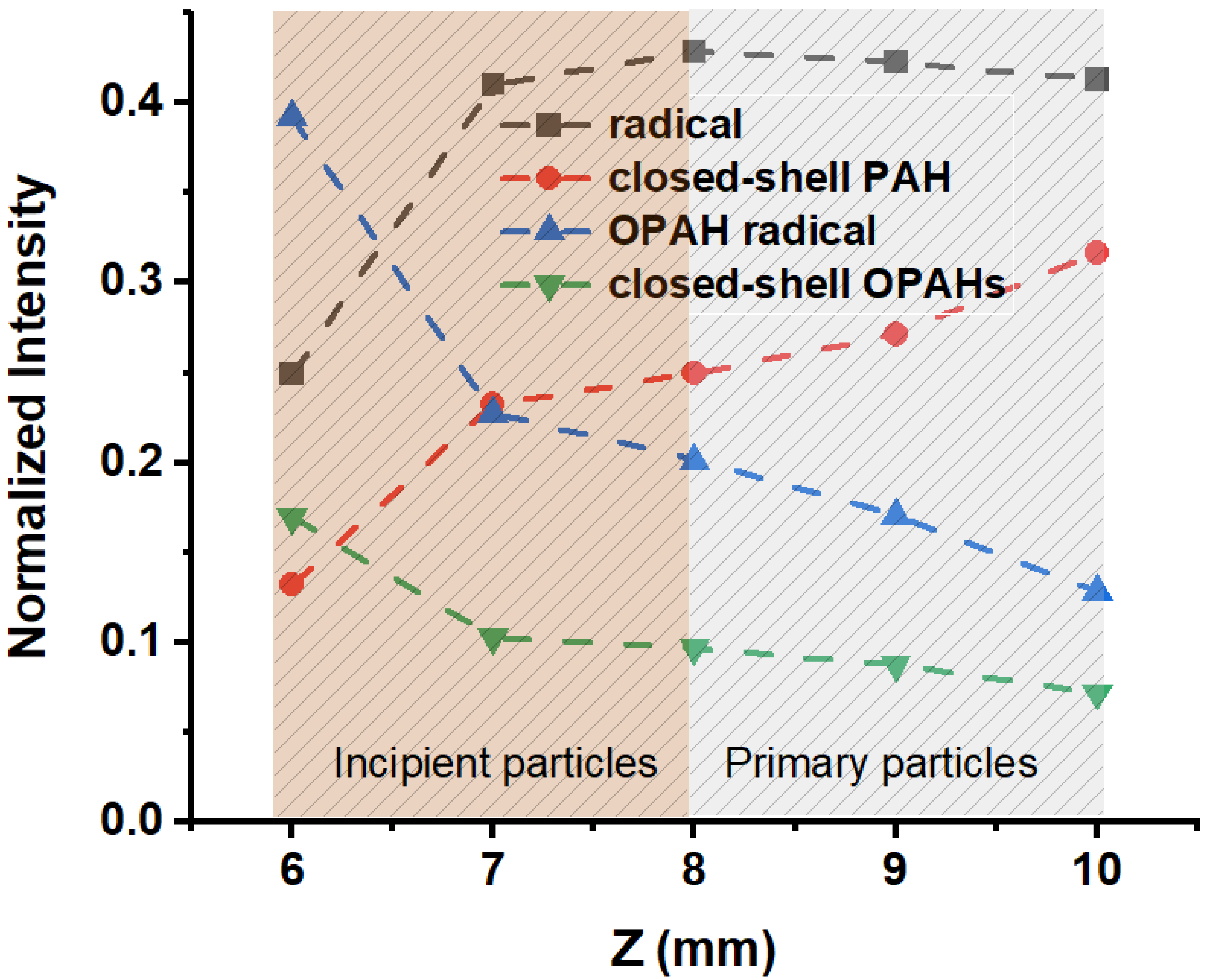
$C_{30}H_{14}$



AFM images from Commodo et al., CnF, 2019, Schulz et al., PROCI, 2019, and Lieske et al., ACS NANO, 2023

Implications for clustering mechanism

- Oxygenated species (OPAH radicals and closed-shell OPAHs) are maximum at 6 mm and decrease significantly with height
- Concurrently, hydrocarbon radicals are increasing
  - ➢ *Oxygenated species form hydrocarbon radicals by decomposition?*
- Hydrocarbon radicals, likely π radicals, increase in incipient particles while closed-shell PAHs increase in primary particles
  - ➢ *Are π radicals forming incipient particles by covalent bonding and orbital overlap?*
  - ➢ *Do closed-shell PAHs participate in soot growth via dispersive interactions?*



Key messages

- Oxygen may have counterintuitive effects on soot formation

- If you want to mitigate soot formation and emissions at source, choose a fuel and combustion conditions that do not favor aromatic π radicals formation

Acknowledgements

- Competitive Research Grant, KAUST (URF/1/4688-01-01)
- Air Force Office of Scientific Research (award number FA8655-25-1-7003)
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Thanks

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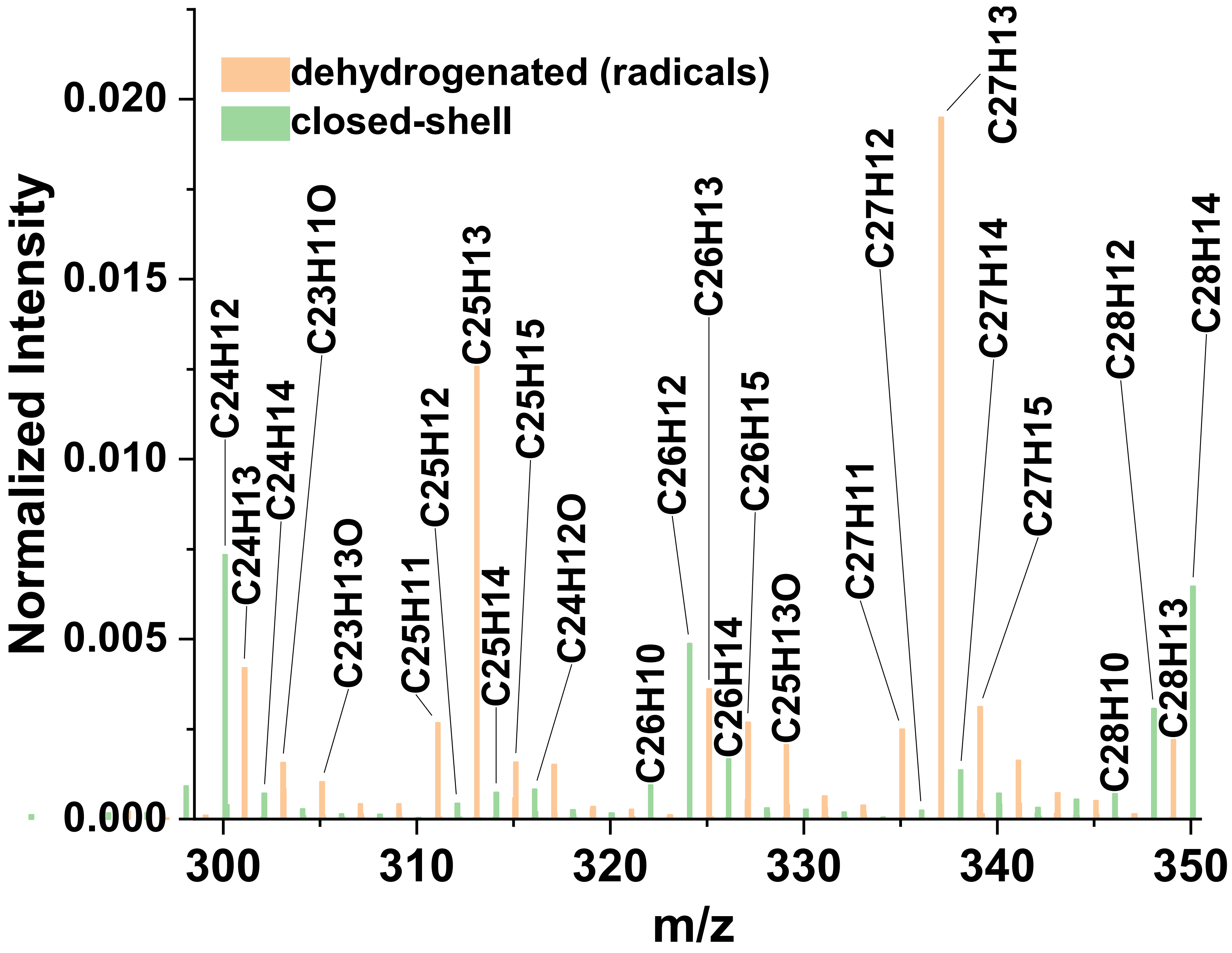
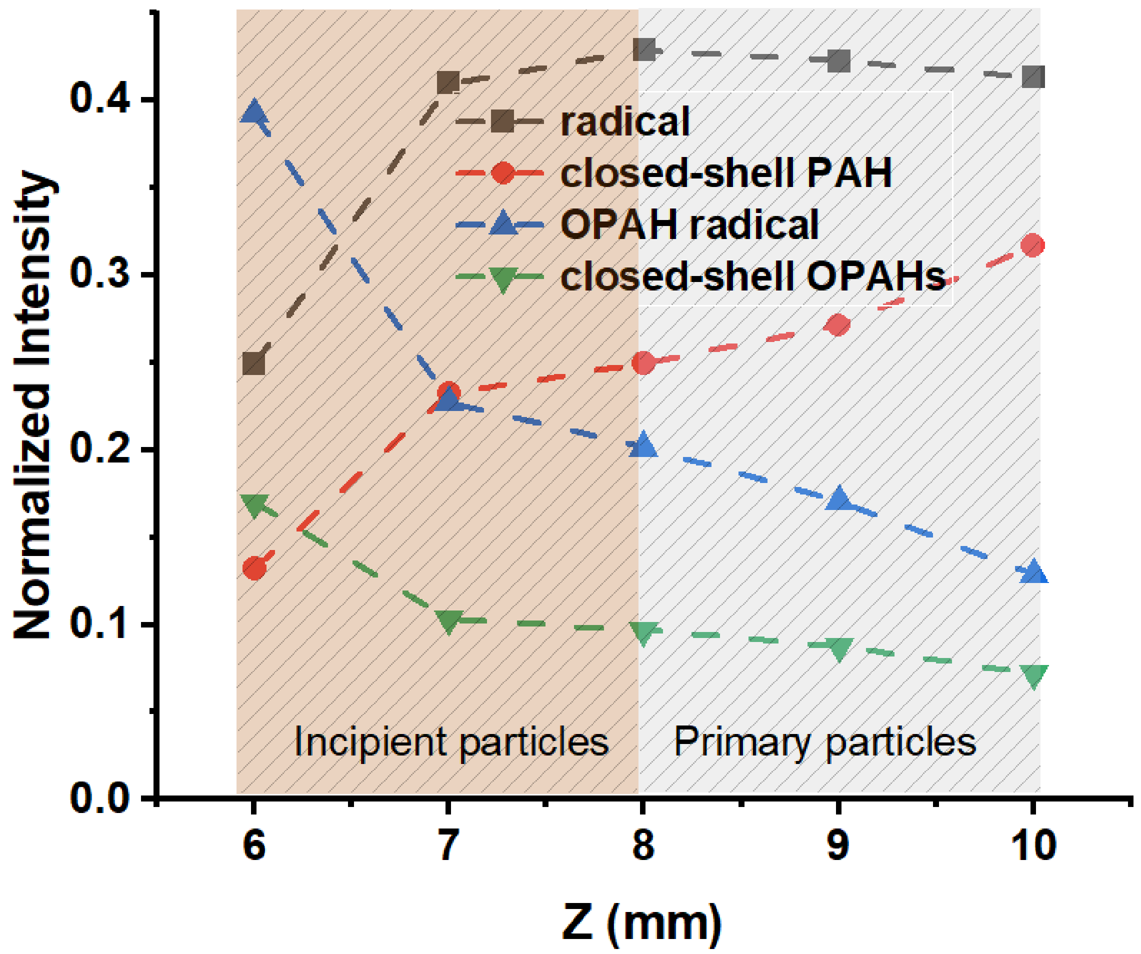
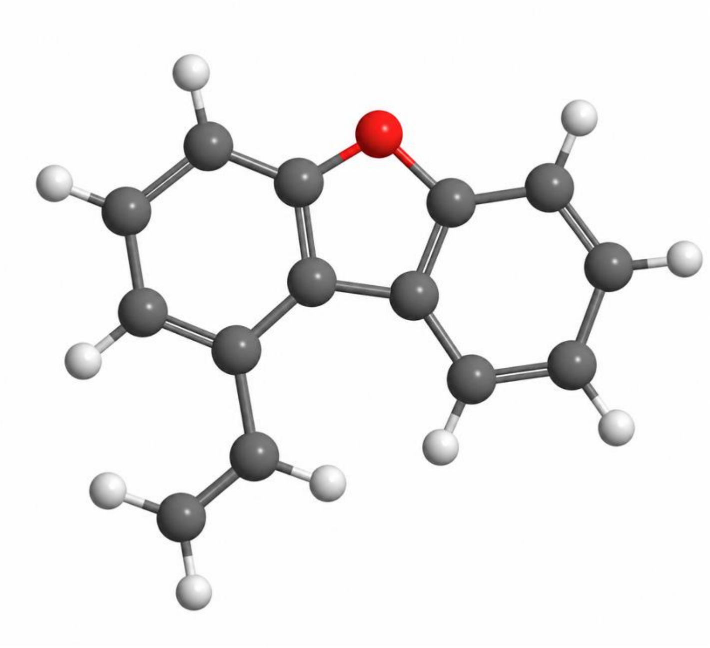
Types of species detected



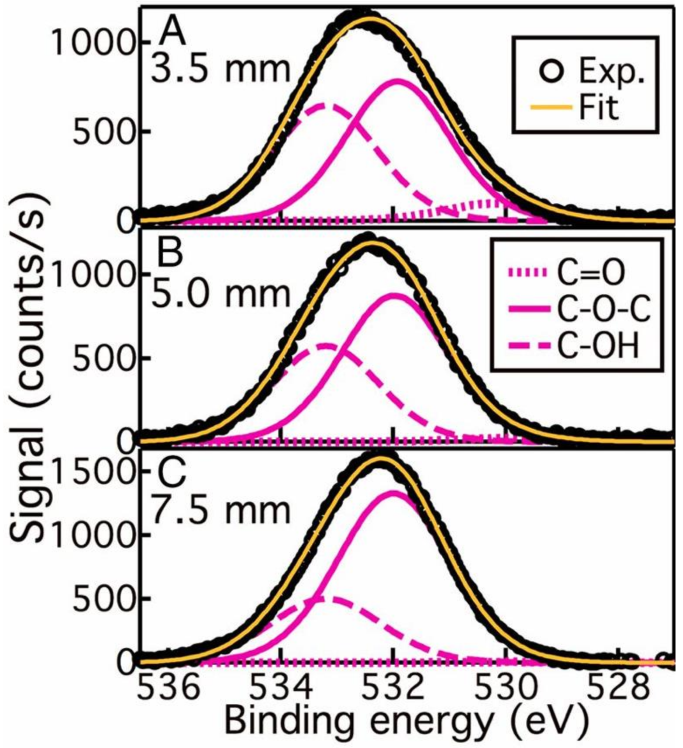


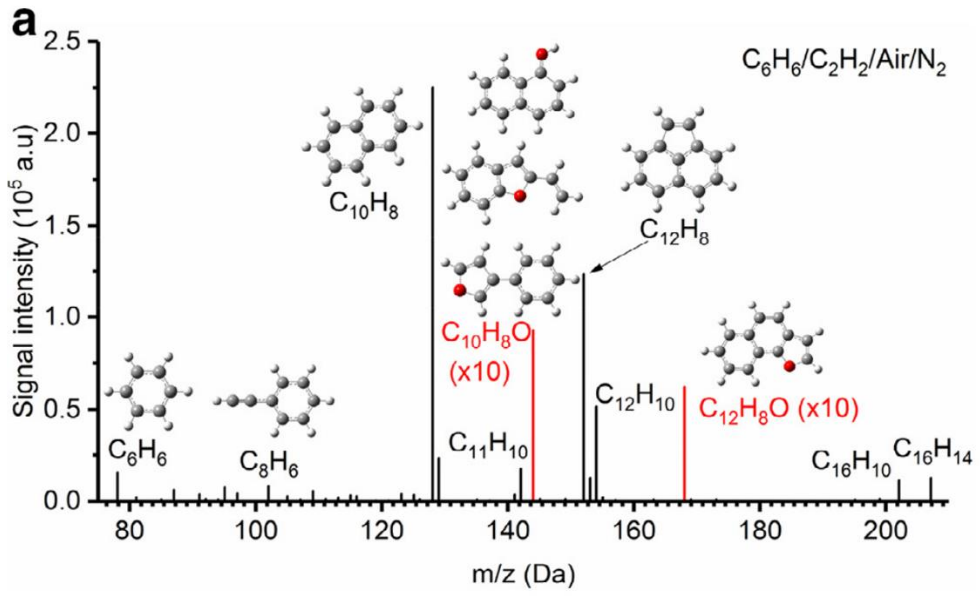
Role of oxygen in inception is not clear

- Oxygenated PAHs (OPAHs) have been detected in the gas phase and also in soot



- OPAHs can include hydroxyl, carbonyl, or cyclic ether types

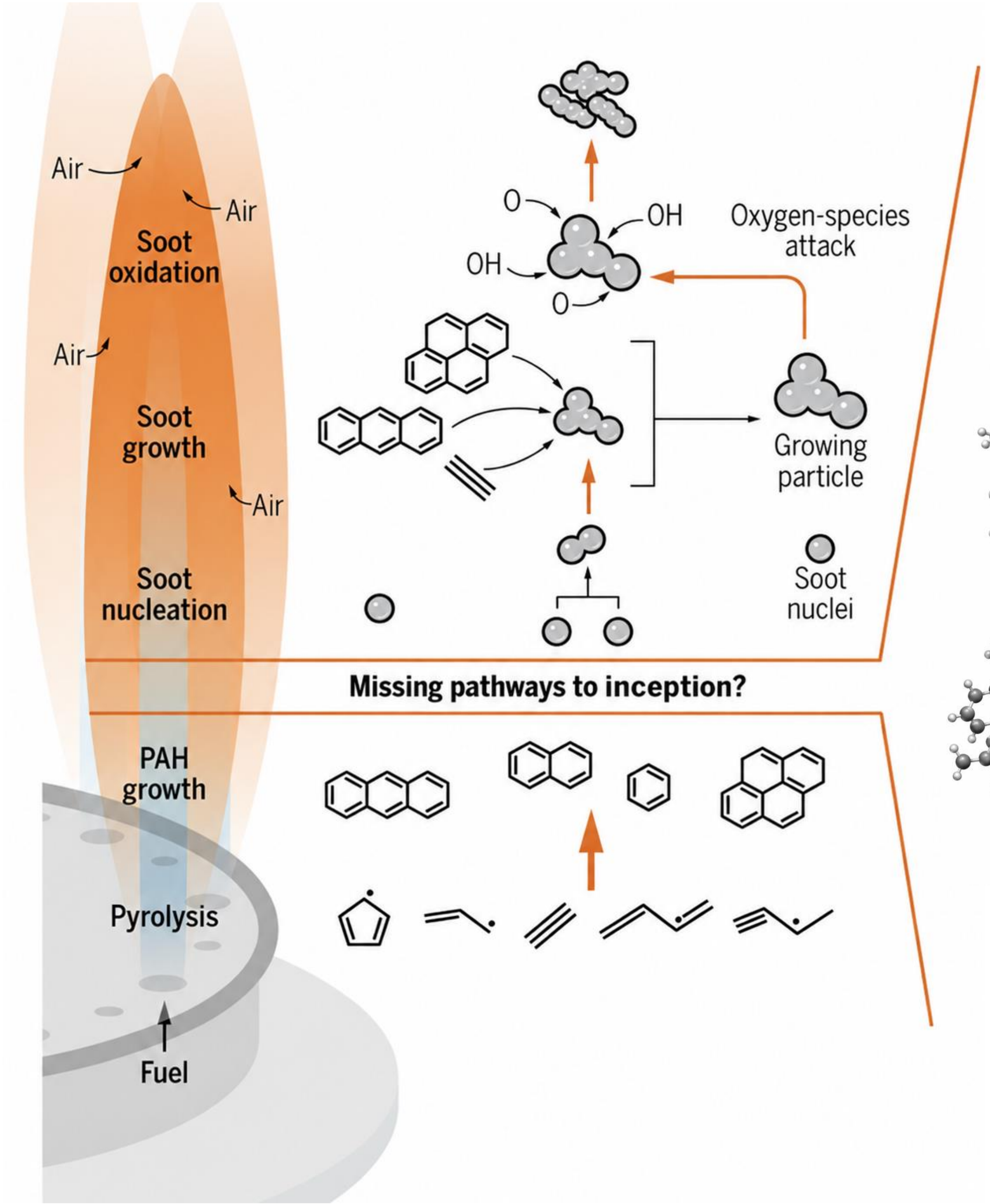


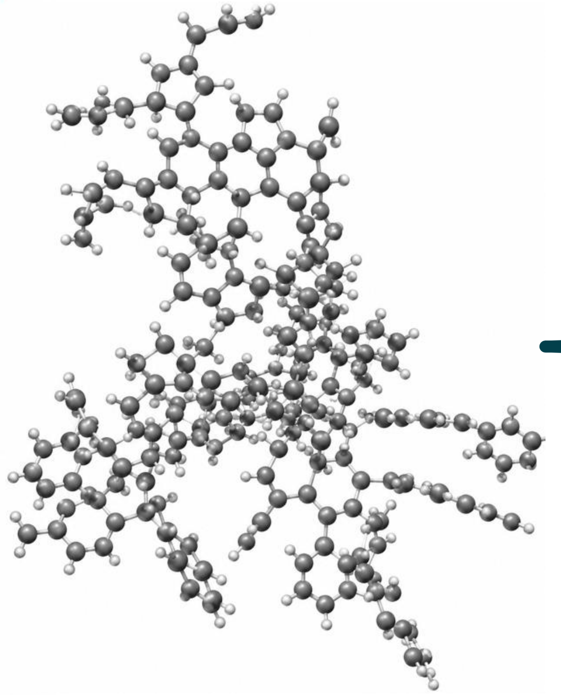


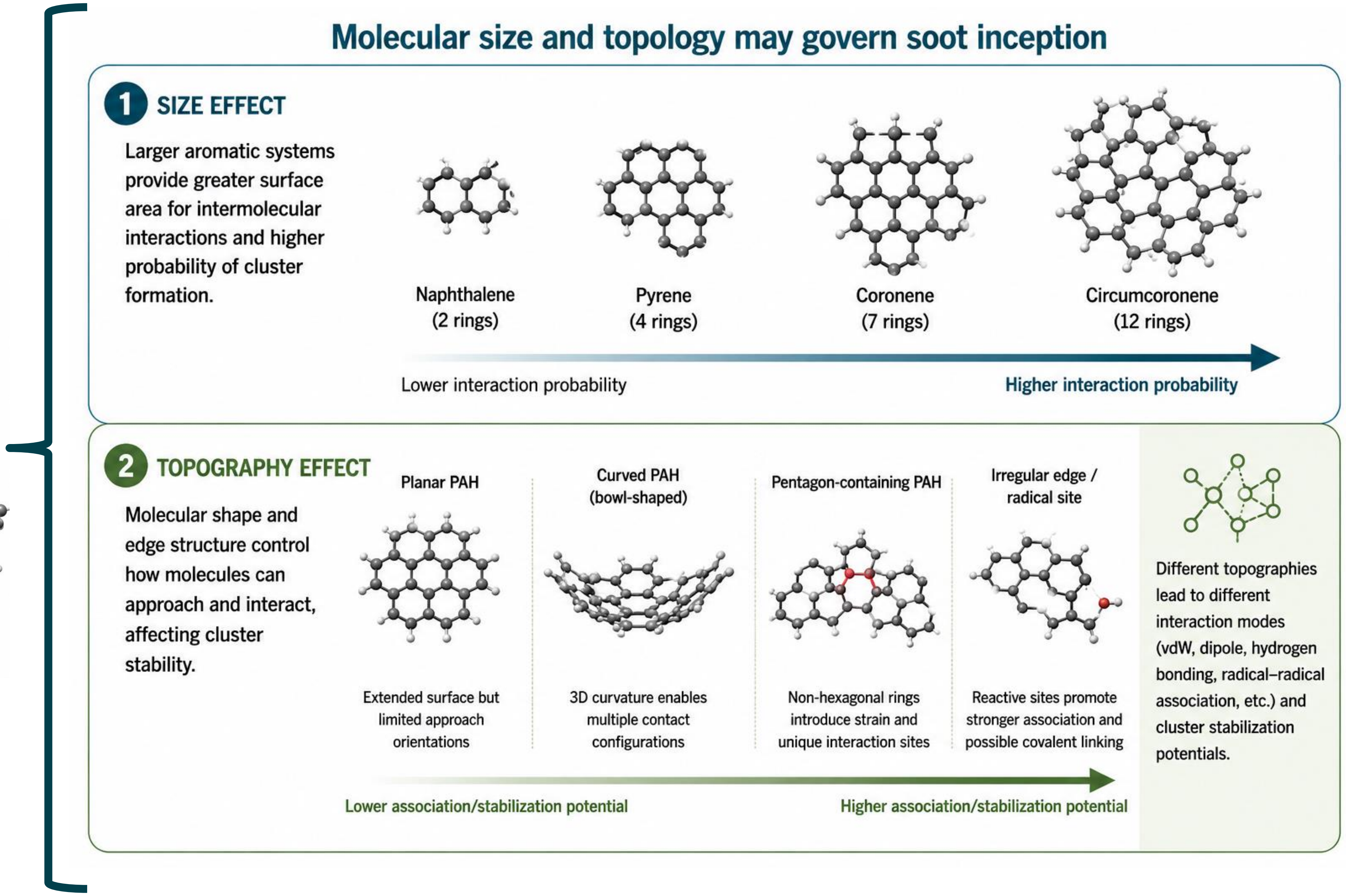
- However, it is not clear how oxygen participates in the clustering process

Johansson et al., PNAS, 2016
Liu et al., CnF, 2019

Inception: the key missing puzzle in flame chemistry







Thomson and Mitra, Science, 2018
Johansson et al., Science, 2018

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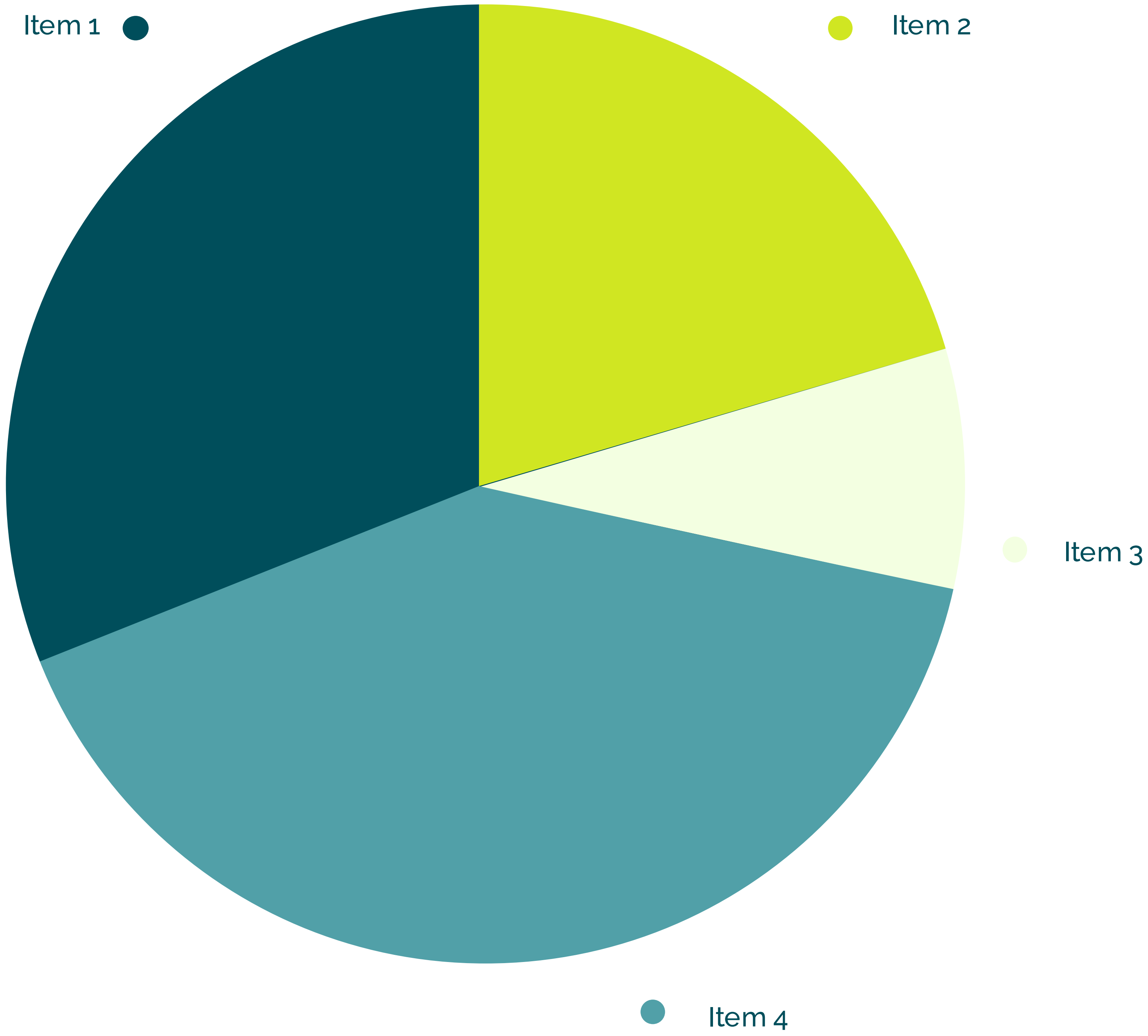

1.Davis M. *Scientific Papers and Presentations*, Academic Press, San Diego, CA.. 1997. 2.Day R. *How to Write and Publish a Scientific Paper*, 4th Edition, Oryx Press, Phoenix, AZ. 1994. 3.Mc Millan V. *Writing Papers in the Biological Sciences*, 3rd Edition, Bedford/St. Martin's, Boston, MA. 2001.

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