TOYOTA CENTRAL R&D LABS., INC.

In-cylinder Soot Nanoparticle Formation Mechanism

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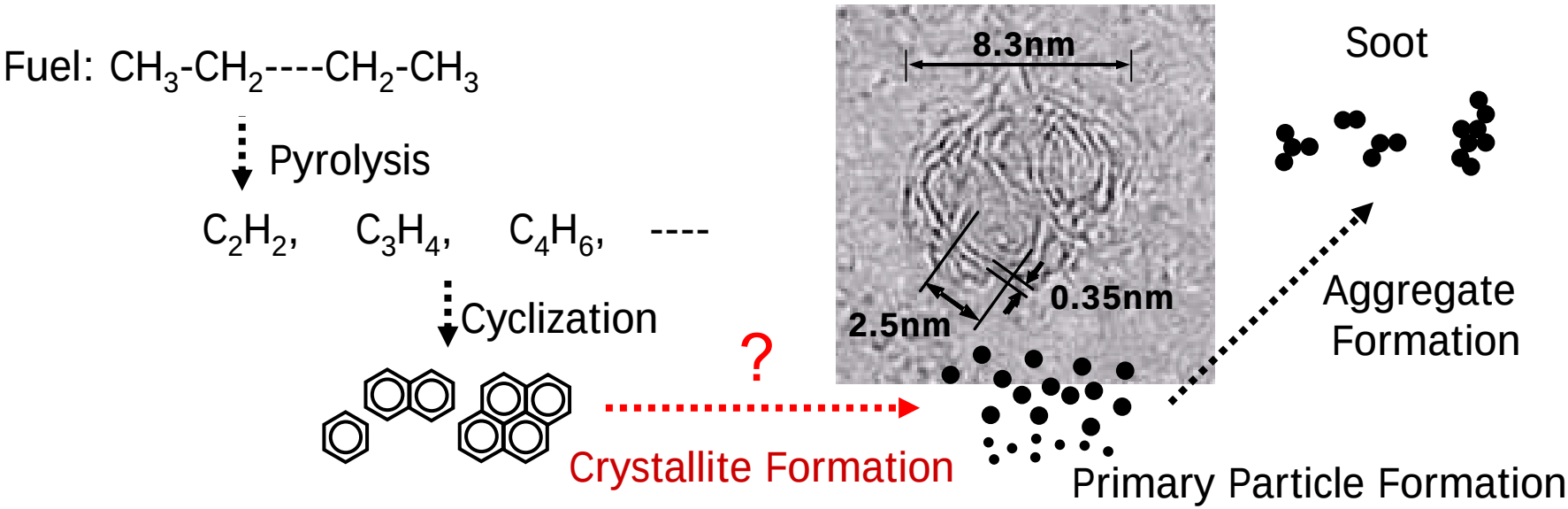
BACKGROUND

- It is important to clarify formation and oxidation processes of carbonaceous soot particles for understanding health effects of soot particles.
- But, any researchers have not resolved formation process of primary soot nanoparticles yet.



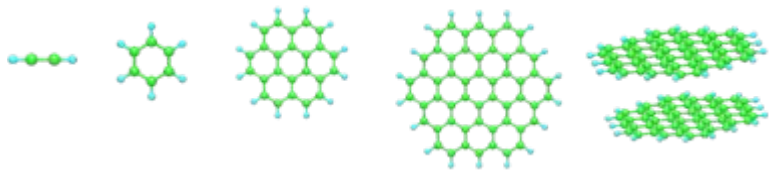
OBJECTIVE

- The objective of our study is to clarify the formation process of primary soot nanoparticles via crystallites in engine combustion.

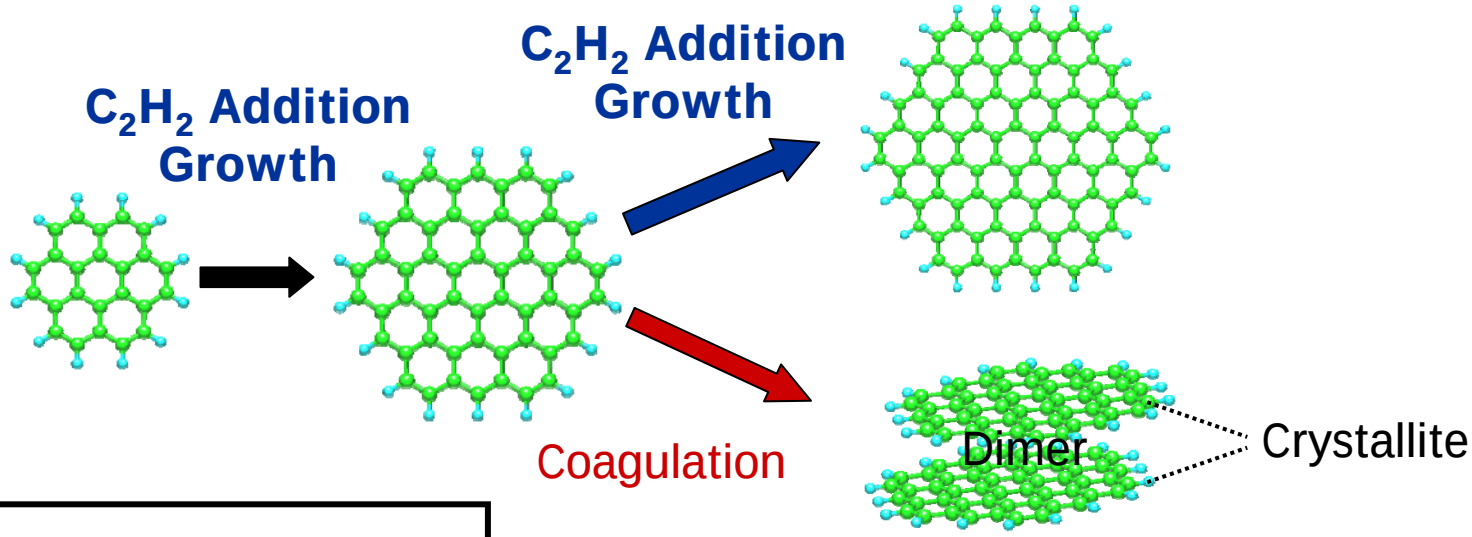
1. Theoretical analysis for the crystallite formation

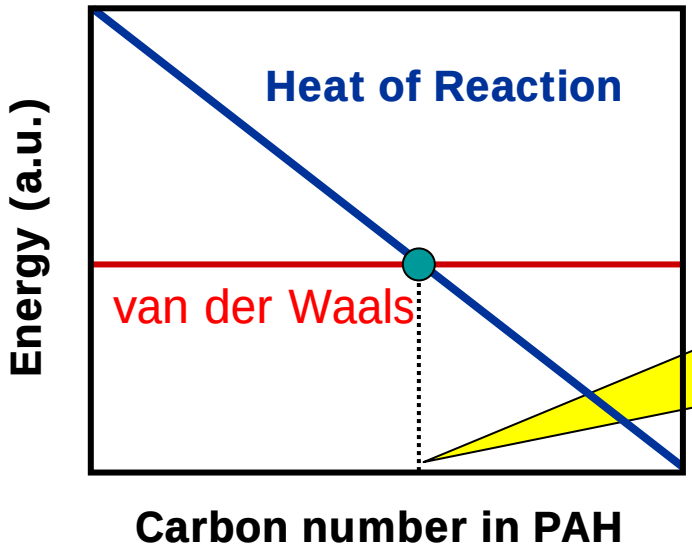
2. Single cylinder engine experiment and particle analysis

Theoretical Analysis



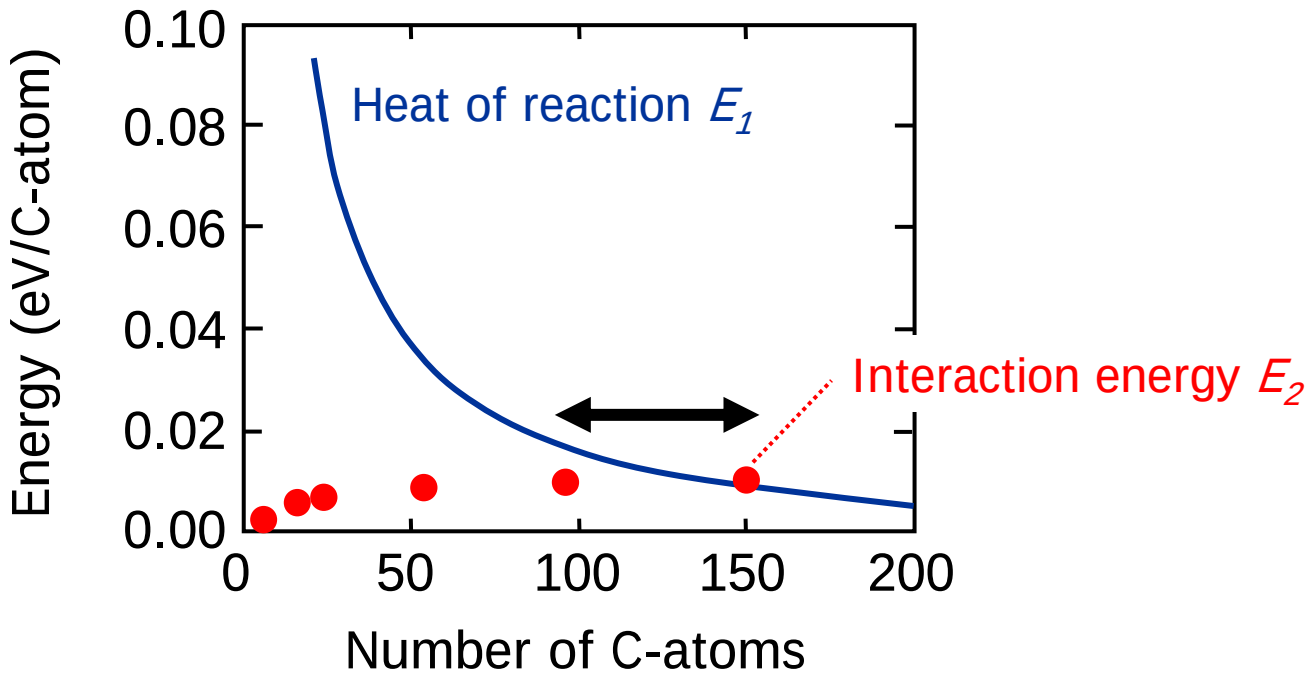
CRYSTALLITE FORMATION





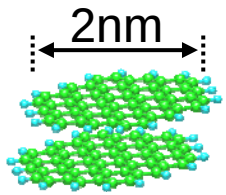
Size of PAH which begins to make a dimer is estimated by mathematical model utilizing Monte Carlo method.

ESTIMATION OF CRYSTALLITE SIZE

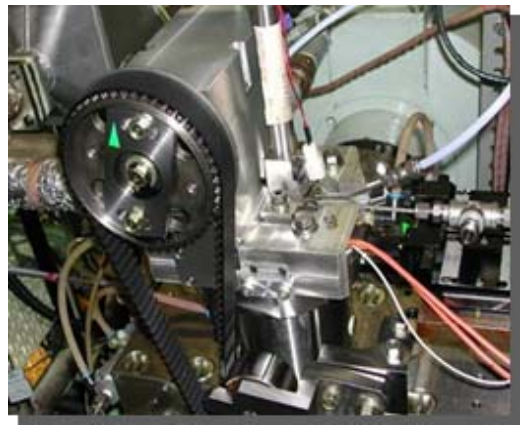


- When the carbon number composing the PAH is more than 100, the PAH molecules start to coagulate for generating graphene dimer.

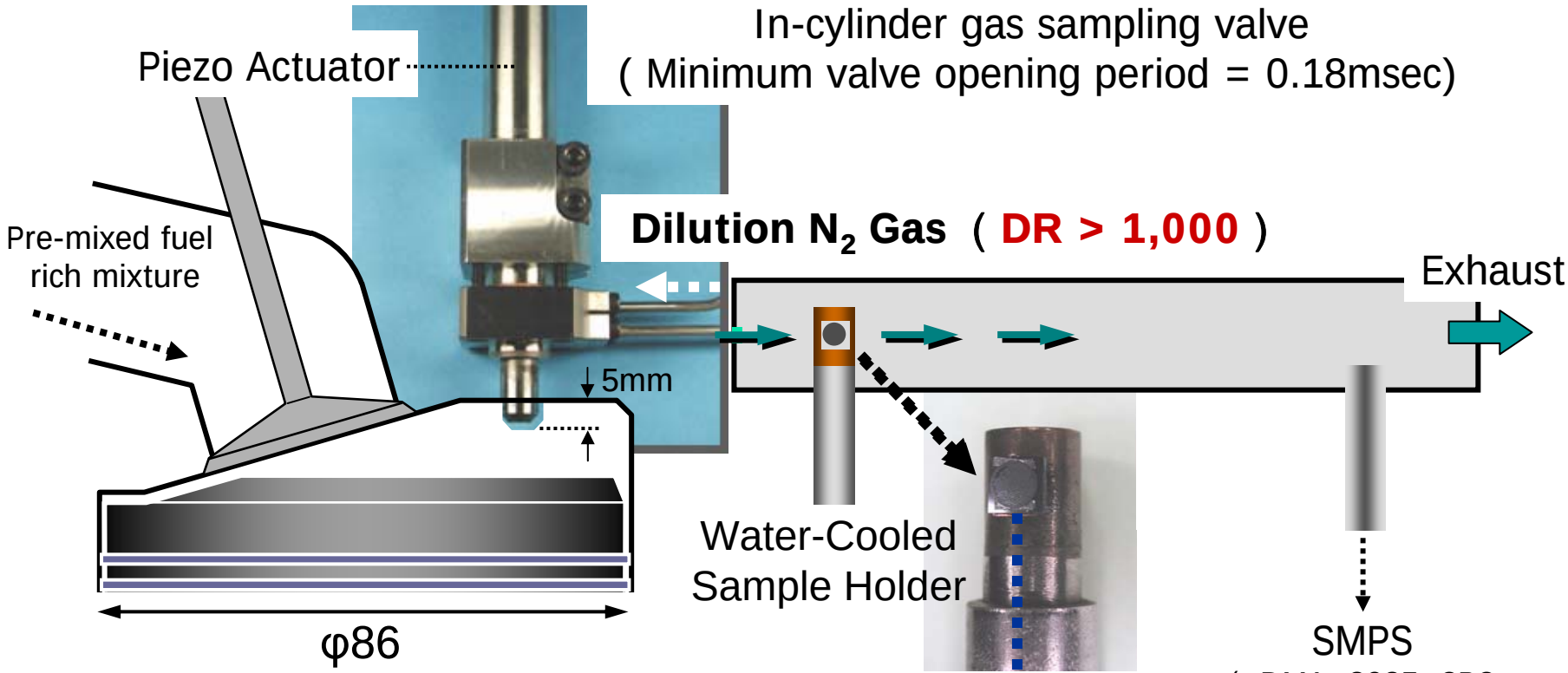
→ Crystallite diameter corresponds to about 2nm.



Engine Experiment



EXPERIMENTAL SET-UP

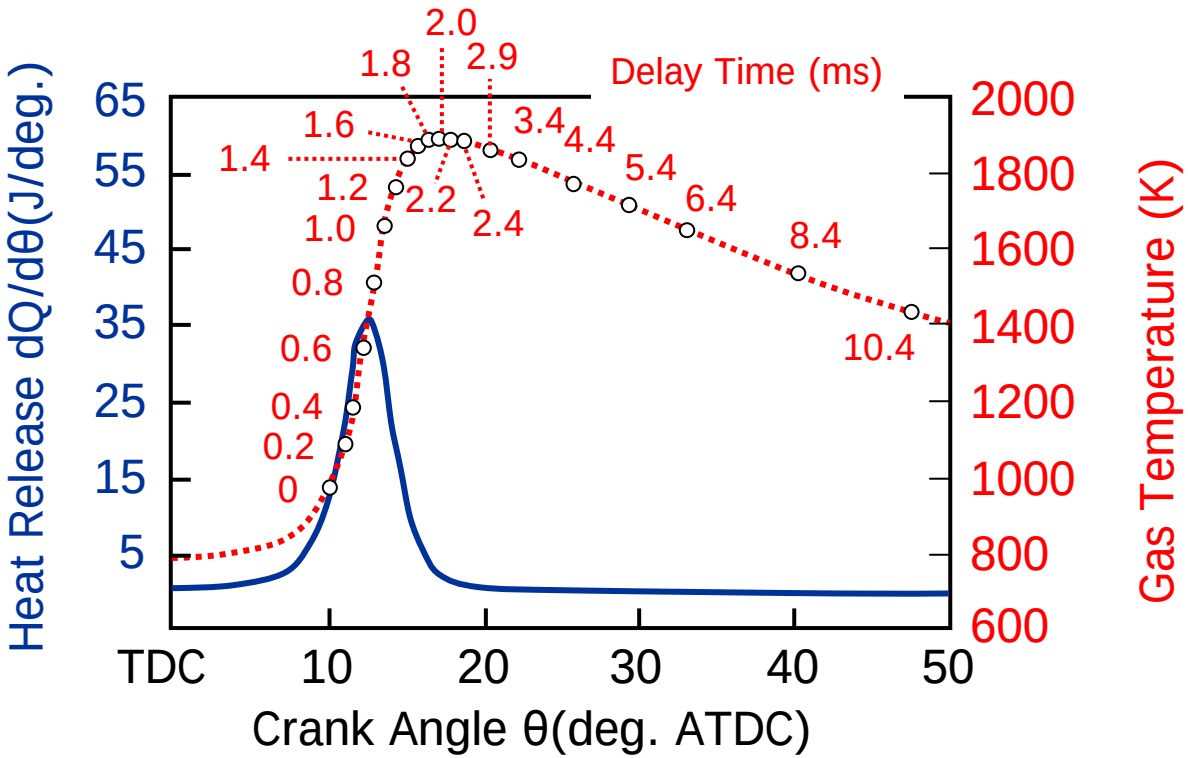


/ Single cylinder HCCI engine
(Displacement: 499cc, CR: 12)
/ Fuel : n-Heptane
/ Equivalence Ratio: 1.5-3.0

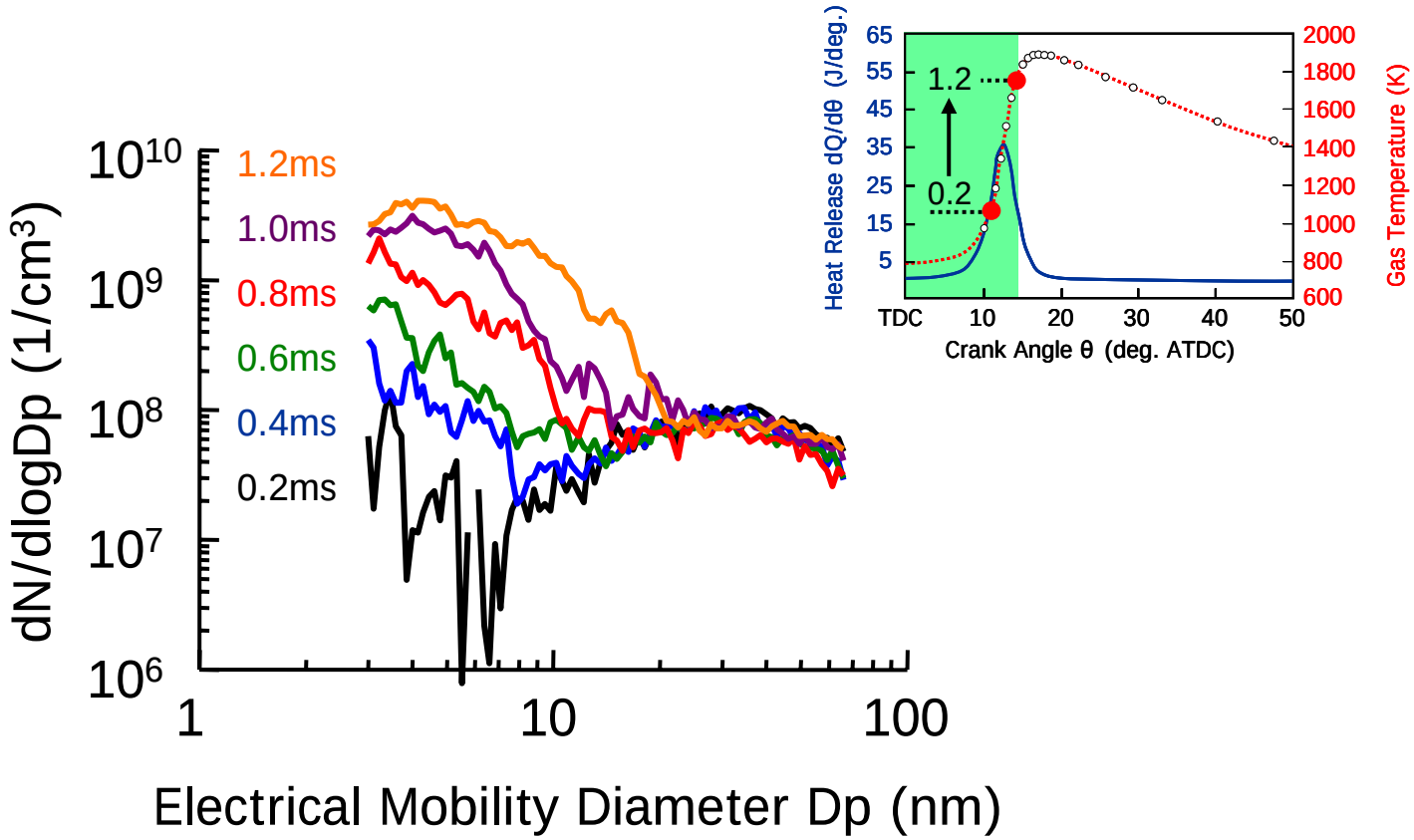
Micro grid for measurement of TEM
Mica sheet for measurement of AFM
Silicon plate for measurement of TOF-SIMS

IN-CYLINDER PARTICLE SAMPLING

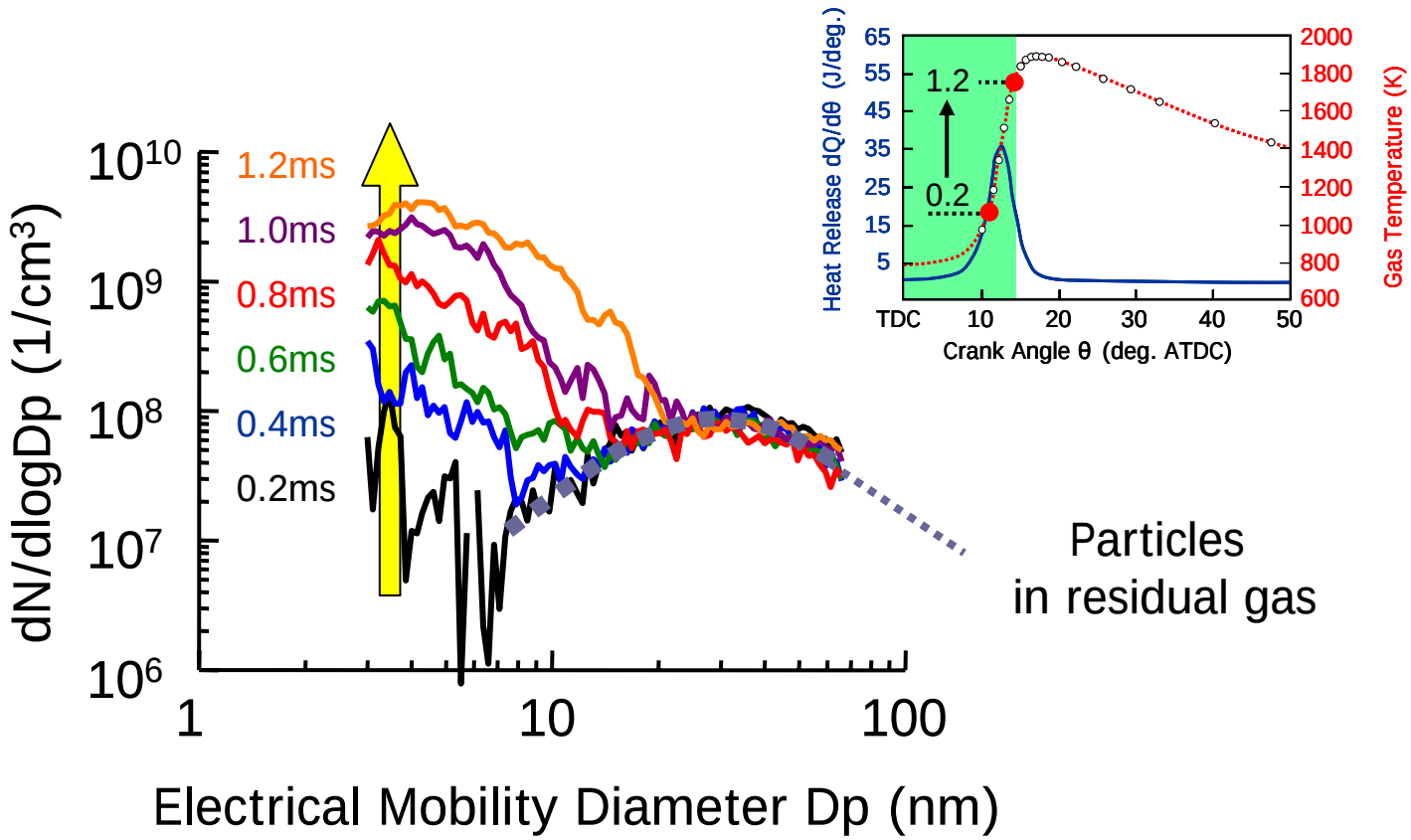
Fuel: n-heptane, Equivalence Ratio : 1.93, Engine Speed: 600rpm



CRYSTALLITE FORMATION

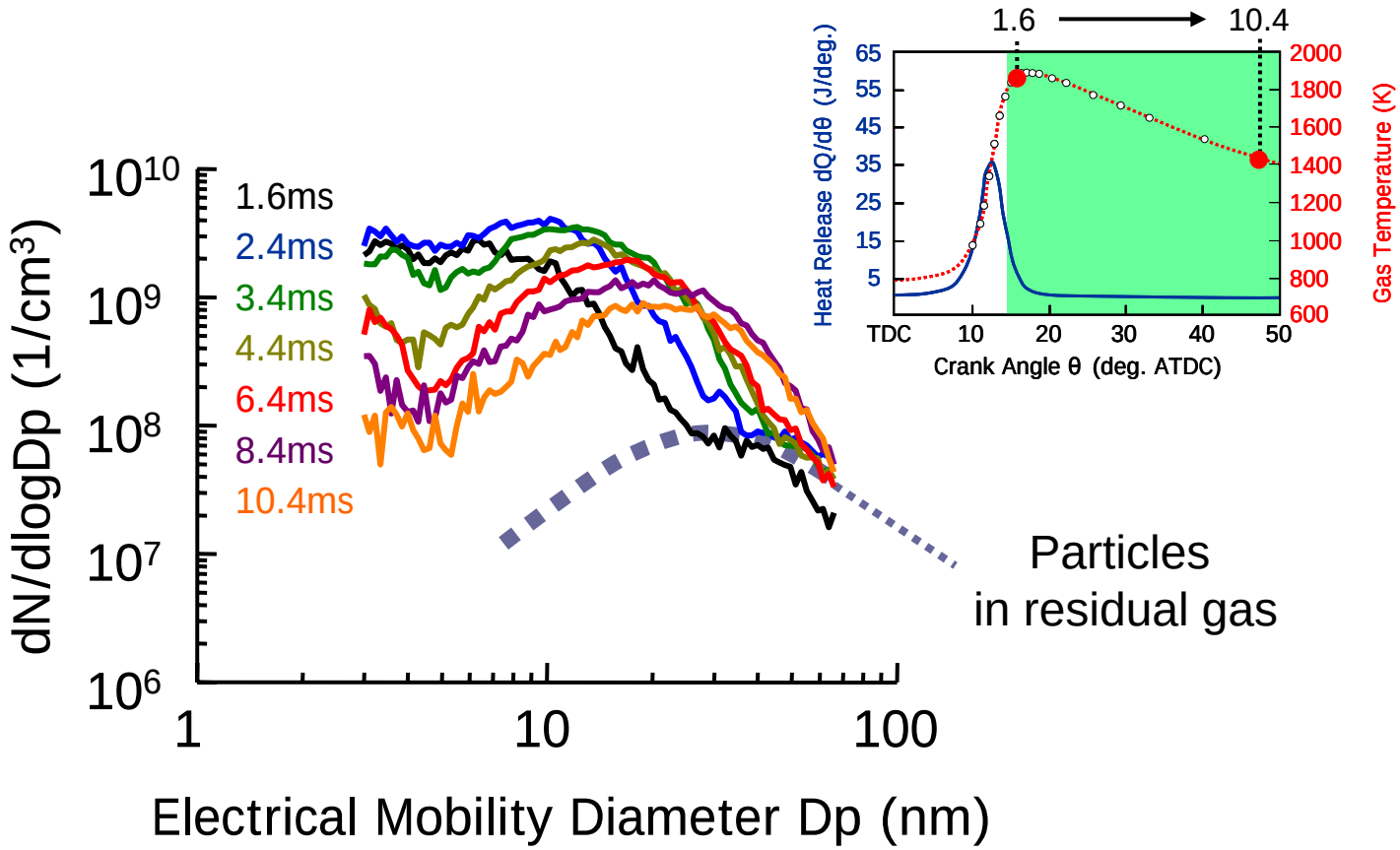


CRYSTALLITE FORMATION

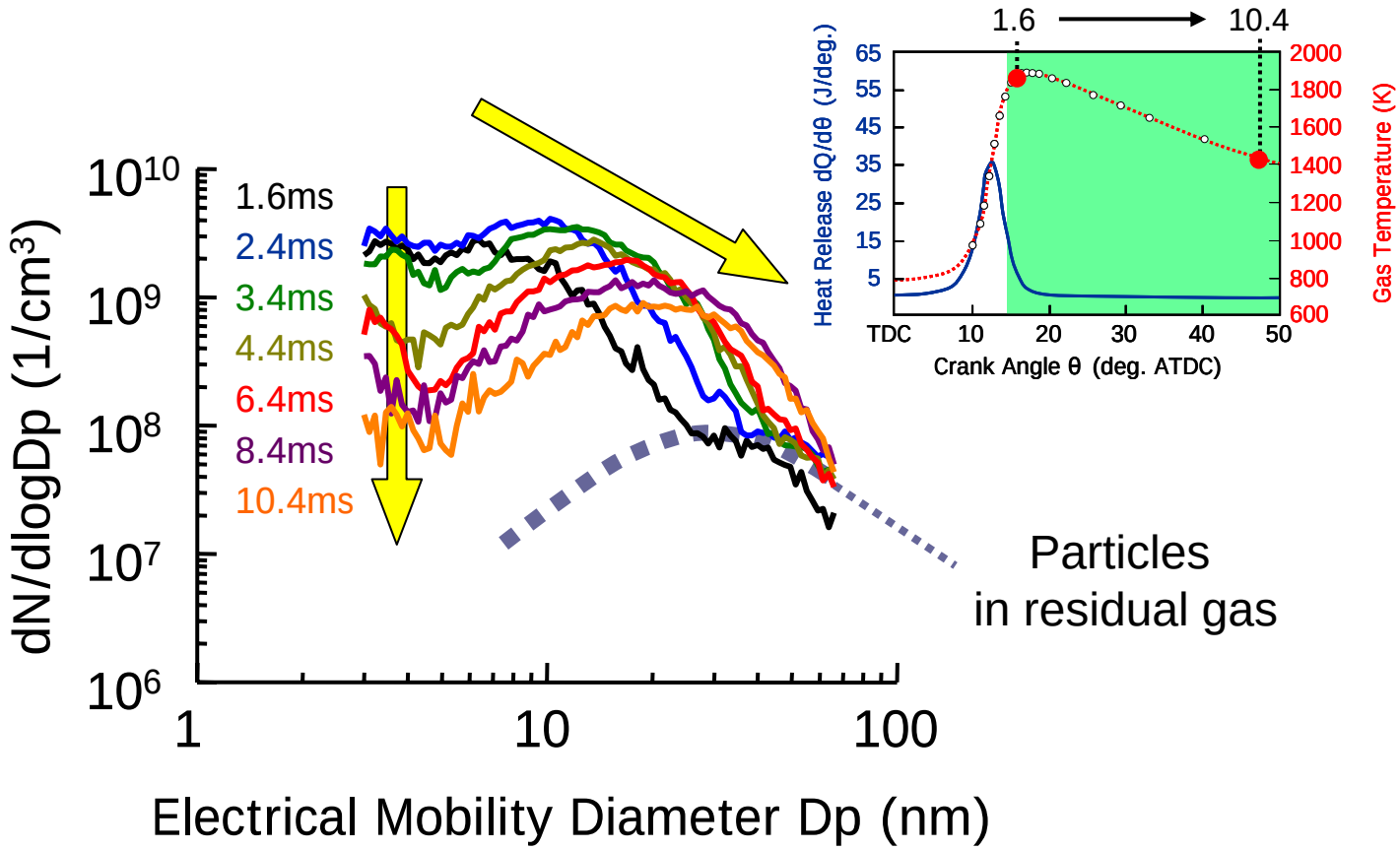


- Formation of crystallites progresses with the increase in in-cylinder gas temperature.

PRIMARY PARTICLE FORMATION

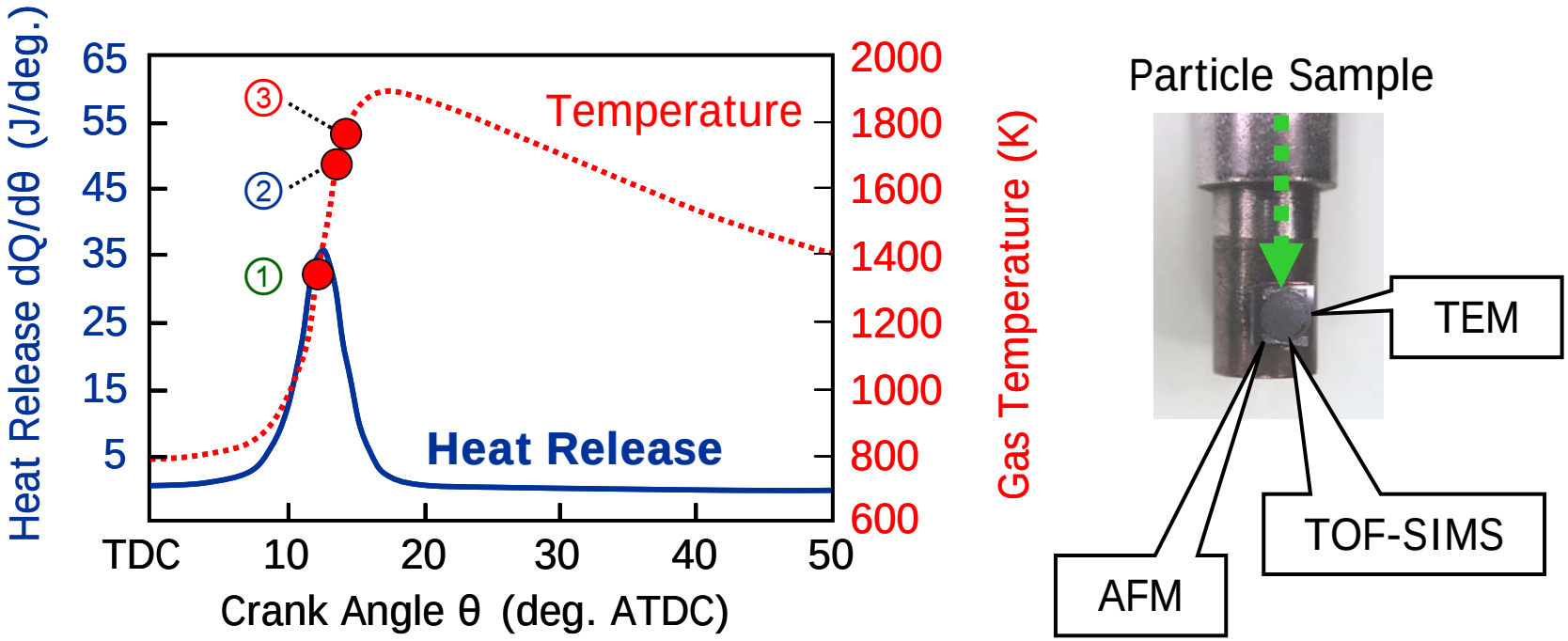


PRIMARY PARTICLE FORMATION



- Primary soot particles are formed by coagulation of crystallites in the latter half of engine combustion.

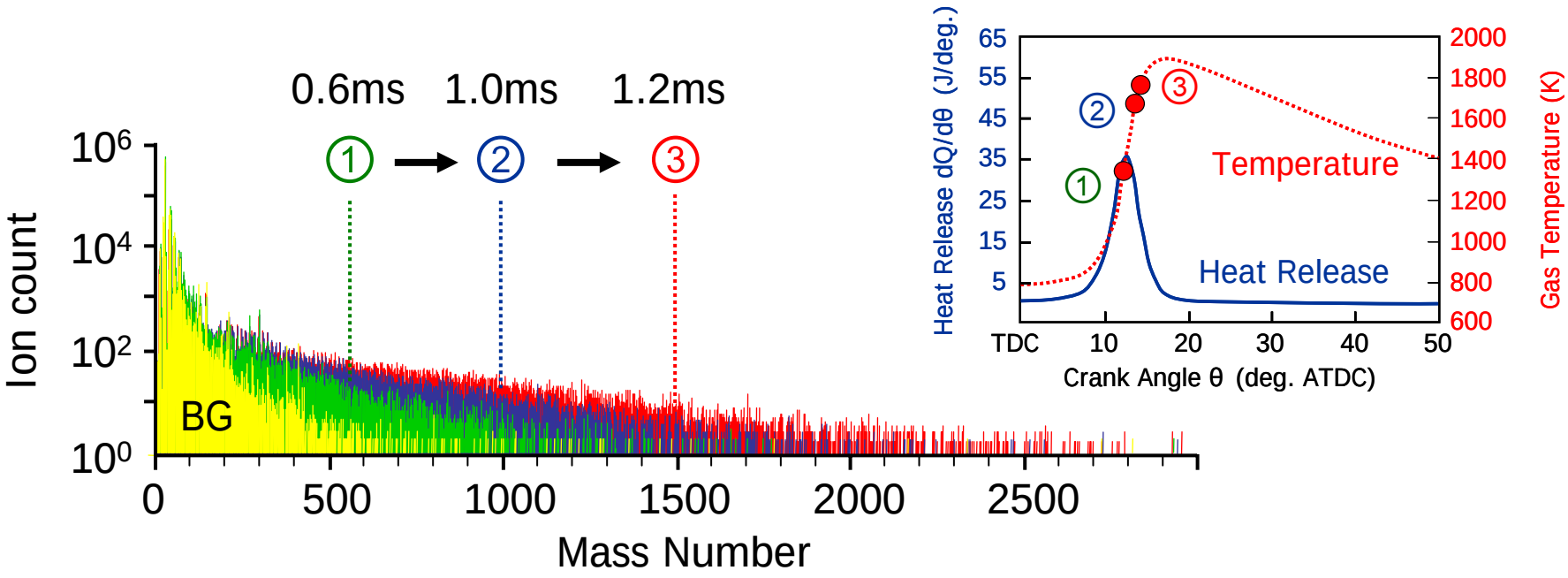
DETAILED ANALYSIS OF CRYSTALLITE



- TOF-SIMS: Molecular weight of crystallite
- AFM: Dimer formation process
- HR-TEM: Morphology of primary soot particle

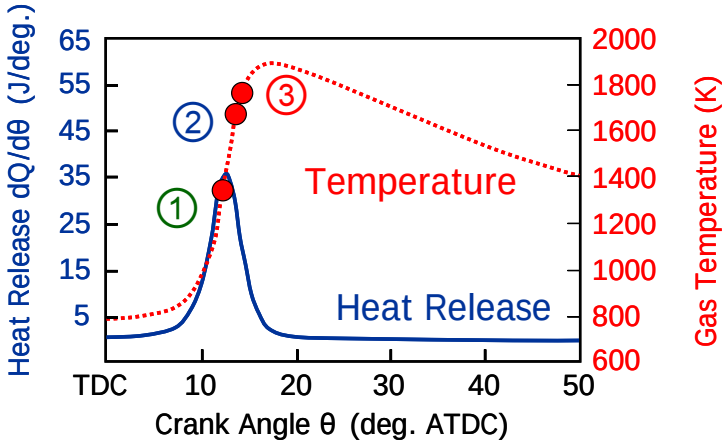
MOLECULAR WEIGHT OF CRYSTALLITE

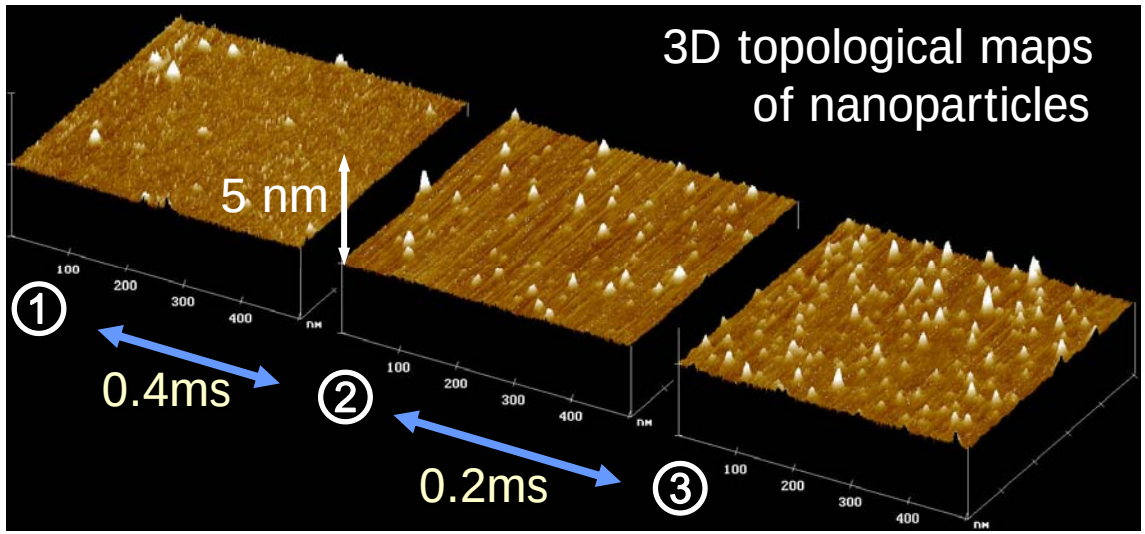
TOF-SIMS: Time of Flight Secondary Ion Mass Spectrometer



- Molecules having more than 1,000 in mass number are formed in the formation process of crystallites. → > C_{100} giant PAHs

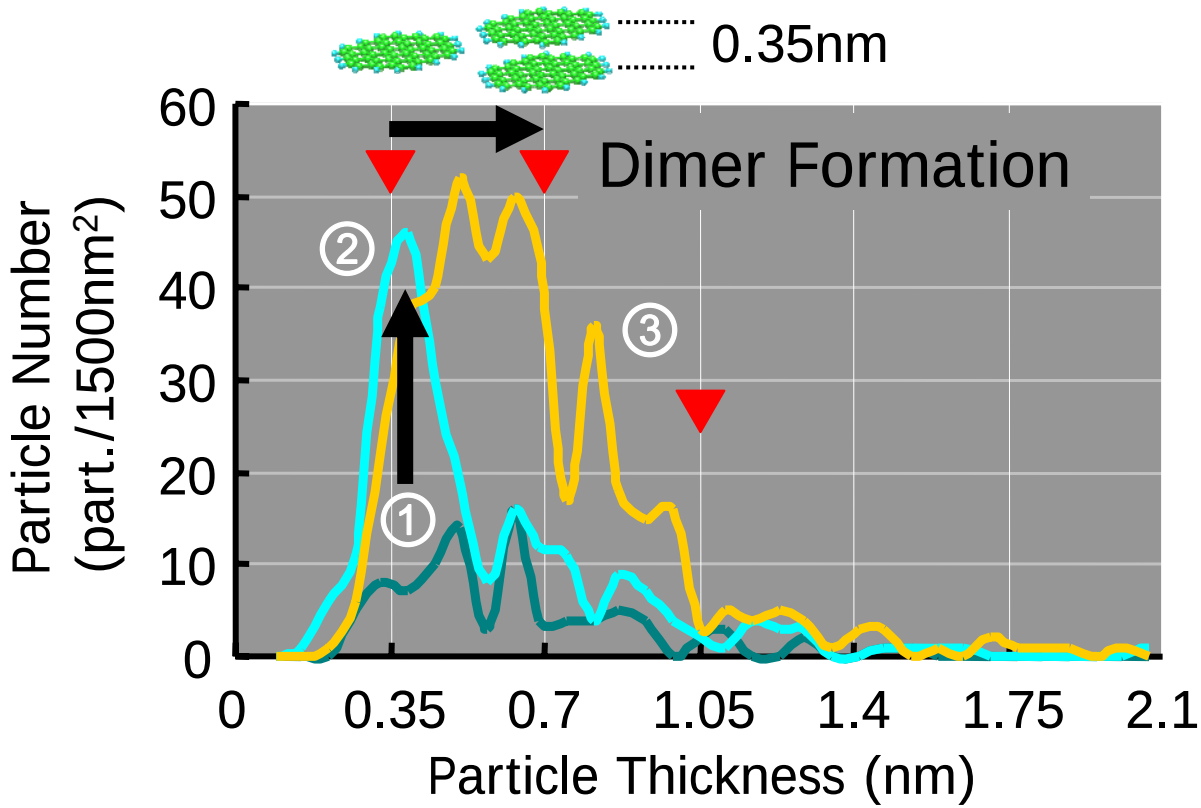
DIMER FORMATION 1 -AFM ANALYSIS-





AFM: Atomic Force Microscope

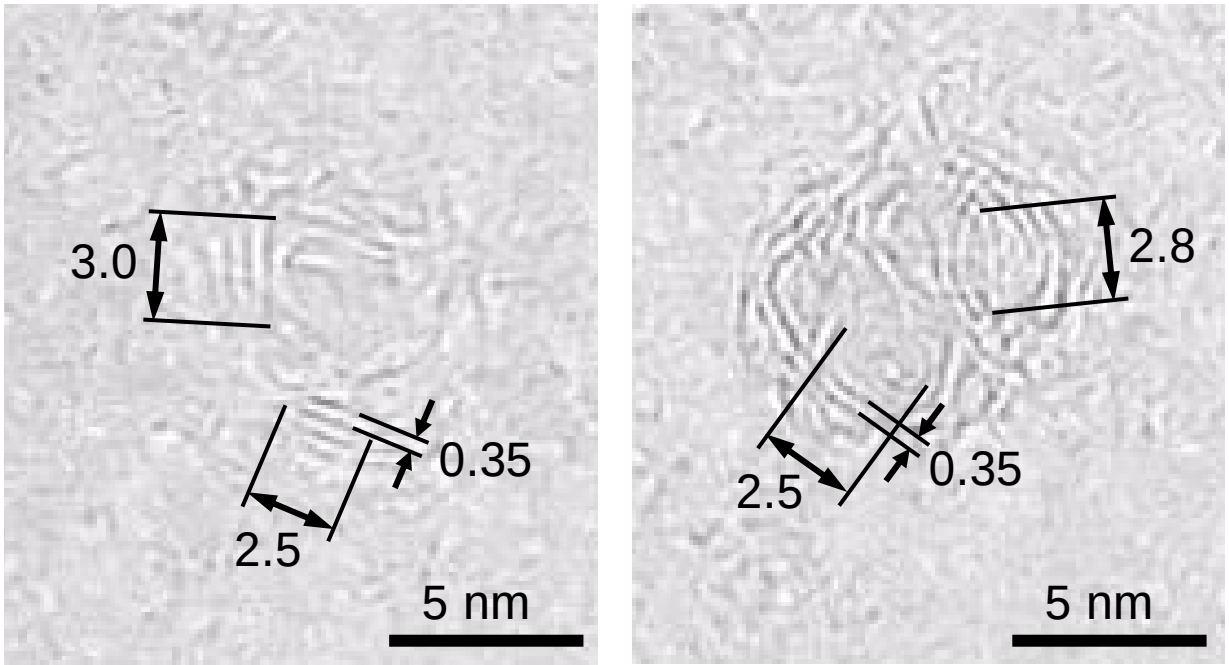
DIMER FORMATION 2



- Change of particle thickness corresponds to monomer, dimer and trimer of graphene crystallites.

MORPHOLOGY OF PRIMARY PARTICLE

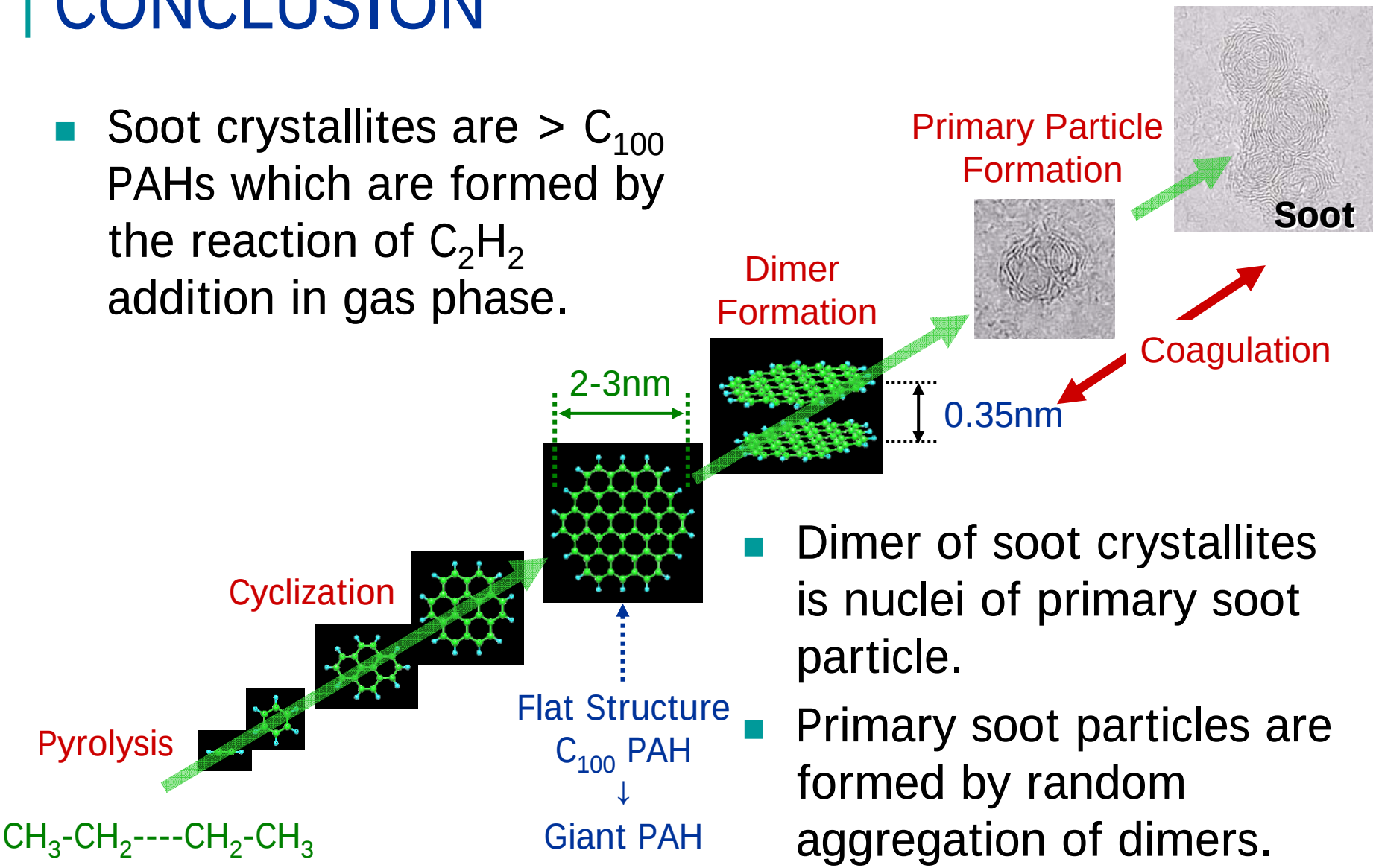
HR-TEM: High Resolution-Transmission Electron Microscope



- In-cylinder sampled soot nanoparticle consists of random aggregation of flat structure giant PAH dimers and trimers.

CONCLUSION

- Soot crystallites are > C_{100} PAHs which are formed by the reaction of C_2H_2 addition in gas phase.

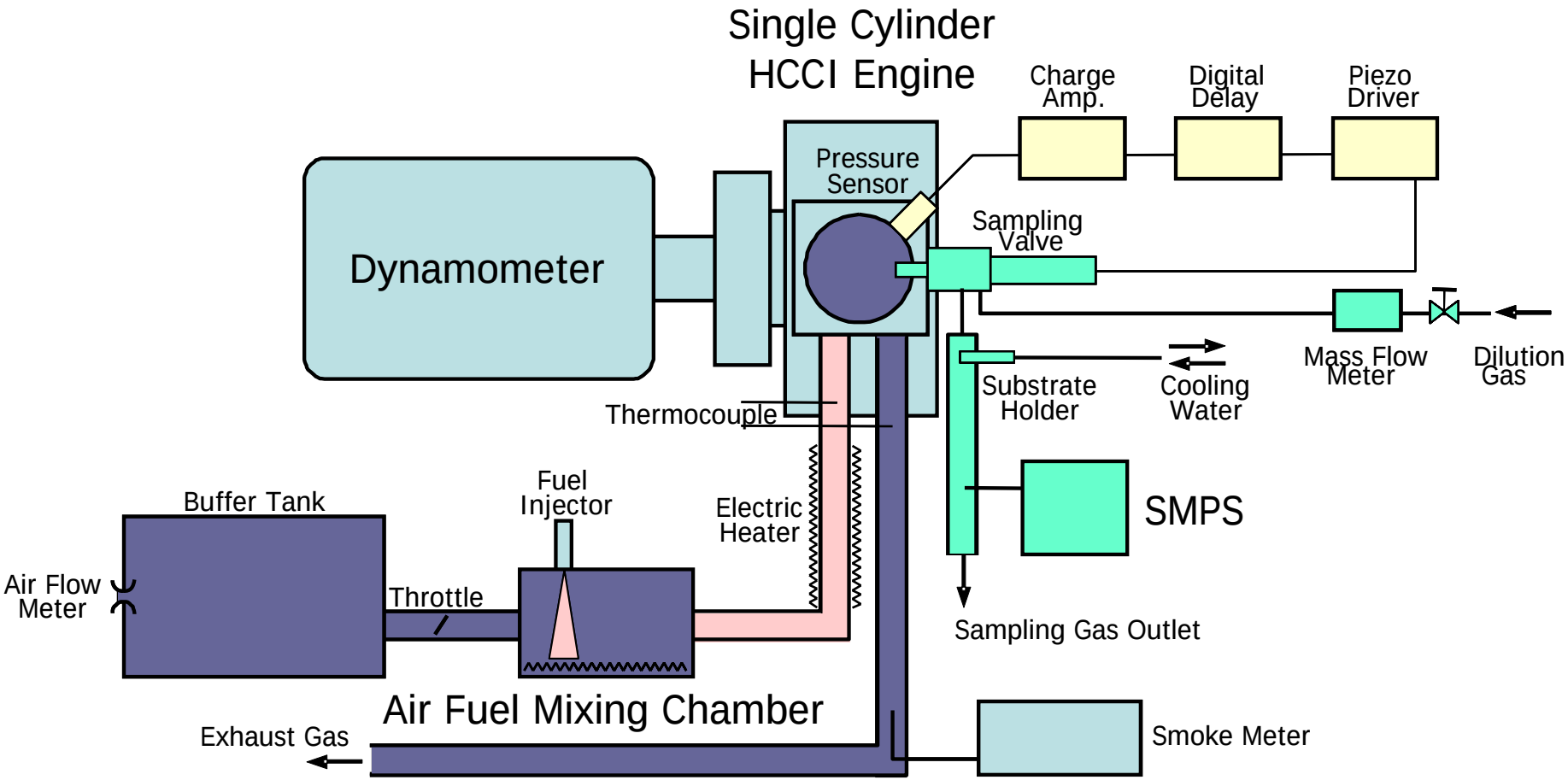


- Dimer of soot crystallites is nuclei of primary soot particle.
- Primary soot particles are formed by random aggregation of dimers.

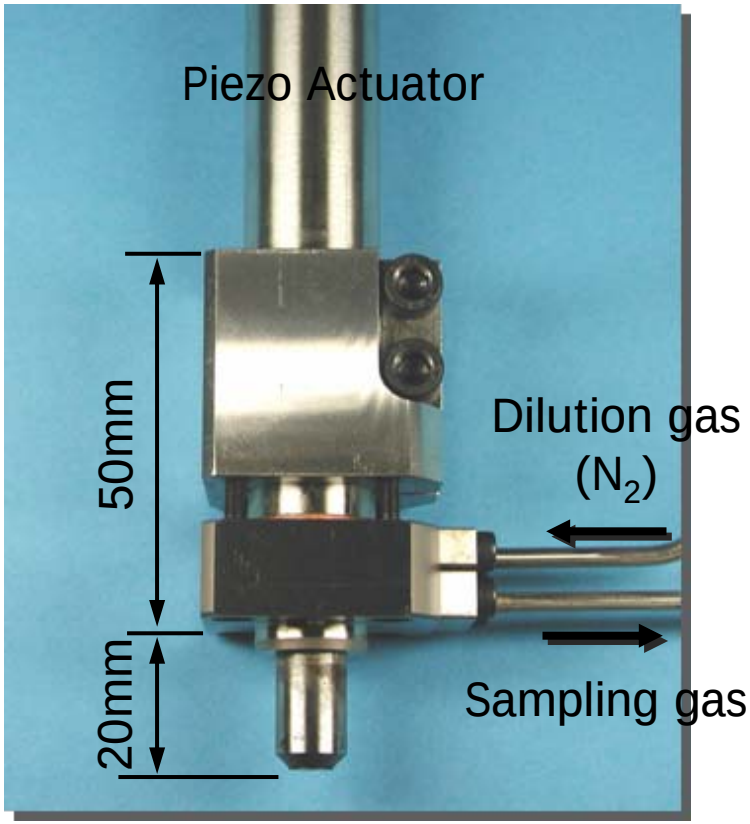
Thank you very much for your attention!!

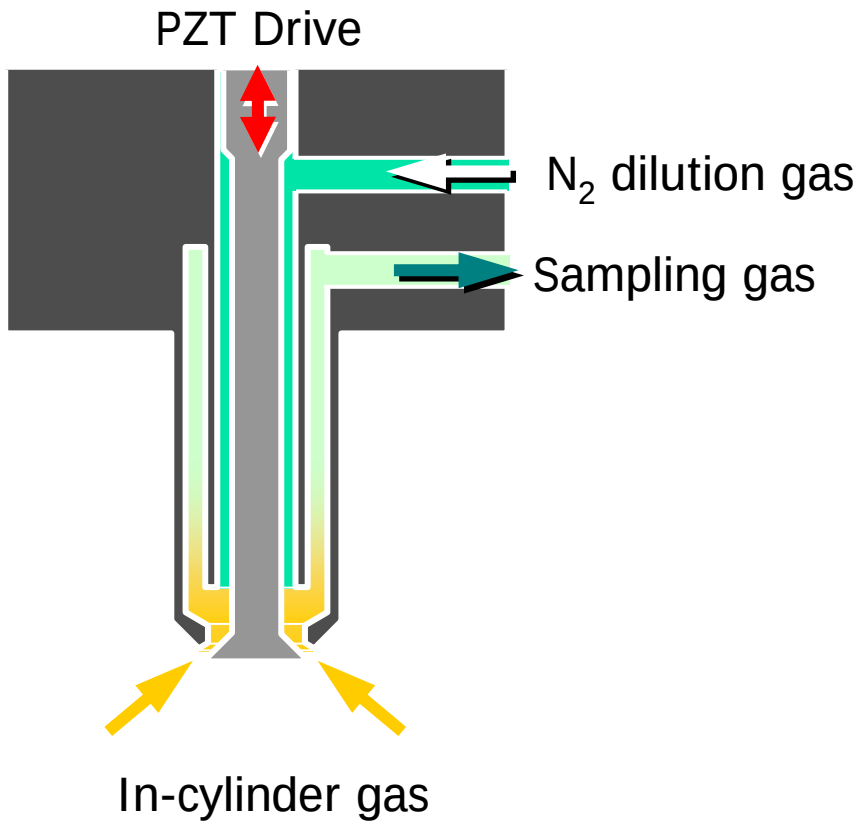
Appendix

ENGINE CONTROL SYSTEM



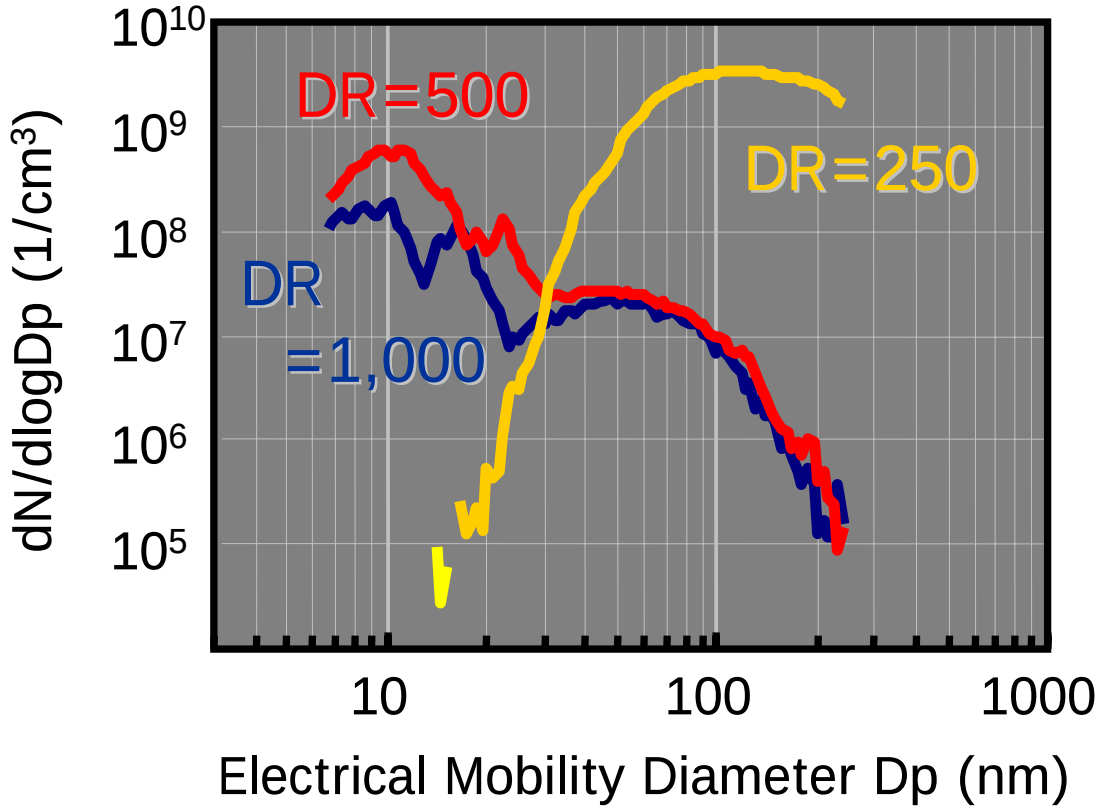
FAST IN-CYLINDER GAS SAMPLING VALVE





- PZT drive valve opening period: 0.18msec
- N_2 dilution system (Dilution ratio > 1,000)

DILUTION RATIO EFFECT

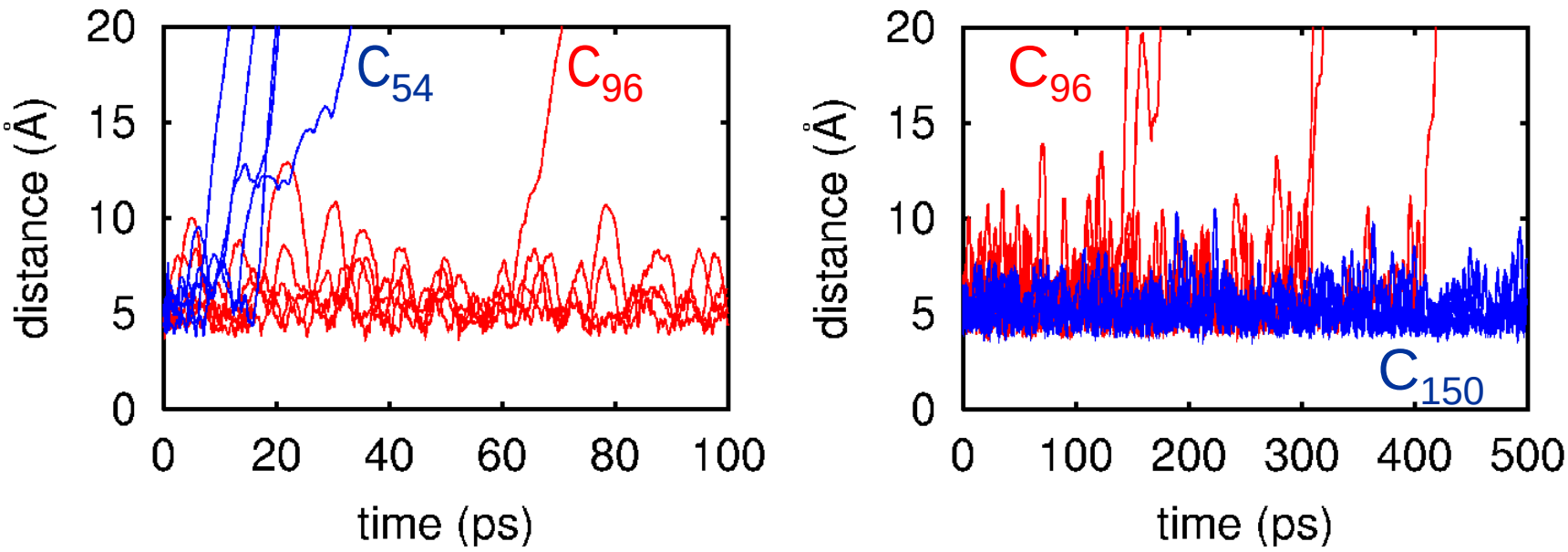


- More than 1,000 of DR was kept to measure real number weighted particle size distribution.

STABILITY OF DIMER 1

-Molecular dynamics calculation-

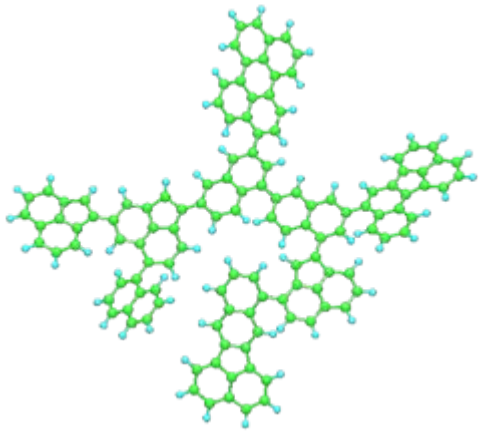
face to face distance of PAH dimer (T=1500K, P=50atm)



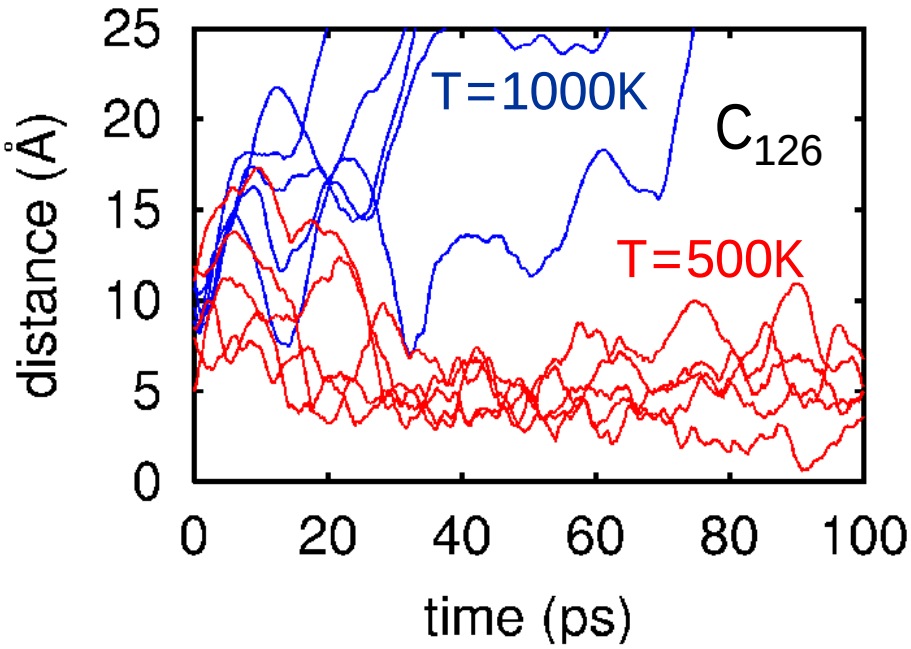
- More than 100 carbon number flat PAH dimer is stable under the condition of 1,500K and 50 atm.

STABILITY OF DIMER 2

Unordered structure
$C_{126}H_{68}$ dimer



-Molecular dynamics calculation-



- Contact area of unordered structure dimer is smaller than that of flat PAH dimer.
- Unordered structure dimer is not formed at 1,000K.