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C2E2 Center for Clean Energy Engineering

# High-Resolution Differential Mobility Analysis (HR-DMA) of sub-10nm Nanoparticles Synthesized by the Reactive Spray Deposition Technology (RSDT)

***Farnaz Khosravi***[1], *Evangelos K. Stefanidis*[2], *Zhiqiao Zeng*[2], *Stoyan Bliznakov*[2,3], *Leonard J. Bonville*[3]
*Radenka Maric*[2,3], and *Francesco Carbone*[1,2,3]

[1] *Department of Mechanical Engineering, University of Connecticut.*
[2] *Department of Chemical and Biomolecular Engineering, University of Connecticut*
[3] *Center for Clean Energy Engineering, University of Connecticut*

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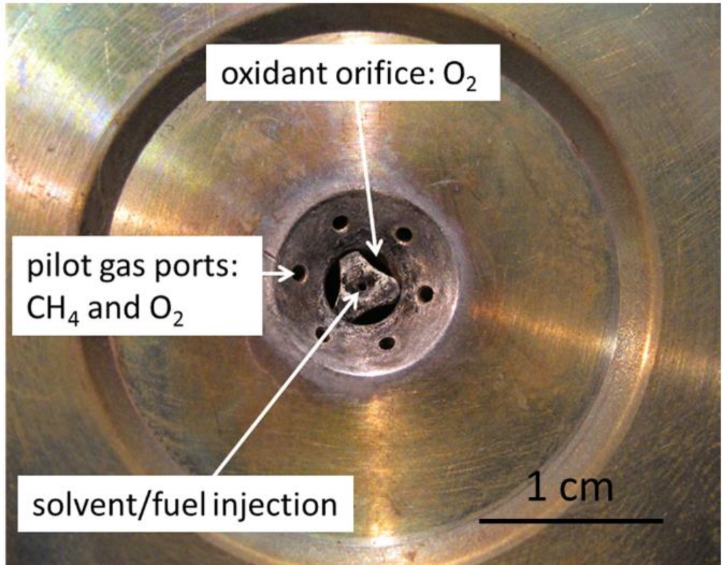
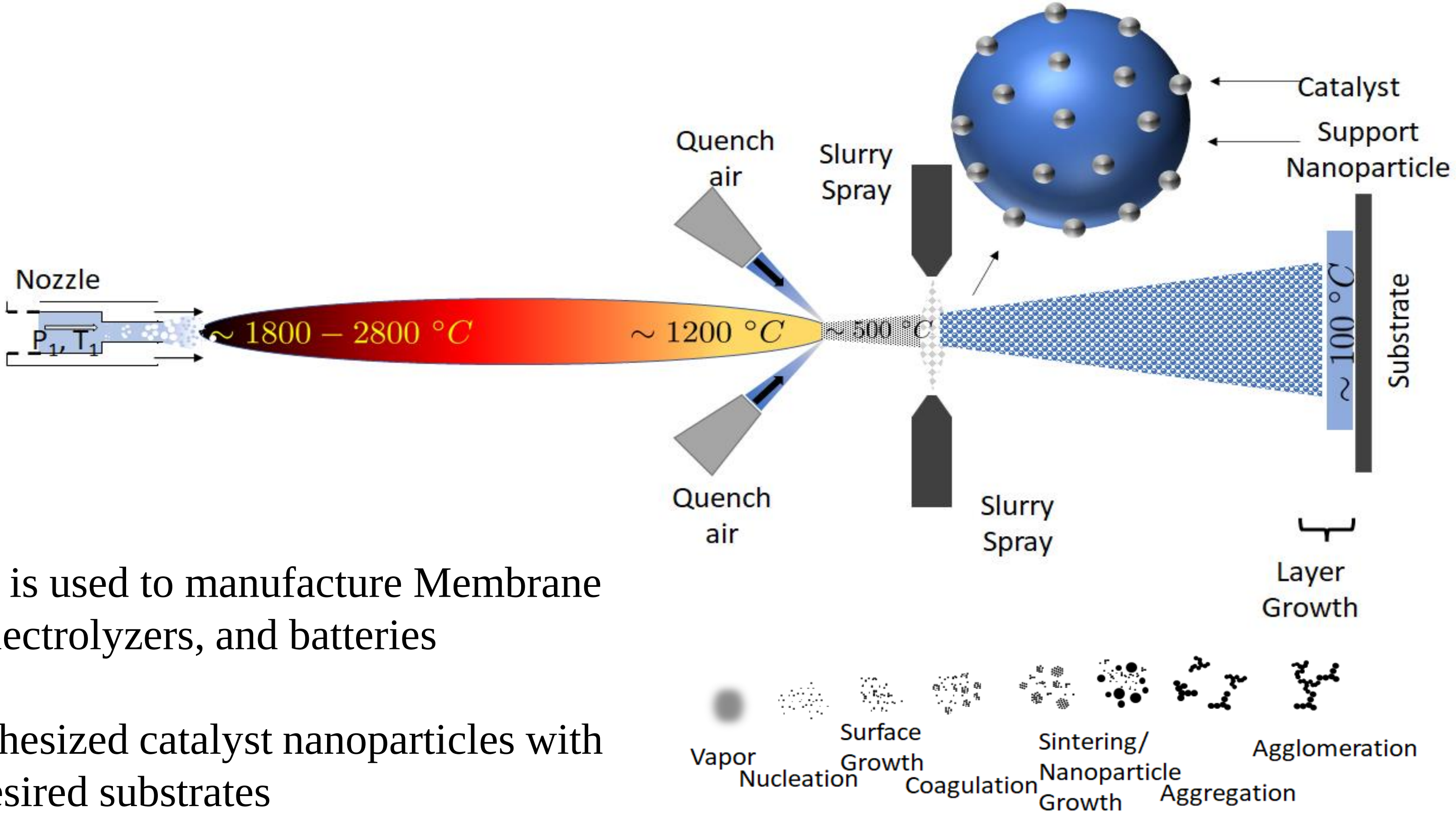
# Reactive Spray Deposition Technology (RSDT)





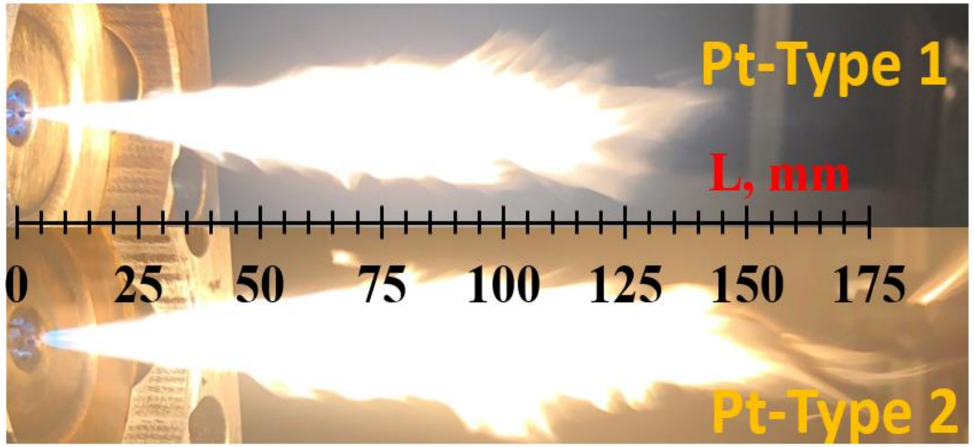




- One-step flame-based process which is used to manufacture Membrane Electrode Assemblies for fuel cell, electrolyzers, and batteries
- Enables the deposition of flame-synthesized catalyst nanoparticles with diameters smaller than 10nm onto desired substrates
- Particle properties are adjusted by controlling the flame boundary conditions

*Yu et al., 2014, J. Electrochem. Soc., 161, F622*
*Roller et al.,2013, Electrochim. Acta, 107, 632-655*

# Investigated RSDT Flames

- Two pairs of flames with same reactants' composition but different reactants' flowrates
- The two flames of each pair differ only because of the presence of Platinum Acetylacetate (PtAcac) in the solution

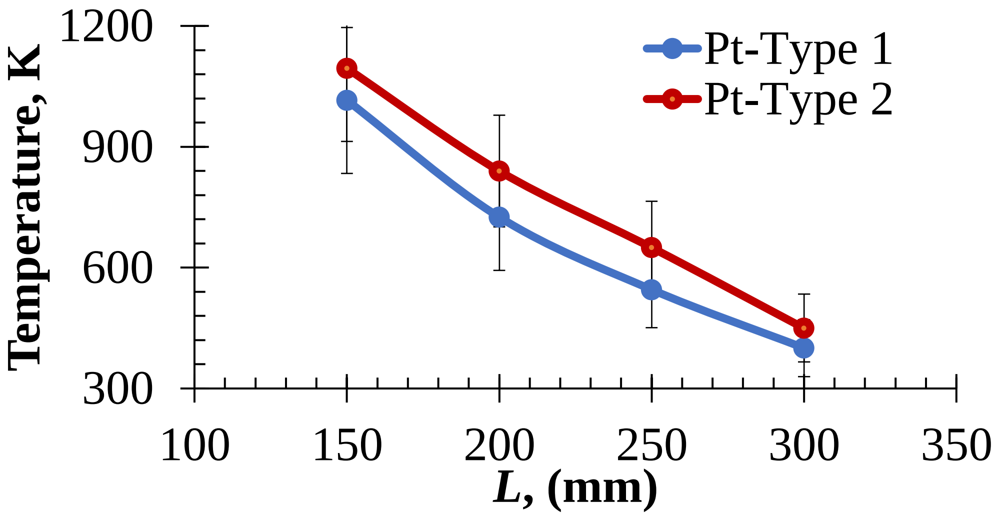



**Solvents in liquid fuel: acetone, xylene, liquid propane**

**Precursor: Platinum Acetylacetonate (PtAcac)**

| Flame | Liquid fuel flow rate, ml/min | $O_2$ flow rate, slpm | Pilot $CH_4$ flow rate, slpm | Pilot $O_2$ flow rate, slpm | Platinum concentration in the fuel |
|---|---|---|---|---|---|
| **Pt-Type1** | **4.0** | **7.3** | 0.55 | 0.55 | 10 mM |
| **Blank 1** | **4.0** | **7.3** | 0.55 | 0.55 | - |
| **Pt-Type2** | **7.0** | **11** | 0.75 | 0.75 | 10mM |
| **Blank 2** | **7.0** | **11** | 0.75 | 0.75 | - |

*The time-averaged flame temperatures*




*Stefanidis et al., 2022, C&F* *Yu et al., 2014, J. Electrochem. Soc., 161, F622*

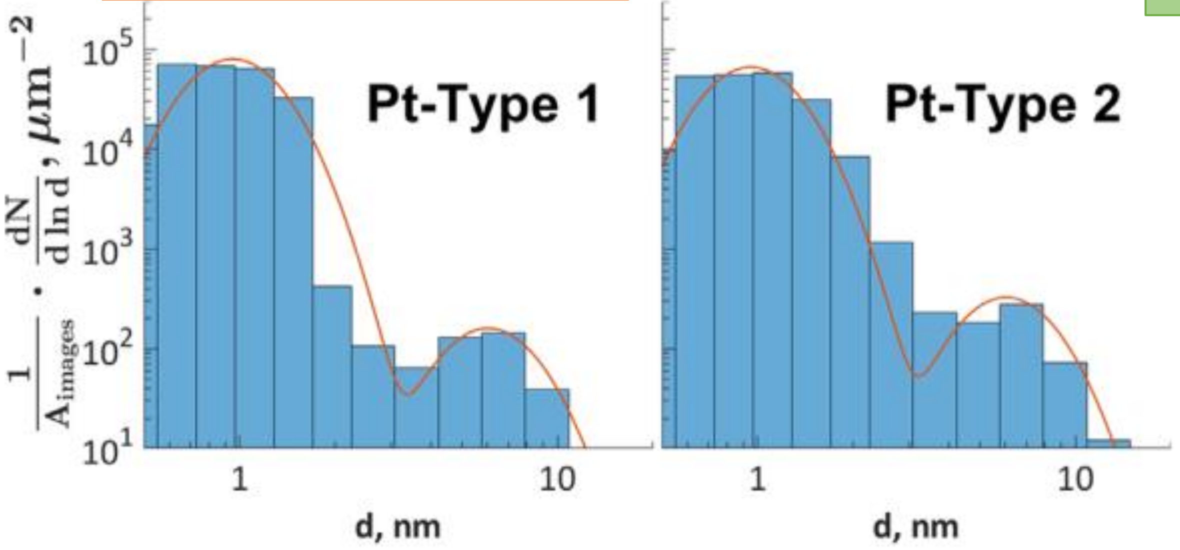
# Background

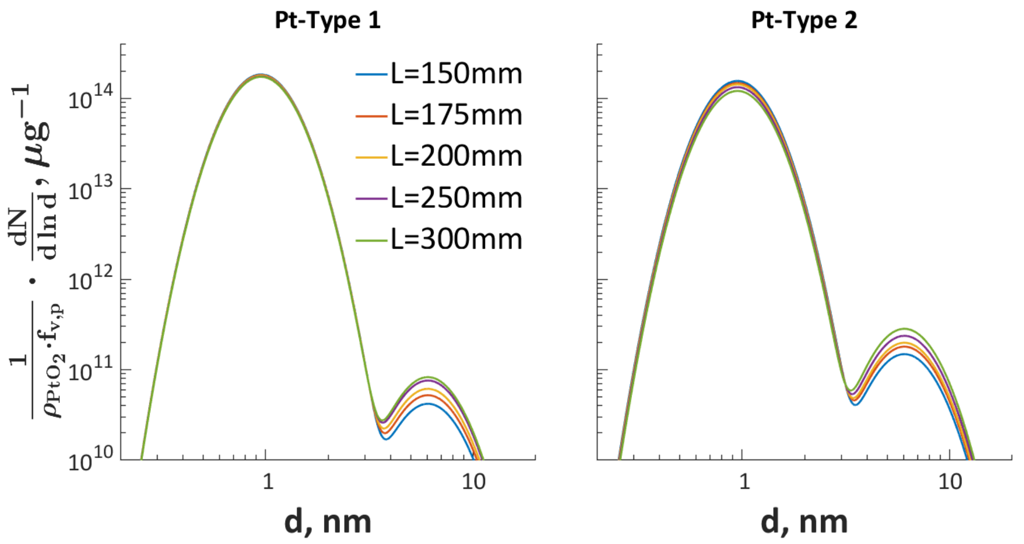
## **In-situ Laser Diagnostics** at different *L*s and **Ex-situ Microscopy Analyses** at *L*=250mm **(Stefanidis et al. 2022)**

- Microscopy image analysis of samples collected at *L*=250mm has revealed a bimodal Size Distribution Function (SDF) composed of two lognormal modes whose median diameters in both flames are 0.95nm and 6.05nm, respectively.
- The number concentration of the second mode, $n_2$, at *L*=250mm in the Pt-Type 2 is larger than in Pt-Type 1 resulting in a larger value of the light scattering equivalent diameter, $d_{6,3}$, and smaller specific surface area.
- The number concentration of each mode (i.e., the SDF) has been estimated from laser diagnostics' measurements of $d_{6,3}$ and volume fraction under the assumption that assuming the modal median diameter do not change across the two flames

$$\frac{d(n)}{\mathrm{d}\,(\ln d)} = \frac{n_i}{\sqrt{2\pi}\cdot\ln\sigma}\ \exp\left[-\frac{\left(\ln d - \ln d_{gm,i}\right)^2}{2\cdot\ln\sigma}\right]$$

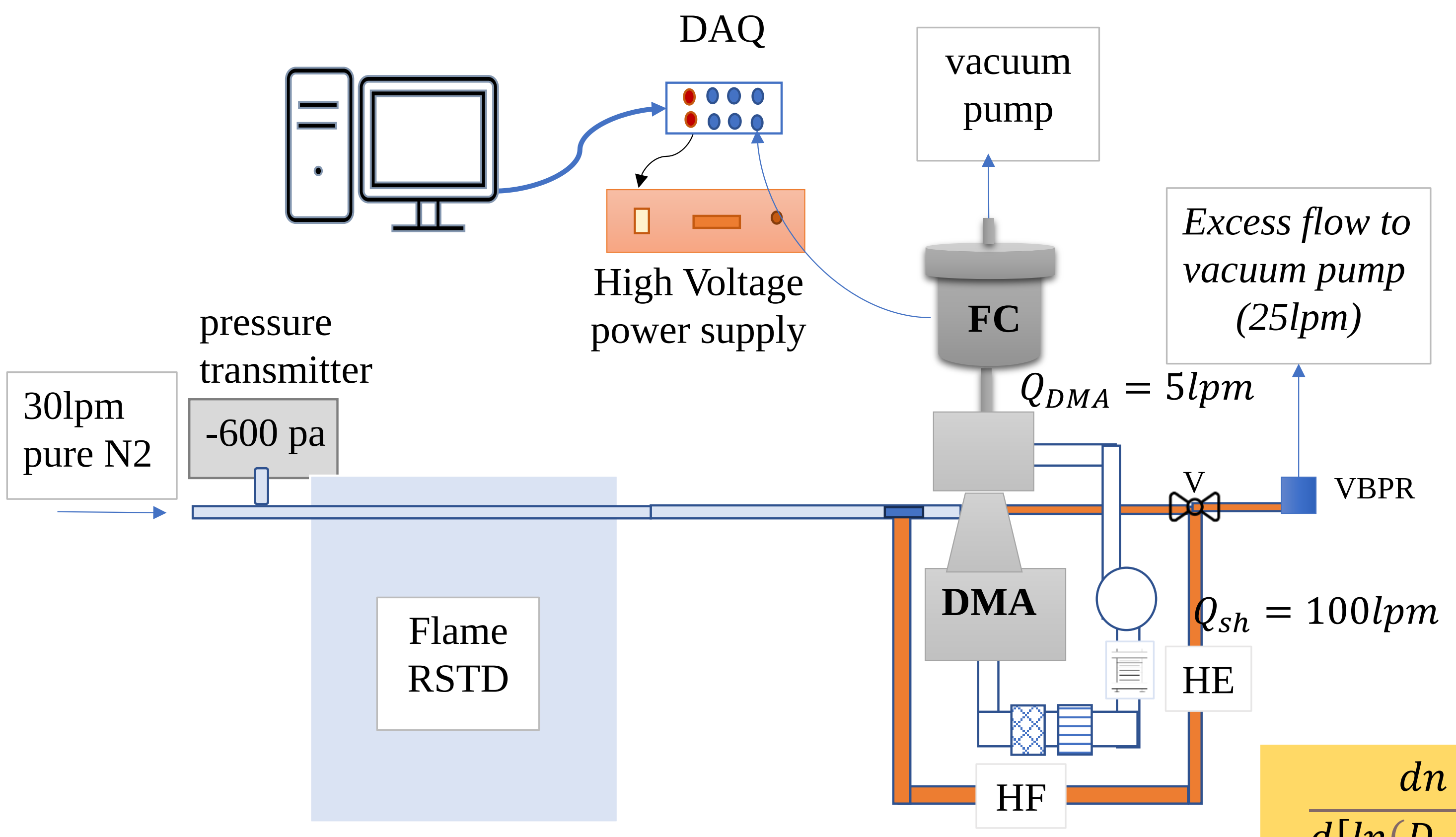
**Sampled at L=250mm**




*Stefanidis et al., 2022, C&F*

# HR-DMA Measurements’ Setup




| Case | $D_{orifice}$ µm | Dilution ratio, DR | Residence time, ms |
|---|---|---|---|
| **A** | 150 | ≈2000 | $\Delta t = 95\ ms$ |
| | 250 | ≈700 | |
| **B** | 150 | ≈2000 | $\Delta t = 56\ ms$ |
| | 250 | ≈700 | |

$$n_{FCE}(D_{DMA}) = \frac{V_{FC}(D_{DMA})}{R.e \cdot Q_{DMA}} \cdot \frac{1}{P_{FCE}(D_{DMA})}$$

$$\frac{dn}{d[ln(D_{DMA})]} = n_{FC}(D_{DMA}) \cdot \frac{2 \cdot Q_{sh}}{Q_{DMA}} \cdot \frac{1}{P_{prob}(D_{DMA})} \cdot \mathrm{DR} \cdot \frac{T_{in-DMA}}{T_{flame}}$$

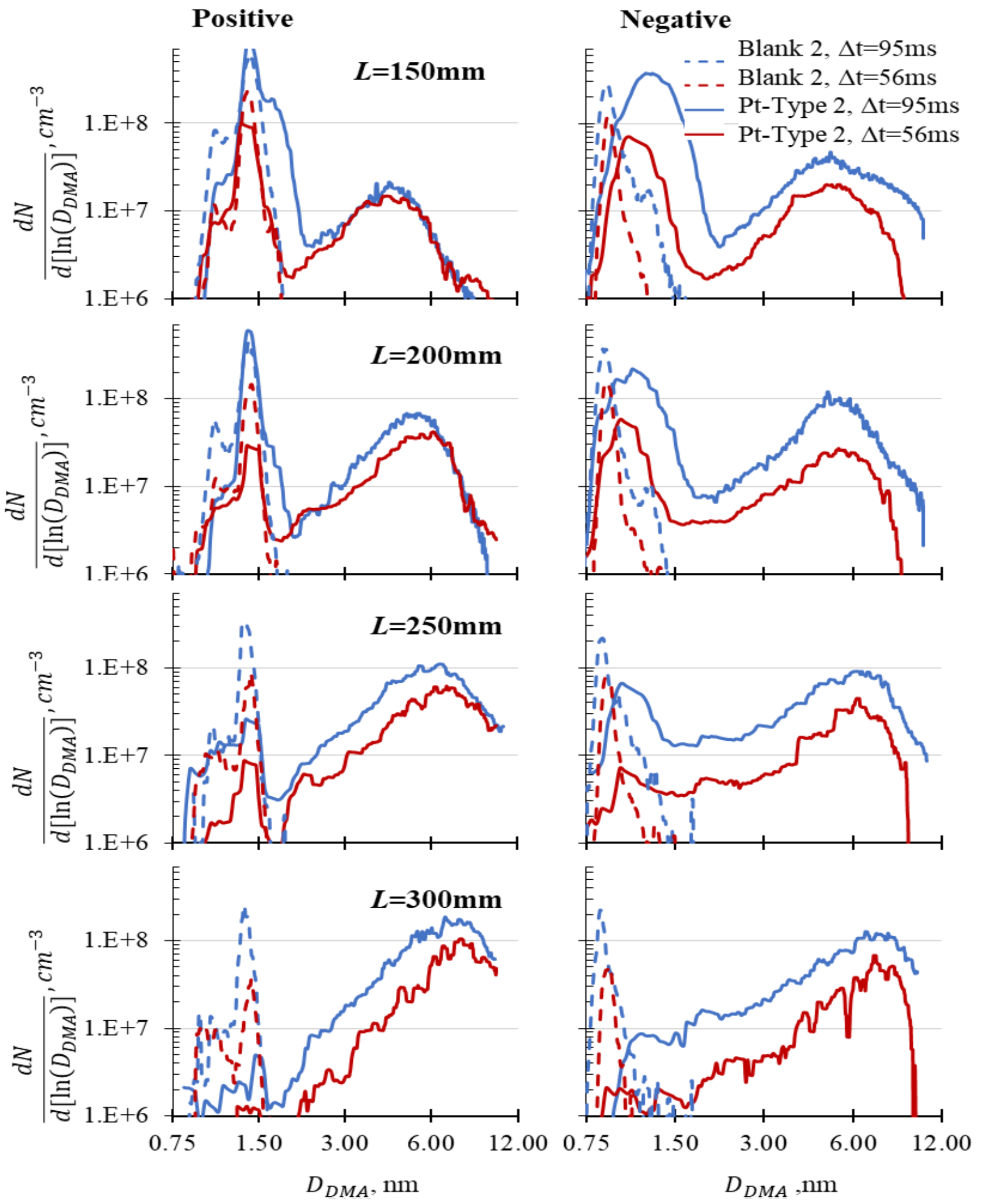
- Measurements rely on natural charging provided by flame chem-ions generated in both the Blank1/2 and Pt-Type1/2

*Fernandez de la Mora, 2017*
*Carbone et al. AST 2016*

# *Effect of residence time in the sampling system*

***Blank2 DR=700*** ***Pt-Type2 DR=700***

- Hydrocarbon chem-ions are all smaller than $D_{DMA}$ =1.6nm and anions are smaller than cations
- HR-DMA results reveal bimodal SDFs of the Pt-Type2 products (especially for measurements in negative polarity)
- A decrease in transport time leads to a decrease in the number concentration of the detected naturally charged nanoparticles at all sampling positions.
- The shape of the second mode is unaffected by the residence time in the sampling probe indicating that coagulation is quenched
- The distinction of the smallest (first mode) nanoparticles from the flame chem-ion is complicated for the measurements with the shortest residence time in the sampling system.

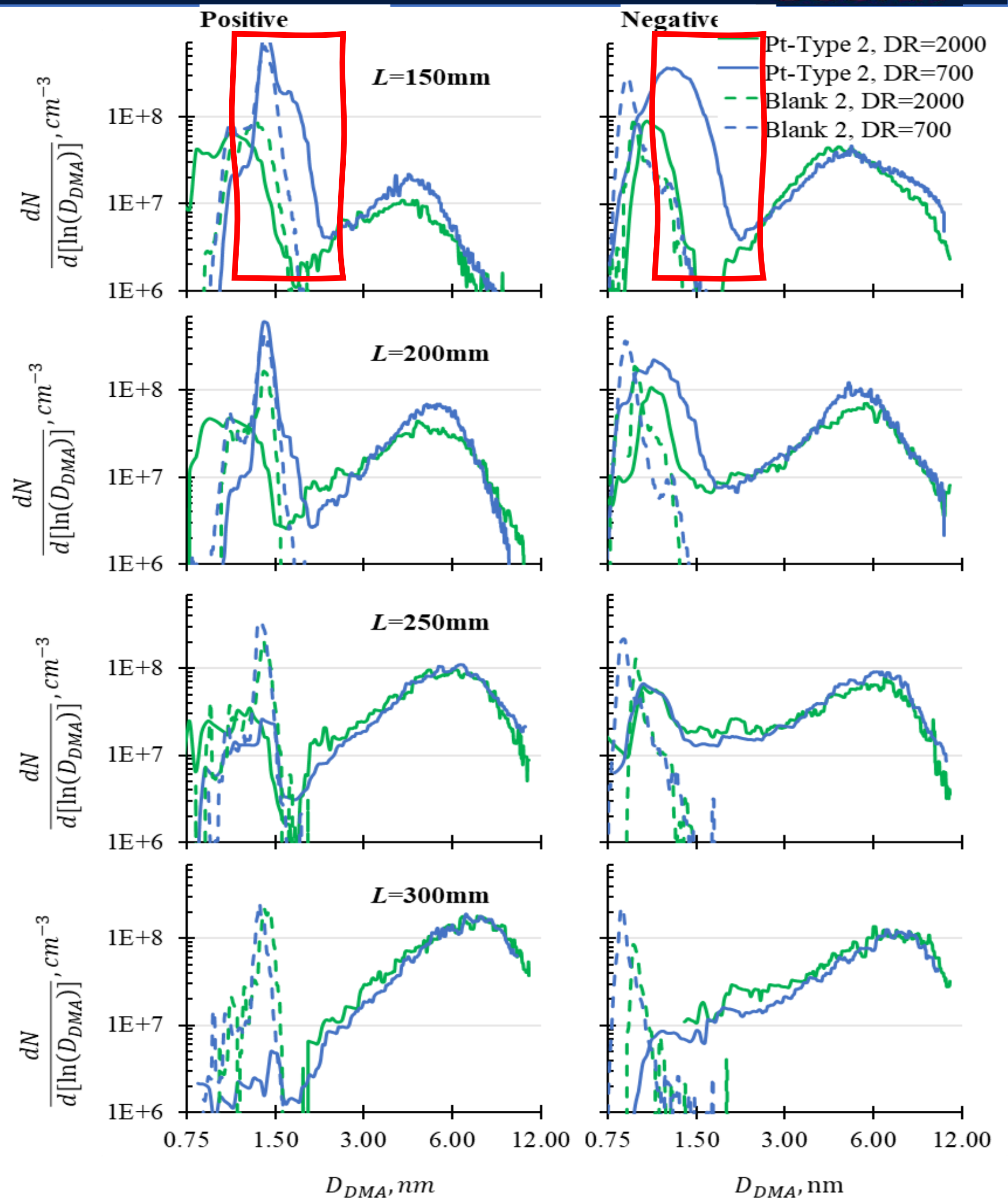


# Effect of sampling Dilution Ratio (DR)

UCONN

***Pt-Type2***
***$\Delta t$ = 95ms (long time)***
***DR=2000 vs DR=700***

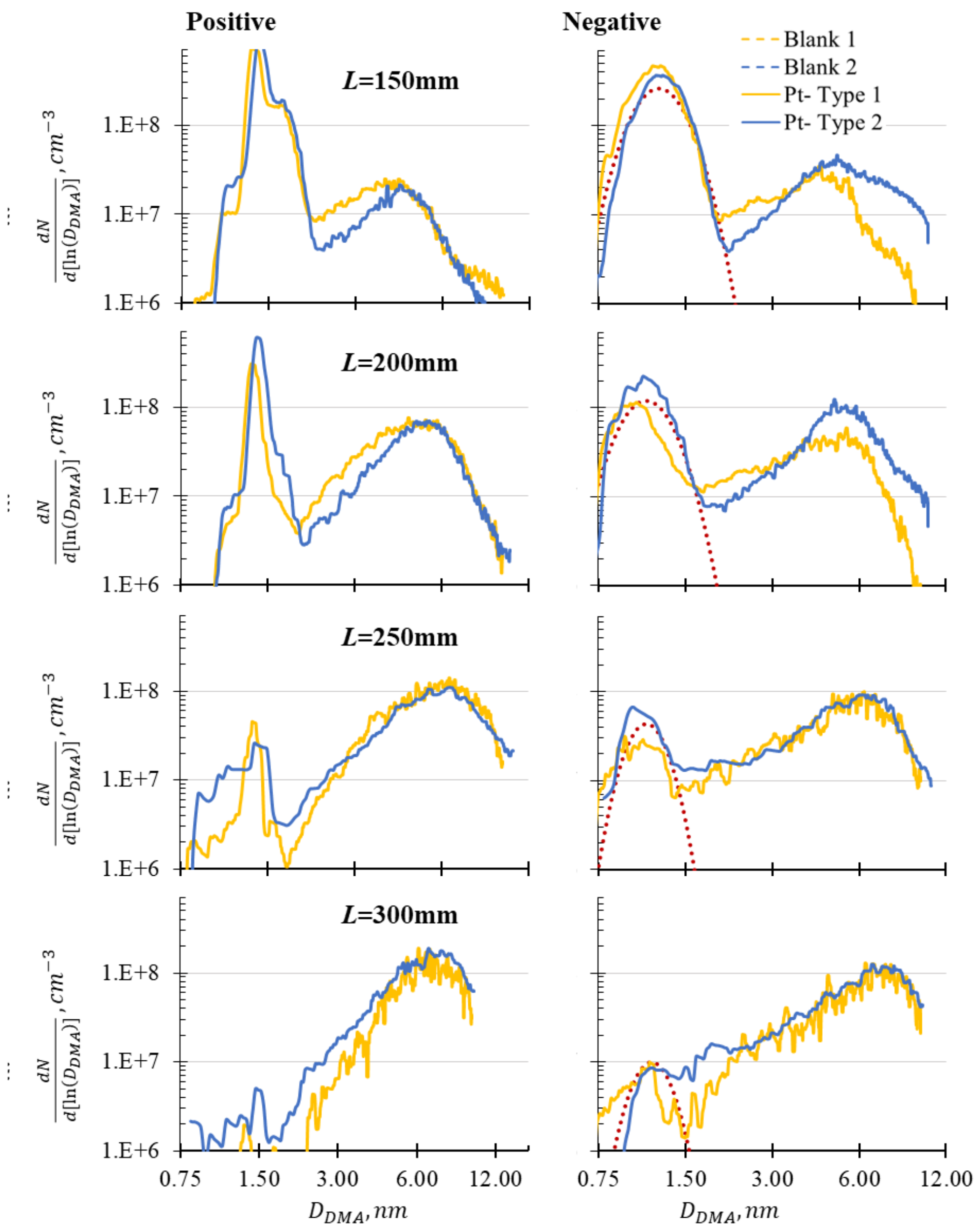
- Lowering DR enables us to measure a larger number of first-mode particles at *L*=150mm after they undergo some coagulation growth in the probing system. Indeed, their growth to larger $D_{DMA}$ separates them form chem-ions and also enhances their ability to get charged in the sampling system.
- DR- and charge polarity independent results are obtained for $D_{DMA}$>2nm with the second mode of naturally charged nanoparticles being approximated by a lognormal distribution
- The shape and center of the first mode is unaffected by dilution at all *L*s but at *L*=150mm



# SDFs measured in Pt-Type1 vs. Pt-Type2

**DR=700 (low dilution)**
**$\Delta t$ = 95ms (long time)**
**Pt-Type1 vs Pt-Type2**

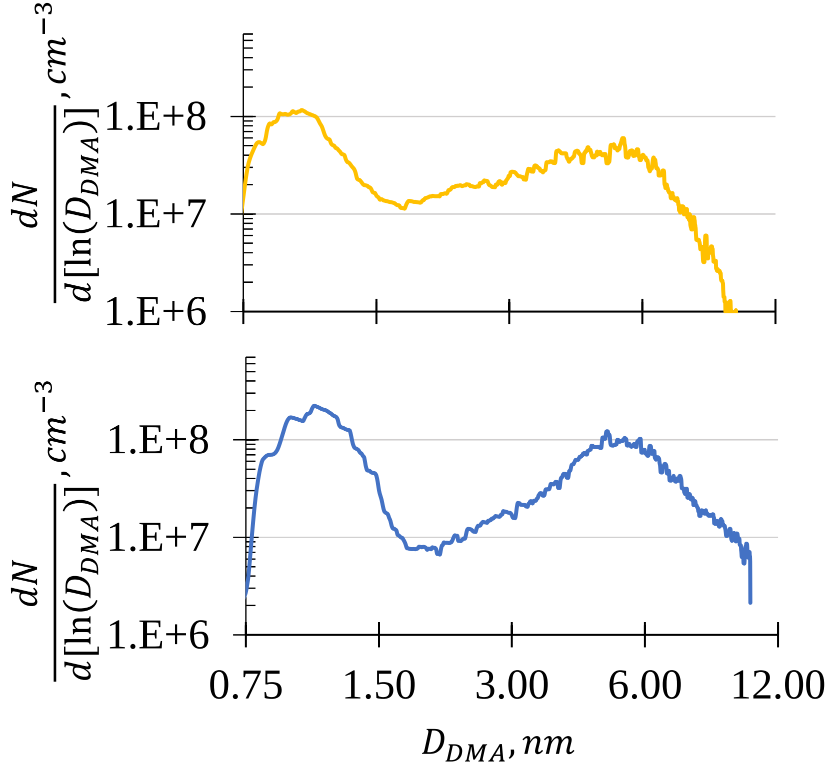
- The second mode exhibits a lognormal distribution with a constant relative width of σ=1.35.
- The center of the second mode shifts from 4nm to 7nm at increasing distances from the fuel nozzle (L)
- A lognormal mode centered at 1.05nm with σ=1.15 fits the SDF of negatively charged first mode nanoparticles (the best distinguishable from chem-ions).
- Any polarity dissymmetry of the Pt nanoparticles in getting charged progressively diminishes as nanoparticle ages in the flame before being sampled at larger *L*s

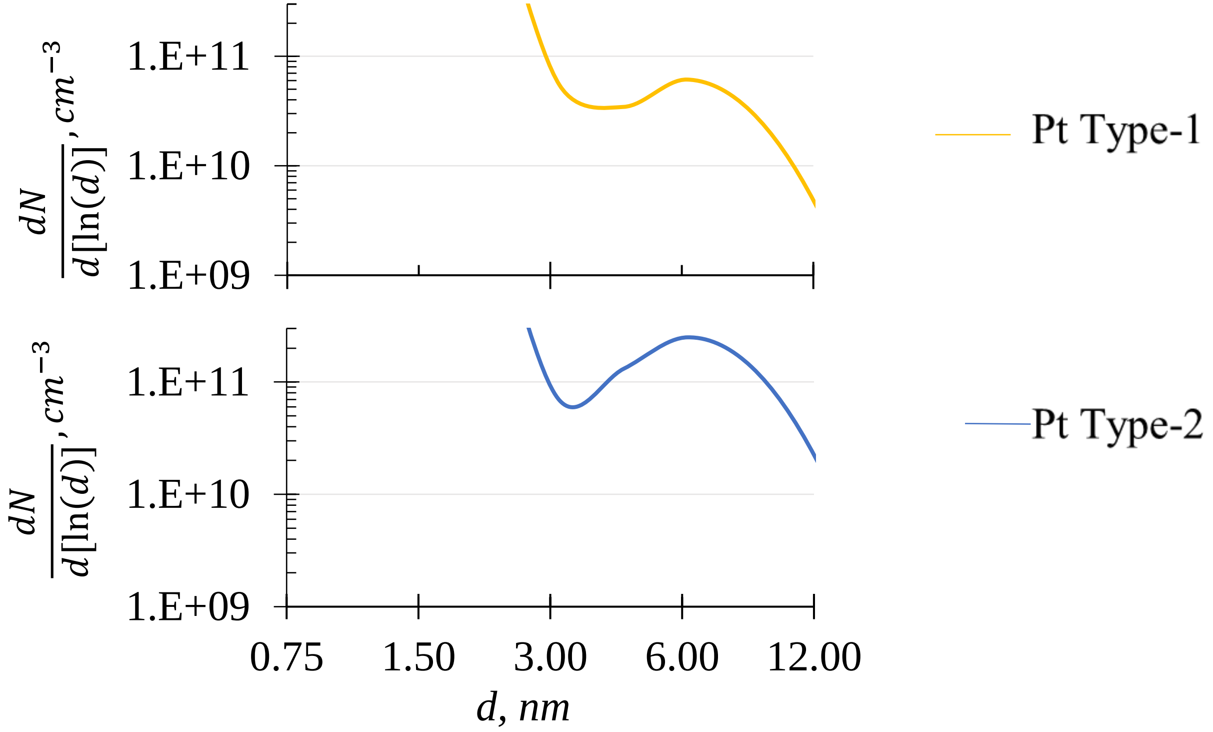


# Comparison with all particles

**$L$=250mm**

**Negative**




- The number concentrations of the naturally charged particles belonging to the second mode are approximately three to four orders of magnitude lower than that of the entire (charged and uncharged) nanoparticle population.
- The number of naturally charged Pt nanoparticles is limited by the available flame chem-ions but their measurements via HR-DMA tracks the shape, median diameter, and width of both modes of the SDF at different $L$s.

# Reprocessing the results of Laser diagnostics

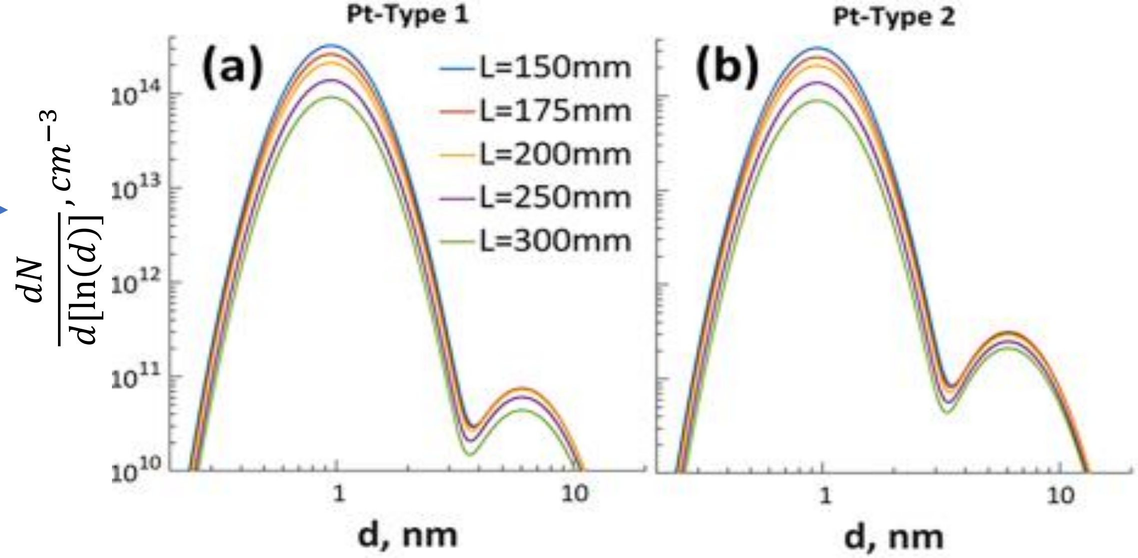
The knowledge of the modal shapes, centers, and width as well as of $d_{6,3}$ and volume fraction, $f_v$, measured by laser diagnostics allow to calculated the number concentrations of the two modes and reconstruct the in-situ SDF at different *L*s

$$\overline{d_{6,3}} = \left(\frac{\overline{d^6}}{\overline{d^3}}\right)^{\frac{1}{3}} = \frac{n_1\overline{d_1^6}+n_2\overline{d_2^6}}{n_1\overline{d_1^3}+n_2\overline{d_2^3}}$$

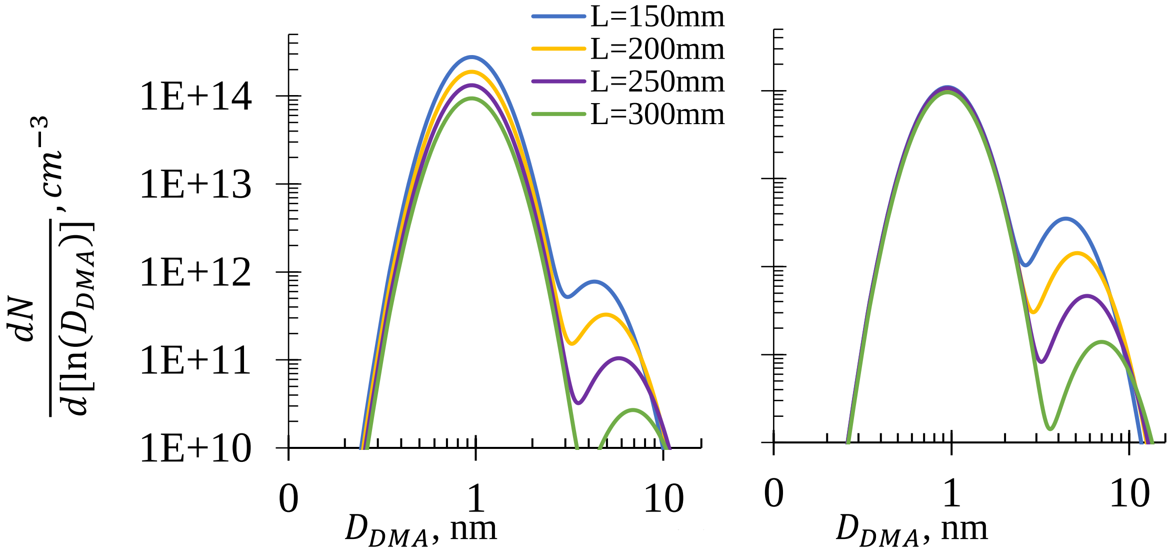
$$f_V = \frac{\pi}{6}\left[n_1\overline{d_1^6} + n_2\overline{d_2^6}\right]$$

| L, mm | σ | $d_{gm}$, nm | |
|---|---|---|---|
| | | Positive | Negative |
| 150 | 1.35 | 4.3 | 4.8 |
| 200 | 1.35 | 5.1 | 5.3 |
| 250 | 1.35 | 5.8 | 5.8 |
| 300 | 1.35 | 7.0 | 7.0 |

Fixed modes as those at *L*=250mm




Modes measured by HR-DMA at different *L*s



# Conclusions



- The Size Distribution Function (SDF) of naturally charged (RSDT synthesized) Pt nanoparticles is bimodal.
- The first mode accounts for both flame hydrocarbon chem-ions and small Pt nanoparticles whose relative contribution to the HR-DMA measurements is difficult to quantify.
- Dilution, time, and charge polarity independent results are obtained clearly only for the second mode.
- The second mode has an approximately log-normal distribution whose center shifts approximately from 4nm to 7nm as the nanoparticle age in the flame in both the Pt-Type1 and Pt-Type2 flames.
- Despite the chem-ions interference, the results of HR-DMA measurements in negative polarity indicate that the first mode also has a lognormal distribution centered at 1.05nm, consistently with microscopy results.
- A combination of HR-DMA and laser diagnostic enable refined measurements of the SDF of the Platinum nanoparticles synthesized in the RSDT in the Pt-Type1 and Pt-Type2 flames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# Thank you For your attention