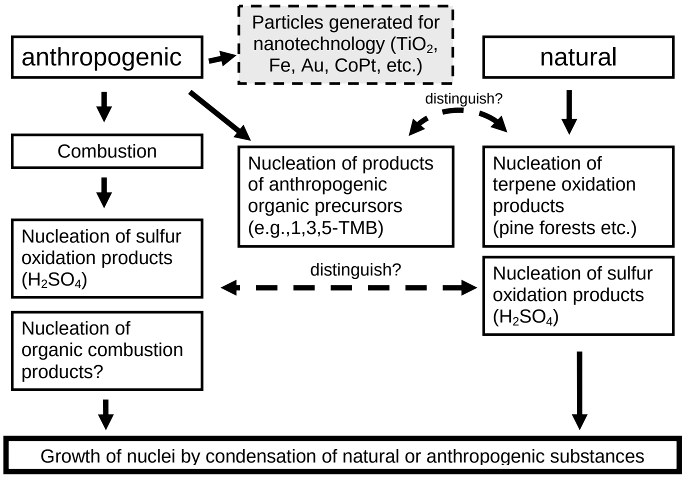
Latest developments in the chemistry of nanoparticles

Johannes Schneider
Particle Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany

The interest in the chemical composition of nanoparticles (particles with diameters smaller than 50 nm) has increased considerably in the recent years, mainly due to two reasons: Firstly, particles with diameters between 10 and 100 nm can penetrate deep into the lungs and are most efficiently deposited in the alveolae. Especially combustion-generated particles which are mainly composed of water-insoluble material are thought to affect human health.Secondly, atmospheric particle formation via gas-to-particle conversion leads to so-called nucleation events with very high particle concentrations. The sources of the precursor gases can either be anthropogenic (sulfuric acid, low-volatile organics) or natural. The natural precursor gases are mainly dicarboxylic acids formed by reaction of vegetation emissions (e.g., terpenes) with ozone or atmospheric radicals.

Sources of nanoparticles in the atmosphere



To understand the mechanisms of particle formation, knowledge of the chemical composition of these newly formed particles is essential. During the last ten years, new methods have been developed in order to investigate the chemistry of nanoparticles. The major problem for chemical analysis of small particles is that particle mass is proportional to the third power of the particle diameter. The mass of a 10 nm particle is by a factor of 1 Million smaller than the mass of a 1 µm particle. Thus, chemical analysis of small particles requires a very high sensitivity of the instruments, a challenge that is accompanied by the difficulties in sampling nanoparticles with respect to diffusion losses and particle evaporation.

Newly developed instruments

The Aerodyne AMS

The Aerodyne Aerosol Mass Spectrometer (AMS) combines aerodynamic focusing and sizing with thermal evaporation, ion impact ionization and analysis of the ions in either a quadruple mass spectrometer (Q-AMS, *Jayne et al.*, 2000) or a Time-of-Flight MS (ToF-AMS, *Drewnick et al.,* 2005). These instruments can quantitatively determine the aerosol mass concentrations as a function of size, but their sensitivity to nanoparticles is limited to particles with d > 30 nm and are therefore only partly suited for nanoparticle analysis. The Q-AMS has been used to study the composition of nucleation particles in diesel exhaust (e.g., *Schneider et al.*, 2005).

The RSMS-3

The RSMS (Rapid Single Particle Mass Spectrometer, *Bein et al.*, 2005) is a laser ablation single particle instrument that overcomes the problem of the small particle size by pre-selecting the particle size with a combination of inlet orifices and a randomly firing ablation laser. With this technique, chemical composition of single particles was reported also in the nanoparticle size range (size classes at 30 and 40 nm).

The TDCIMS

The Thermal Desorption Chemical Ionization Mass Spectrometry (TDCIMS) was developed for real time, quantitative chemical analysis of ultrafine particles (*Voisin et al.*, 2003). The technique combines nanoparticle separation by differential mobility analysis (DMA), collection of the charged particles on an electrostatic precipitator, and highly sensitive chemical analysis provided by selected ion chemical ionization mass spectrometry. Sensitivity tests using laboratory-generated ammonium sulfate particles in the diameter range between 10 and 16 nm showed that sulfate and ammonium can be quantified with as little as 1 pg of collected aerosol mass.

The NAMS

Recently, *Wang and Johnston* (2006) introduced the Nano Aerosol Mass Spectrometer (NAMS) which uses a linear quadrupole behind an aerodynamic lens inlet system in order to guide charged aerosol particles into an ion trap, where the particles are trapped like large ions and subsequently ablated and ionized with a laser pulse. The ions are analyzed in a time-of-flight mass spectrometer. With this instrument, mass spectra of individual aerosol particles in the size range between 7 and 25 nm were obtained.

References

Bein, K. J., Y. Zhao, A. S. Wexler, and M. V. Johnston (2005), Speciation of size-resolved individual ultrafine particles in Pittsburgh, Pennsylvania, *J. Geophys. Res., 110*, D07S05, doi:10.1029/2004JD004708.

Drewnick, F., S. S. Hings, P. DeCarlo, J. T. Jayne, M. Gonin, K. Fuhrer, S. Weimer, J. L. Jimenez, K. L. Demerjian, S. Borrmann, D. R. Worsnop (2005), A new Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS) - Instrument Description and First Field Deployment, *Aerosol Sci. Technol., 39*, 637-658.

Jayne, J. T., D. C. Leard, X. Zhang, P. Davidovits, K. A. Smith, C. E. Kolb, and D. R. Worsnop (2000), Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, *Aerosol Sci. Technol., 33*, 49-70.

Schneider, J., N. Hock, S. Weimer, S. Borrmann, U. Kirchner, R. Vogt, and V. Scheer (2005), Nucleation particles in Diesel exhaust: Composition inferred from in-situ mass spectrometric analysis, *Environ. Sci. Technol.,* 39, 6153-6161.

Voisin, D., J. N. Smith, H. Sakurai, P. H. McMurry, and F. L. Eisele (2003), Thermal Desorption Chemical Ionization Mass Spectrometer for Ultrafine Particle Chemical Composition, *Aerosol Sci. Technol., 37*, 471–475.

Wang, S., and M. V. Johnston (2006), Airborne nanoparticle characterization with a digital ion trap–reflectron time of flight mass spectrometer, *Int. J. Mass Spec.*, doi:10.1016/j.ijms.2006.07.001.

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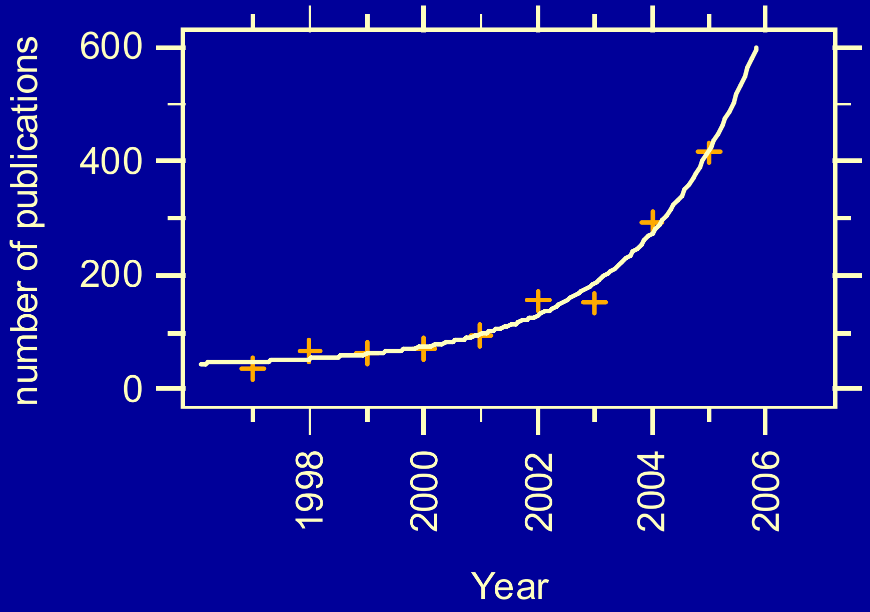
Particle Chemistry Department

Max Planck Institute for Chemistry, Mainz, Germany

10th ETH-Conference on Combustion Generated Nanoparticles
August 21 - 23, 2006

Chemistry of nanoparticles:

Searching the ISI Web of Science for "chemistry AND nanoparticles" yielded 1579 hits (between 1992 and 2006).



Focus:

Atmospheric nanoparticles

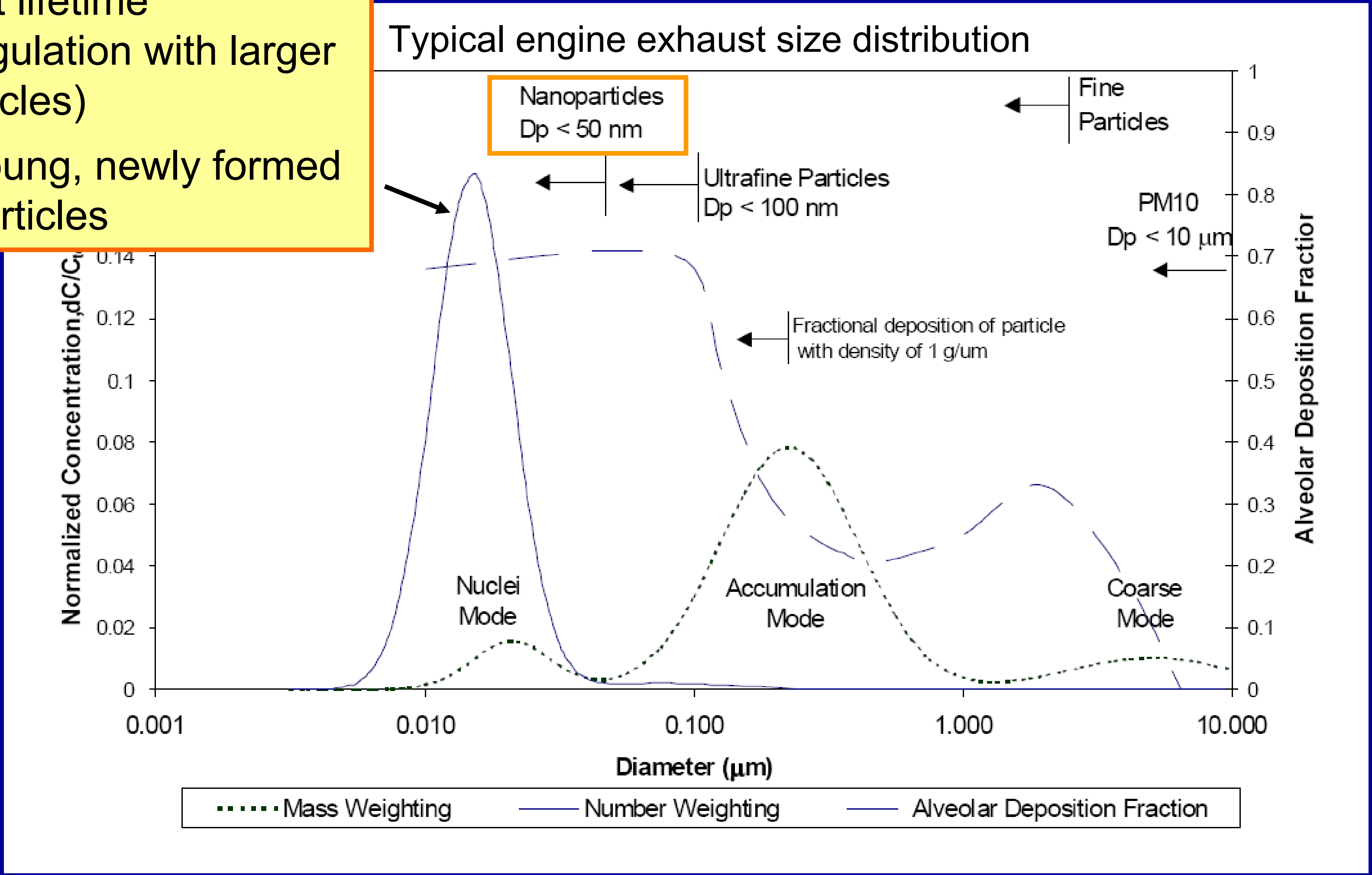
Outline

- Introduction to atmospheric nanoparticles
    - General
    - Sources of atmospheric nanoparticles
    - Observations of nanoparticles
    - Open questions
    - Measurement problems
- Recent instrumental developments and results with respect to chemical composition
    - AMS
    - RSMS
    - TDCIMS
    - NAMS
- Summary and Outlook

Introduction

Short lifetime
(coagulation with larger
particles)

→ young, newly formed
particles

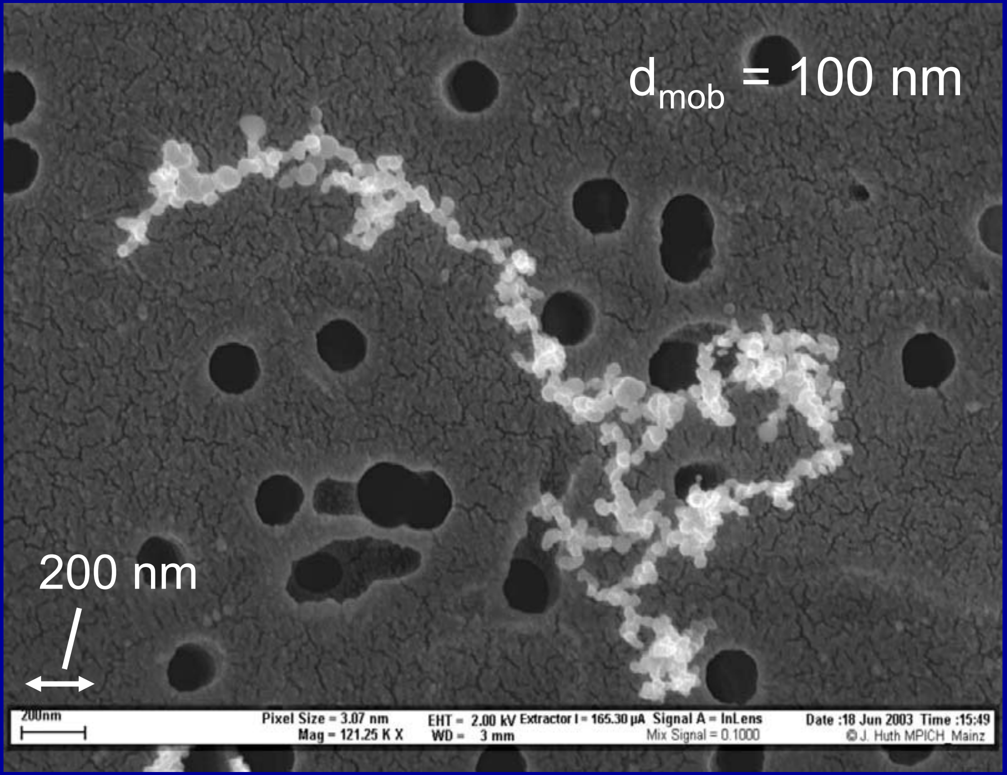


Kittelson, D., et al., *SAE technical paper series*, 2000–01-2212.

Introduction

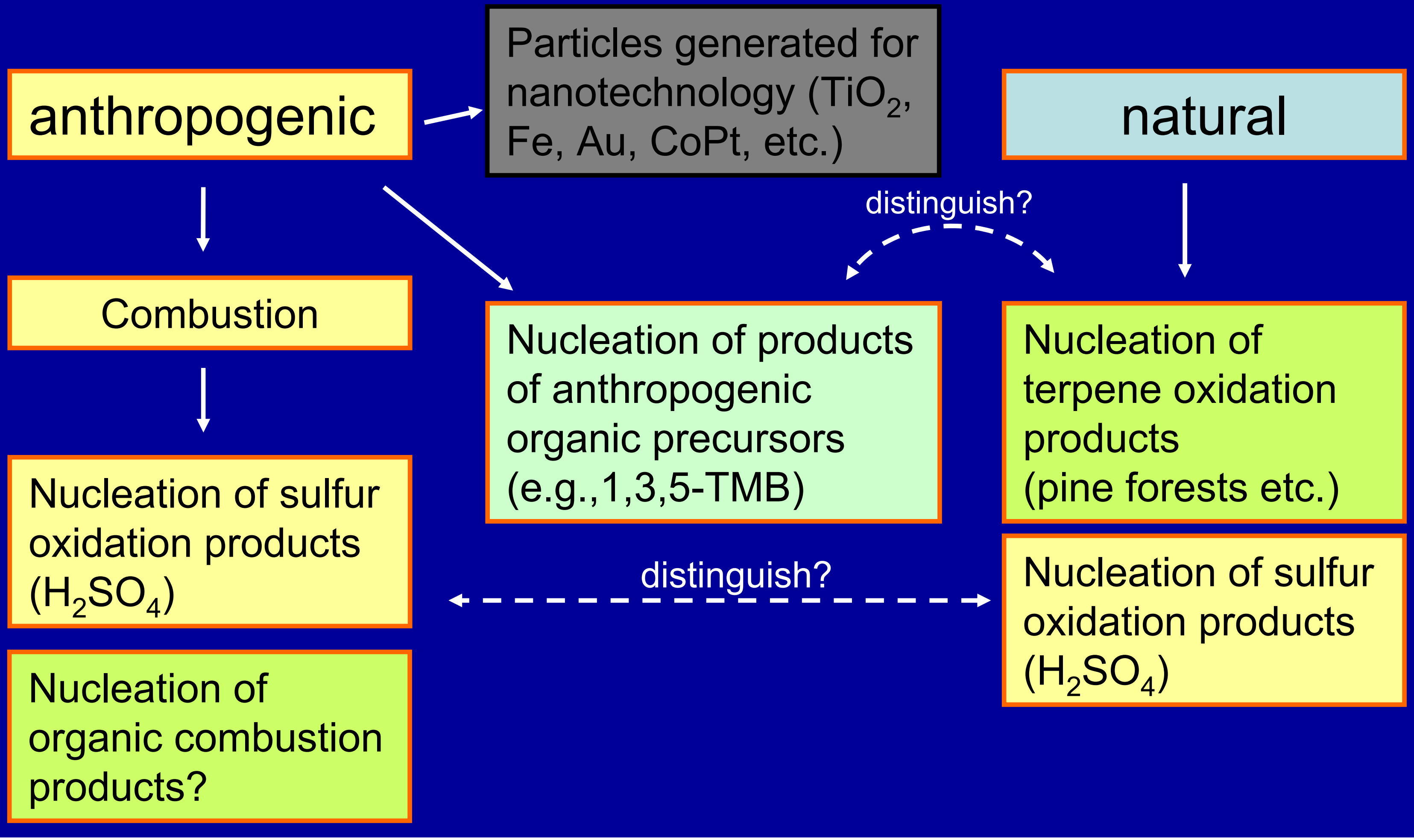
Soot particles:

- agglomerates of primary particles ($d_{pp} \cong 10 - 50$ nm)
- Usually found in the accumulation mode
- Not subject of this presentation



Particle from
biomass burning
(beech)

Sources of nanoparticles in the atmosphere



anthropogenic

Particles generated for nanotechnology (TiO_2, Fe, Au, CoPt, etc.)

natural

distinguish?

Combustion

Nucleation of products of anthropogenic organic precursors (e.g.,1,3,5-TMB)

Nucleation of terpene oxidation products
(pine forests etc.)

Nucleation of sulfur oxidation products (H_2SO_4)

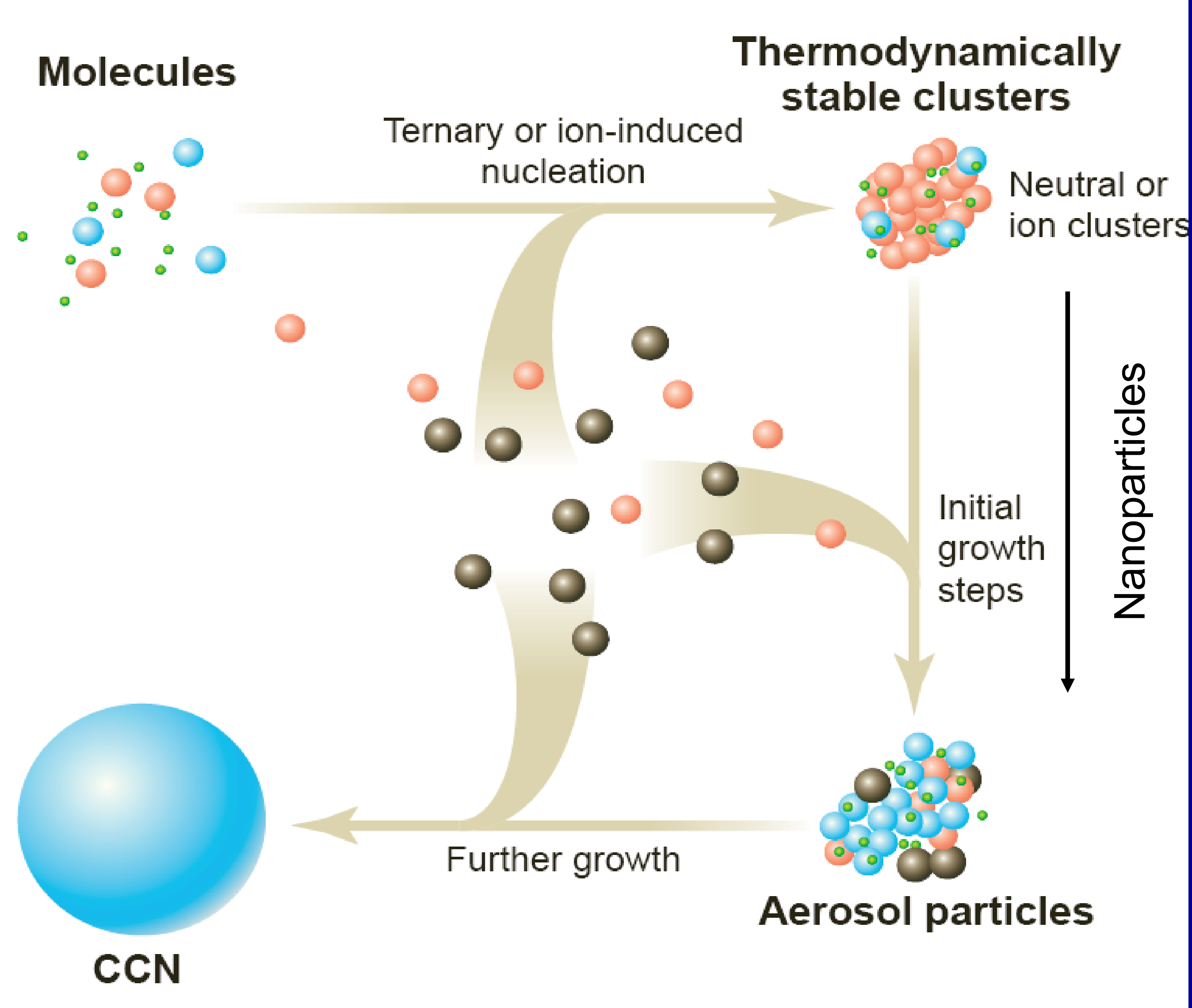
distinguish?

Nucleation of sulfur oxidation products (H_2SO_4)

Nucleation of organic combustion products?

Growth of nuclei by condensation of natural or anthropogenic substances

Introduction



Kulmala, Science, 2003

Introduction

Chemistry:

Sulfur species:

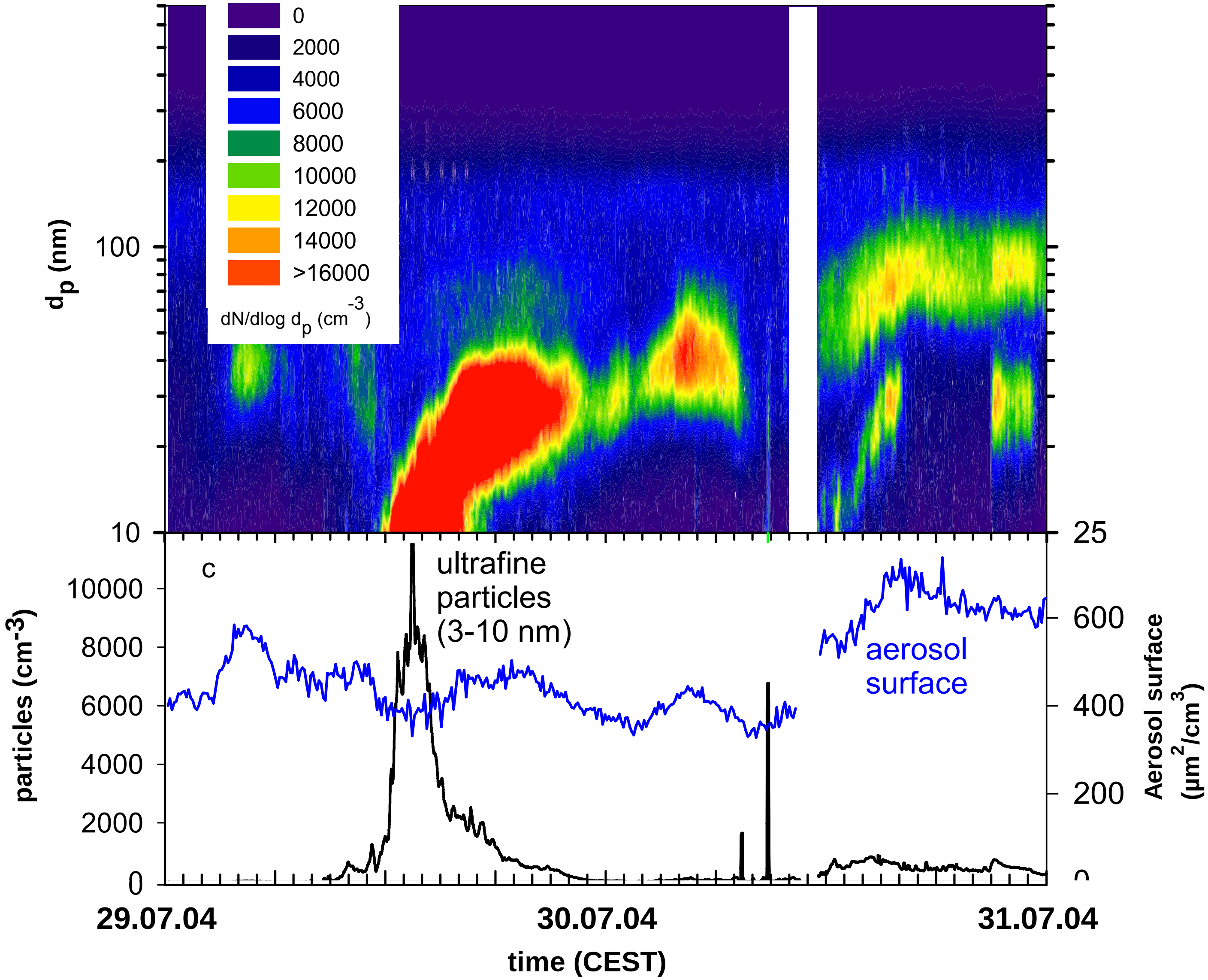
$H_2SO_4 + H_2O \rightarrow$ Particles	binary nucleation
$H_2SO_4 + H_2O + NH_3 \rightarrow$ Particles	ternary nucleation

Organic species:

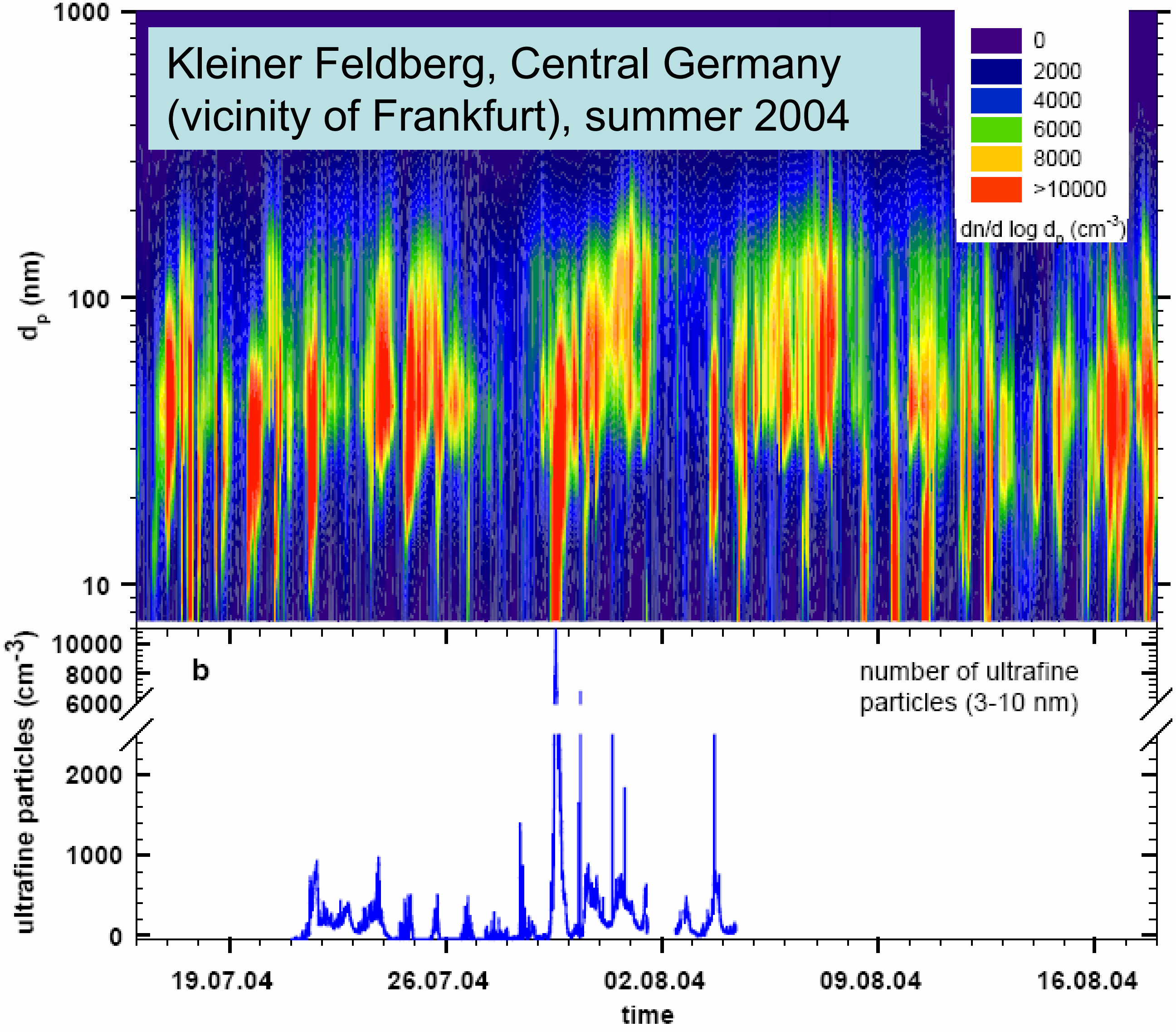
Organic precursor gases (VOCs) $\xrightarrow{O_3,\ OH,\ NO_3}$ products with low vapour pressure (e.g., dicarboxylic acids)

$\longrightarrow$ nucleation, condensation

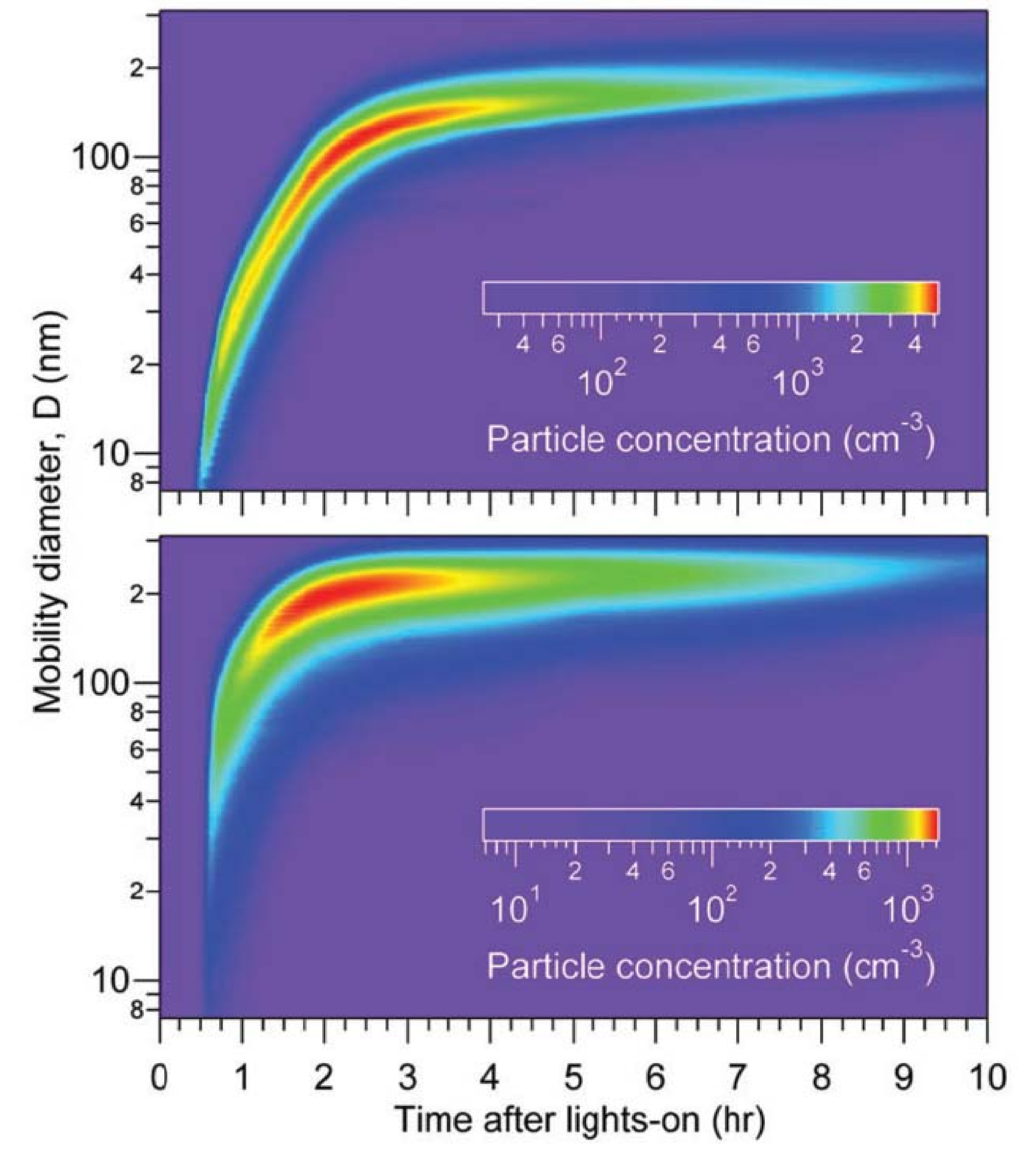
Observations: Nucleation event



Observations: Nucleation event


Kleiner Feldberg, Central Germany (vicinity of Frankfurt), summer 2004

Observations: Laboratory



Anthropogenic precursor gas:

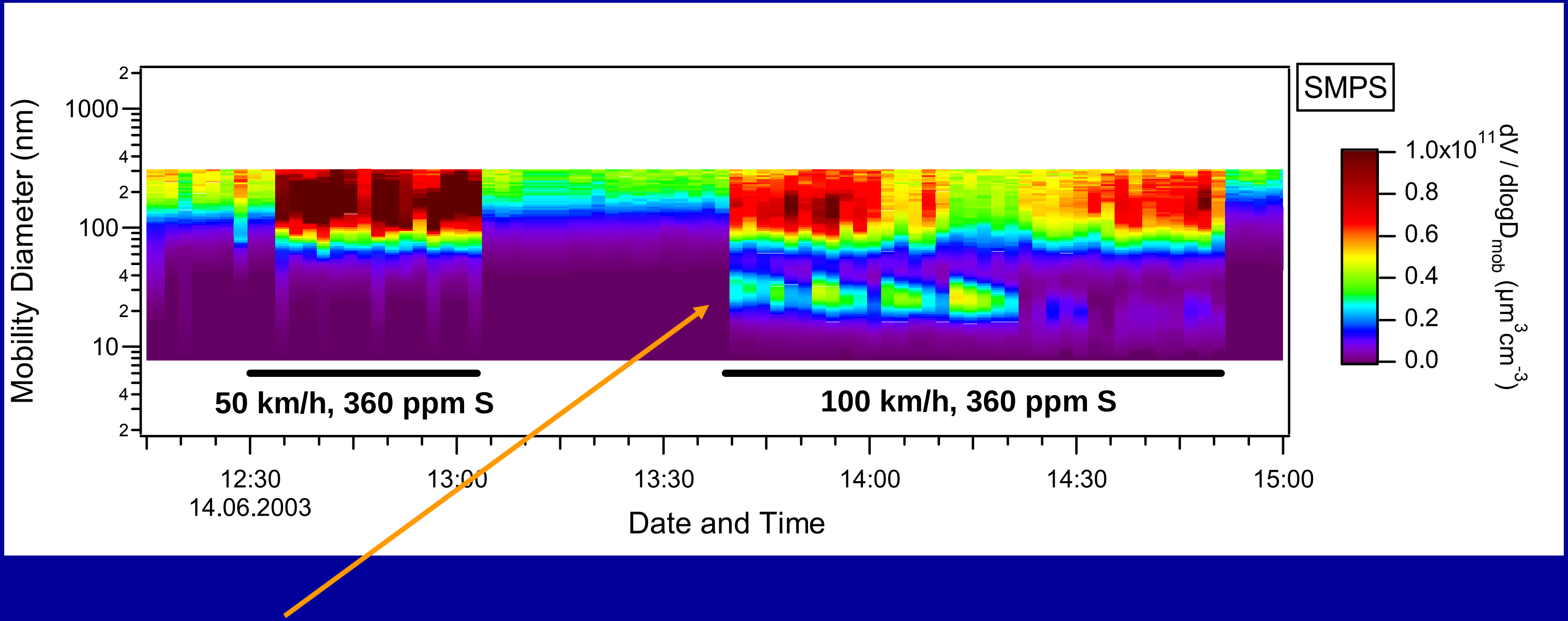
1,3,5-TMB/NO_x/C_3H_6
(650 ppb, 320 ppb, 300 ppb initial mixing ratios) at 50% RH;

Natural precursor gas:

α-pinene/NO_x/C_3H_6
(160 ppb, 130 ppb, 300 ppb initial mixing ratios) at 50% RH.

Baltensperger et al., *Faraday Discuss.*, 2005

Observations: Diesel exhaust



Individual car chasing on test track:
Nanoparticle formation in diesel exhaust with high fuel sulfur content under high load

Schneider et al., *ES&T*, 2005

Open questions

Open questions:

- Organic mass concentrations needed in laboratory experiments to trigger nucleation are much higher than found in ambient atmosphere
- Which chemicals trigger the nucleation? (Organics or H_2SO_4? Binary or ternary? Natural or anthropogenic sources?)
- Which gaseous substances condense on the nuclei and lead to particle growth?
- Can we distinguish between natural and anthropogenic sources?

Measurement problems

Measurement problems:

- Particle mass is very small :
  mass of a 10 nm particle (1 g/cm^3): $5x10^{-19}$ g
- Sampling problem: diffusion losses
- Off-line methods: Long sampling times
  → low time resolution
  (nanoparticle events occur on short time scales)
  → loss of volatile substances from substrate
  → condensation of gas-phase compounds on filter
  → chemical reactions of unstable compounds

→ On-line methods preferred for analysis of atmospheric nanoparticles

Instruments

Recently developed on-line methods

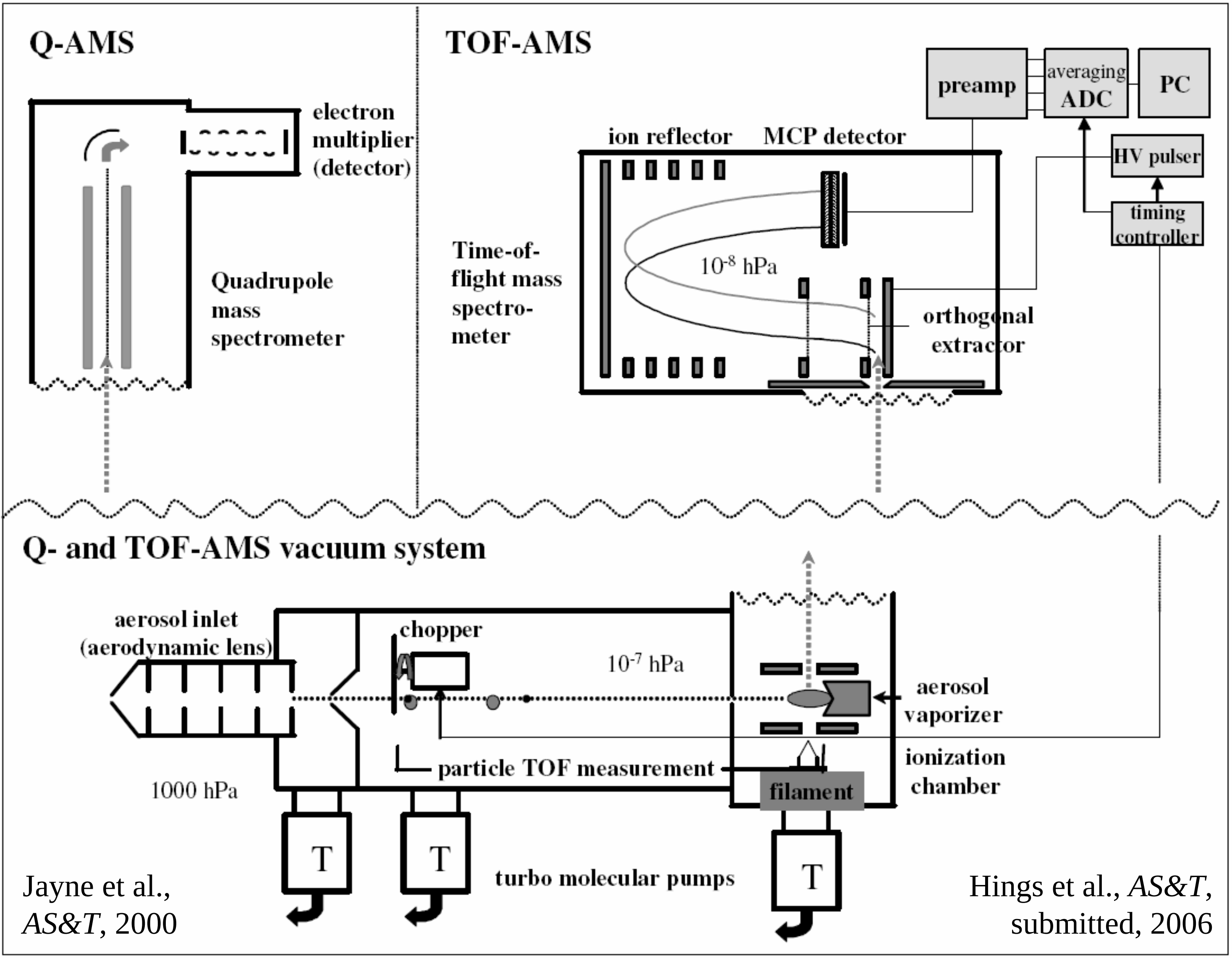
(on-line: analyis of particles directly upon sampling)

Aerosol mass spectrometers

- AMS (Q, ToF) (Aerodyne Inc.)
- RSMS-3 (A. Wexler, U California)
- TDCIMS (J. Smith, NCAR)
- NAMS (M. Johnston, U Delaware)

Instruments

Aerodyne Aerosol Mass Spectrometers (Q-AMS, ToF-AMS)



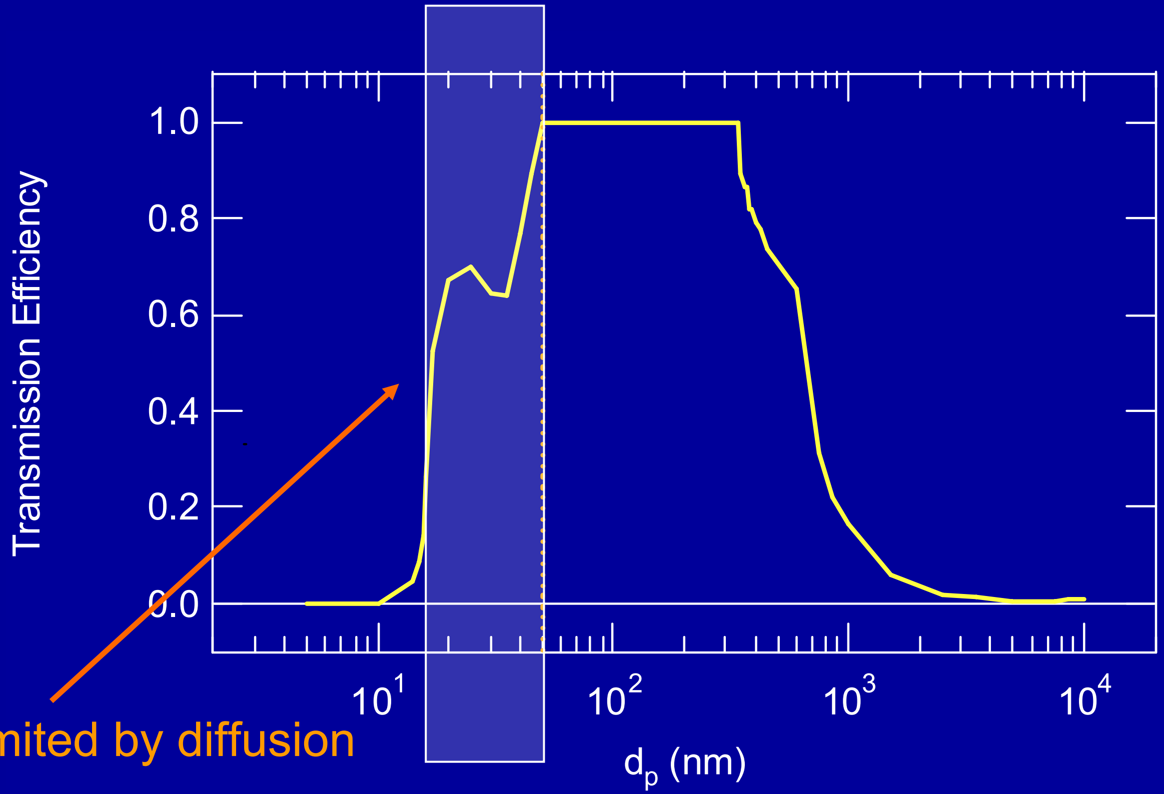
Jayne et al., *AS&T*, 2000

Hings et al., *AS&T*, submitted, 2006

Instruments

Aerodyne AMS: Aerodynamic lens transmission curve

Substantial transmission between 20 and 50 nm

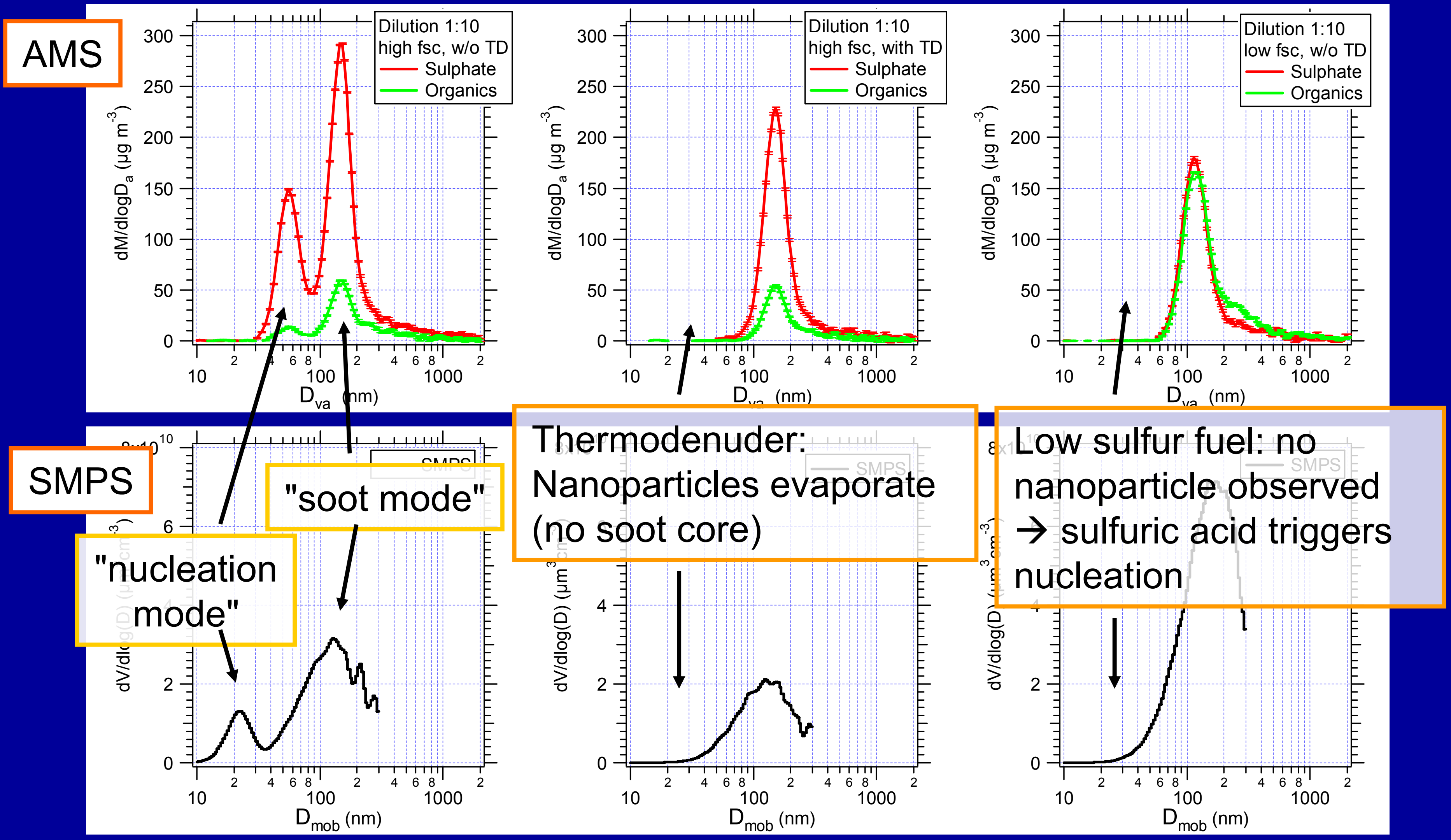


Focusing limited by diffusion

Zhang et al., *AS&T*, 2004

Q-AMS Results

Nanoparticles in diesel exhaust (chassis dynamometer)



"nucleation mode"

"soot mode"

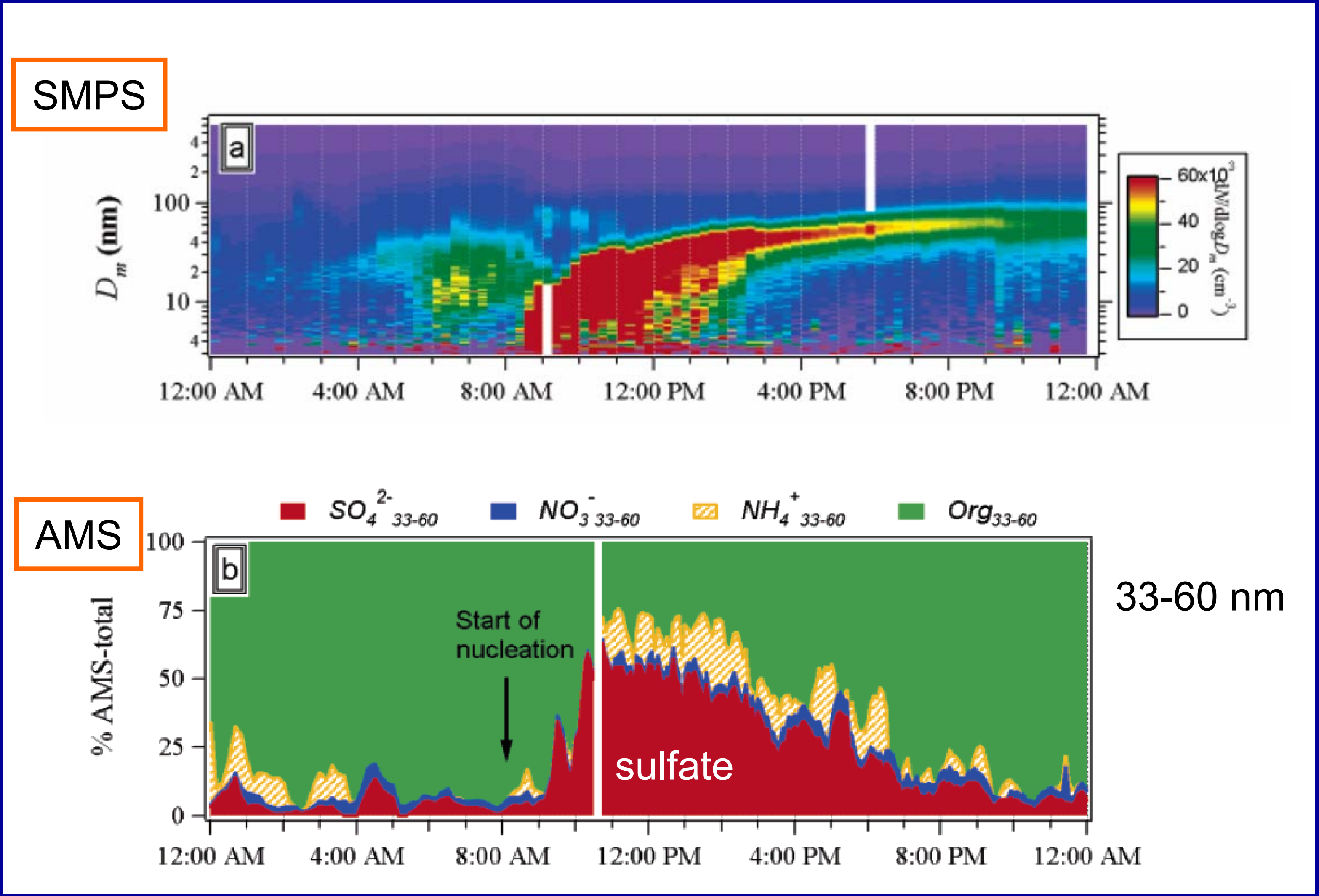
Thermodenuder: Nanoparticles evaporate (no soot core)

Low sulfur fuel: no nanoparticle observed → sulfuric acid triggers nucleation

Schneider et al., *ES&T*, 2005

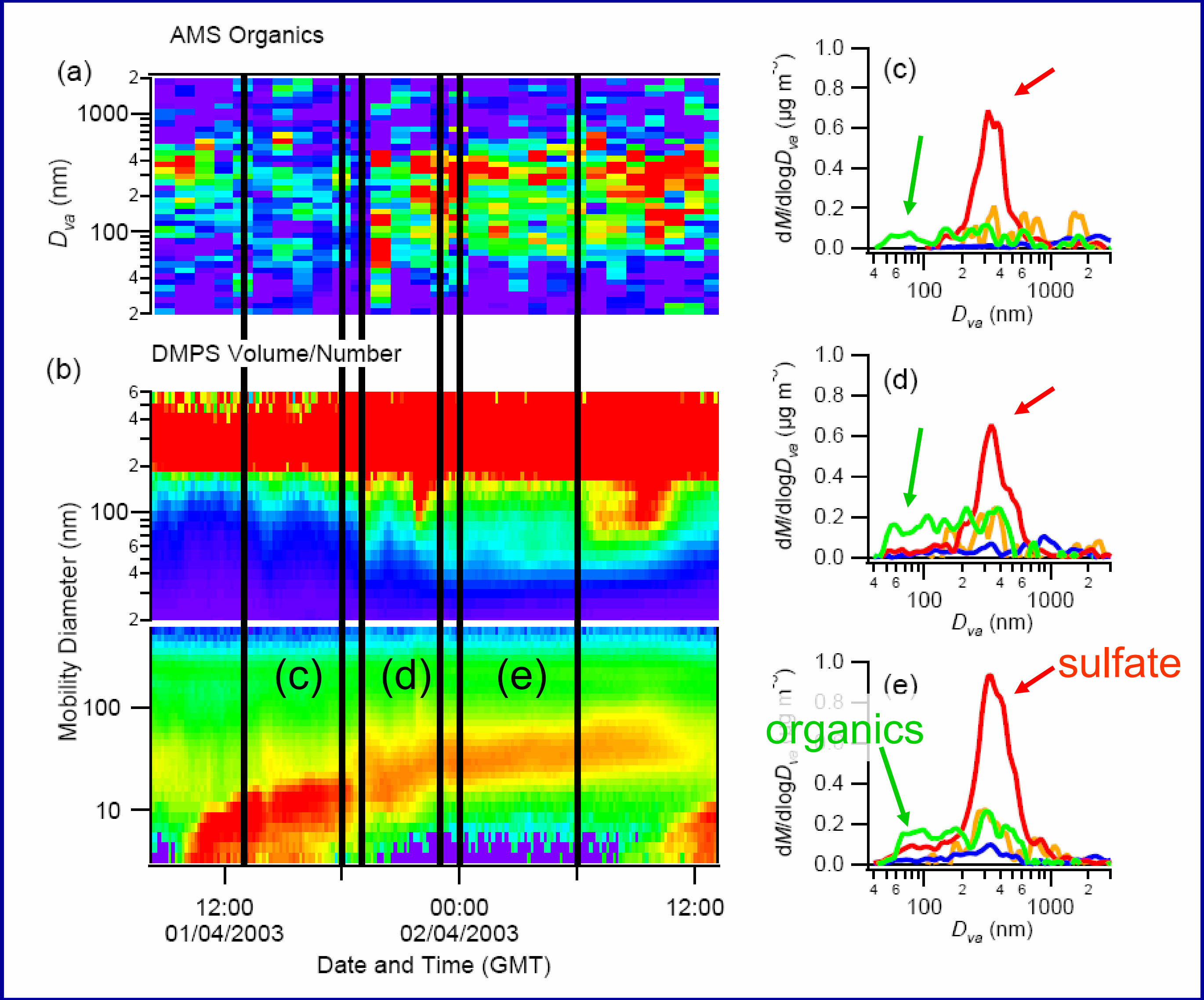
Q-AMS Results

Nucleation event observed at Pittsburgh, Sept. 2002



Zhang et al., *ES&T*, 2006

Q-AMS Results



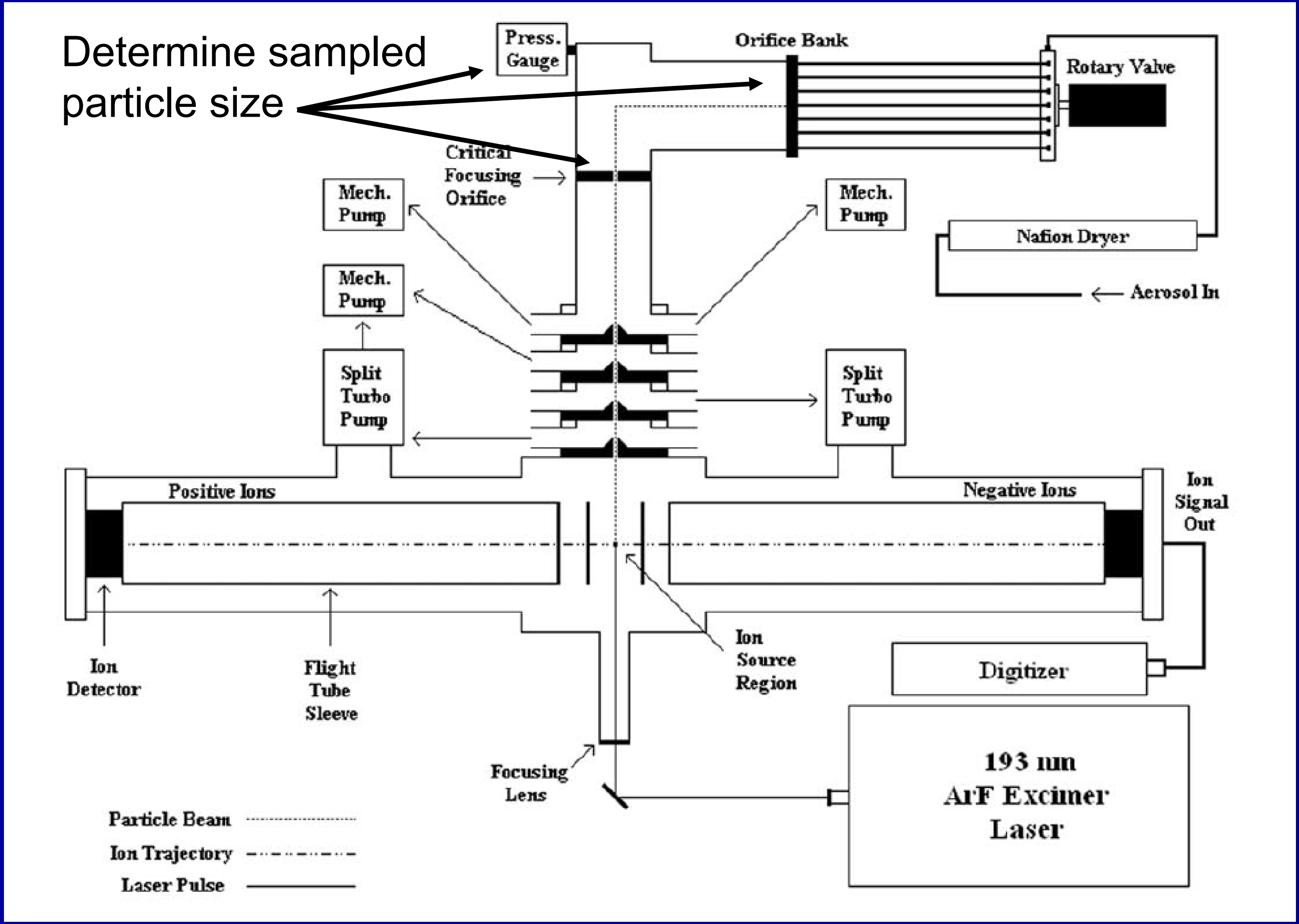
Nucleation event observed during the QUEST 2 project (March/April 2003, Hyytiälä, Finland)

Particles below 100 nm consist mainly of organics

Allan et al., *ACP*, 2006

Instruments

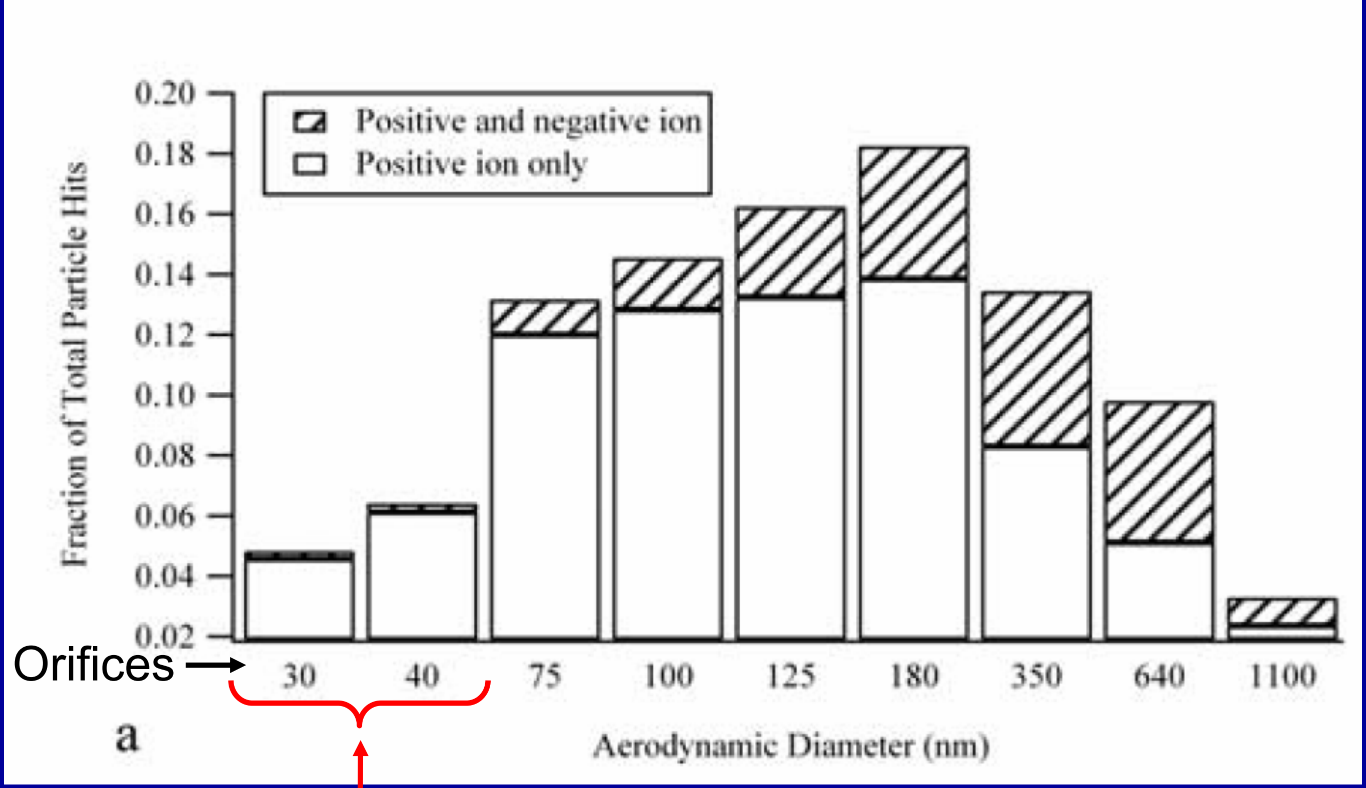
RSMS-3, Rapid Single Particle Mass Spectrometer



Determine sampled particle size

Bein, Zhao, Wexler, Johnston, *JGR*, 2005

RSMS-3 Results



smallest two size channels include nanoparticles
But: "no true size distribution"

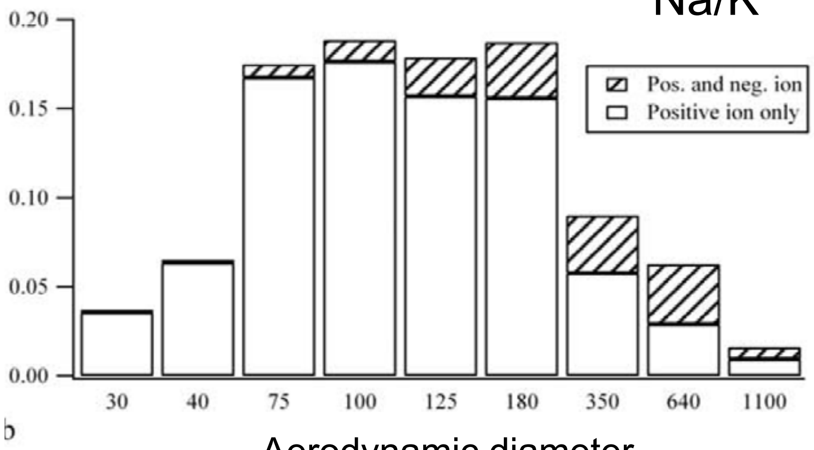
Bein, Zhao, Wexler, Johnston, *JGR*, 2005

RSMS-3 Results

Pittsburgh, Sept. 01 –Sept. 02

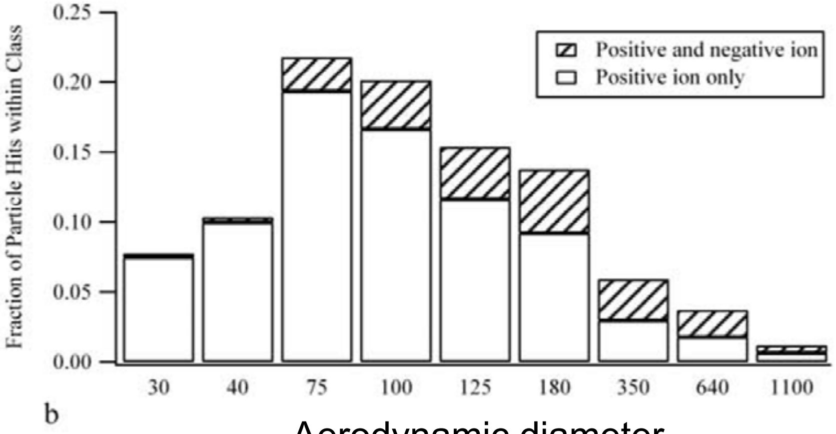
Fraction of particle hits within class

Na/K



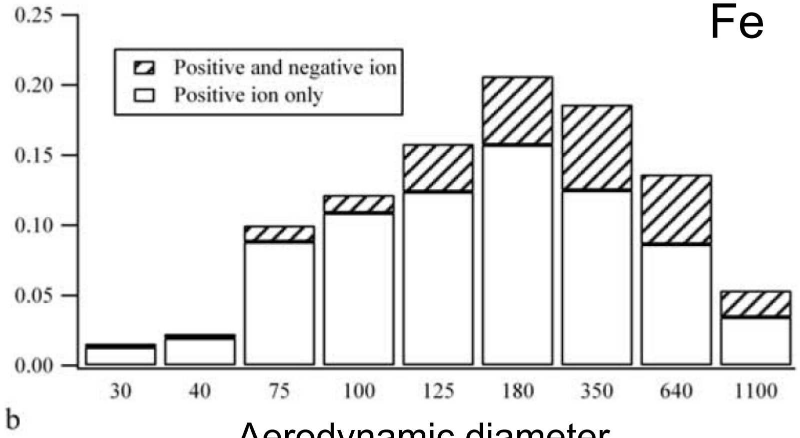
Aerodynamic diameter

EC/OC



Aerodynamic diameter

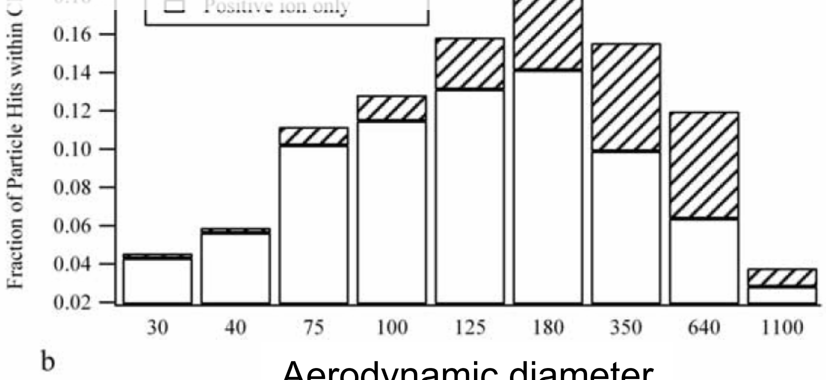
Fe



Aerodynamic diameter

This class dominated the sampled aerosol (54.4%)

OC/NH_4NO_3

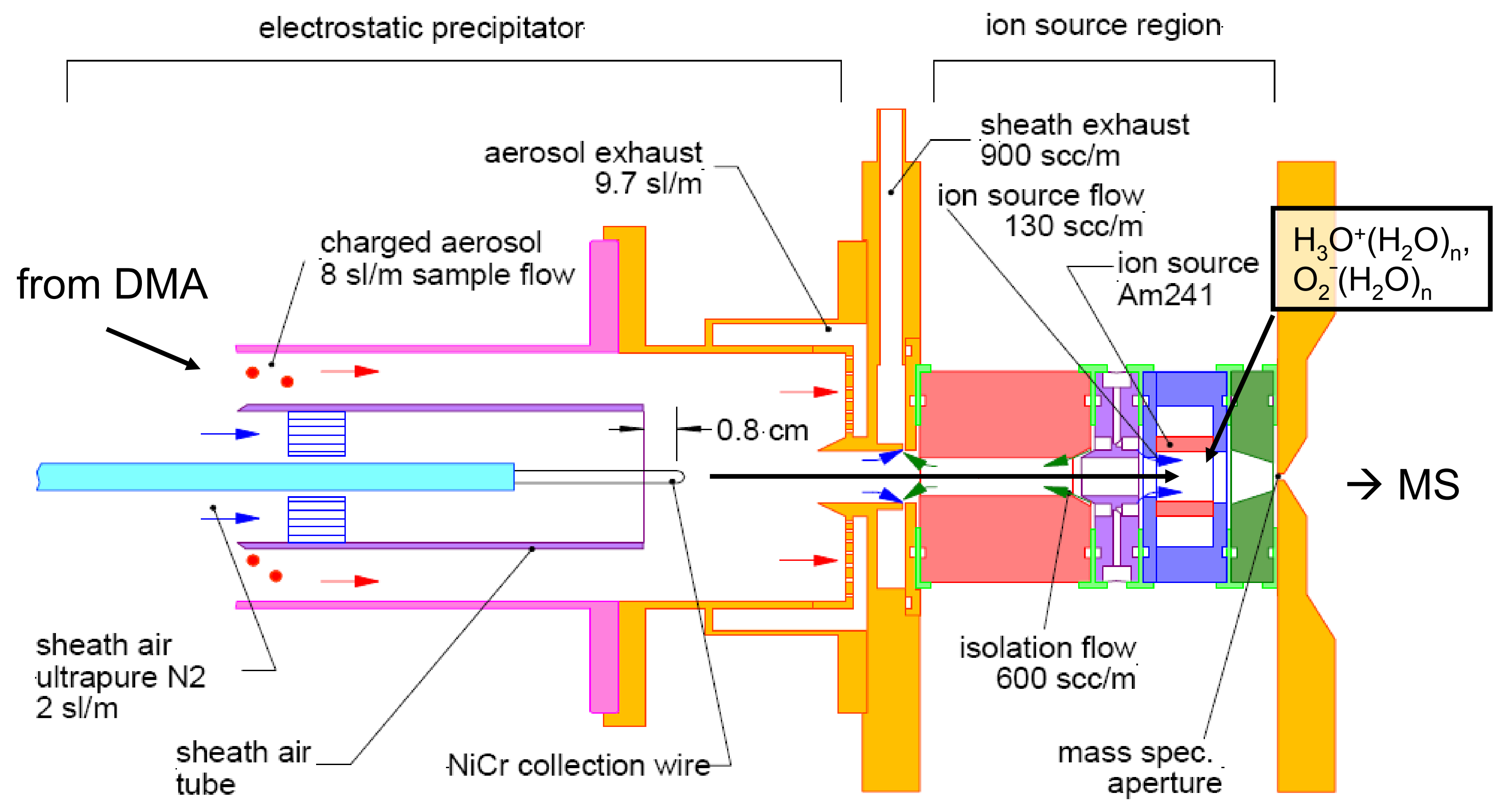


Aerodynamic diameter

Bein, Zhao, Wexler, Johnston, *JGR*, 2005

Instruments

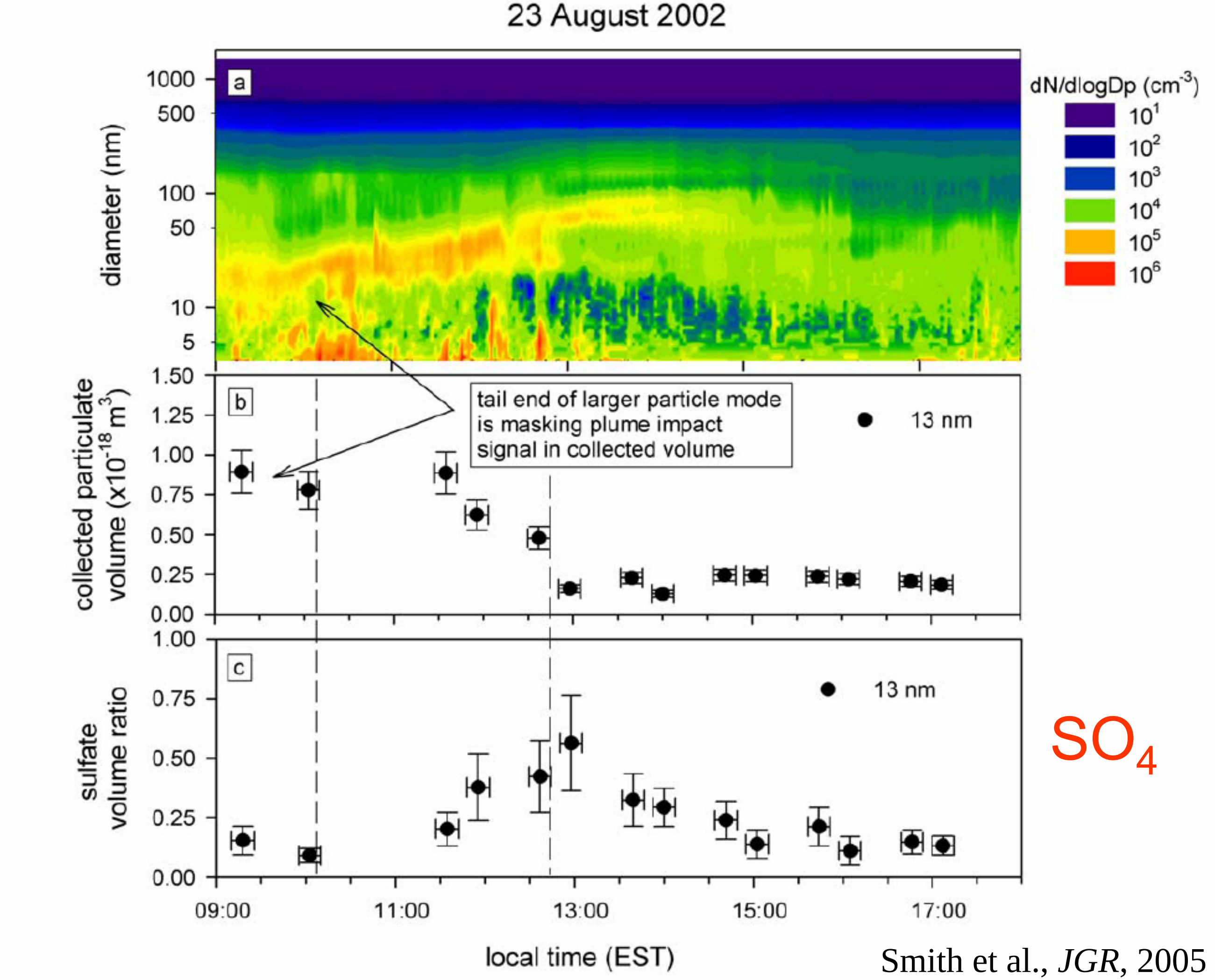
Thermal Desorption Chemical Ionization Mass Spectrometry (TDCIMS)



D. Voisin, J. N. Smith, et al., *AS&T*, 2003

TDCIMS-Results

Aerosol Nucleation and Real-time Characterization Experiment, Atlanta, 2002

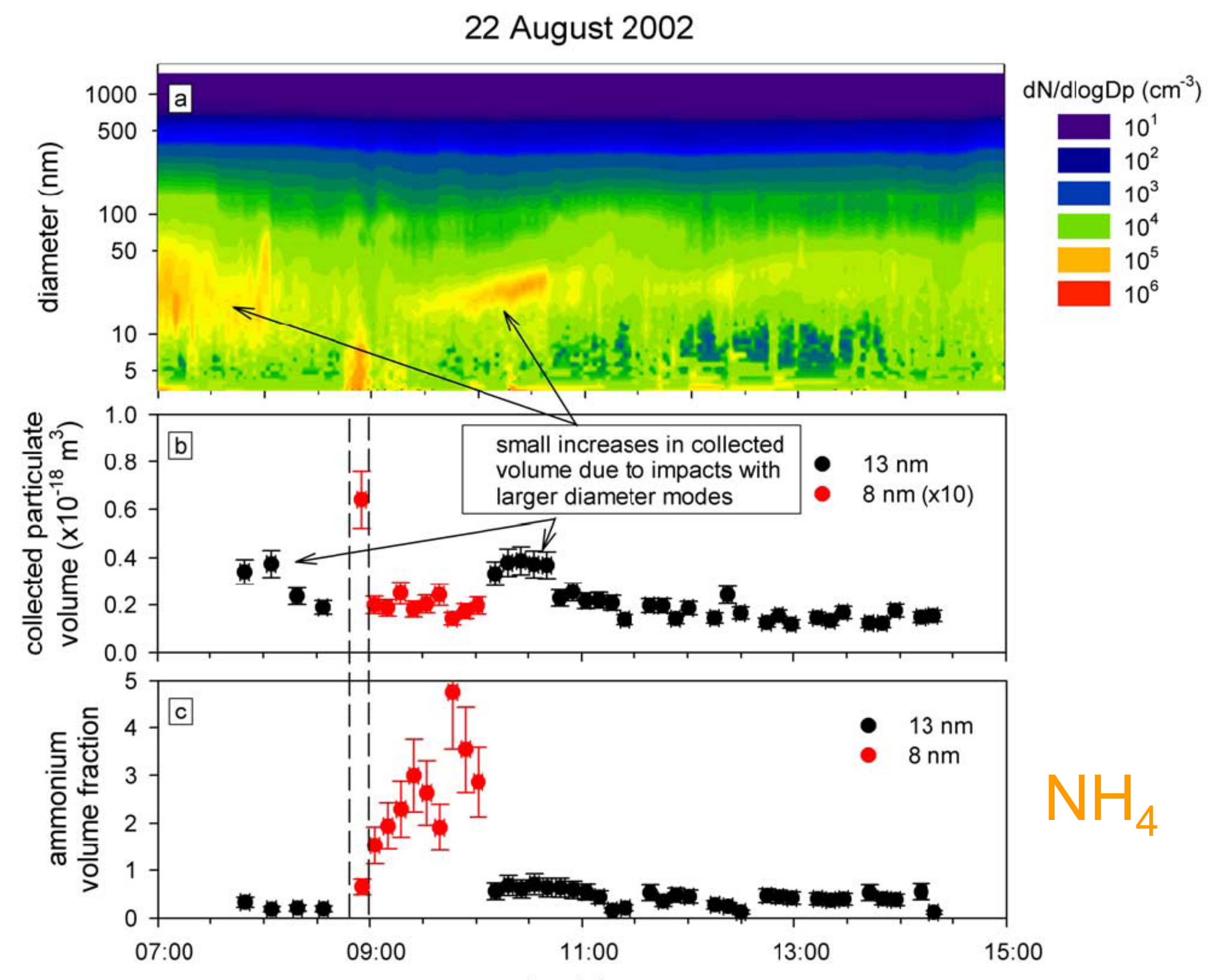


tail end of larger particle mode is masking plume impact signal in collected volume

SO_4

Smith et al., *JGR*, 2005

TDCIMS-Results



small increases in collected volume due to impacts with larger diameter modes

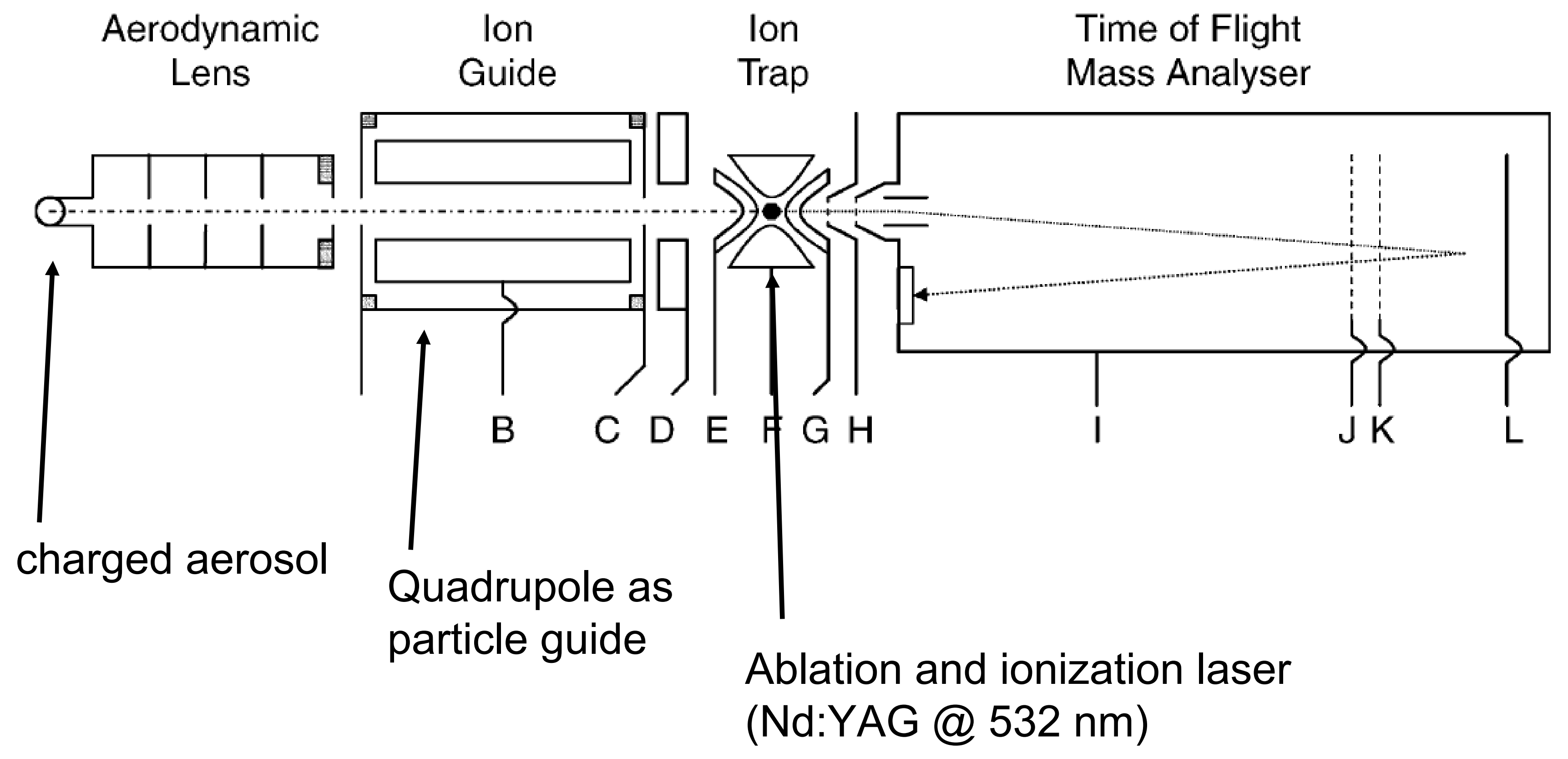
Smith et al., *JGR*, 2005

No other compounds identified during nucleation events

Ammonium and sulfate are essential → ternary $H_2SO_4/H_2O/NH_3$ nucleation

Instruments

NAMS (NanoAerosol Mass Spectrometer)



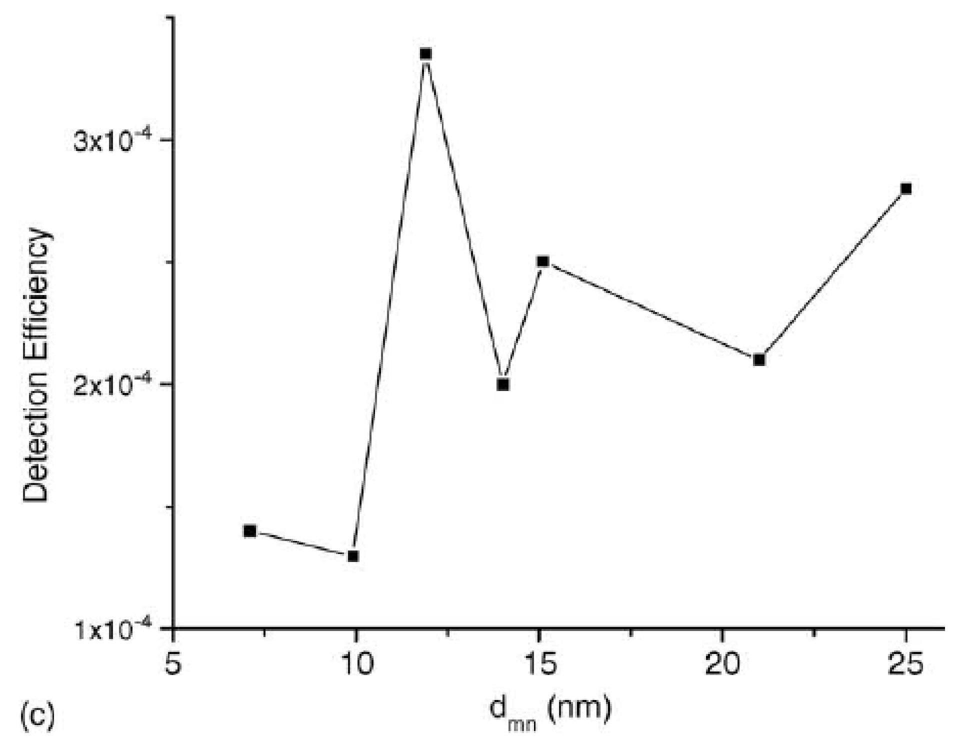
charged aerosol

Quadrupole as particle guide

Ablation and ionization laser (Nd:YAG @ 532 nm)

Wang and Johnston, *IJMS*, in press, 2006

NAMS Results

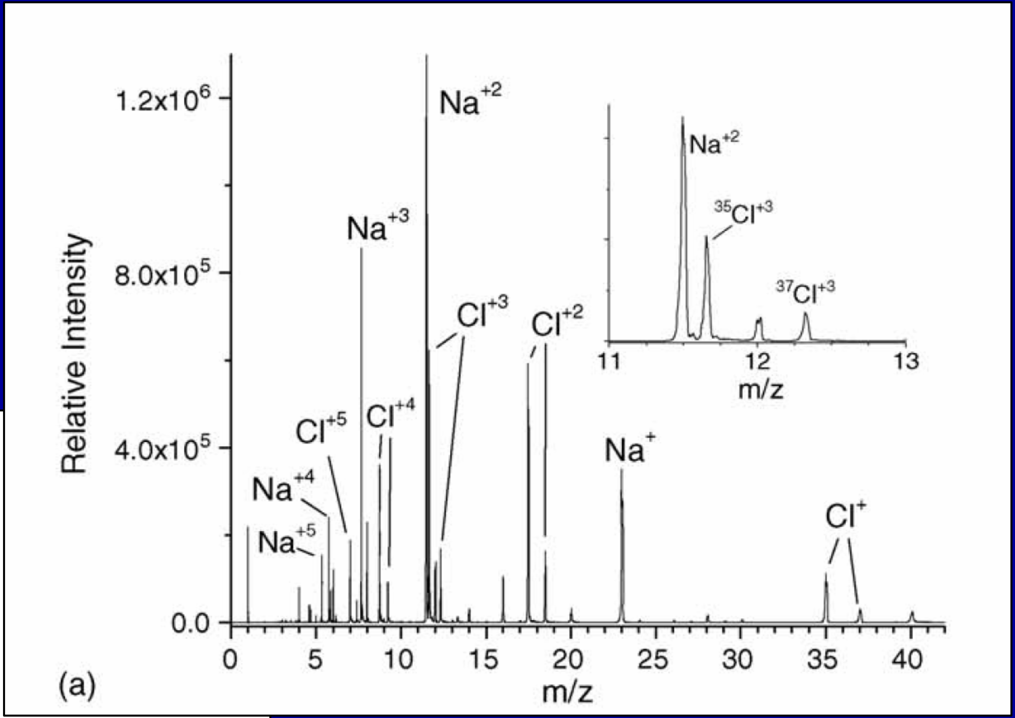


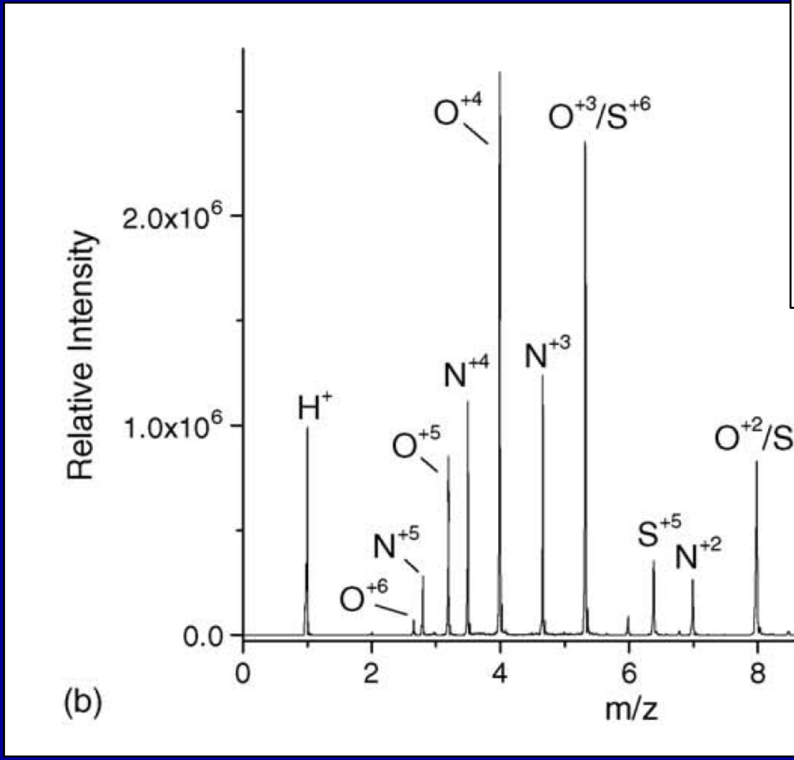
- Mass normalized diameters between 7 and 25 nm
- Single particle analysis
- Size selection with ion trap
- No field data reported yet (new development)

Wang and Johnston, *IJMS*, in press, 2006

NAMS Results

NaCl
(16 nm, 100 spectra averaged)





$(NH_4)_2SO_4$
(20 nm, 100 spectra averaged)

Wang and Johnston, *IJMS*, in press, 2006

Summary and Outlook - 1

- Atmospheric nanoparticles are typically composed of sulfate, ammonium and organics.

- Depending on the location and the sources, either of these components can dominate the composition.

- When SO_4 and NH_4 dominate, nucleation is most likely triggered by $H_2SO_4/H_2O/NH_3$ ternary nucleation.

- When organics dominate, the nucleating agent is not clear. The amount of $H_2SO_4/H_2O/NH_3$ that is needed to form the primary nucleus may be too small to be detected by the instruments.

Summary and Outlook - 2

- Laboratory experiments are not yet able to reproduce atmospheric organic nucleation under realistic atmospheric conditions → indication of additional nucleating agent in atmosphere (H_2SO_4?)

- Diesel exhaust nanoparticle formation has been shown to be triggered by sulfuric acid.

- Recent developments (TDCIMS, NAMS) have high potential to reveal further insight into nanoparticle chemistry.

- Some problems still exist:
  - Thermal desorption instruments are not sensitive to all chemical components (refractory material)
  - Laser ablation not quantitative (for molecules)

Thank you for your attention.