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Nanoparticle formation in modern Diesel vehicle exhaust:

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Talk given at 13 ETH conference on *Combustion Generated Nanoparticles*, Zürich, 22-24 June 2009

Nanoparticle formation in modern Diesel vehicle exhaust:
New insights from innovative exhaust measurements of key precursor gases

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For more information see

paper in preparation

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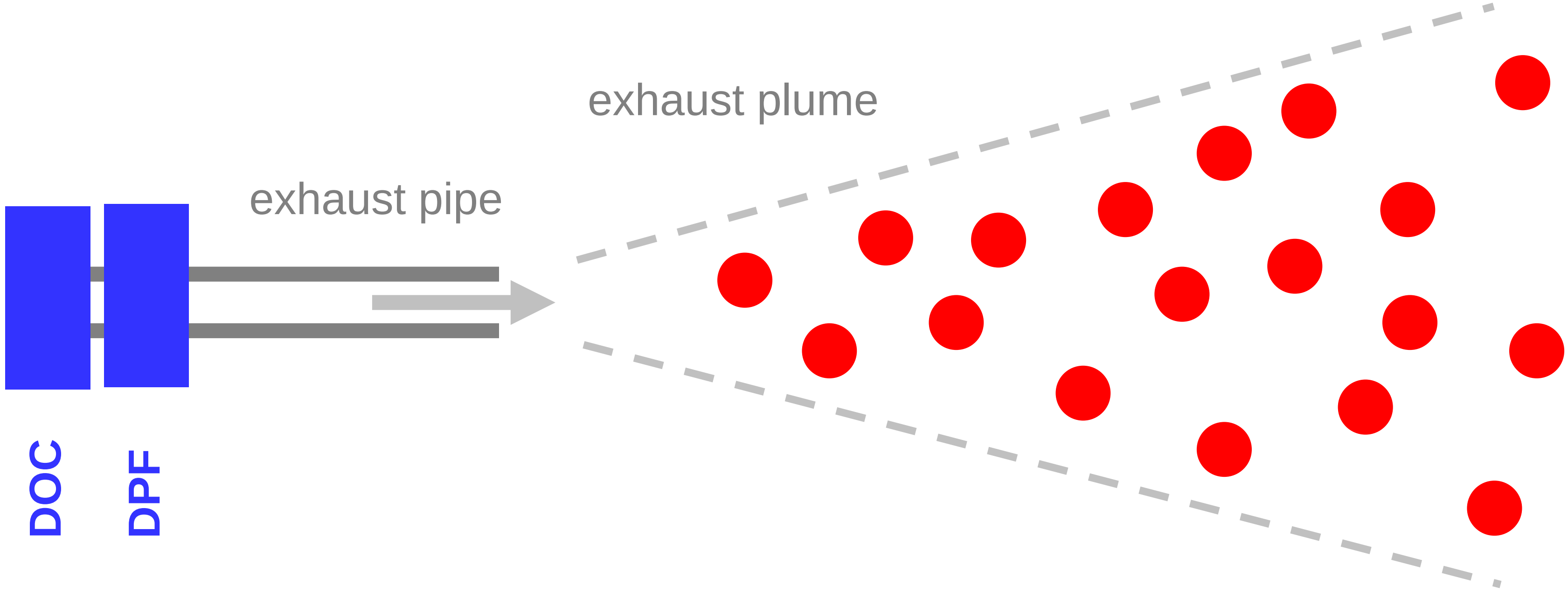
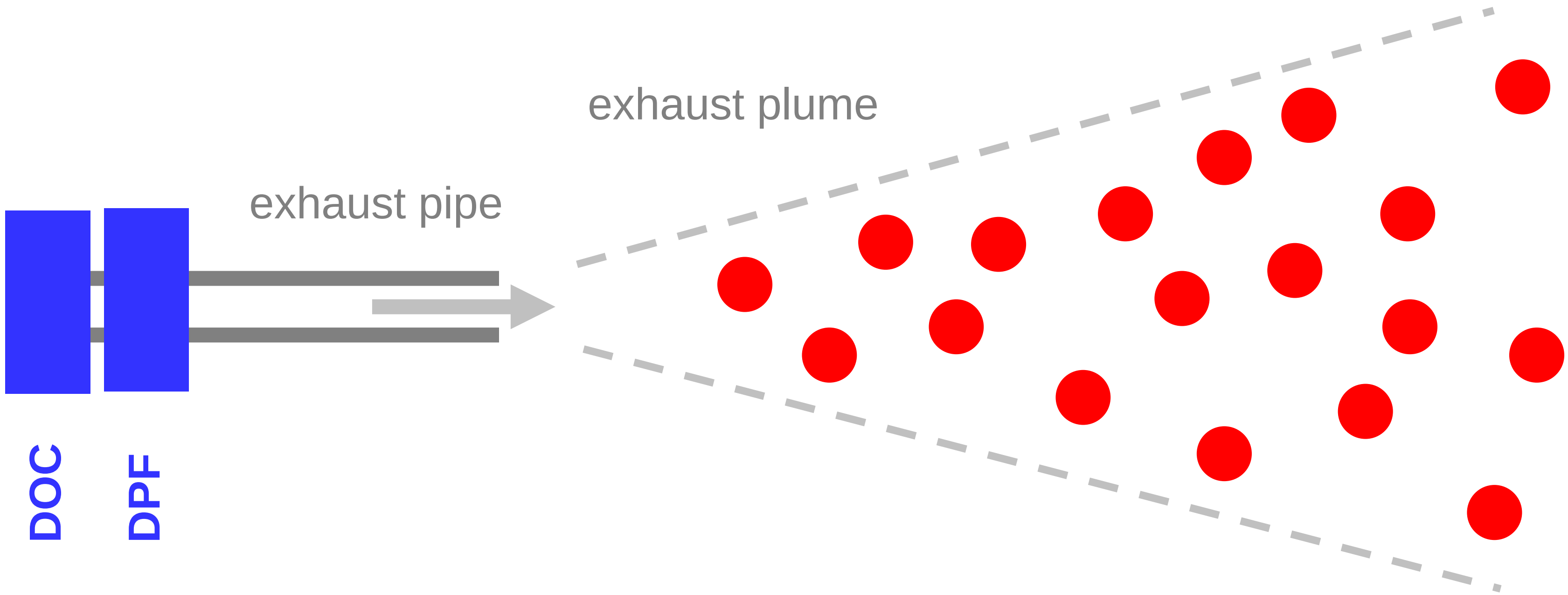
Modern Diesel vehicles equipped with after treatment systems (DOC + DPF)



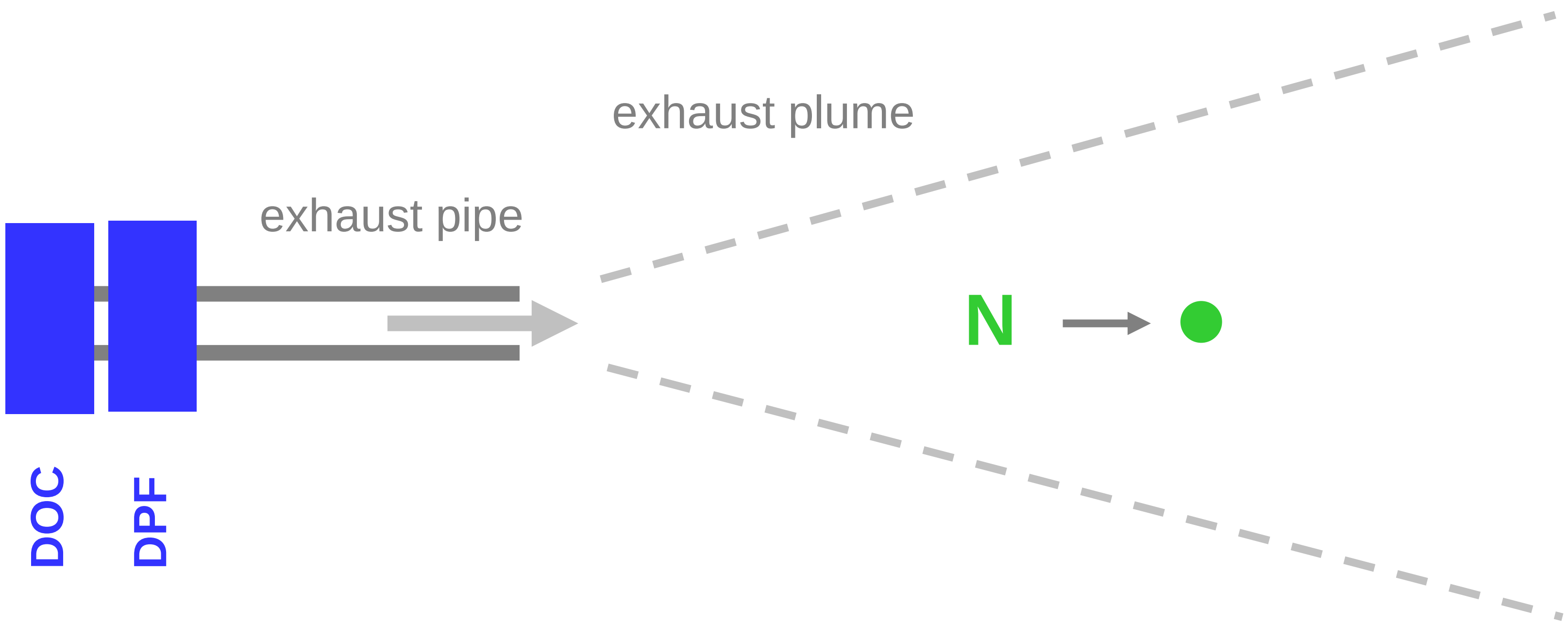
- Semi-volatile particles (D=10 nm) are present in large concentrations

Diesel exhaust : with after treatment (DOC + DPF)

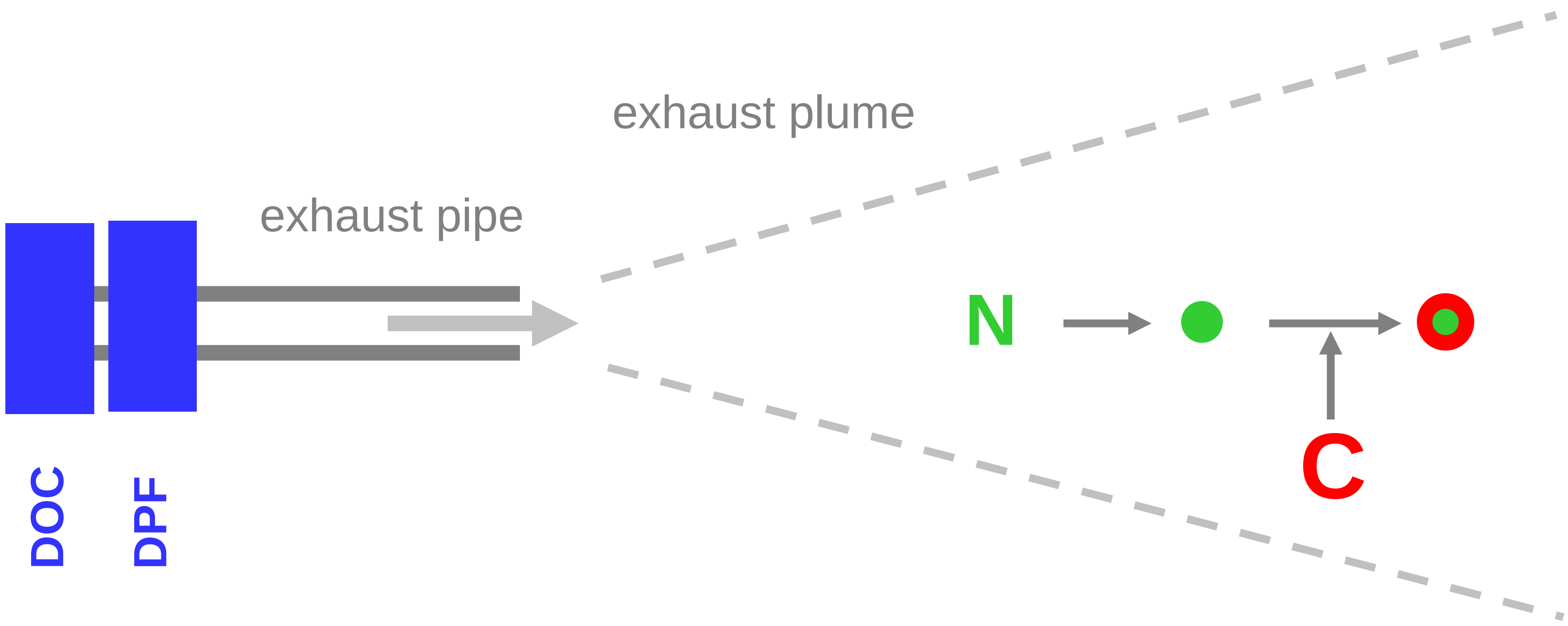


- Semi-volatile particles (D=10 nm) are present in large concentrations
- Must be formed downstream of DPF
- Requires presence of nucleating gases (**N**) and condensing gases (**C**)

Diesel exhaust : with after treatment (DOC + DPF)



Diesel exhaust : with after treatment (DOC + DPF)



Nucleation particles (NUP)

- Mechanism of formation and chemical nature only poorly understood
- NUP precursor gases not known

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- Mechanism of formation and chemical nature only poorly understood
- NUP precursor gases not known
- di-acids are conceivable candidates
  (have low saturation vapor pressures due to efficient hydrogen-bonding)

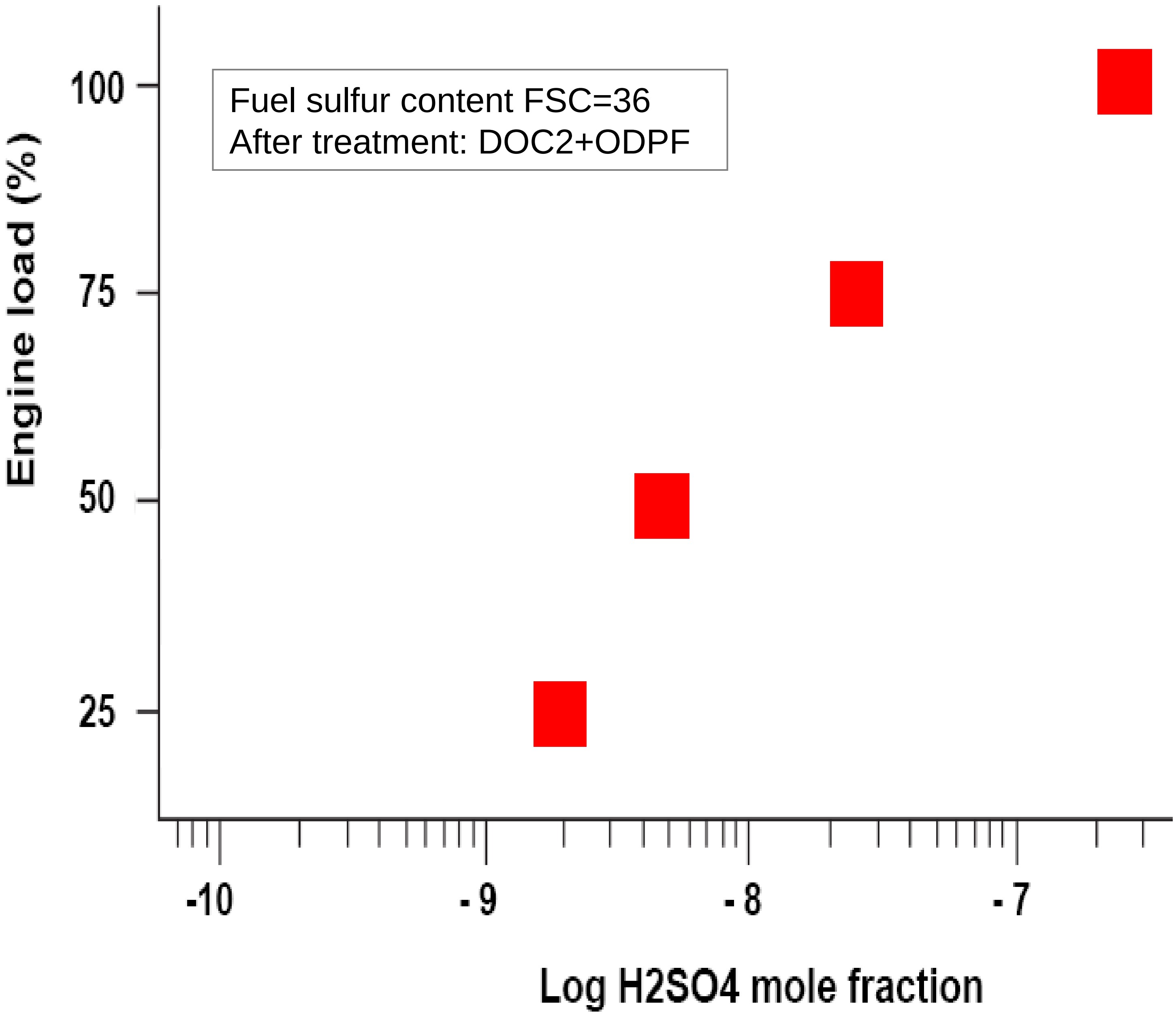
Experiments at MAN engine test lab (Nuernberg)

- **NUP precursor gas**: measurements (acids)
- **Measurement method**: IMR-ITMS (developed by ***MPIK Heidelberg)***
- **On-line :** heated exhaust
- **Off-line :** sampling on stainless steel surface, followed by thermodesorption
- Heavy duty Euro 4 Diesel vehicle **engine**:
  - MAN 323 kW , 6 cylinder turbo charged common rail
  - displacement: 10.6 l, torque: 2220 Nm
- **Parameters** varied during measurements : FSC , ATS , EL

On-line measurements

Sulfuric acid

Example of an on-line measurement of gas-phase H2SO4 in heated Diesel exhaust



H2SO4 formation increases with:

- Fuel sulfur content FSC
- Engine load EL
- Aftertreatment system ATS

„Fuel sulfur conversion fraction F“

- Diesel engine without ATS : F < 1%
- Diesel engine with ATS : F < 20-30 %

Comparison: Air craft exhaust plumes

Sulfur conversion efficiency

„Fuel sulfur conversion fraction F"

- Diesel without ATS : about 1%
- Diesel with ATS : about 20-30 %
- Jet air craft : about 2-4 %

Diesel vehicle exhaust:

Di-carboxylic acids

Di-carboxylic acids

- Various DCA have been observed
- DCA are correlated with H_2SO_4

Off-line measurements

- **Sampling**

  of exhaust components on heated stainless steel surface

- **Thermodesorption**

  stepwise increase of temperature (to 420 C)

- **IMR-ITMS measurement**

  of desorbed gases

Example of sampler measurement

Sampler 16

NI-CIMS

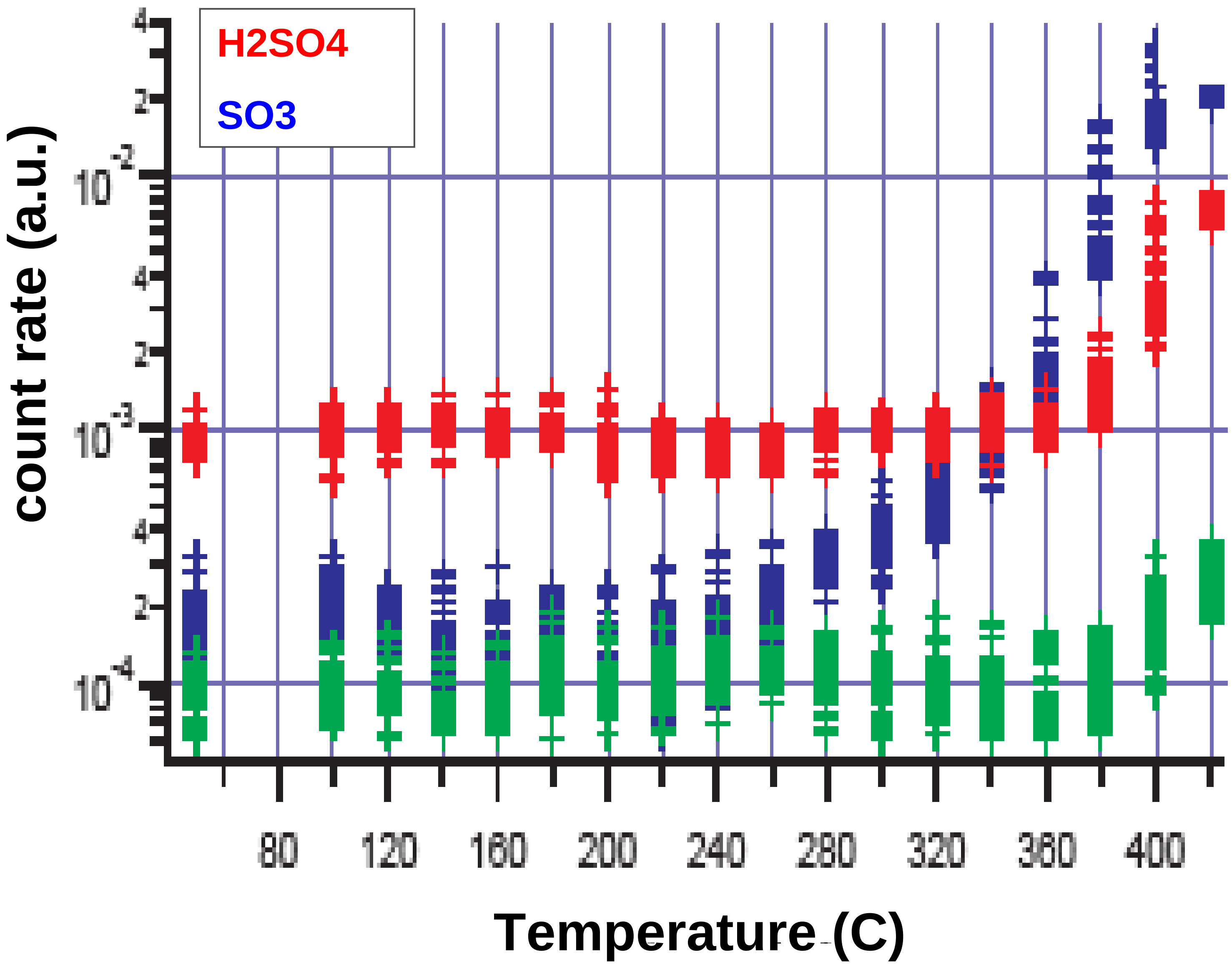
Sampling-T: 50 C

Thermodesorption: - 400 C

FSC=6 ppmM

no ATS !

Example of an off-line measurement of gas-phase H2SO4 and SO3



Thermodesorption of H_2SO_4

- H_2SO_4 condensate is more stable than H_2SO_4/H_2O condensate
- H_2SO_4 condensate does not seem to be ammonium sulfate ! (measured desorbed NH_3 is much less than H_2SO_4)

Di-carboxylic acids

Relative abundances of thermodesorbed acids

(for T= 120 C)

Ion Identification

- High precission mass measurements

- Fragmentation studies of mass selected ions:

  - for different collision energies

  - for different collision gas atoms (He , Ar)

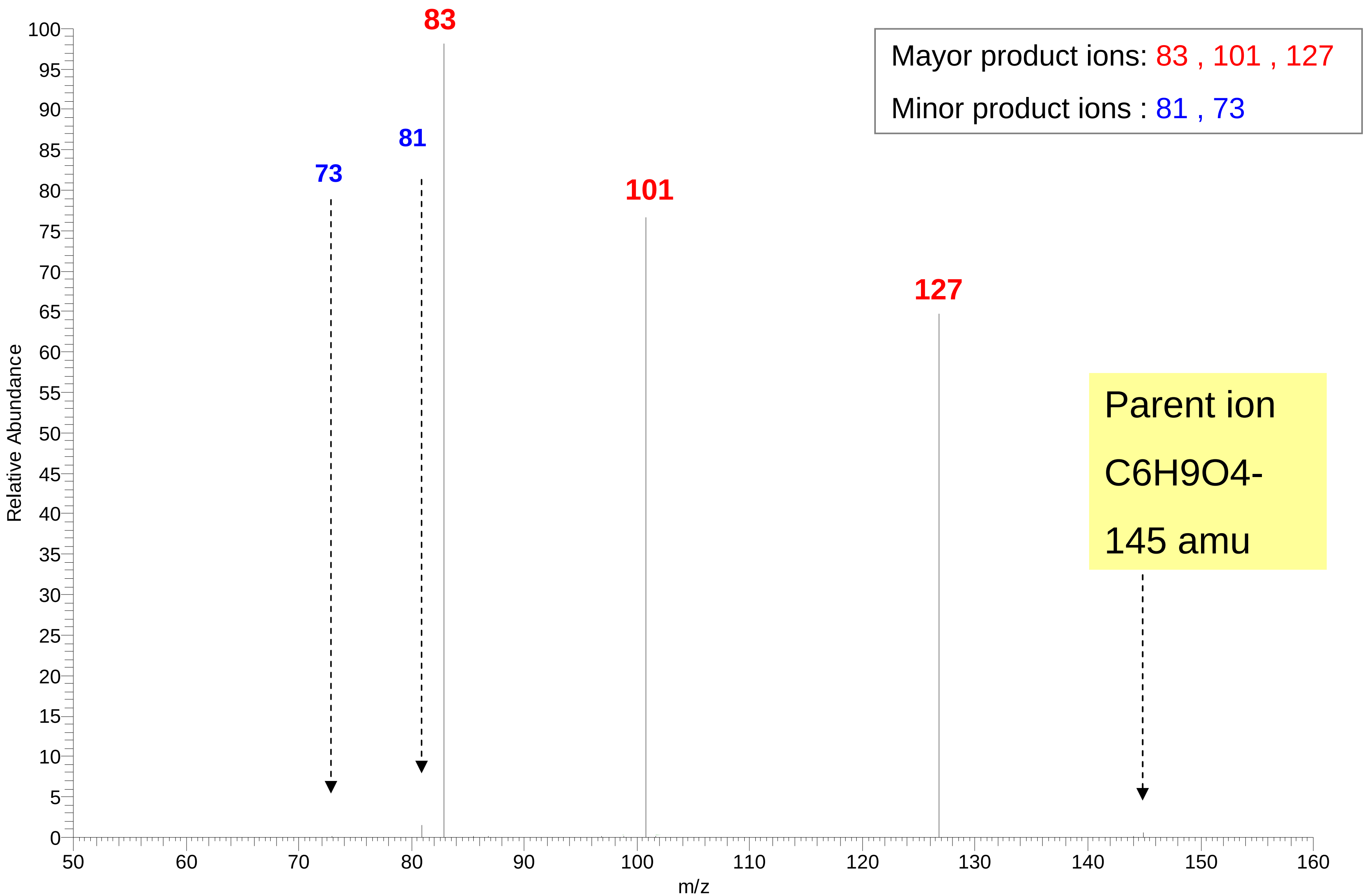
Fragmentation studies

Example:

Adipic acid $C_6H_{10}O_4$

Adipic acid

MS-MS mass spectrum: parent ion C6H9O4- ; colission gas He ; CE = 30 eV



Aerosol formation and growth

Conclusions

- $H2SO4$ increases with EL
- $H2SI4$ increases with FSC
- $H2SO4$ increases whith ATS
- Strong $H2SO4$ store and release effects

Summary and Conclusions

- H2SO4 increases with EL
- H2SI4 increases with FSC
- H2SO4 increases whith ATS
- Strong H2SO4 store and release effects
- Organic acids correlated with H2SO4
- NUP conc. increases with H2SO4
- NUP diameter increases with H2SO4
- NUP volume conc. încreases with H2SO4
- NUP occasionally correlated with acids other than H2SO4

- For more information see paper in preparation (contact: **frank.arnold@mpi-hd.mpg.de**

ThankYou

for your interest