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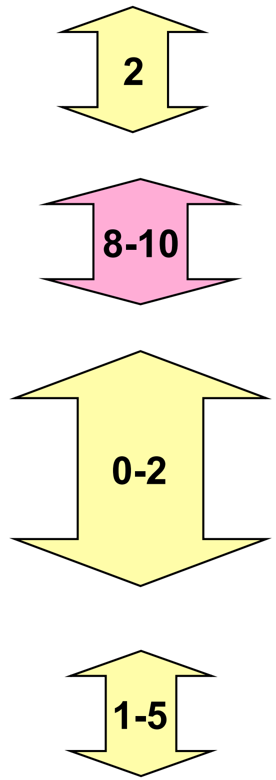
Vapours contributing to atmospheric particle formation and growth

Concentration levels

- **Air, 1 atm, 25°C** — **$\sim 2.5 \times 10^{19}/cm^3$**
- **Water RH100%, 25 °C** — **$\sim 7.7 \times 10^{17}/cm^3$**
- **Ammonia 1-10 ppt** — **$\sim 1\text{-}10 \times 10^{7}/cm^3$**
  - **ppt parts per trillion $1/10^{12}$**
  - **ppb parts per billion $1/10^{9}$**
- **Sulphuric acid** — **$\sim 10^{5}\text{-}10^{7}/cm^3$**
- **Aerosol particles** — **$\sim 10^{2}\text{-}10^{4}/cm^3$**



What is required from a vapour to nucleate in the atmosphere

Atmospheric nucleation is almost always multicomponent

- If some molecule is really strongly attracted **to others of the same type**, it is unlikely to make it to the gas phase
  - Potential molecules formed in the air by chemical reactions
  - Organic oxidation products, **sulphuric acid**

- Possible ”pairs” of compounds strongly attracted to each other:
  - **Acid – base**
  - **Anion – cation**
  - H-bond **donor – acceptor** pairs
  - *E.g.* H_2SO_4 – NH_3 – H_2O *contains all three interaction types!*

Hydrochloric acid (HCl)+ methylamine (CH_3NH_2)

Courtesy of Jim Smith, National Center for Atospheric Research (NCAR), Boulder , USA/
University of Esatern Finland

Experimental challenges:
Diameter - number of molecule conversions

- **Diameter 0.4 nm = 1 molecule**
- **Diameter 1 nm ~ nucleation = 15 molecules**
- **Diameter 2.5 nm = 100-200 molecules**
  - **Composition represents the molecules related to growth**
- **Diameter 20 nm = ~10^5 molecules**

R↯R^2↯R^3

Atmospheric particle composition measurements: indirect methods

- Hygroscopicity
  - E.g. HTDMA: detection limit ~4 – 10 nm, depending on the particle concentrations (the sample needs to survive through 2 DMA systems)
  - CPCB: 2 – 10 nm, data interpretation challenging
- Volatility
  - VTDMA: detection limits similar to HTDMA measurements
- Density
  - E.g. ELPI-based systems, > 10 nm particles

Atmospheric particle composition measurements: direct methods

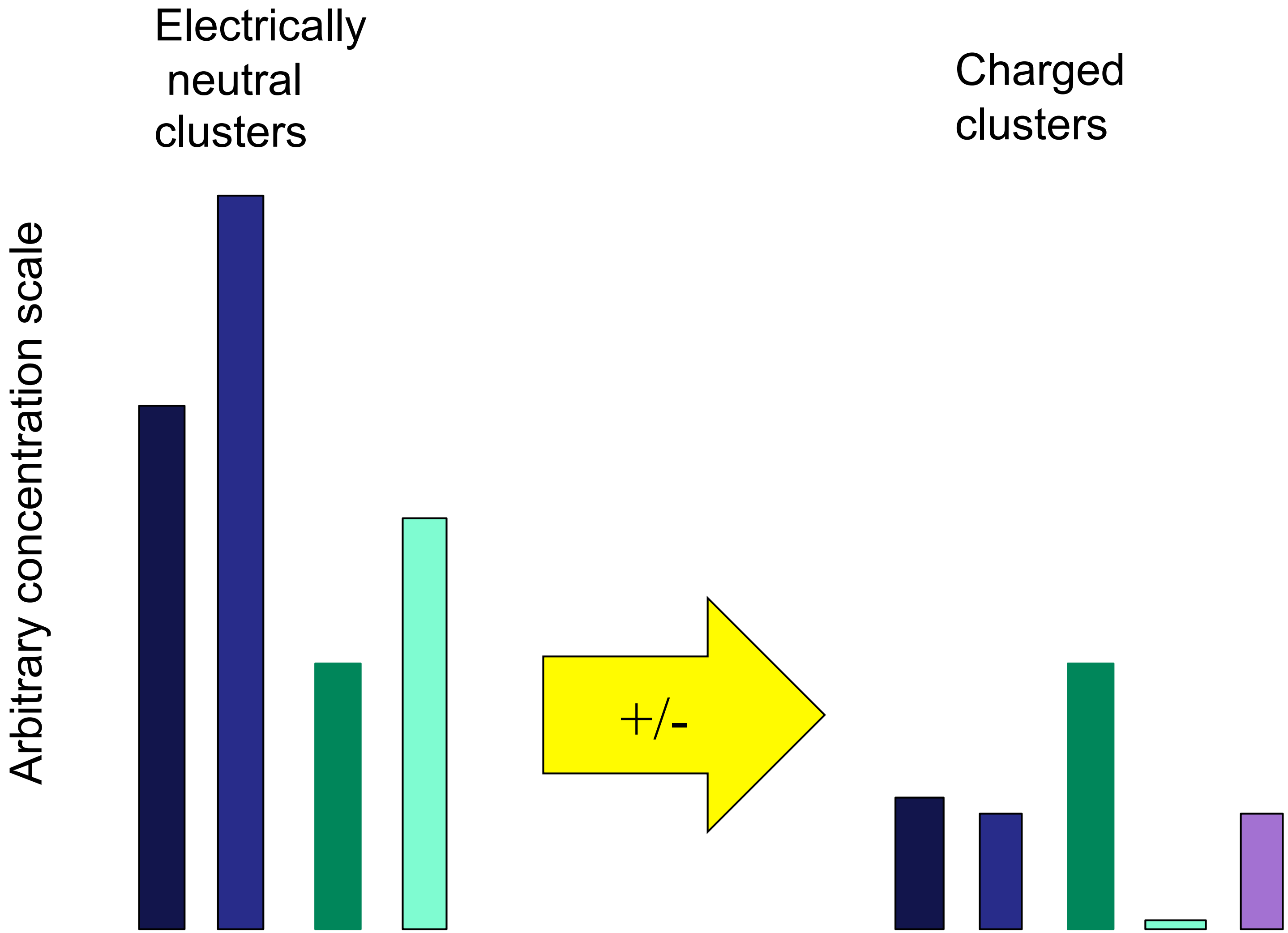
- Filter sampling + spectrometric analysis
  - Large enough masses needed to be collected
    - Typically 1-2 samples a day
    - Large particles dominate the samples

- Mass spectrometers
  - CIMS: Chemical Ionization Mass Spectrometer
  - AMS: Aerosol Mass Spectrometer
  - API-ToF Atmospheric Pressure Interface time-of-flight MS
    - Large enough mass needs to collected
    - Difficult to distinguish clusters from gas molecules
    - Trade-off between size, mass and time resolution and sensitivity
    - Charging affects the sample

Neutral-charged dilemma in atmospheric mass spectrometry

- Most molecules and nanometer-scale clusters **neutral**
- All mass-spectrometric methods for studying clusters require them to be **charged**
- **Charging options**:
  - in the **instrument** (chemical ionization, corona charging, …)
  - in **nature** (cosmic rays, radon)
  - **violent** (e.g. corona discharge)
    - all clusters are charged, some/all may break up
    - new/artificial ions & cluster types may be formed.
  - **gentle** charging (*e.g.* chemical ionization)
    - depends on composition
    - some clusters may not be charged
    - something may leave the cluster due to charging

Charging may change the relative abundances of clusters



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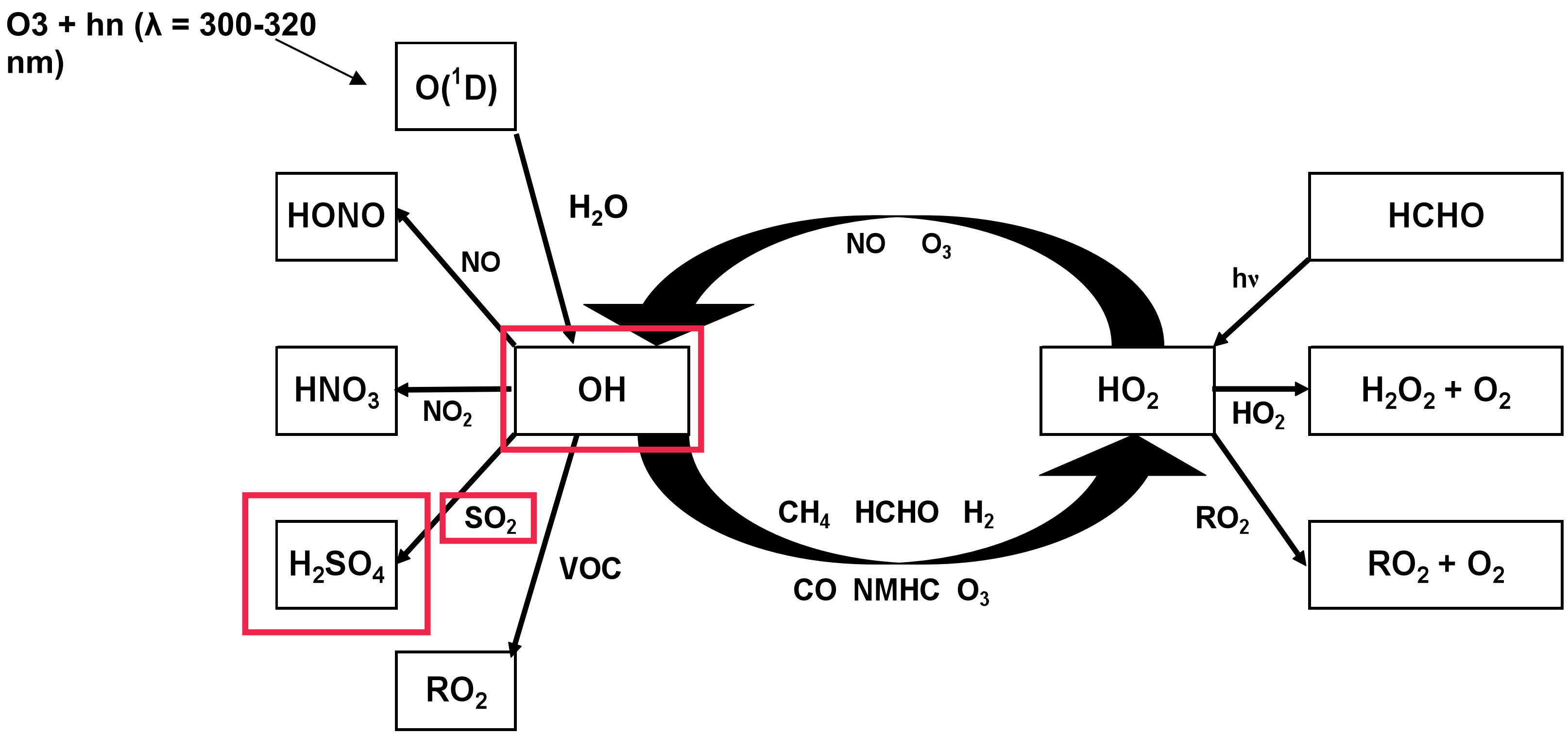
Sulphuric acid, ammonia and amines

Atmospheric production of sulphuric acid

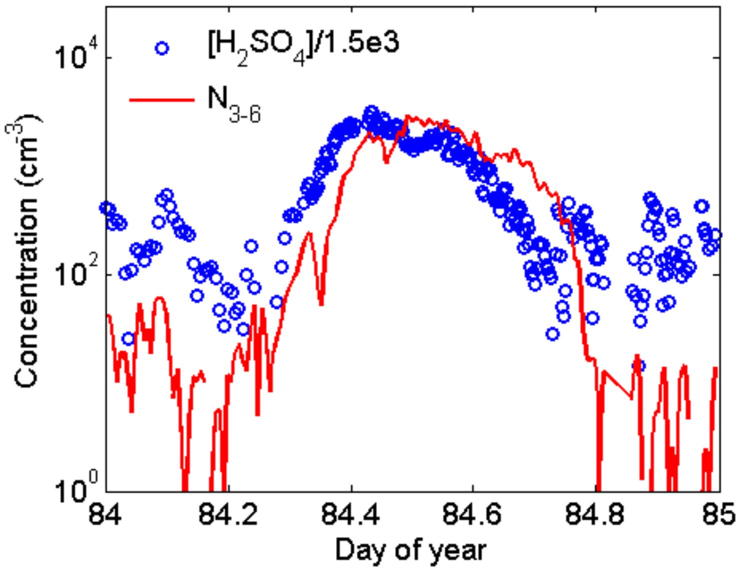
- H_2SO_4 produced by oxidation of SO_2 by OH

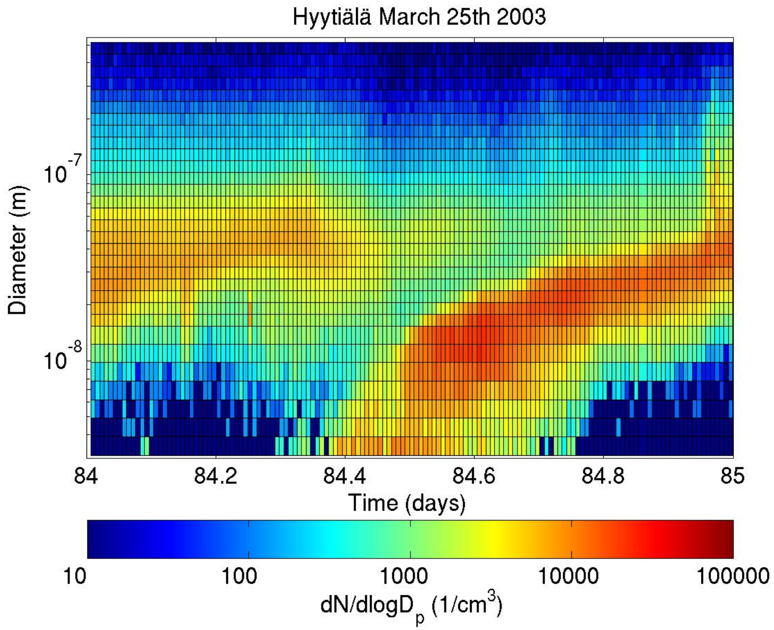


- Main sink the condensation on aerosol particles (CS)

Boy et al., *ACP* 2005

Close correlation between atmospheric particle formation and sulphuric acid



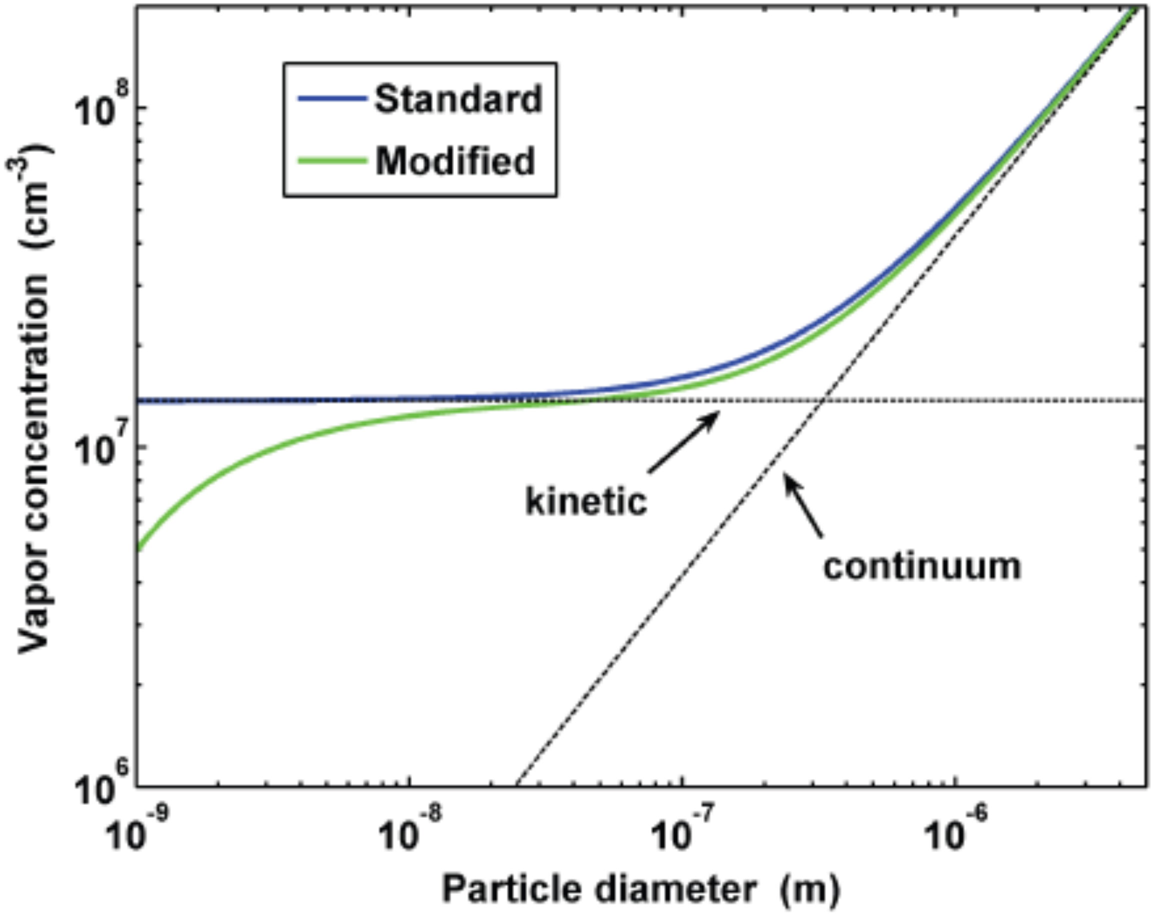


- Time delay of some minutes to hours

- Proportionality: J= A $[H_2SO_4]^{1...2}$
- A < kinetic collision rate (≈kinetic rate/100)

Sulphuric acid cannot explain nanoparticle growth rates

Vapour concentration required for 1 nm/h



- Typical particle growth rates 1-20 nm/h

- Typical sulphuric acid concentrations ~10^6 cm^{-3}

Nieminen et al., 2010

$J= A [H_2SO_4]^{1...2}$
What does slope 1-2 mean?

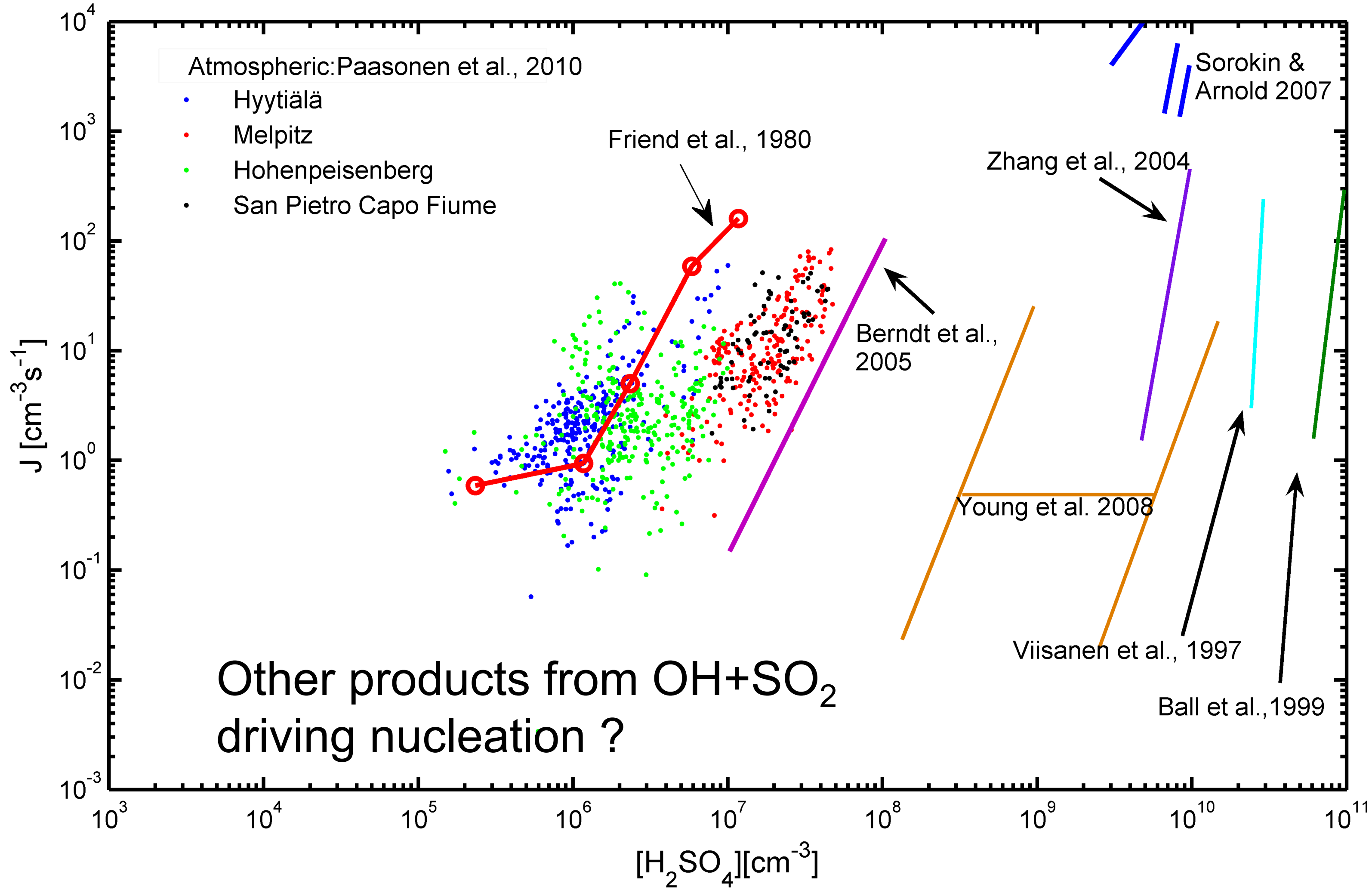
- before atmospheric H_2SO_4 measurements classical picture: slope around 7-8

- observed slope 1-2 induced a revolution in thinking

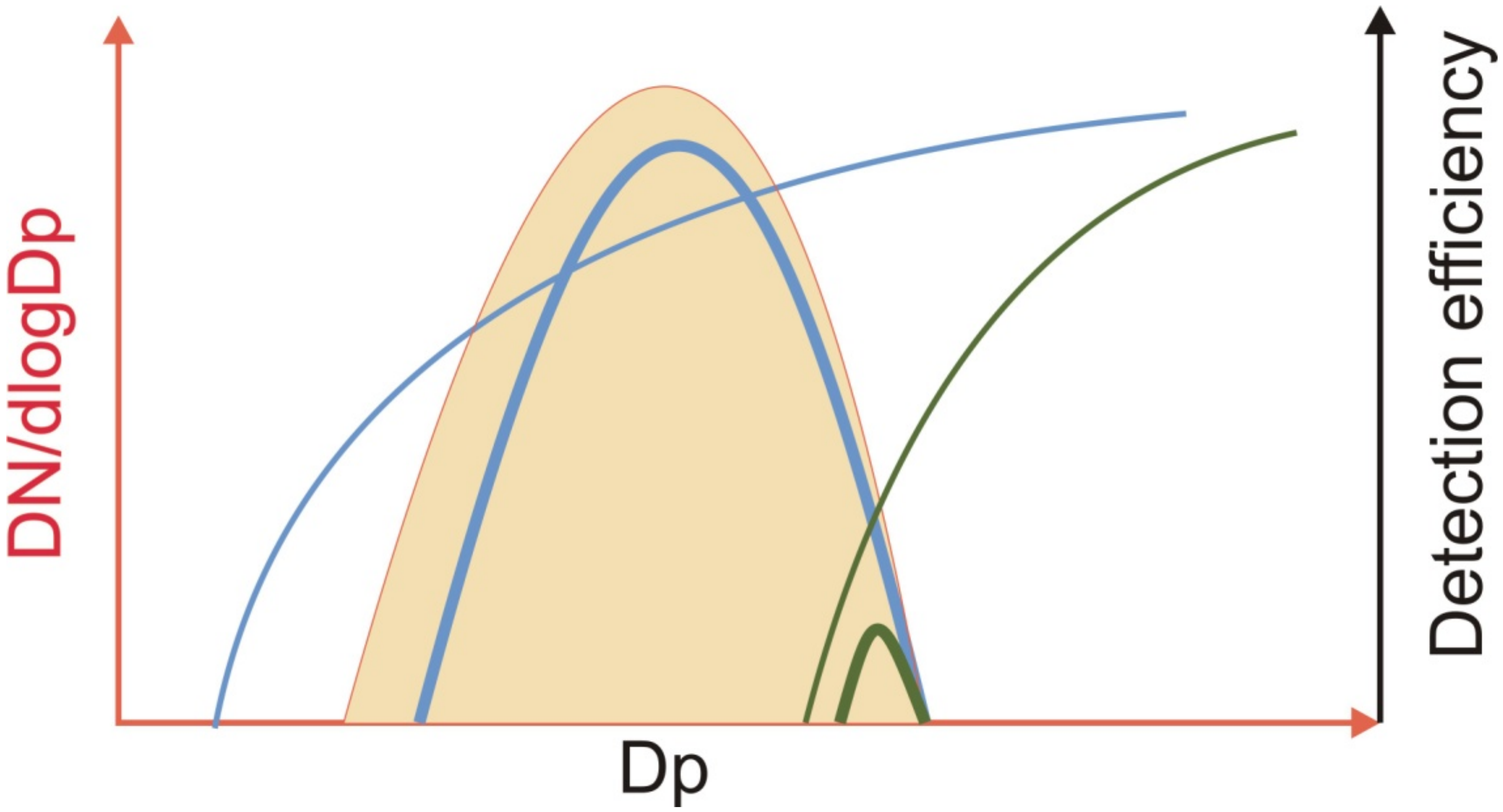
- 2 would be the slope if every collision of 2 sulphuric acid would result in stable particles
  "kinetically controlled ~~nucleation~~"
- magnitude of pre-factor A shows that it is not every collision

- 1 would be slope if only 1 sulphuric acid were needed to "activate" some unknown compound/cluster

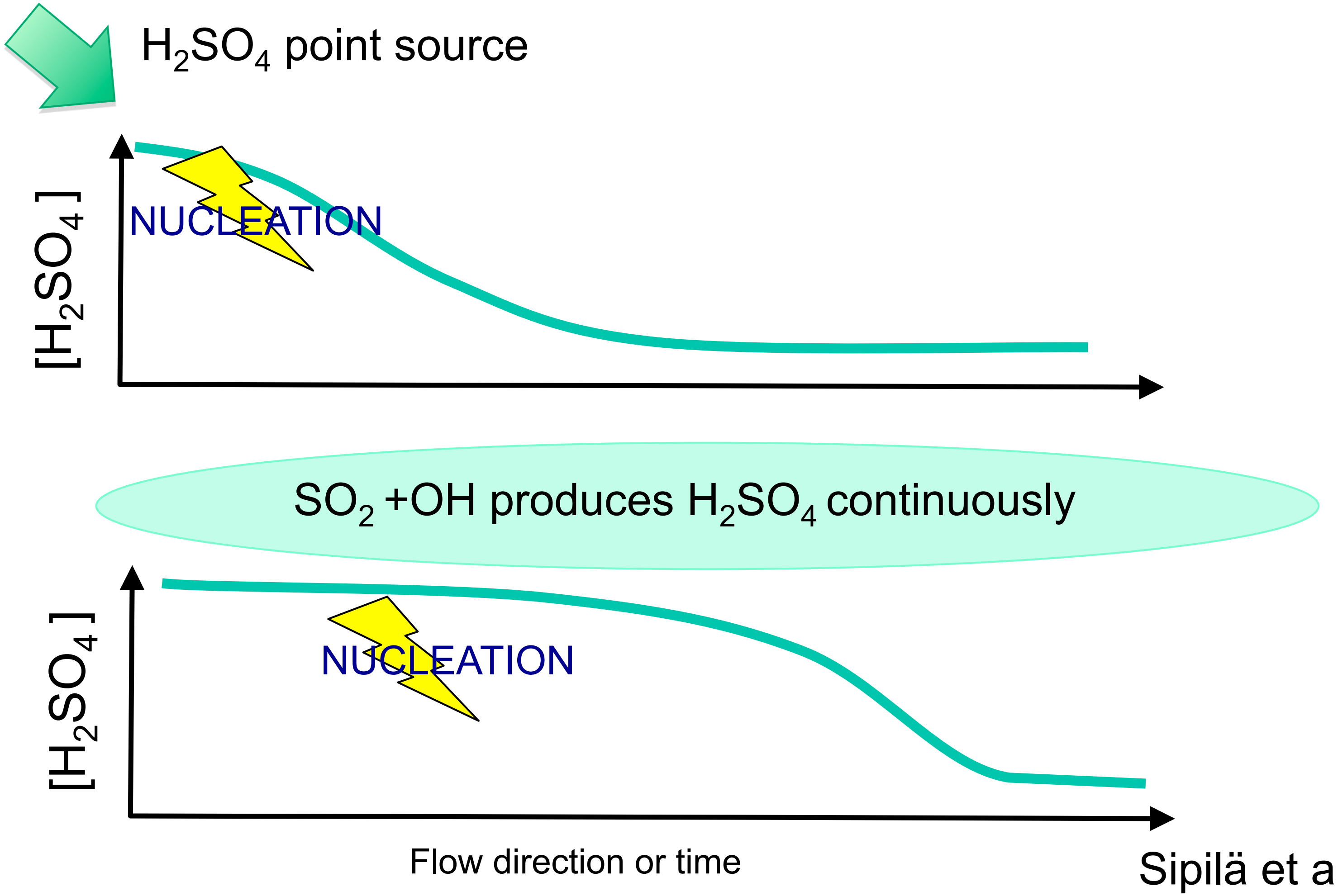
Flow tube experiments on $H_2SO_4 + H_2O$ conflicting?



Only small fraction of nucleated particles counted with traditional instruments



Sulphuric acid concentration not always high enough to grow nucleated particles to detection limit before they are lost (walls, coagulation)



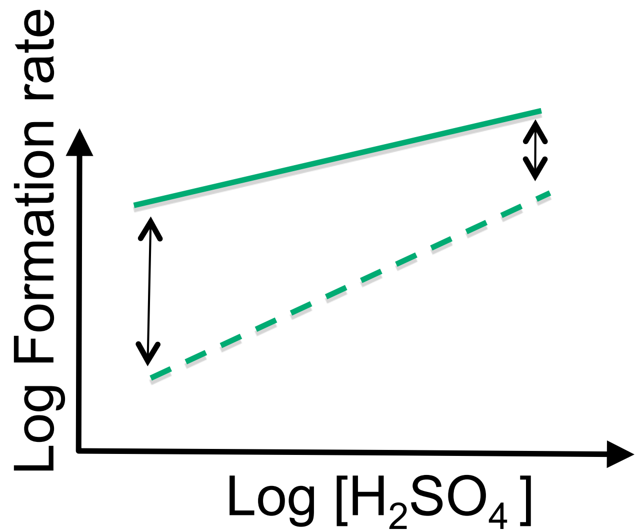
Sipilä et al, Science, 2010

Mismatch due to different particle detection instruments and sulphuric acid profile

- Only clusters that have grown to the detection limit of the instrument are counted
  - clusters lost to walls or by coagulation
  - for reliable results you need to detect very small clusters

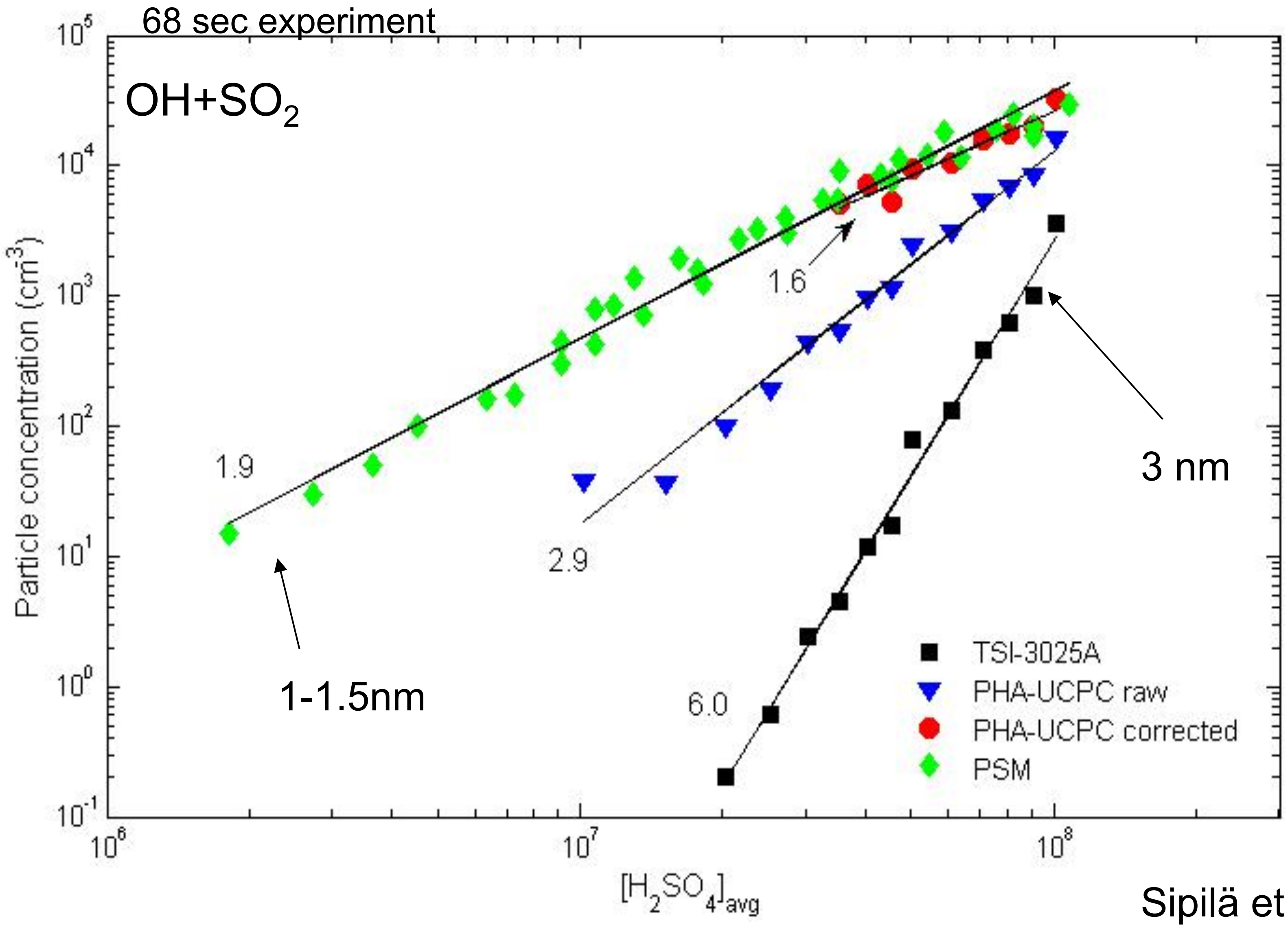
- Low sulphuric acid concentration enough for nucleation
  - growth slow

- Lower [H_2SO_4], lower survival rate
  ➔ apparent slope larger



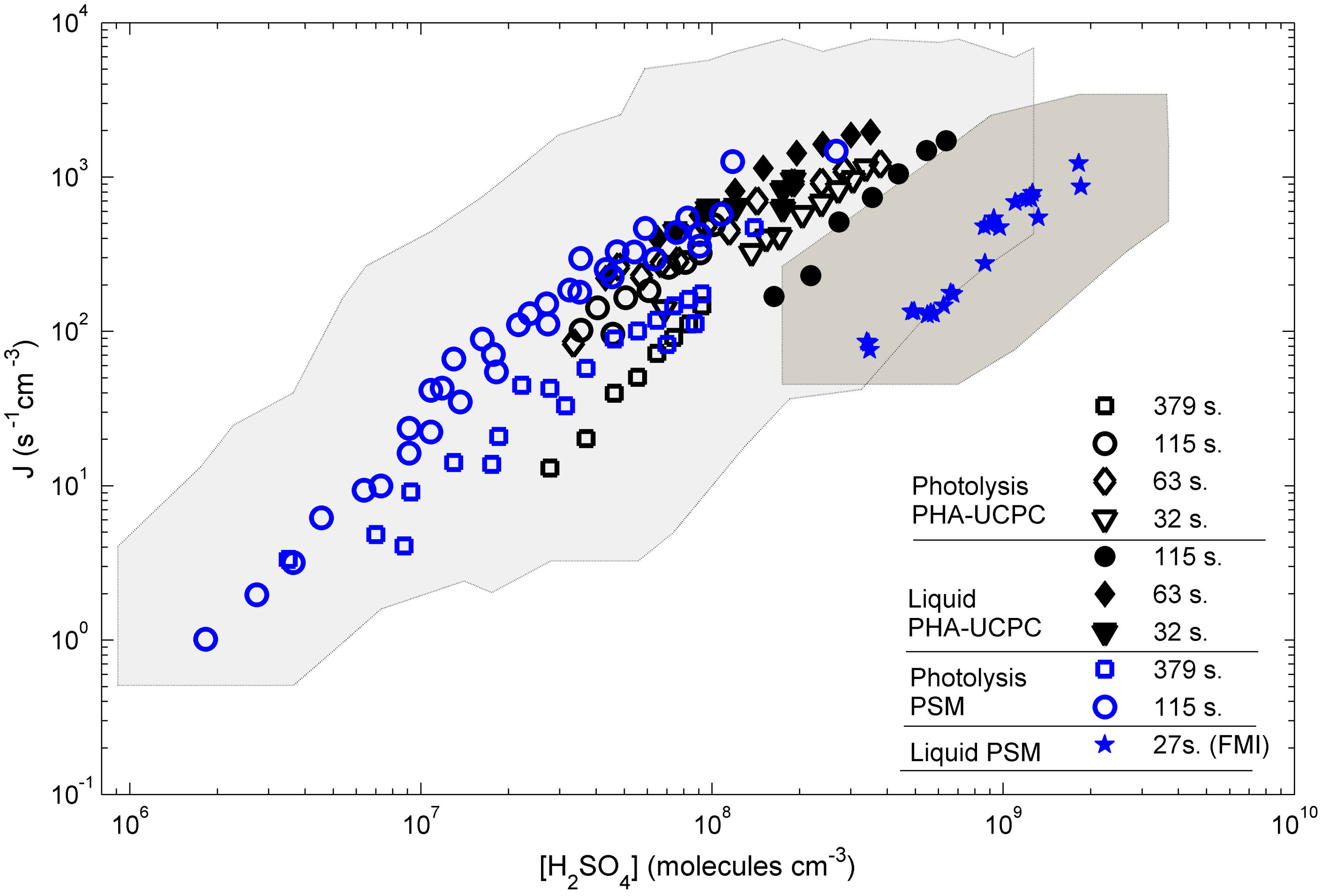
Sipilä et al, Science, 2010

Insensitive detector does manipulate the results



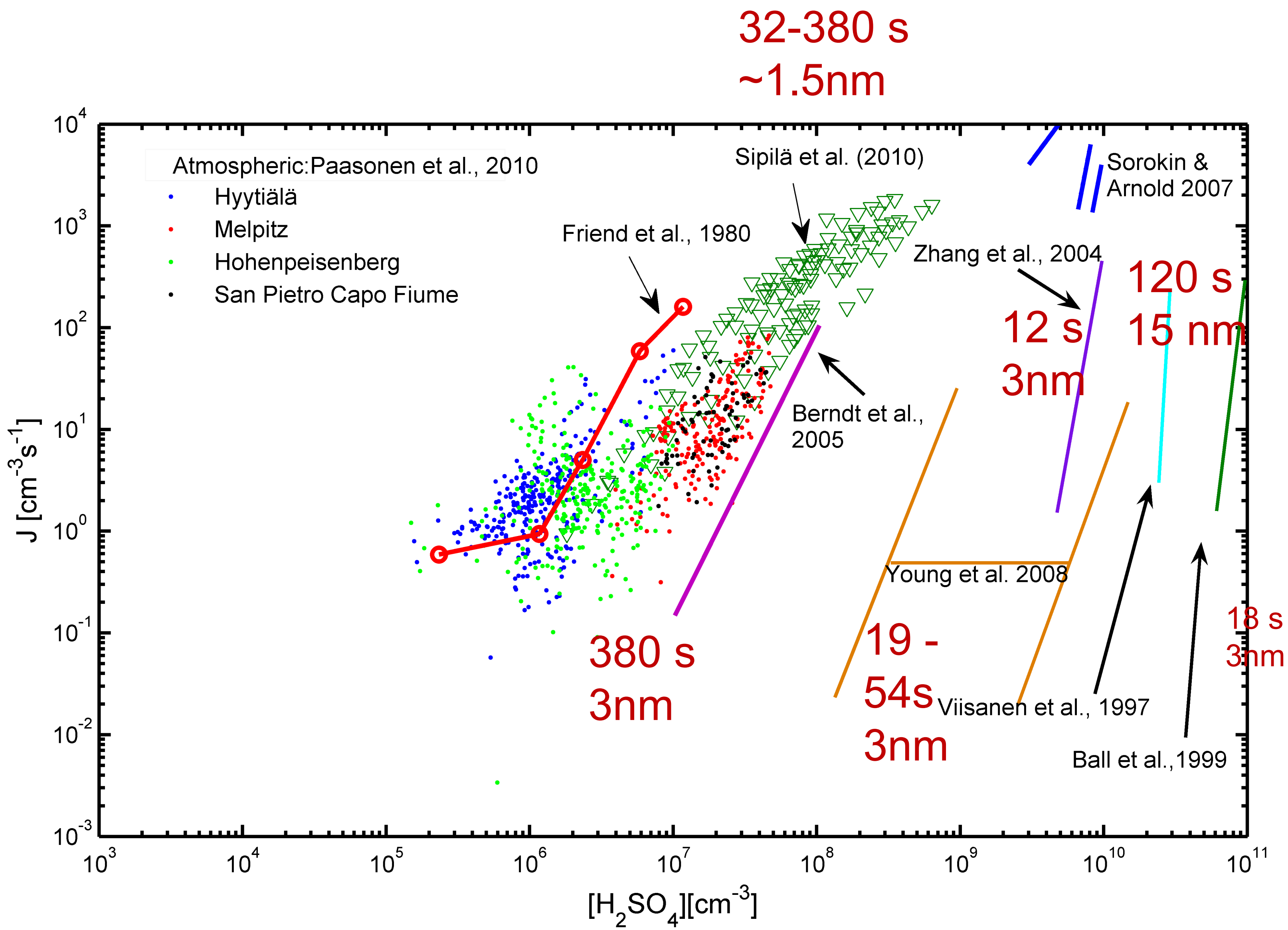
Sipilä et al., Science, 2010

New instruments with low detection treshold: in-situ and liquid sample data merge



Sipilä et al, Science, 2010

New instruments with low detection treshold: in-situ and liquid sample data merge



Sulfuric acid & nucleation: summary of observations

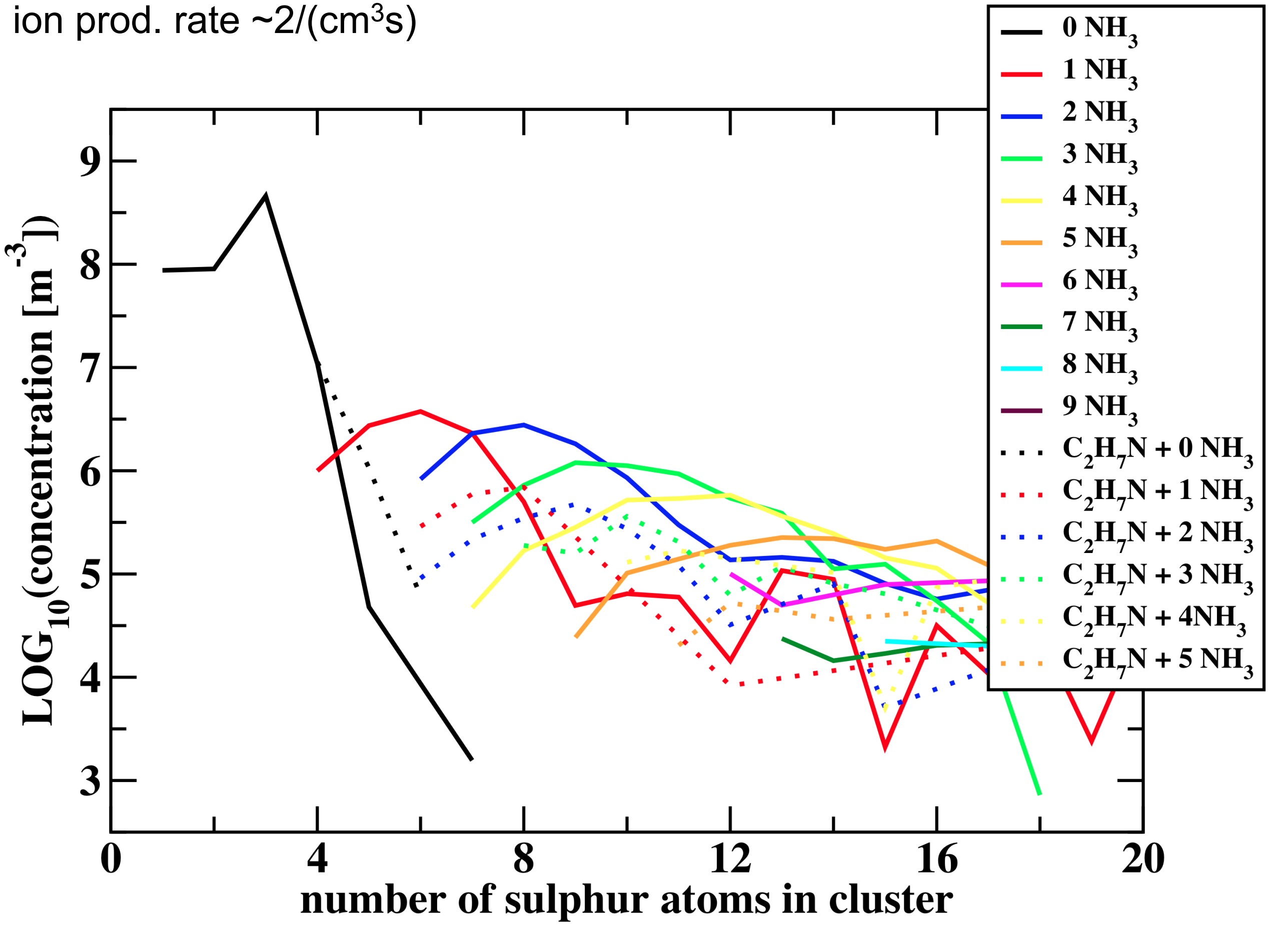
- Sulphuric acid one of the very few ”common factors” for nucleation observed **around the world**.
  - Sulphuric acid – water nucleation (& ions) likely to be dominant in the **upper troposphere**
  - Near **ground level**, H_2SO_4 + H_2O is not enough
  - Some third compounds needed
- Acid likes base: only a few basic compounds in the gas phase ammonia and amines most prominent

Gas phase measurements of trace gases difficult

- Continuous, reliable H_2SO_4 field measurements are rare
- NH_3 measurements even more rare, detection limit high
- Amine measurements in the gas phase almost nonexistent
- Dimethylamine observed in larger particles (filter samples) especially during nucleation events

Atmospheric pressure Interface time-of-flight mass spectrometry (API-Tof/MS) at CLOUD experiment in CERN

T = 19 °C, RH = 38% H_2SO_4] = 5×10^8/cm^3 J_3 = 5 /(cm^{3}s)
ion prod. rate ~2/(cm^{3}s)



Trace amounts of ammonia and amines present even in cleanest conditions

Concentrations below current detection limit

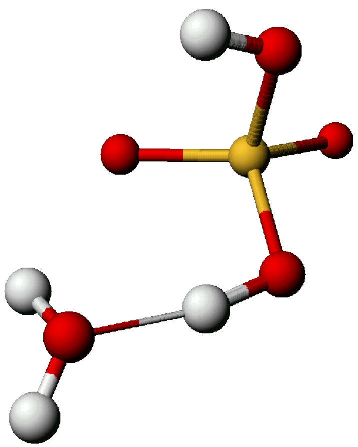
…but…

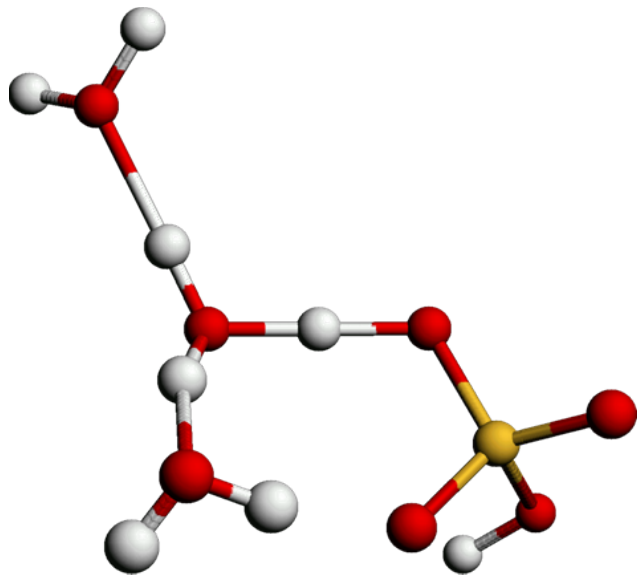
comparable with sulphuric acid concentration when nucleation occurs

Number of sulphur atoms n= 1 HSO_4^- + (n-1) H_2SO_4

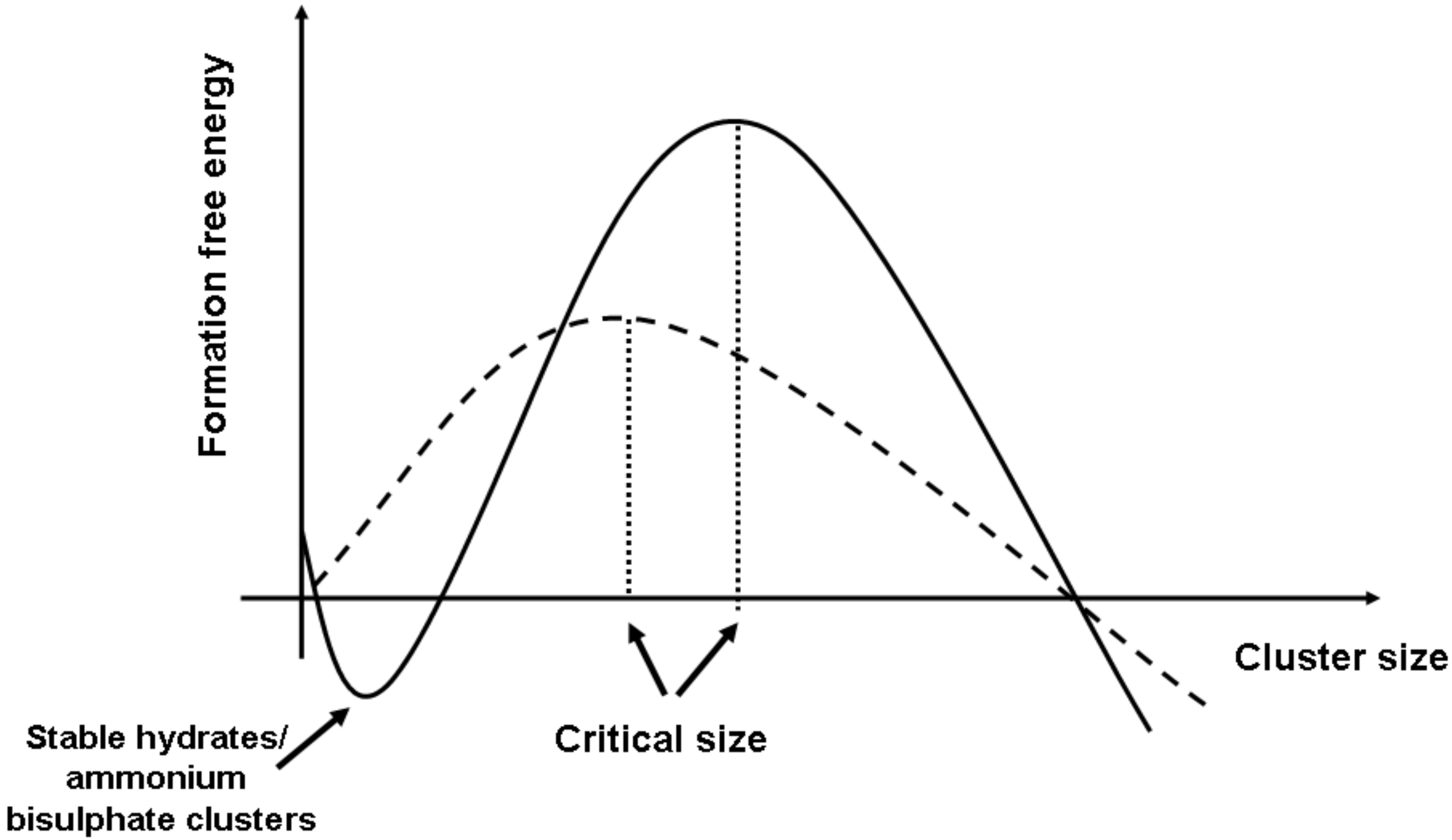
Specific issues with sulphuric acid

- Sulphuric acid forms pre-nucleation clusters
  - hydrates with water
  - small clusters with ammonia and amines

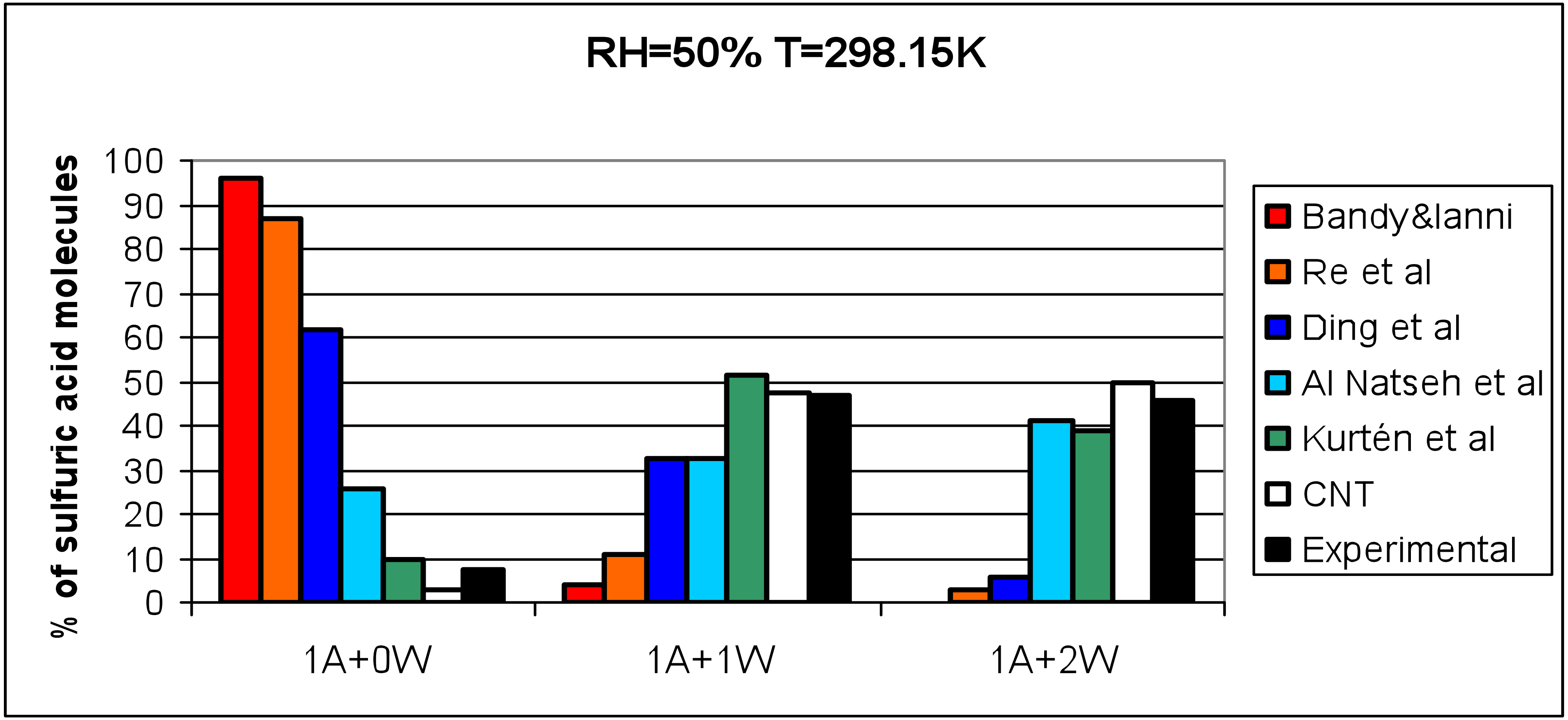


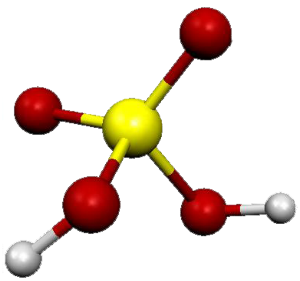


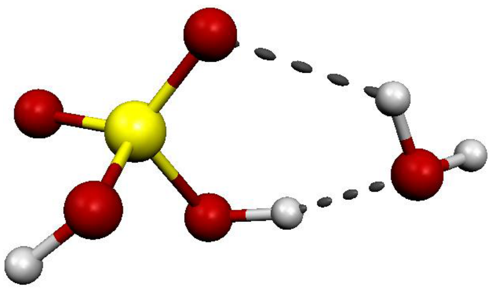
The effect of hydrate formation on the free energy curve

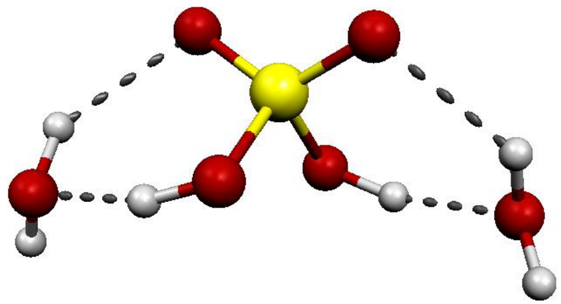


Extent of sulphuric acid hydration according to different models

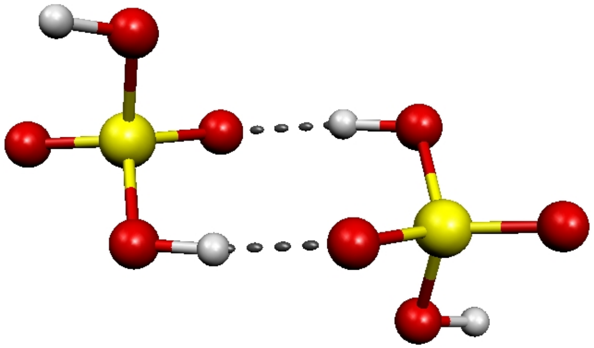




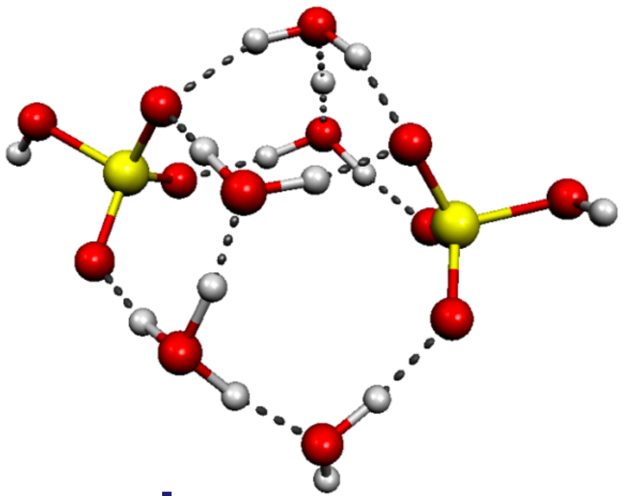




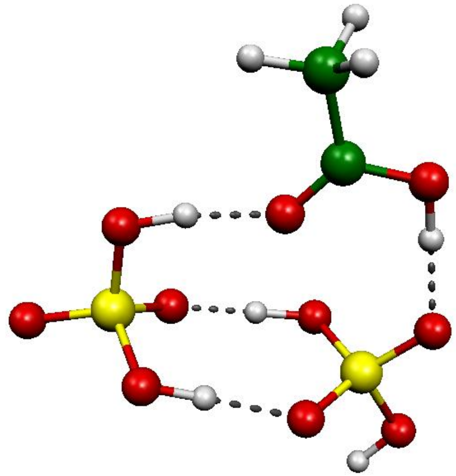
Evaporation of sulphuric acid from a two-acid cluster



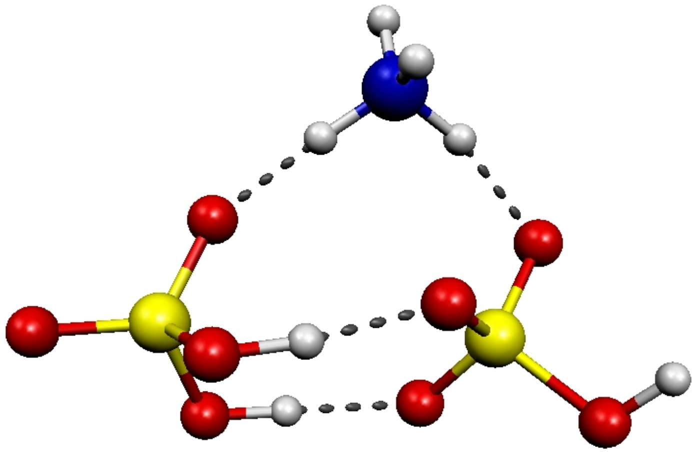
pure sulfuric acid
$k_{evap} \approx 10^{\mathbf{4}}$ $(10^{2}...10^{6})$ s^{-1}



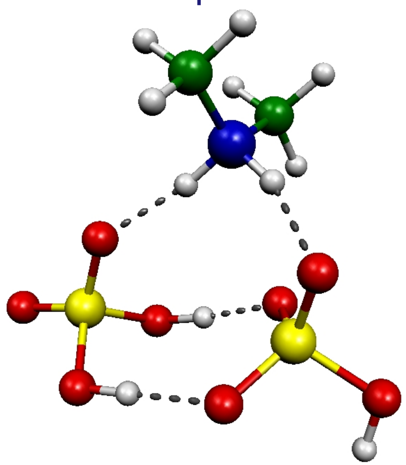
water
$k_{evap} \approx 10^{\mathbf{2}}$ $(1...10^{4})$ s^{-1}



small organic acids
$k_{evap} \approx 10^{\mathbf{8}}$ $(10^{6}...10^{10})$ s^{-1}

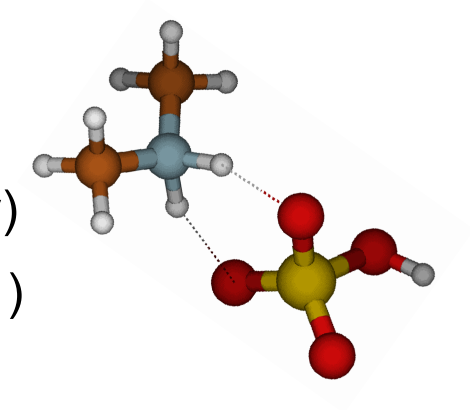


ammonia
$k_{evap} \approx 10^{\mathbf{-1}}$ $(10^{-3}...10)$ s^{-1}



amines
$k_{evap} \approx 10^{\mathbf{-4}}$ $(10^{-6}...10^{-2})$ s^{-1}

Interpreting charged cluster measurements: CIMS

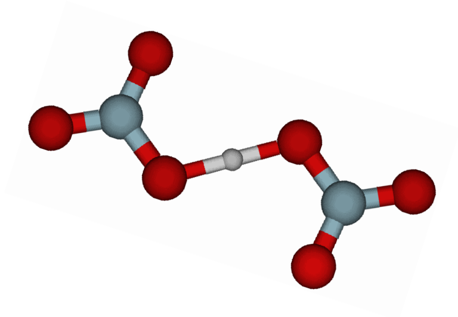


- Nitrate – based **CIMS** (Chemical Ionization Mass Spectroscopy) selective to sulphuric acid(≈ only acid stronger than nitric acid)

- (NO_3^- + H_2SO_4 → HNO_3+HSO_4^-)
- NO_3^-•HNO_3 + H_2SO_4→2HNO_3+HSO_4^- bisulphate ion formation

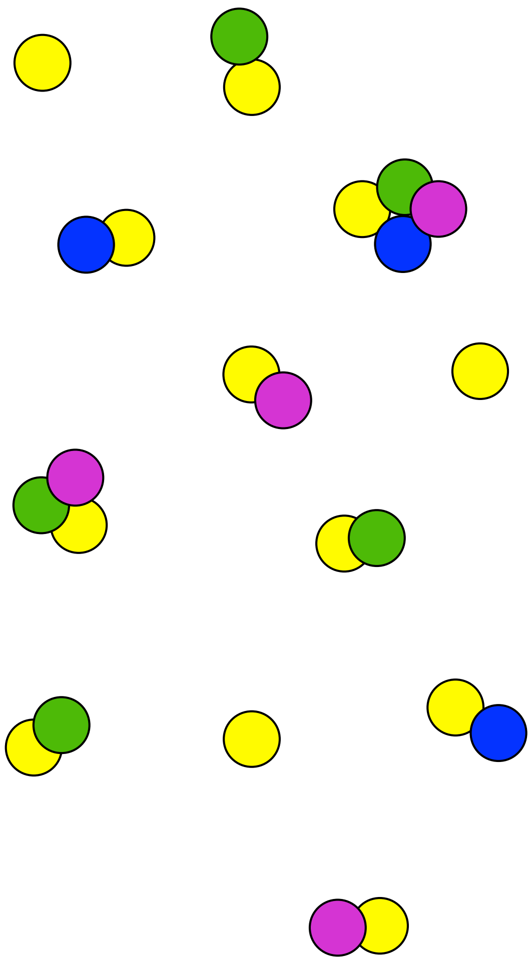
- Measurements of “total” [H_2SO_4] may not measure **base-containing** sulphuric acid clusters (*e.g.* sulphuric acid – amine/ammonia clusters)

- NO_3^-•HNO_3 does **not have high enough proton affinities** to charge all sulphuric acid – containing clusters



- NO_3^-•HNO_3 + H_2SO_4• C_2H_7N → ?
- NO_3^-•HNO_3 + H_2SO_4• NH_3→ ?

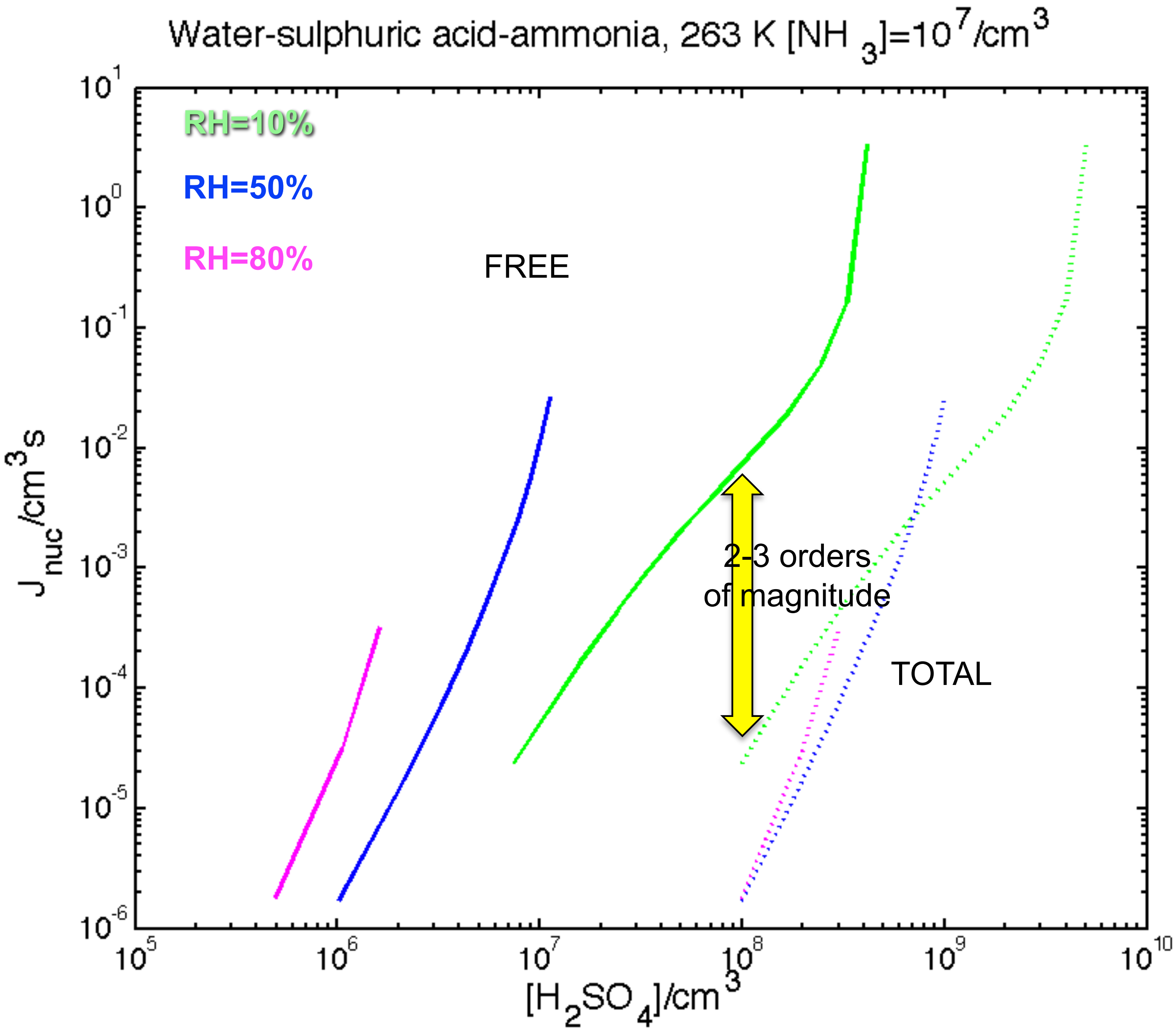
What do we measure when we measure the "sulphuric acid concentration"?



All yellow balls	=12
Free yellow balls	=3
Free + attached to blue only	=5
Free + attached to blue only + attached to green only	=8
Free+ attached to blue only+ 30% of attached to green only	=6

99,… % of sulfuric acid molecules attached to water & trace gas molecules

For theorists it is important to know what the measured sulphuric acid concentration represents



Formation of H_2SO_4 dimers unlikely to occur without a stabilising compound X

- X probably leaves when “dimers” are charged/ enter vacuum

- The M/D ratio changes from ~100 to ~200 in RH range from 16 to 57% at 25 ^oC.

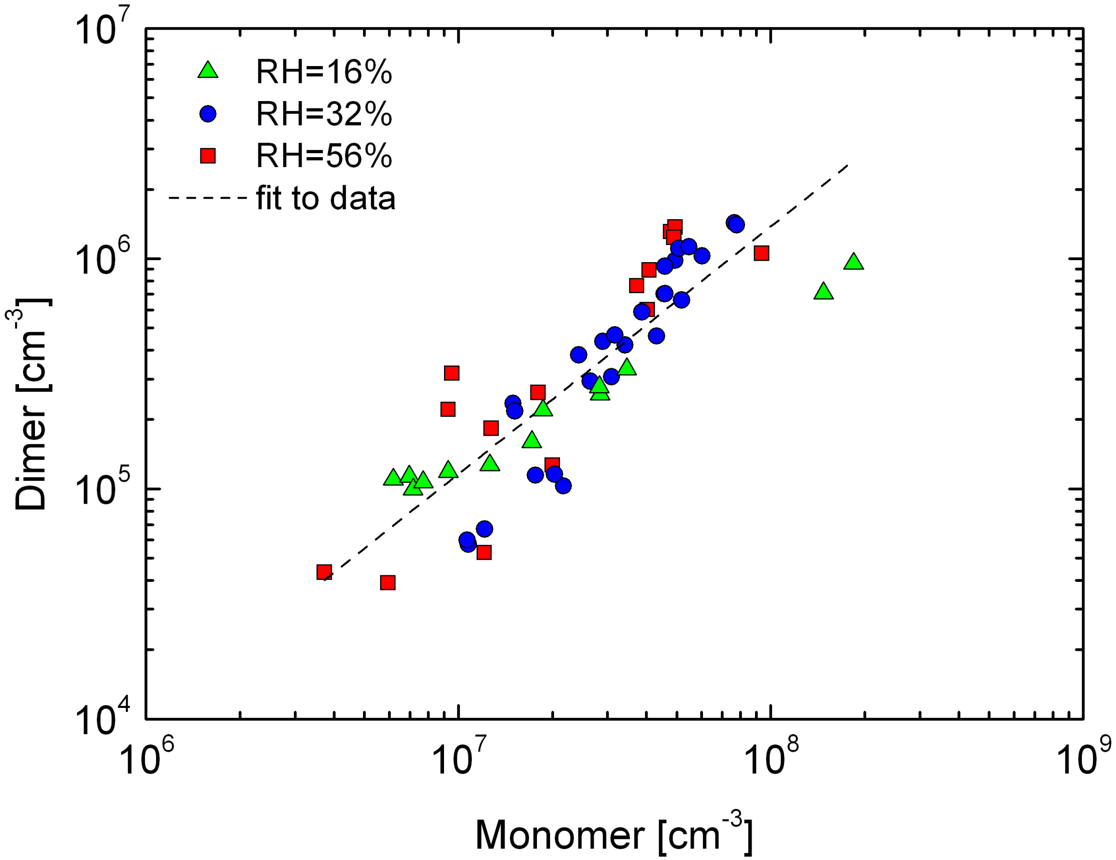
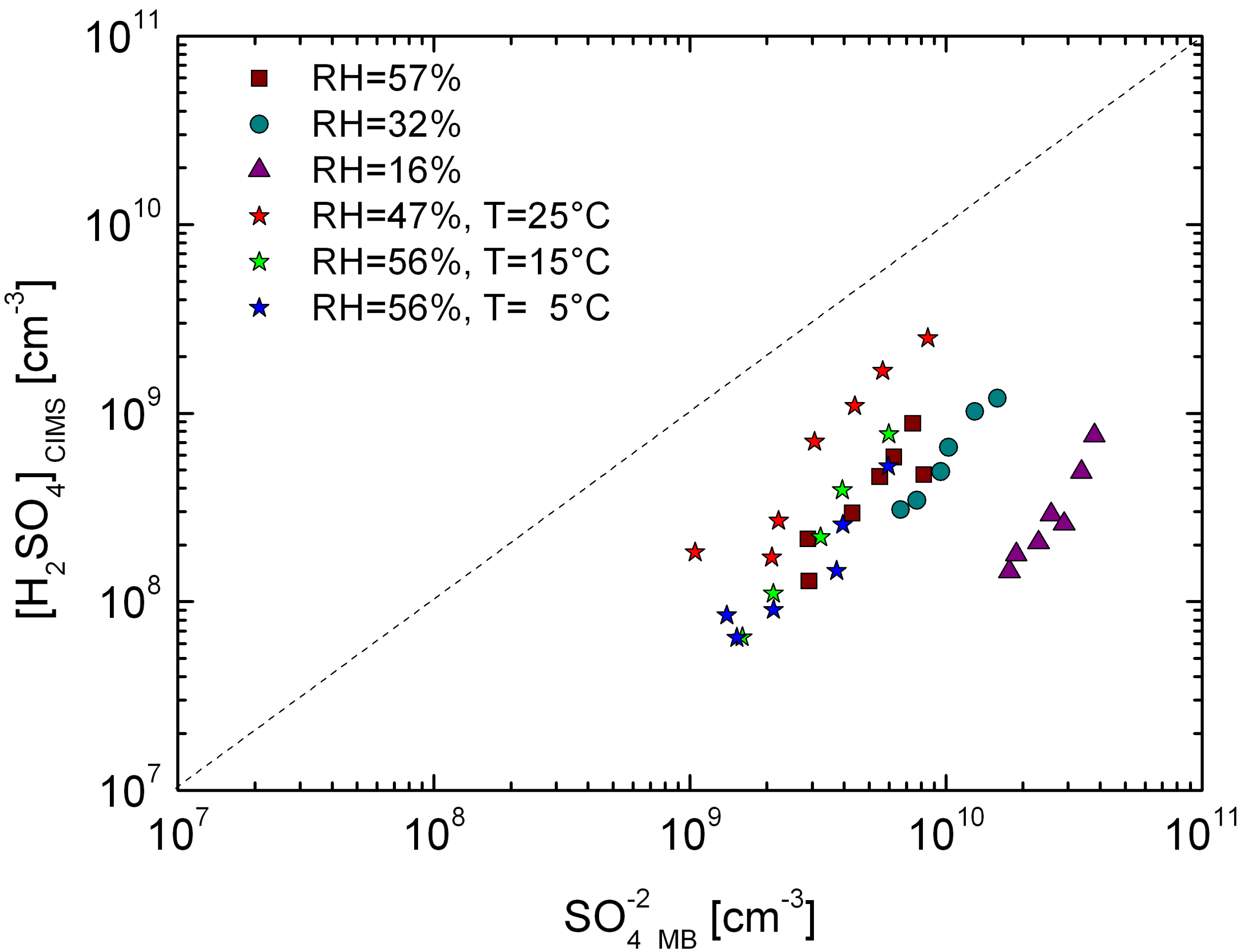


Figure Kimmo Neitola et al
Finnish Meteorological Institute

CIMS counts about 20% at RH ~50% and only about 1% at RH ~16% of total sulfate concentration measured with bubblers



Shielding of H_2SO_4 molecules by water molecules by hydration

- CIMS showed decreasing count on decreasing RH, discrepancy with hydration

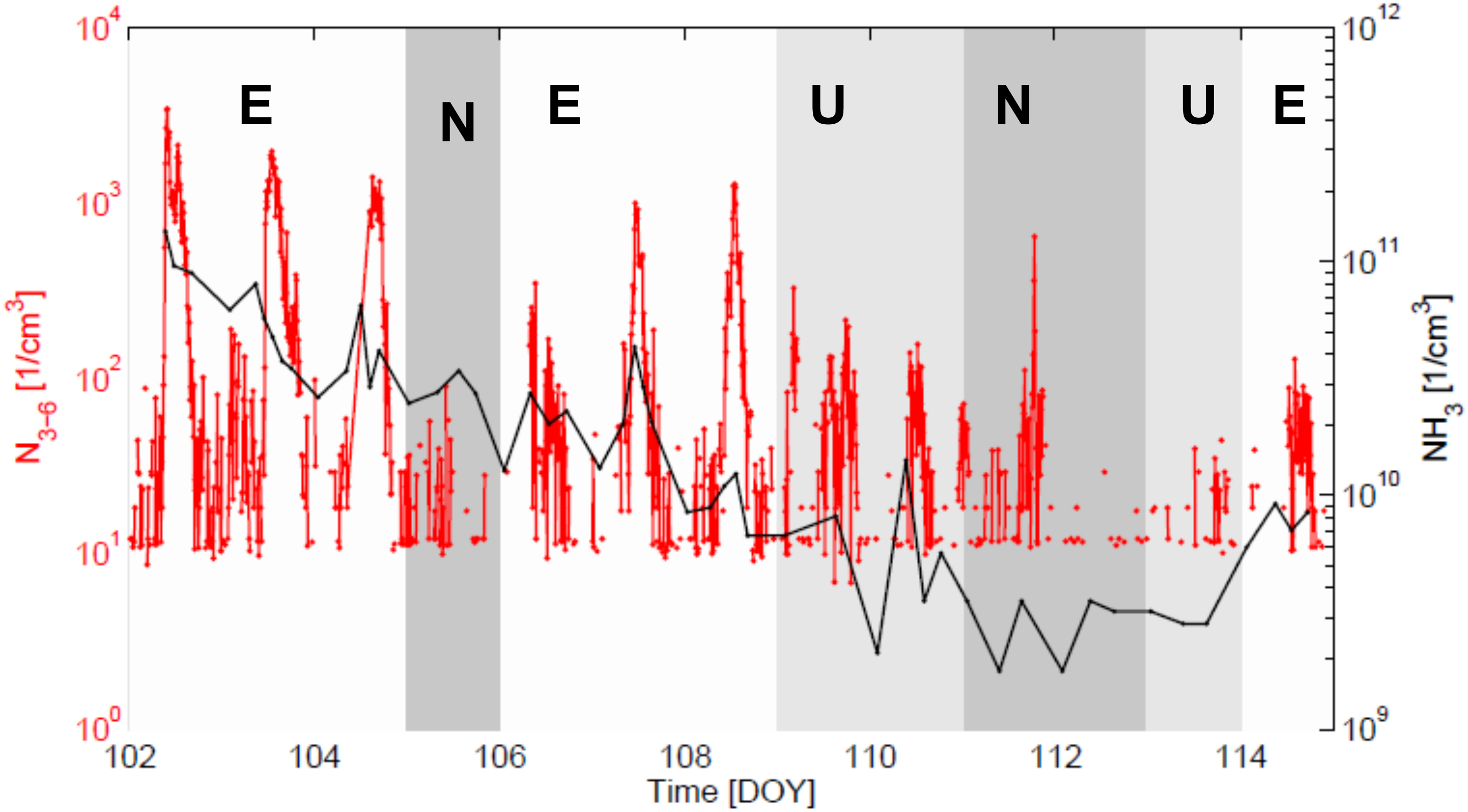
Shielding by ammonia (forming ammonium sulfate or bisulfate) from water

- The IC det. limit for ammonia is 0.02 mg/l → order of magnitude higher than H_2SO_4 conc.

Figure Kimmo Neitola et al
Finnish Meteorological Institute

Atmospheric results from Hyytiälä: Ammonia vs. particle formation rates

- In Hyytiälä no clear signs of correlation

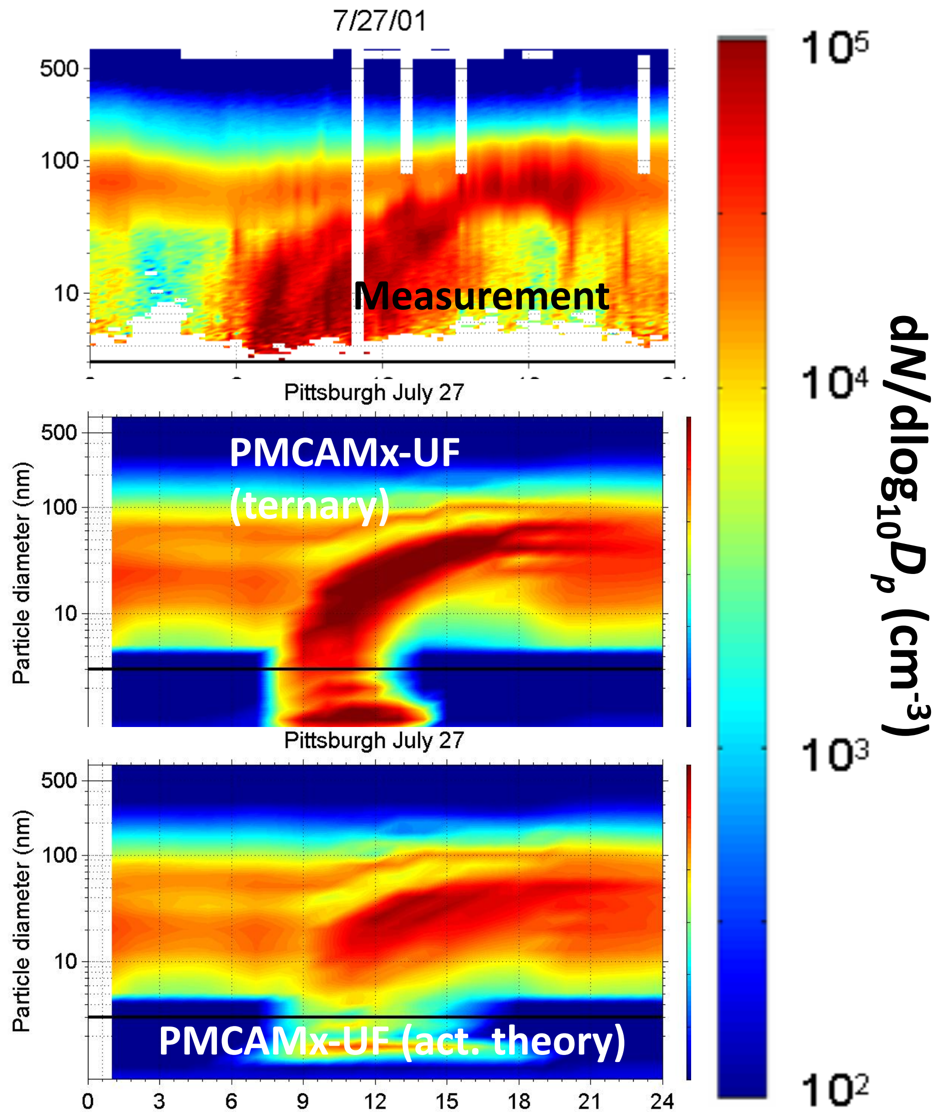


- What if ammonia is important but not limiting?

Sulphur-rich atmosphere of Pittsburgh: Implications on the role of ammonia / amines

- Results from Pittsburgh, PA, USA:
  - Regional air quality model PMCAMx-UF
  - Semi-empirical parameterization based on ternary nucleation model seems to work best
  - Sulphuric acid explains nearly all of the growth too!

- Ammonia a tracer for amines?



Jung et al., AST 2008

Most serious problem of using classical nucleation theory in atmospheric nucleation?

- Extent of proton transfer
  - CNT assumes bulk liquid – in practise complete proton transfer ?
  - BUT in smallest cluster no proton transfer

➔ Serious overbinding

$(H_2SO_4)(NH_3) \rightarrow H_2SO_4 + NH_3$

k_{evap}, CNT = 3×10^{-8} 1/s

k_{evap}, Quantum chemistry = 2×10^{5} 1/s