Effects of high RH on α-pinene SOA phase partitioning

Göteborg summer school 26/06/2008

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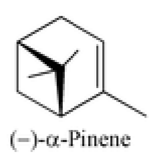
Motivation

- Current atmospheric models cannot account for observed organic aerosol mass.
- Identify mechanisms that contribute to increasing predicted secondary organic aerosol (SOA) mass.
- The influence of humidity on SOA gas-particle phase partitioning is one such potential effect.

Outline

- partitioning theory
  - why expect a humidity effect on SOA phase partitioning?
- the experiments
- preliminary results
  - what did we observe?
  - future work/challenges
- my other PhD project
  - surfactant partitioning in activating cloud droplets

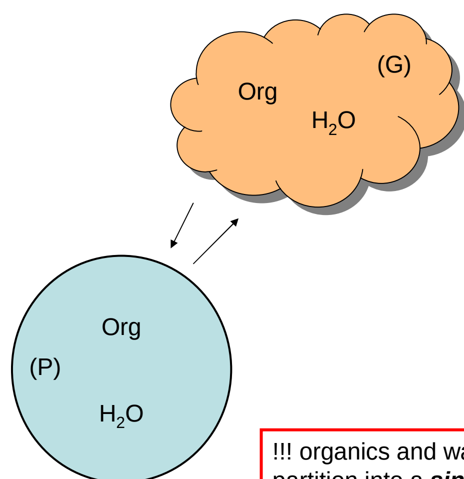
The experimental system



↓ O_3

organic products

$[H_2O]$



!!! organics and water partition into a ***single*** condensed phase

SOA phase partitioning

reference: Presto and Donahue (EST 2006)

- the effective gas phase saturation mass concentration **c***
  - related to the partial pressure of a species in solution
  - the saturation vapor pressure of the *pure* liquid species, with the properties the species posesses in a given *solution*
- the partitioning coefficient **ξ**
  - ratio of the mass concentration of a species *in solution* to the *total* mass concentration in gas phase and solution

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Effective gas phase saturation concentration, c*

$$p_i = p^0_{i,P}\gamma_i\chi_{i,P}$$ **Raoult's law**

$$p_i = \frac{c_{i,G}}{W_i}RT$$ **ideal gas law**

$$c_{i,P} = \chi_{i,P}\frac{W_i}{\overline{\overline{W}}}$$ **mass fraction in solution**

$$c_i^* \equiv \frac{c_{i,G}}{c_{i,P}} = \frac{p^0_{i,P}\gamma_i\overline{W}}{RT}$$ ***effective* gas phase *saturation* mass concentration**

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c* depends on SOA composition

- c* depends on the particle *composition*
  - » activity coefficient
  - » mean molar weight

$$c_i^* = \frac{p_{i,P}^0 \gamma_i \overline{W}}{RT}$$

- composition *change* => c* change if
  - » activity coefficient change
  - » mean molar weight change

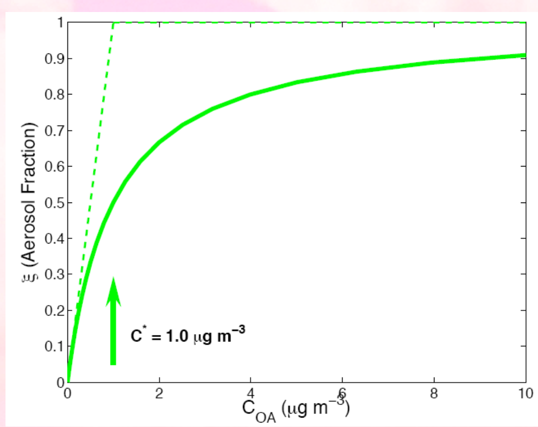
$$\chi_i' \rightarrow \chi_i'' :$$

$$\frac{c_i^{*''}}{c_i^{*'}} = \frac{\gamma_i'' \overline{W}''}{\gamma_i' \overline{W}'}$$

Partitioning coefficient, ξ

$$\xi_i = \frac{1}{1 + \frac{c_i^*}{c_{OA}}}$$

$$c_{OA} = \sum_i c_i \xi_i$$



RH effect on SOA phase partitioning

- o increasing RH => SOA *hygroscopic* growth
- o if water and organics mix in solution
  - » increase absorbing c_{OA}
  - » decrease W_{avg} => decrease c* (if pseudo-ideal)
- o both will increase ξ_i => increase resulting c_{OA}

$$\xi_i = \frac{1}{1+\frac{c_i^*}{c_{OA}}}$$

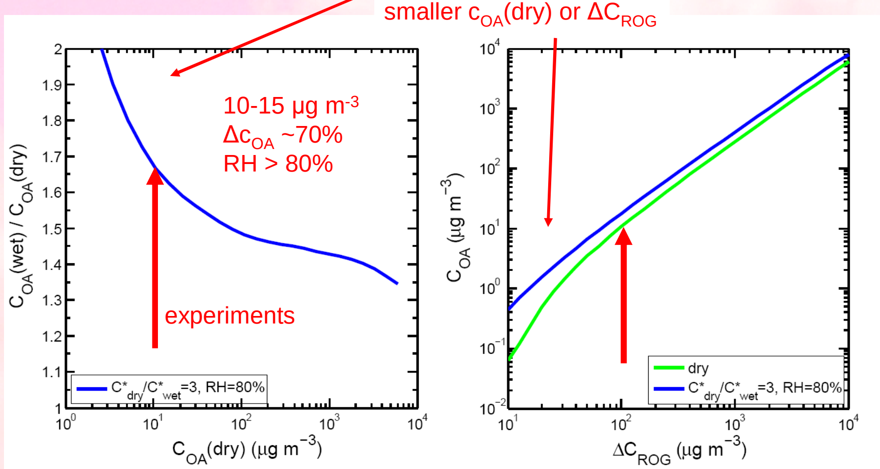
$$c_{OA}\uparrow, \xi_i \uparrow, c_{OA}\uparrow$$

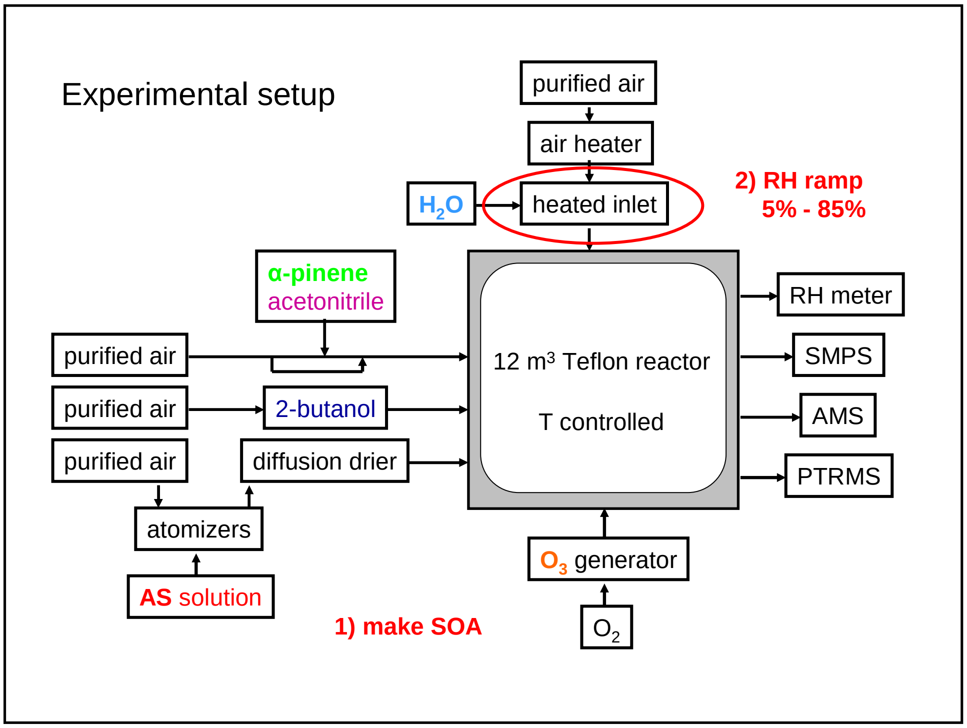
$$\overline{W}\downarrow, c_i^* \downarrow, \xi_i \uparrow, c_{OA}\uparrow$$

c* 'wet shift'

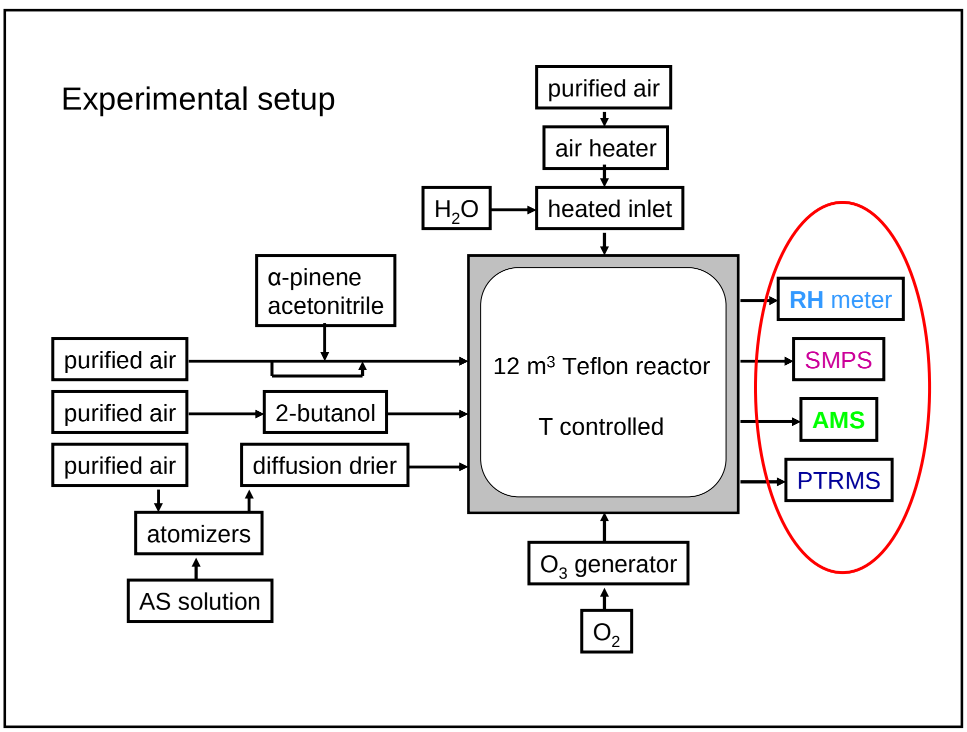
c* 'wet shift' - depends on initial c_{OA}

larger effect of c* wet shift
smaller c_{OA}(dry) or ΔC_{ROG}





Experimental setup
purified air
air heater
H_2O
heated inlet
2) RH ramp
5% - 85%
α-pinene
acetonitrile
RH meter
purified air
12 m³ Teflon reactor
SMPS
purified air
2-butanol
T controlled
AMS
purified air
diffusion drier
PTRMS
atomizers
O_3 generator
AS solution
1) make SOA
O_2



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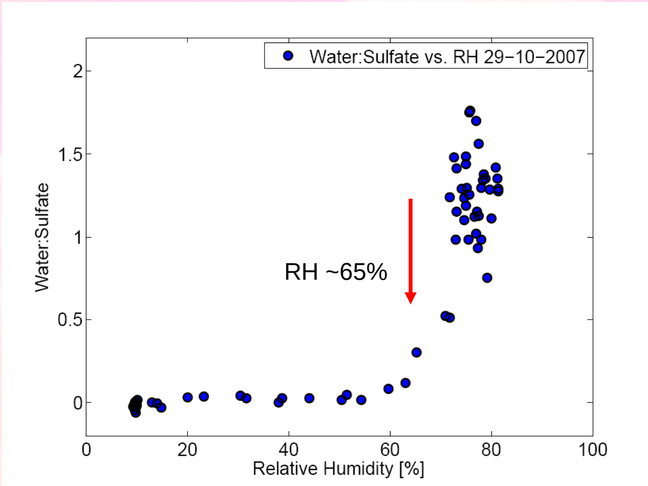
Hygroscopic growth

max RH ~85%

particles take up water at RH ~65%

DRH(pure AS) = 80%



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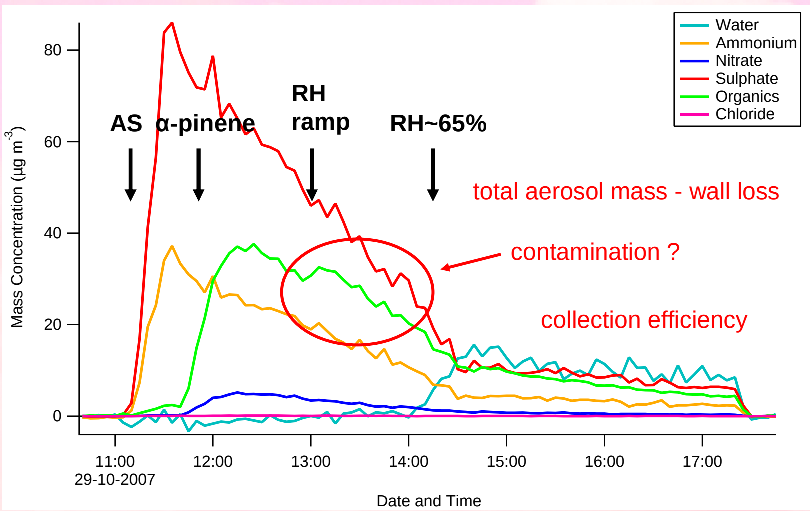
Aerosol mass composition timeseries (AMS)



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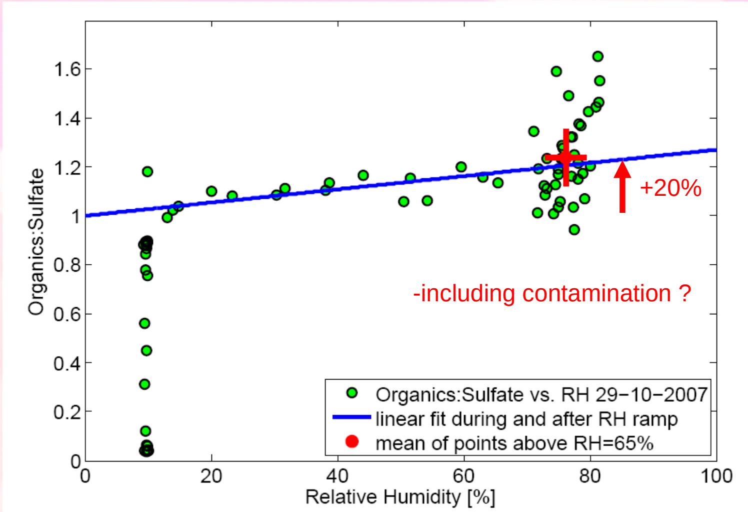
Observed SOA mass growth



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Predicted SOA mass growth

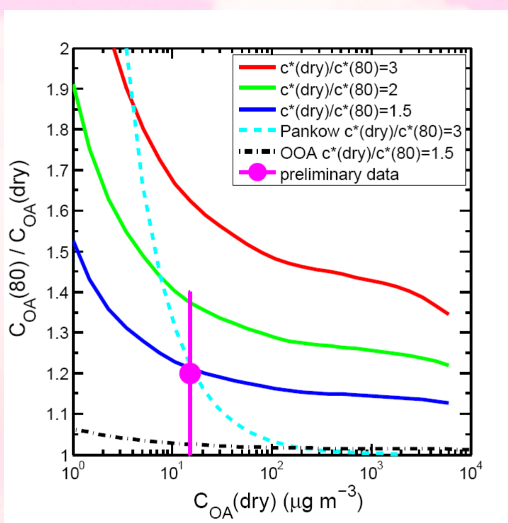
references:
Presto and Donahue (EST 2006)
Chang and Pankow (acpd 2008)

We observed:

Δc_{OA} ~20%
for c_{OA} ~15 µg m^{-3}
at RH ~85%

Consistent 'wet shift':

c*(dry)/c*(wet) ~1.5 ±0.5



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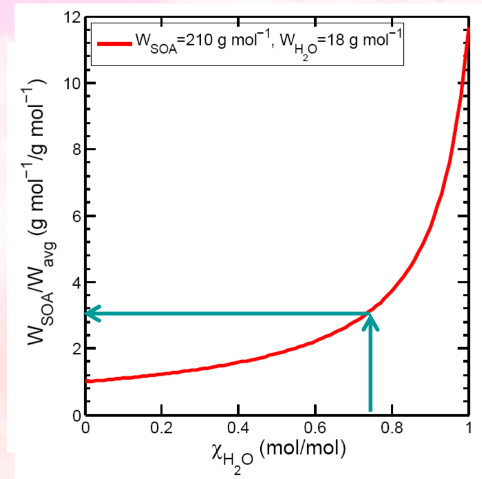
Observed SOA water content from hygroscopic growth

- α-pinene SOA diameter GF=1.08 at RH=85%
  [Varutbangkul et al., ACP 2006, 2367]
- corresponds to aerosol $\chi(H_2O)=0.75$
- corresponds to decrease in W_{avg} from W_{SOA} by factor 3



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Humidity effect on SOA mass?

- at most (incl. contamination), we observed an a-pinene SOA mass growth of ~20%
  - » we did not see a large RH effect on SOA mass
- the observed SOA mass growth is consistent with a c* 'wet shift' of ~1.5
  - » this is about half the c* 'wet shift' expected from the effect of pure SOA hygroscopic growth on OA W_{avg}
- there may be an additional γ-effect on c*:
  - » pseudo-ideality not valid assumption
  - » γ_{org} increasing with water uptake (no surprise)

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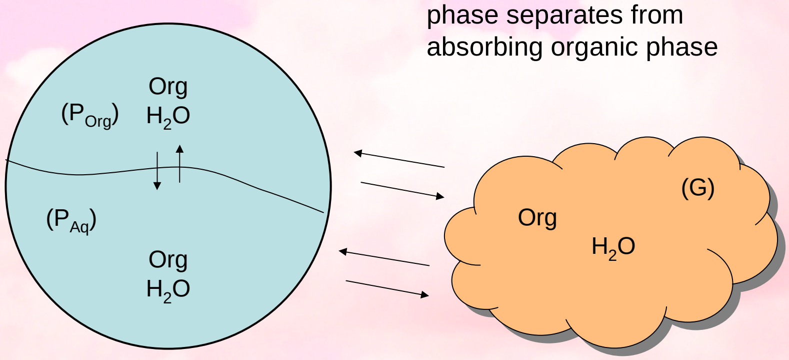
Particle phase separation

experimental evidence

W_{avg} effect smaller for given total water uptake if aqueous phase separates from absorbing organic phase



Future work

- contamination correction => better constrain SOA growth
- phase separation: water content of absorbing organic phase
- activity coefficients: AIM model including organics
- experiments w. other terpenes/mixed terpenes

Take-home message #1

- The predicted effect of RH on SOA gas-particle phase partitioning is highly dependent on the assumed dry SOA volatility distribution.

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Take-home message #2

- If the particle phase separates into distinct organic and aqueous phases, the effect of a given total water uptake into the aerosol phase on SOA gas-particle phase partitioning will be much less than if the water and organics partition into a single absorbing organic aerosol phase.

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Surfactants in cloud droplet activation

- cloud droplet activation: Köhler theory
- surfactant partitioning in an aqueous droplet
- results and future work

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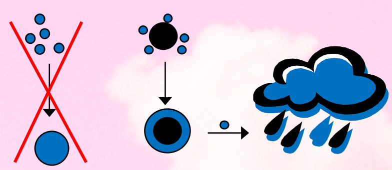
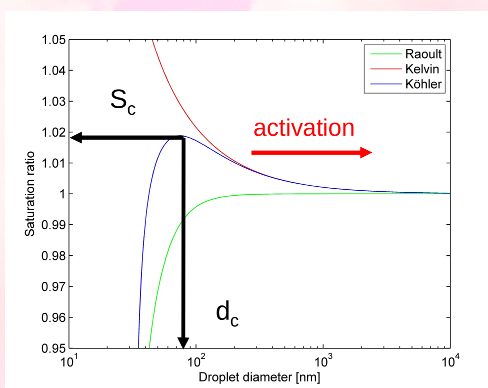
Cloud droplet activation



- Köhler equation

$$S = \frac{p_w}{p_w^0} = a_w \exp\left(\frac{4 v_w \sigma}{RTd}\right)$$

- critical point (S_c,d_c)
- activated droplet $d>d_c$



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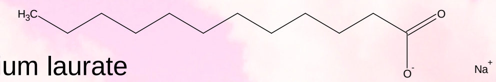
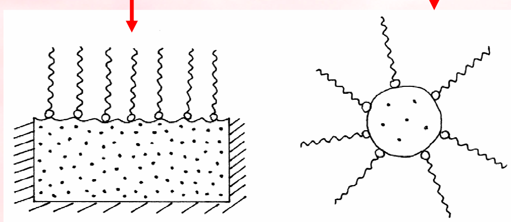
Surfactant partitioning

=> greater predicted S and S_c

Sorjamaa et al. (acp 2004)



- surfactants decrease σ
- fatty acid sodium salts: sodium laurate
- preferentially concentrate in the surface
  - » surface-bulk partitioning
- microscopic droplets have large *surface area-to-bulk volume* ratio
- smaller equilibrium surface area and bulk volume concentrations

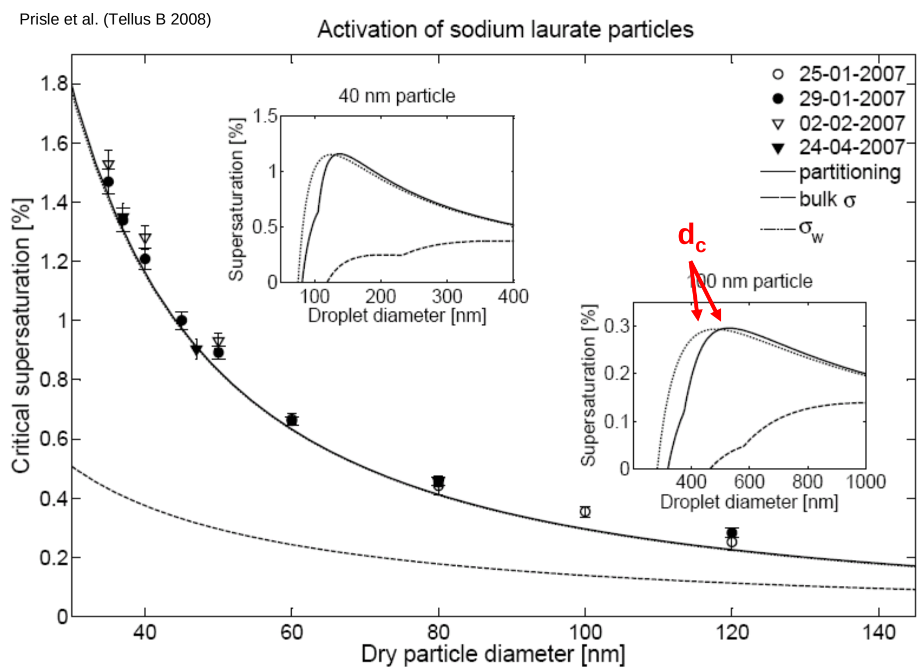


$$S = \frac{p_w}{p_w^0} = a_w \exp\left(\frac{4\nu_w \sigma}{RTd}\right)$$

a_w lowered less

σ lowered less

Prisle et al. (Tellus B 2008)



Take-home message #3

- If the surfactant properties are accounted for in predicting cloud droplet activation, the effect of surfactant partitioning between the droplet bulk and surface must be accounted for in both Kelvin and Raoult terms of the Köhler equation, else particle critical supersaturatiions are considerably underestimated.

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Thank you – see you at EAC2008!

- Acknowledgements are due:
  - Profs. Neil Donahue and Spyros Pandis (CMU)
  - Gabi Engelhart (CMU)
  - Prof. Ari Laaksonen (FMI)
  - Riikka Sorjamaa (Univ. Kuopio), Tomi Raatikainen (FMI)
  - CCAR, BACCI & EUCAARI

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