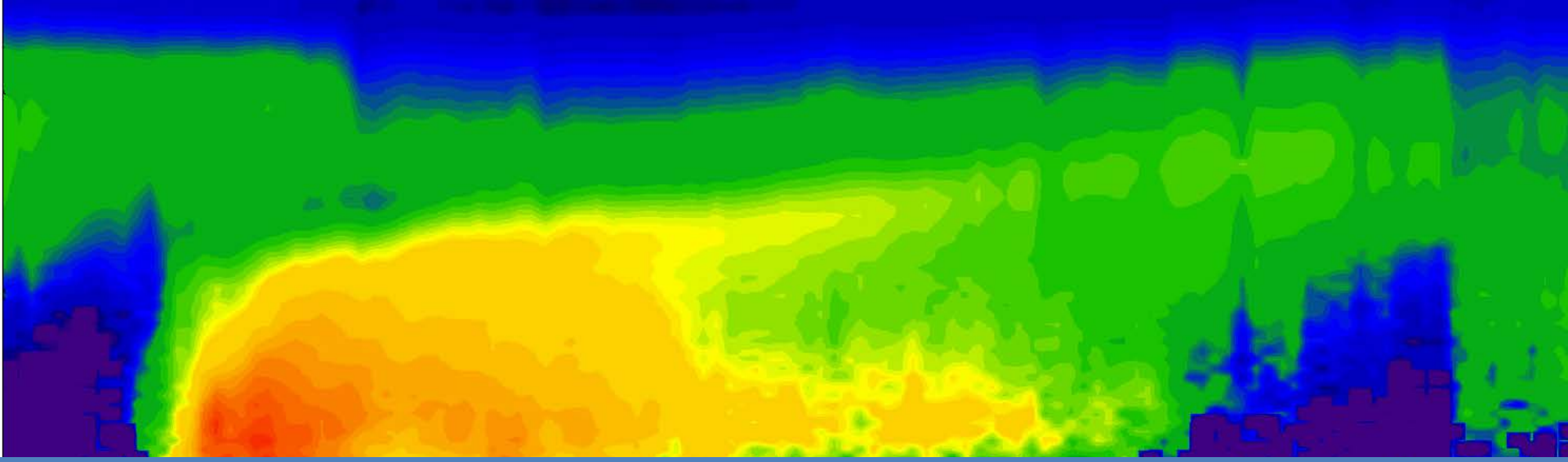


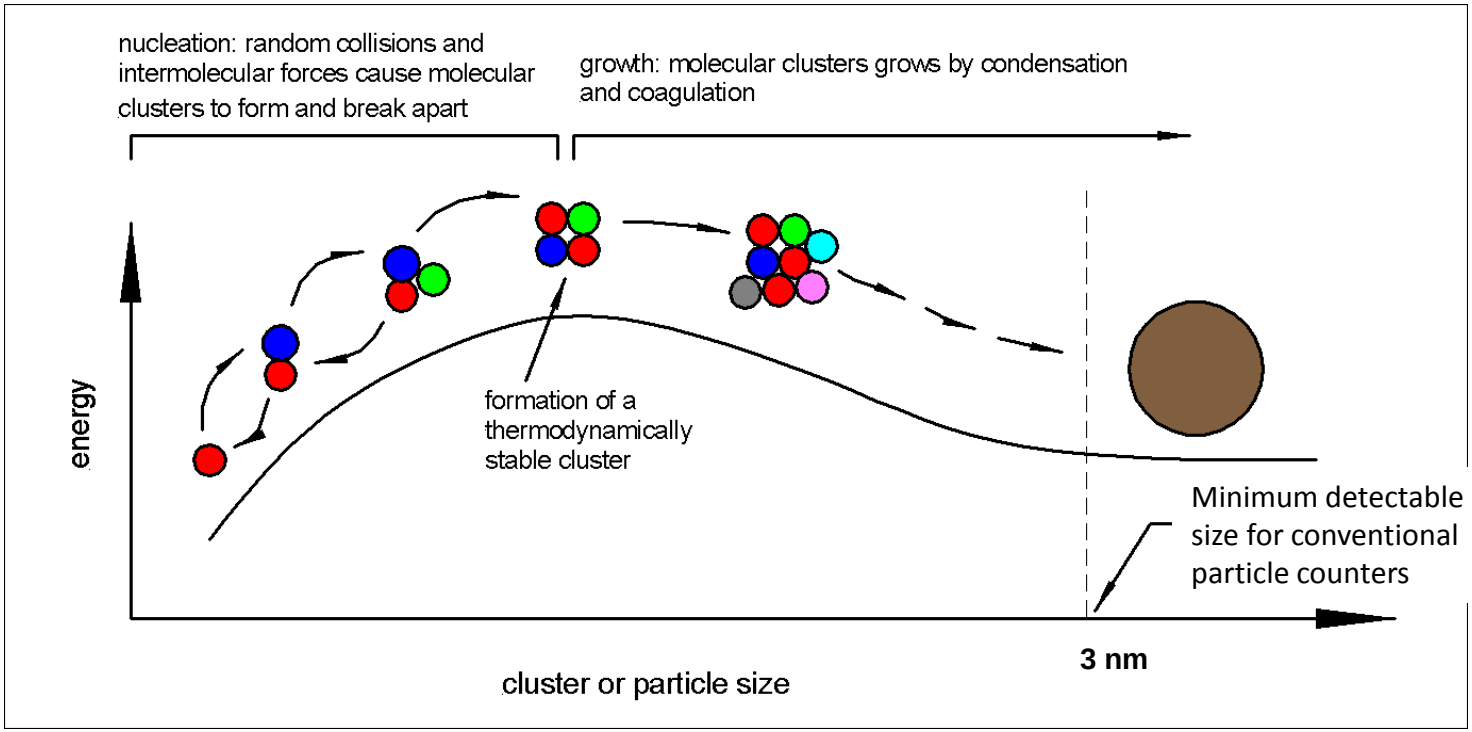
Progress Report: ASR New Particle Formation Research

Jim Smith, Peter McMurry,
and the New Particle Formation Focus Group

18 March 2013
DOE ASR Science Team Meeting

Background: New Particle Formation

New Particle Formation = Nucleation + Growth

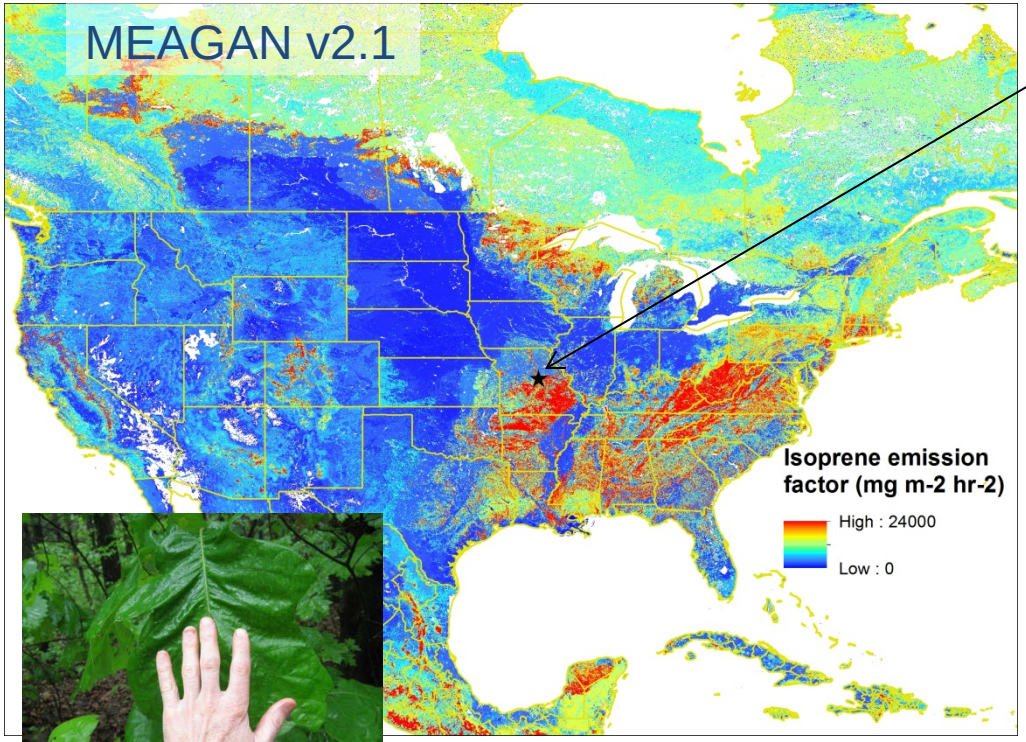


McMurry, Smith et al. in Aerosol Measurement Techniques, 2009.

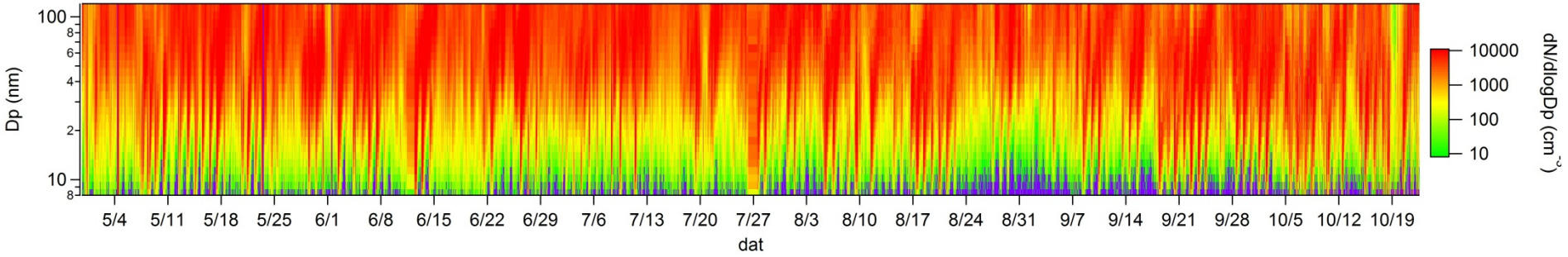
Objectives of the ASR New Particle Formation Focus Group:

Using field and laboratory observations, develop models for nucleation rates and growth rates of atmospheric nanoparticles that can be incorporated into **regional and global models**.

New particle formation in an isoprene-dominated forest



Particle Investigations at a Northern Ozarks Tower – NOx, Oxidant, Isoprene Research (PINOT-NOIR)
where: MOflux site (Columbia, MO)
when: 1 May – 31 Oct 2012
what: 8 nm – 3 μm size distr.
$N_{1.5\text{-}3nm}$: 1 Aug – 31 Oct
VOCs, trace gases and H2SO4



Smith et al., unpublished

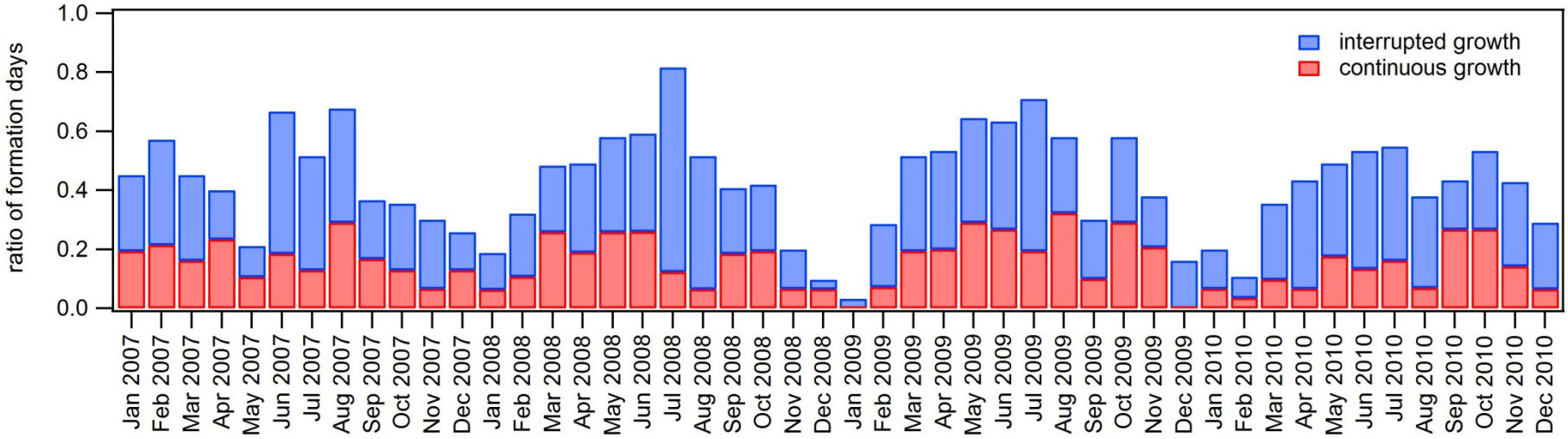
Southern Great Plains New Particle Formation Study (NPFS-2013)

Dates: 13 April – 23 May 2013
Location: ARM Southern Great Plains site

Objective: Study new particle formation and its impact on clouds and climate

Measurements @ Guest Instrument Facility (UMN, Augsburg, NCAR, UDel):

- nanoparticle composition (TDCIMS and NAMS)
- particle size distribution: 1.5 nm to 1 mm (SMPS + DEG-CPC)
- aerosol gas phase precursors (ammonia, amines, sulfuric acid, VOCs; CIMS)
- Vertically-resolved aerosol size distribution (SMPS on tethered balloon)
- Spatial extent of new particle formation (satellite site ~200km from main site)



Biogenic Aerosols- Effects on Clouds and Climate

Objective: Study the impacts of biogenic aerosol on clouds, precipitation and climate.

where: SMEAR II Station, Hyytiälä, Finland
when: 1 Feb – 30 Sept 2014
what: AMF2 supplements SMEAR II observations by providing cloud and vertical profiling, including radars, radiometers, lidar, balloon soundings, etc.

More details on Wed, 1:30pm

Experiments at CLOUD in Geneva, Switzerland

DOE ASR Science Team members participating in CLOUD:

- Smith: chemical composition of growing nanoparticles
- Worsnop: composition of charged and neutral clusters
- Donahue: experiment planning
- Seinfeld: experimental development (Radial DMA)

CLOUD results 1: H_2SO_4 + NH_3 + ions

LETTER

25 AUGUST 2011 | VOL 476 | NATURE | 429

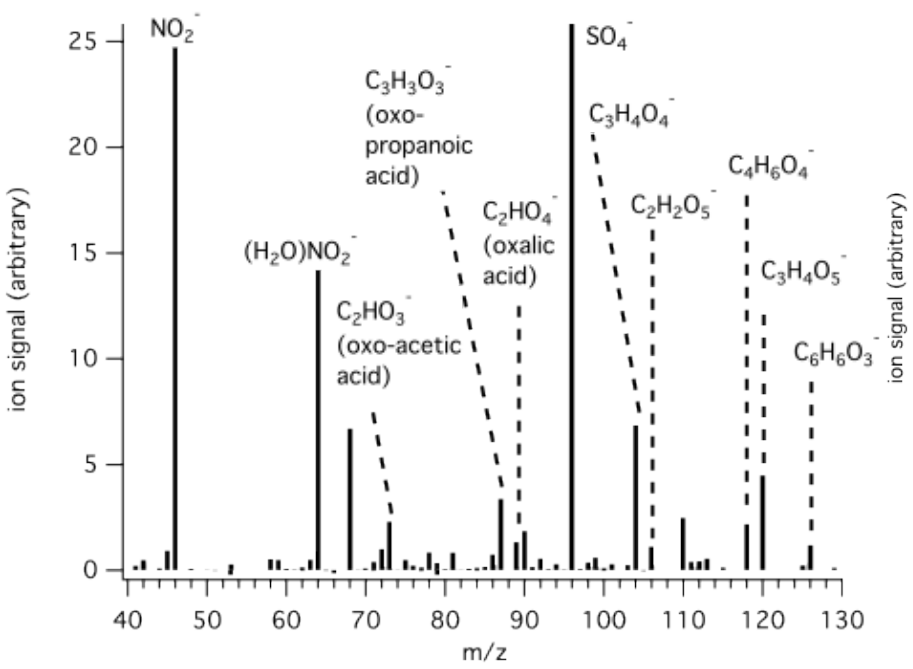
doi:10.1038/nature10343

Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation

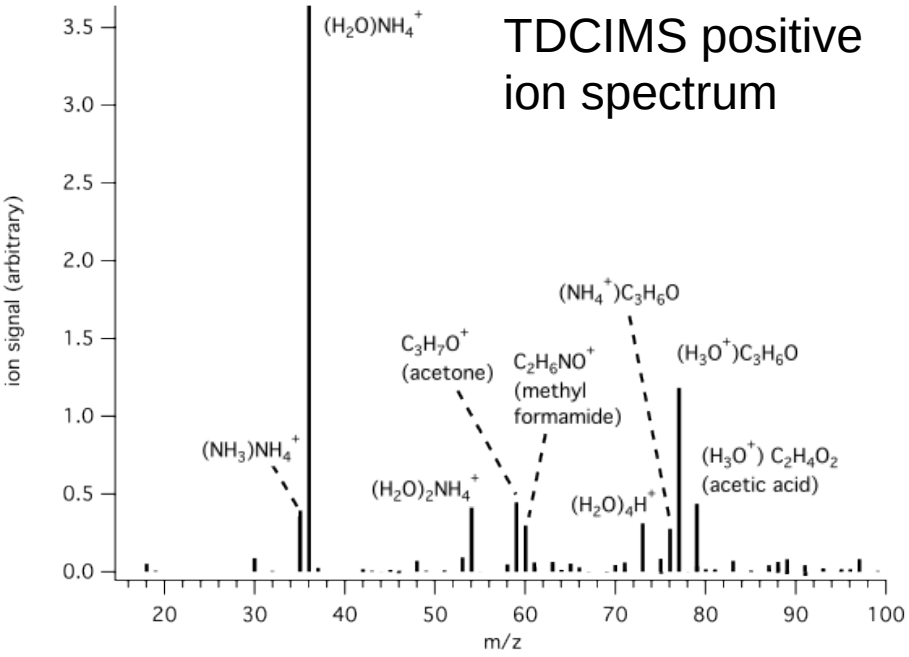
Jasper Kirkby[1], Joachim Curtius[2], João Almeida[2,3], Eimear Dunne[4], Jonathan Duplissy[1,5,6], Sebastian Ehrhart[2], Alessandro Franchin[5], Stéphanie Gagné[5,6], Luisa Ickes[2], Andreas Kürten[2], Agnieszka Kupc[7], Axel Metzger[8], Francesco Riccobono[9], Linda Rondo[2], Siegfried Schobesberger[5], Georgios Tsagkogeorgas[10], Daniela Wimmer[2], Antonio Amorim[3], Federico Bianchi[9,11], Martin Breitenlechner[8], André David[1], Josef Dommen[9], Andrew Downard[12], Mikael Ehn[5], Richard C. Flagan[12], Stefan Haider[1], Armin Hansel[8], Daniel Hauser[8], Werner Jud[8], Heikki Junninen[5], Fabian Kreissl[2], Alexander Kvashin[13], Ari Laaksonen[14], Katrianne Lehtipalo[5], Jorge Lima[3], Edward R. Lovejoy[15], Vladimir Makhmutov[13], Serge Mathot[1], Jyri Mikkilä[5], Pierre Minginette[1], Sandra Mogo[3], Tuomo Nieminen[5], Antti Onnela[1], Paulo Pereira[3], Tuukka Petäjä[5], Ralf Schnitzhofer[8], John H. Seinfeld[12], Mikko Sipilä[5,6], Yuri Stozhkov[13], Frank Stratmann[10], Antonio Tomé[3], Joonas Vanhanen[5], Yrjo Viisanen[16], Aron Vrtala[7], Paul E. Wagner[7], Hansueli Walther[9], Ernest Weingartner[9], Heike Wex[10], Paul M. Winkler[7], Kenneth S. Carslaw[4], Douglas R. Worsnop[5,17], Urs Baltensperger[9] & Markku Kulmala[5]

Measuring nanoparticles created in the world's cleanest chamber: a-Pinene + SO_2 oxidation

TDCIMS negative ion spectrum



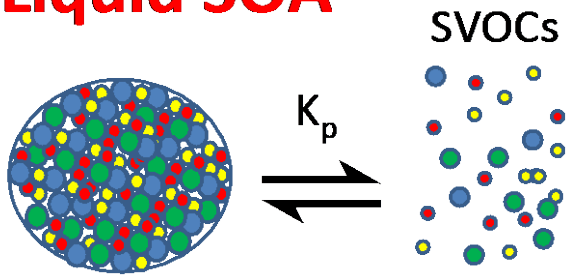
TDCIMS positive ion spectrum



Laboratory studies at UC Irvine to understand SOA phase effects

- Models underestimate SOA in air
- Discrepancies could be rooted in how models treat SOA growth

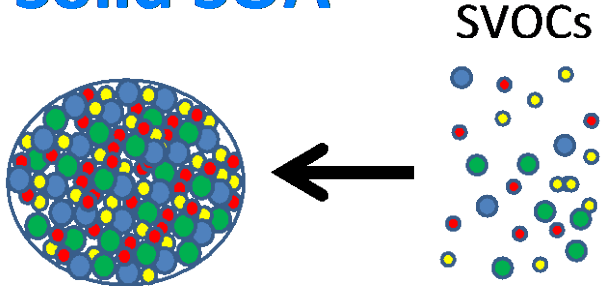
Liquid SOA



⇒ **SOA as a low viscosity liquid**
⇒ **Instantaneous gas-particle partitioning (K_p)**
⇒ **Fast diffusion**
⇒ **Reversible SVOC uptake**

Equilibrium partitioning, assuming low viscosity *Liquid* SOA, is most widely used in models (Hallquist et al., 2009; Kanakidou et al., 2005; Jimenez et al., 2009; Pankow et al., 1994; O'Donnell et al. 2011; Baek et al., 2011; Parikh et al., 2011)

Solid SOA

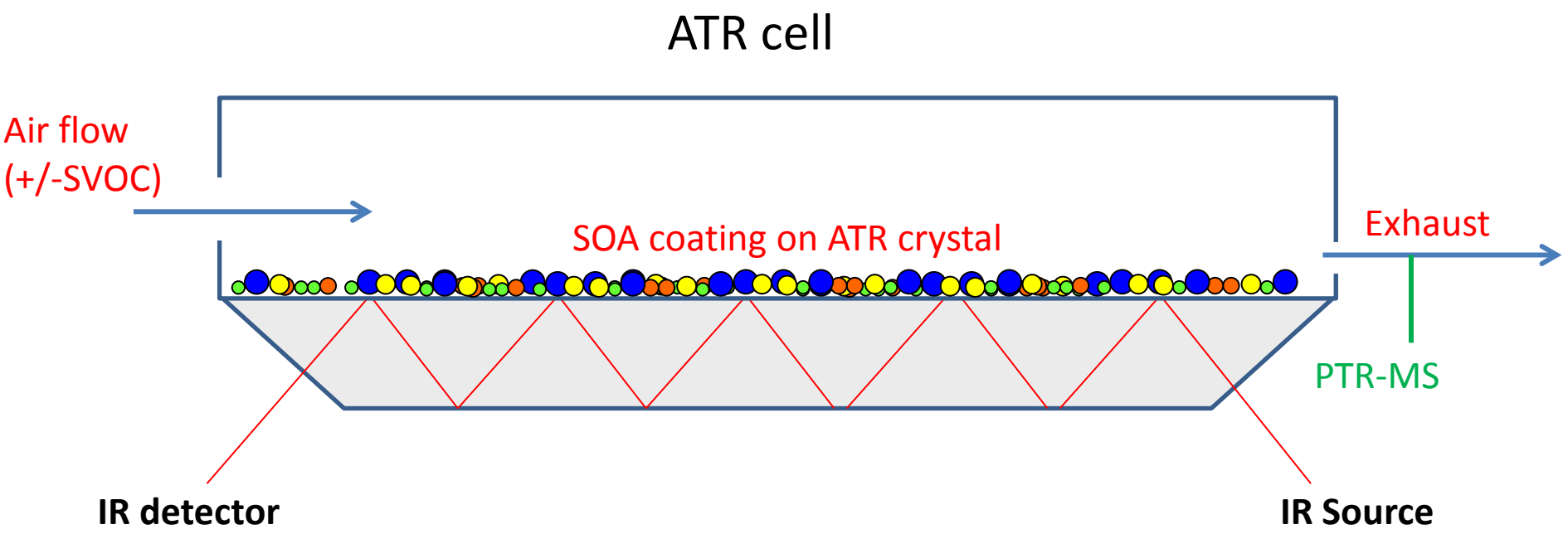


⇒ **SOA as a high viscosity semi-solid/tar**
⇒ **Slow diffusion**
⇒ **Irreversible SVOC uptake**

Recent studies show that aerosols are semi-solid or glassy (Zobrist et al., 2008; Virtanen et al., 2010 and 2011; Vaden et al., 2010 and 2011; Cappa and Wilson, 2011; Koop et al., 2011; Saukko et al., 2012; Zelenyuk et al., 2012; Shiraiwa et al., 2012; Mikhailov et al., 2012; Tong et al., 2012; Abramson et al., 20012)

and the uptake of SVOCs seems to be better represented by a condensation mechanism (Perraud et al., 2012; Kleinman et al., 2012; Riipinen et al., 2011)

Attenuated Total Reflectance FTIR Experimental Set up



SOA evaporation

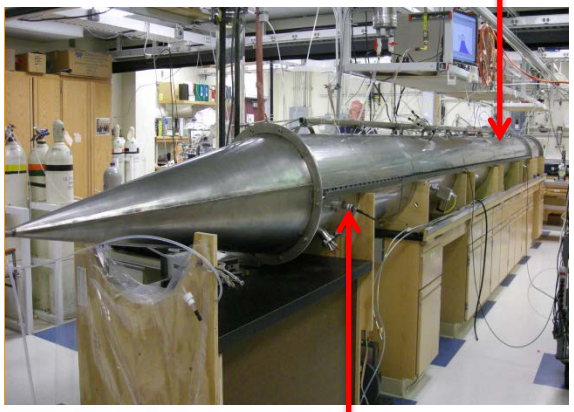
- IR spectrum of SOA coating
- IR signal monitored as a function of time
- Evaporation rate and IR spectrum of evaporated material obtained

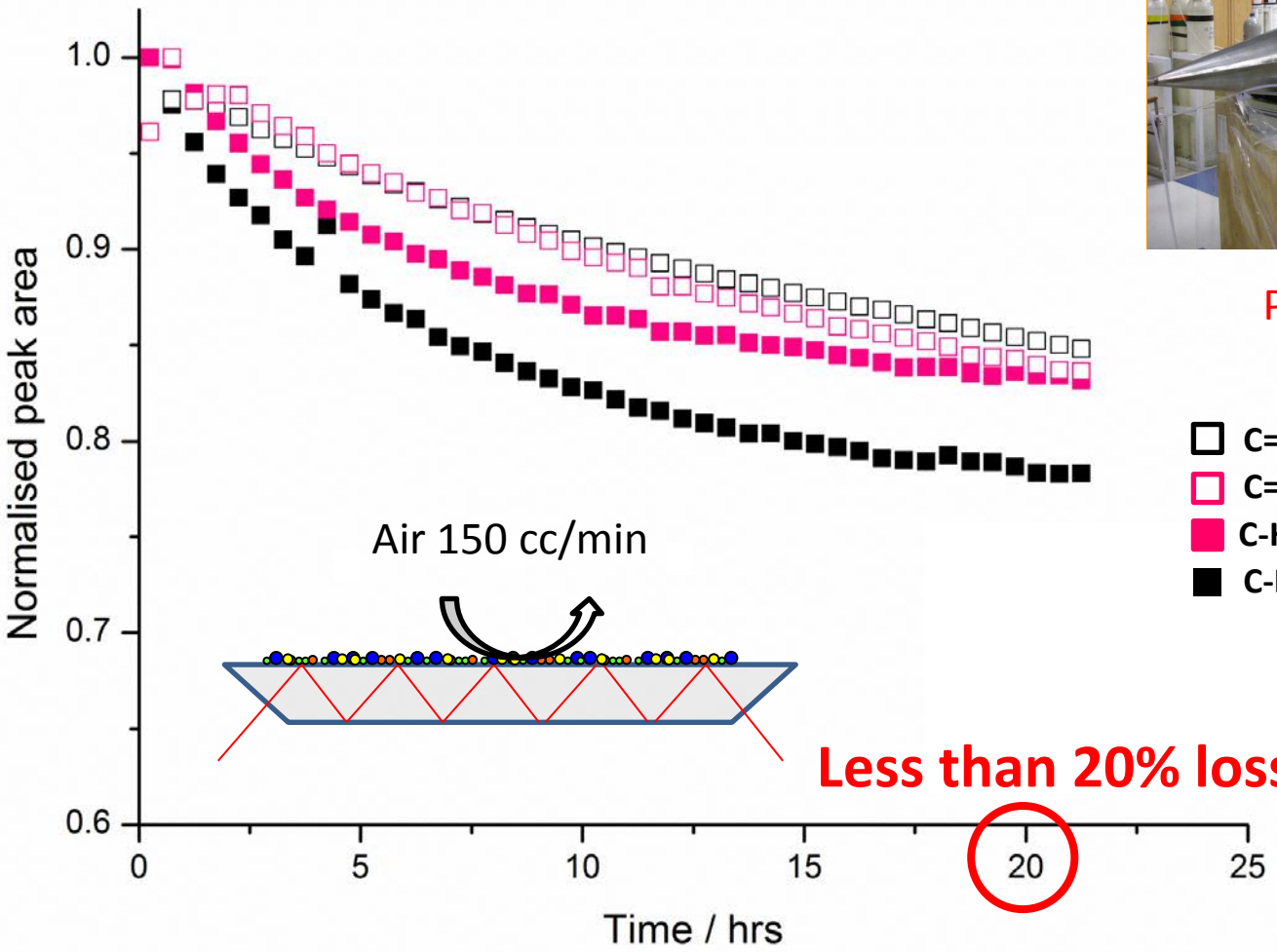
$RONO_2$ uptake

- $RONO_2$ uptake rate
- $RONO_2$ flow replaced with air
- $RONO_2$ loss rate

Results: a-pinene + o3 SOA Evaporation at room temperature

⇒ Very little evaporation at either port/reaction time



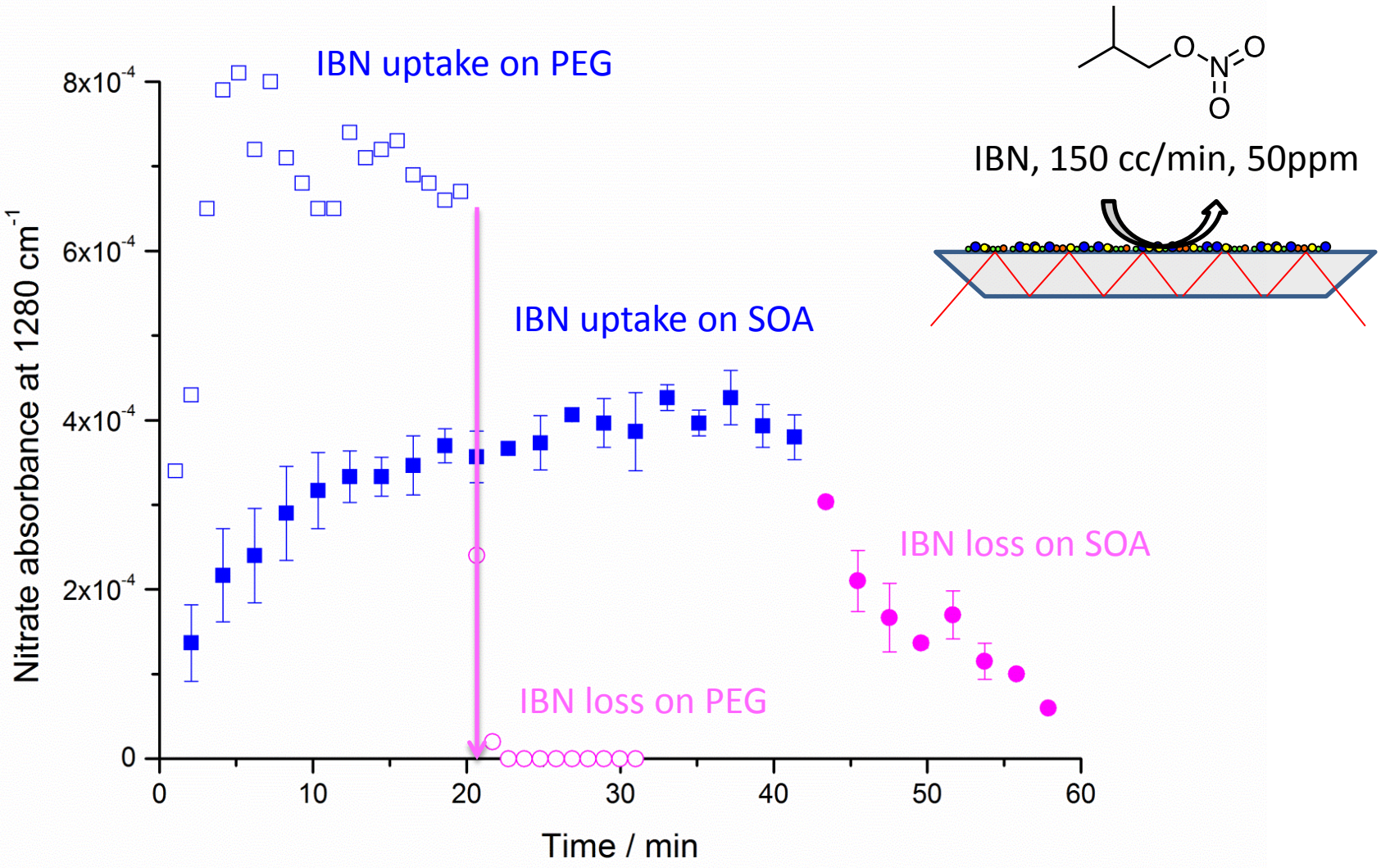


Less than 20% loss in 22 hrs!

Results: Isobutyl nitrate uptake/loss experiment

⇒ Fast loss of IBN → Liquid PEG

⇒ Loss of IBN on SOA is slower → much more viscous



Effect of adsorption on initial cluster growth and new particle formation

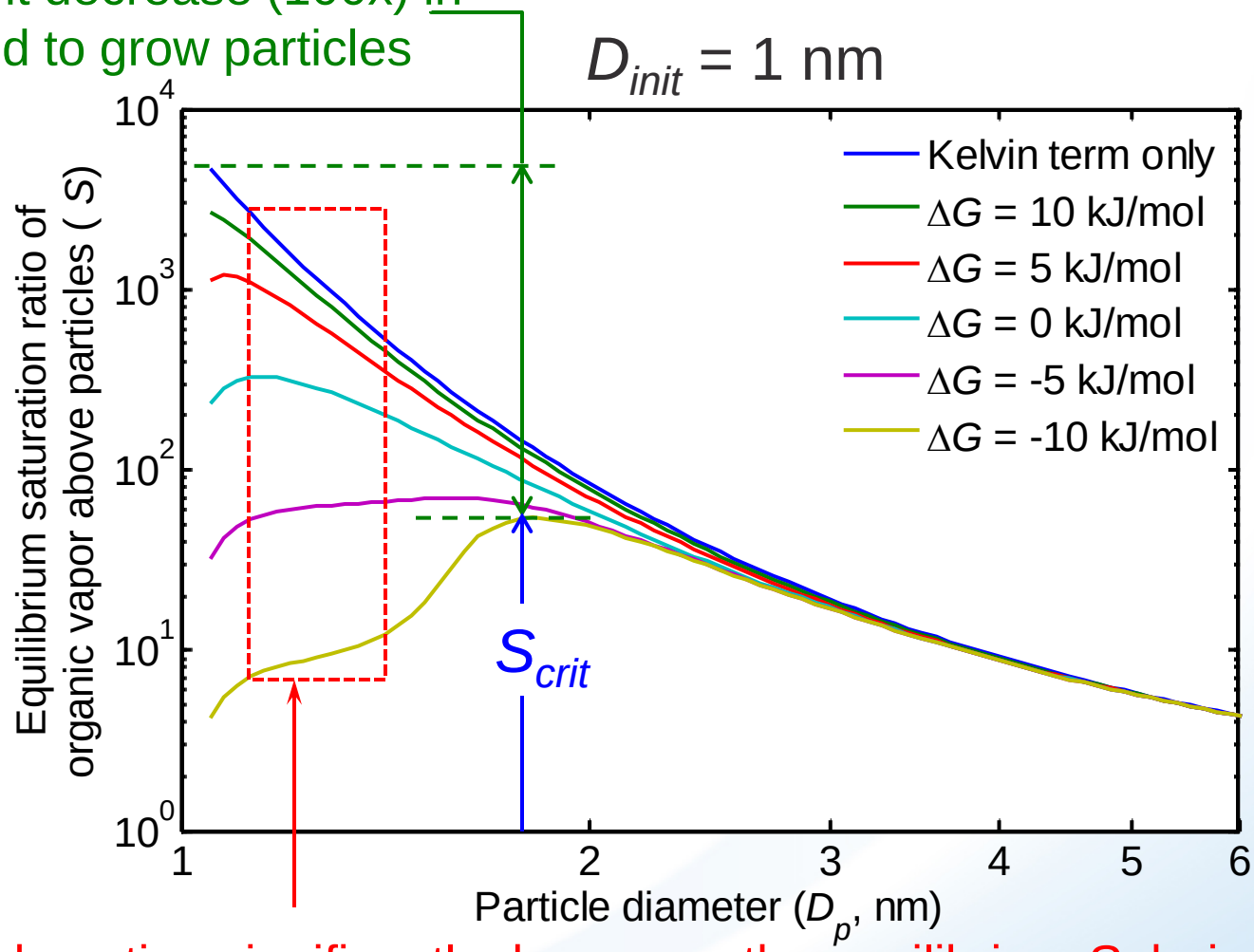
- Adsorption of organic molecules onto the surface of clusters, not considered previously, may significantly reduce the saturation ratio required for the condensation of organics to occur.
- This may provide a physico-chemical explanation for the enhanced initial growth by condensation of organics despite the strong Kelvin effect.

Equilibrium *S* over growing particles:

$$S = \frac{C_\infty}{C_{Sat}} = \underbrace{\frac{\left[c-\theta(c-2)\right]-\sqrt{c^2(\theta-1)^2+4\theta c}}{2\theta(1-c)}}_{\text{Adsorption(<1)}} \cdot \underbrace{\exp\left(\frac{4\nu\sigma}{RTD}\right)}_{\text{Kelvin effect}}$$

Effect of adsorption on equilibrium *S*

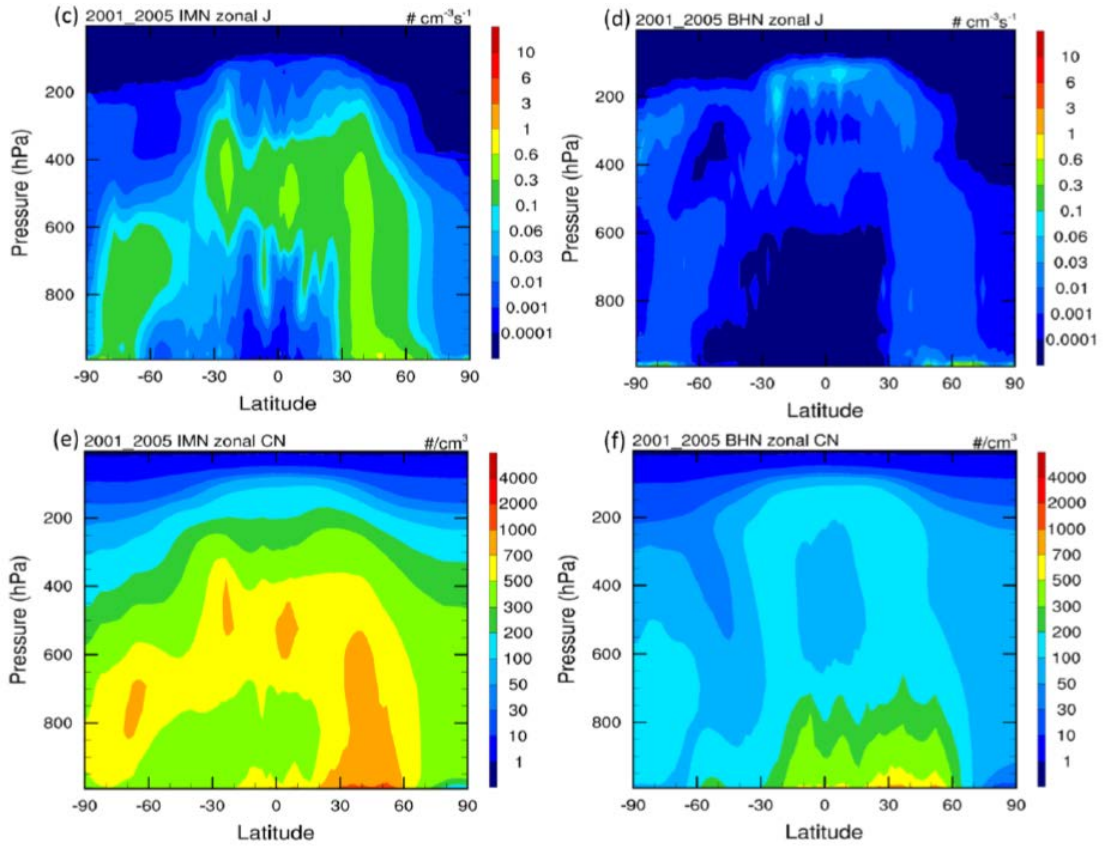
Significant decrease (100x) in *S* required to grow particles



Adsorption significantly decreases the equilibrium *S* during the initial growth of clusters

Effect of ionization on aerosol formation, CCN and cloud radiative forcing

Xiaohong Liu, R.C. Easter, S. Ghan (PNNL)
F. Yu (SUNY- Albany)



Nucleation rate *J*, and total particle number concentration, averaged over all longitudes, simulated with (left) and without (right) ion-mediated nucleation.

Shortwave cloud forcing (SWCF) changed by -3.67 W m^{-2}, and longwave cloud forcing by +1.78 W m^{-2} due to ionization. This SWCF change is much higher than that of a previous study (-1.15 W m^{-2}) based on a different ion nucleation scheme and climate model (Kazil et al. 2010)

From Yu et al., ACP, 2012

Pacific Northwest
NATIONAL LABORATORY

CAM5 aerosol nucleation work

- *Planned improvements:*
  - Include an explicit "nucleation" mode for fresh particles. Present treatment grows fresh particles to Aitken size using current time-step conditions, accounting for coagulation loss. Growth time often exceeds model time step.
  - Incorporate new findings for fresh particle growth rates (Kuang and Wang, BNL), including organics (SOA), which are currently not considered.
  - Improve time-splitting of aerosol dynamics processes (better numerical techniques).
  - Better represent fresh particle loss processes and gas concentrations under fractional cloudiness conditions.
  - Treat sub-grid variations in RH, T, H_2SO_4.
- *Preliminary results:*
  - Eliminating time-split of H_2SO_4 production and condensation significantly increases nucleation. New particle formation up 400% globally, Aitken number up 160%, accumulation number up 20%.
  - Aitken number evaluation (limited): Aircraft profiles improved; marine BL now too high.

Closing thoughts …

- ASR sponsored a special symposium on New Particle Formation at the American Assoc. for Aerosol Research (AAAR) meeting last fall. With these funds, we were able to award travel grants to 10 students who presented their work at the symposium.
- International collaborations are developing (e.g., Finnish research). What additional opportunities does this present, and how can ASR encourage this?
- How can we improve our national effort? Are we doing enough to involve atmospheric modelers in our observational work?
- **For more science and discussion on New Particle Formation, attend the breakout session Tuesday, after lunch.**