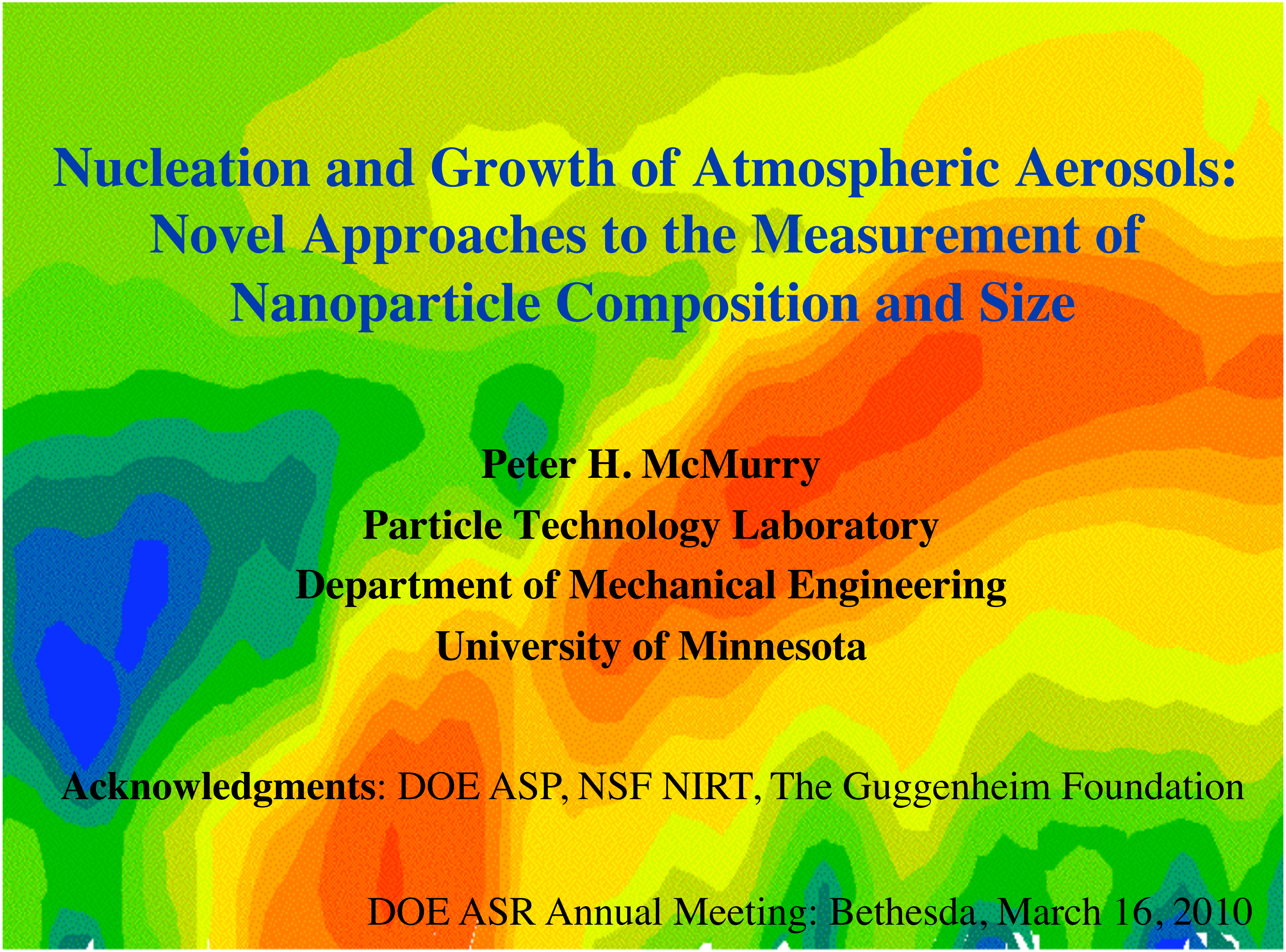


Nucleation and Growth of Atmospheric Aerosols: Novel Approaches to the Measurement of Nanoparticle Composition and Size

Peter H. McMurry
Particle Technology Laboratory
Department of Mechanical Engineering
University of Minnesota

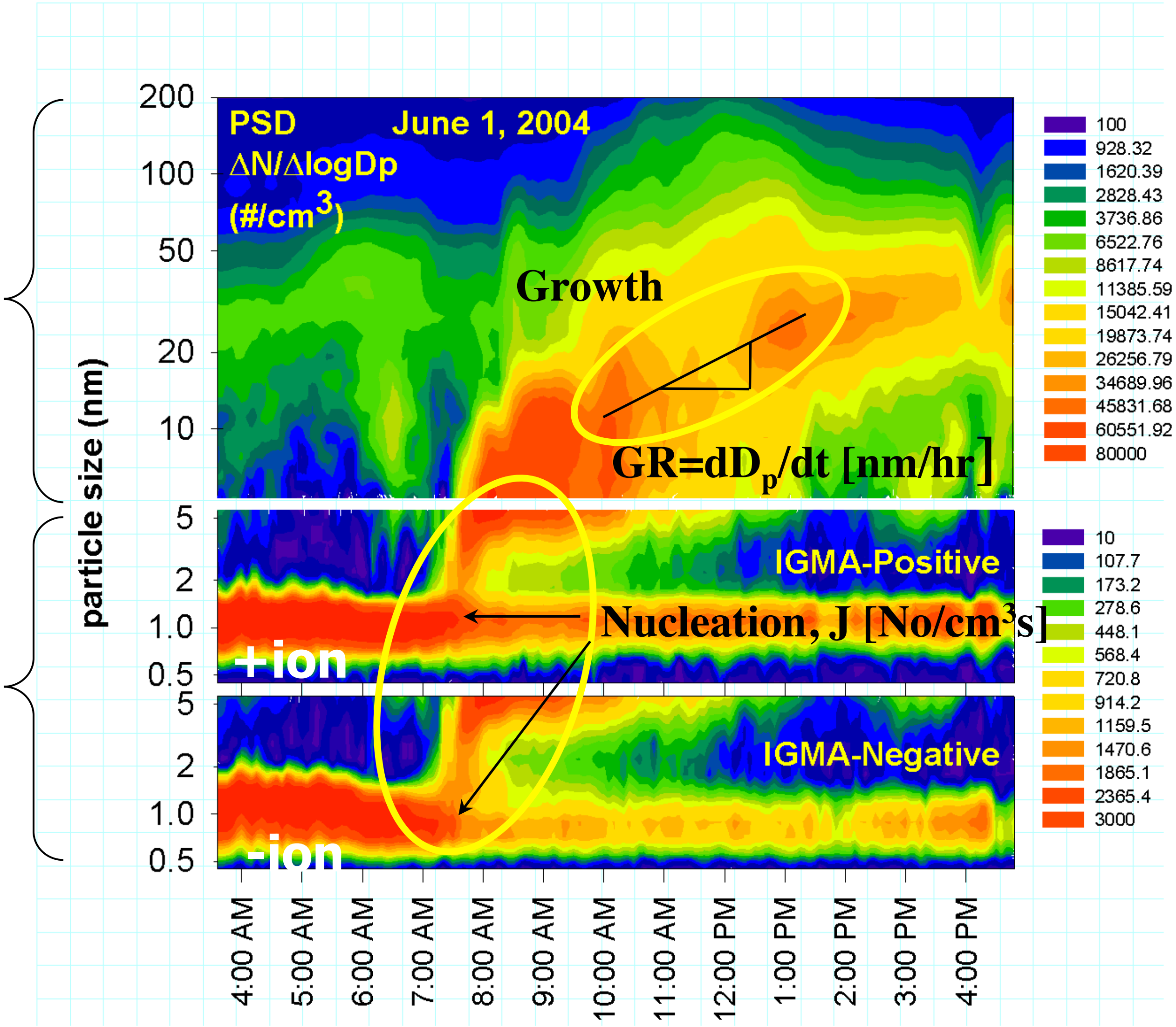
Acknowledgments: DOE ASP, NSF NIRT, The Guggenheim Foundation

DOE ASR Annual Meeting: Bethesda, March 16, 2010

New Particle Formation (NPF) Event, Boulder. Distinguishing Nucleation from Growth

Size Distribution of all charge states

Size Distribution of Charged Particles (Ions)



Iida et al., *JGR*., **111**: 2006

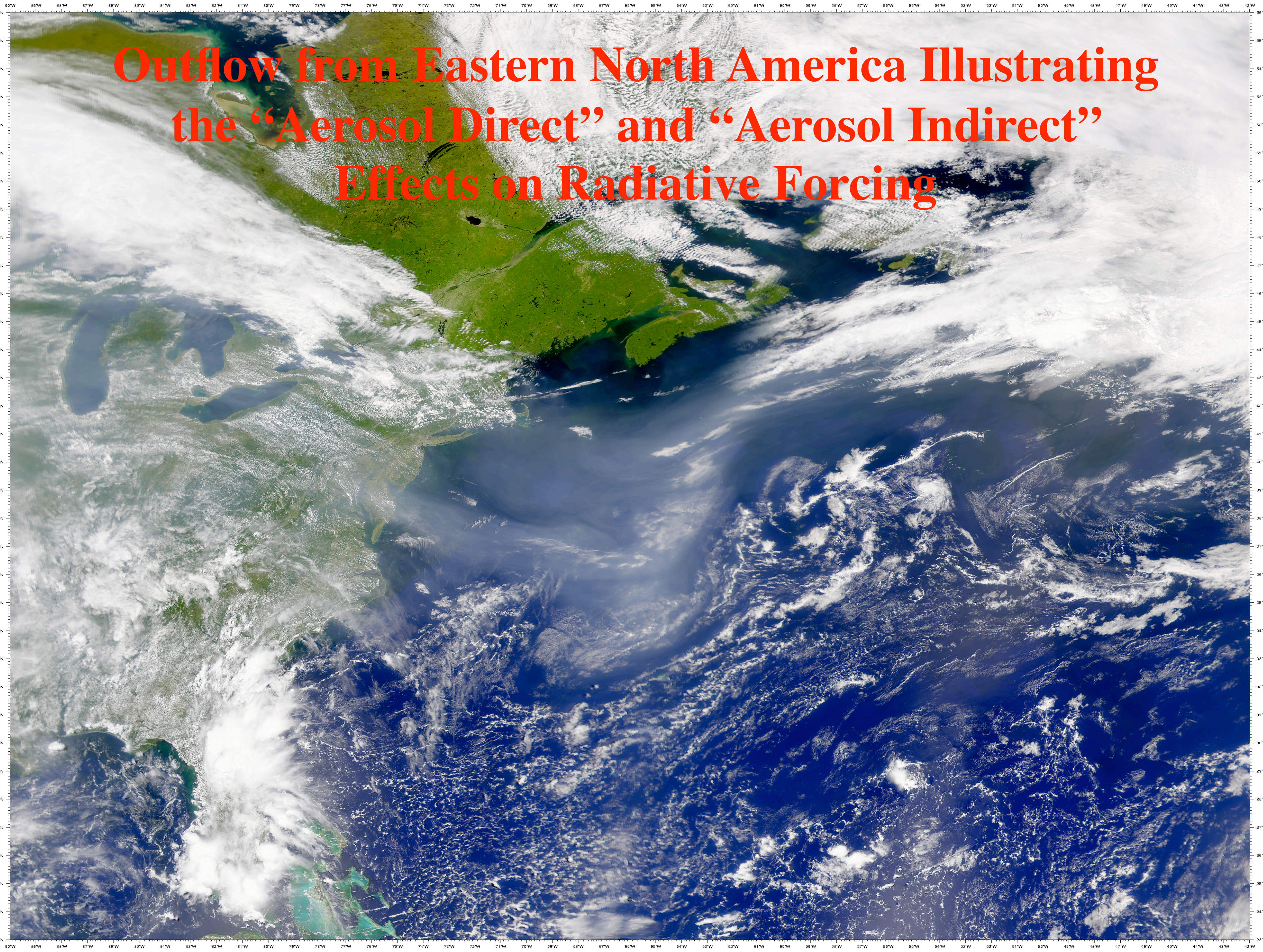
Regarding Atmospheric Nucleation, *John Aitken* Wrote a Century Ago:

"The great difficulty in investigations of this kind is the extremely minute quantities of matter which produce surprising results and make the work full of pitfalls for the hasty."

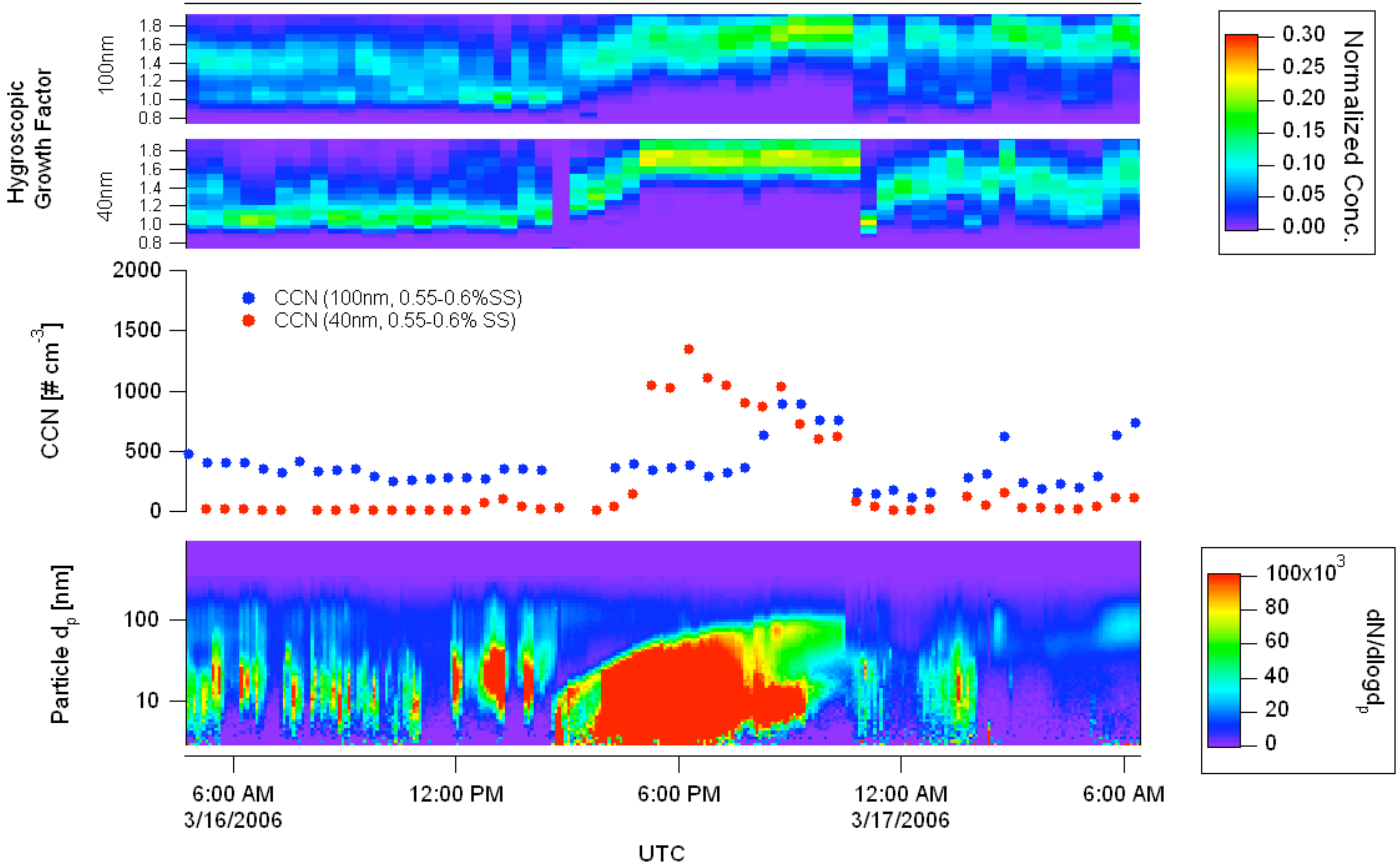
Coworker Acknowledgments

Jim Smith	NCAR & U. E. Finland	TDCIMS, H NanoTDMA, **etc.**
Fred Eisele	NCAR	Cluster CIMS, **etc.**
Jun Zhao	NCAR	Cluster CIMS
Jingkun Jiang	UMN	NPG, DEG
Chongai Kuang	UMN, BNL	DEG SMPS, Cluster Dynamics
Modi Chen	UMN	DEG SMPS
Jacob Scheckman	UMN	Nano TDMA
Mari Titcombe	UMN	Cluster CIMS
Brent Williams	UMN	Nano TDMA
Kelley Barsanti	NCAR, Port. State	Aerosol Thermodynamics
Thanos Nenes	Georgia Tech.	CCN Measurements
Sara Lance	Georgia Tech., NOAA	CCN Measurements
David Hanson	Augsburg College	AmpMS

Outflow from Eastern North America Illustrating the "Aerosol Direct" and "Aerosol Indirect" Effects on Radiative Forcing

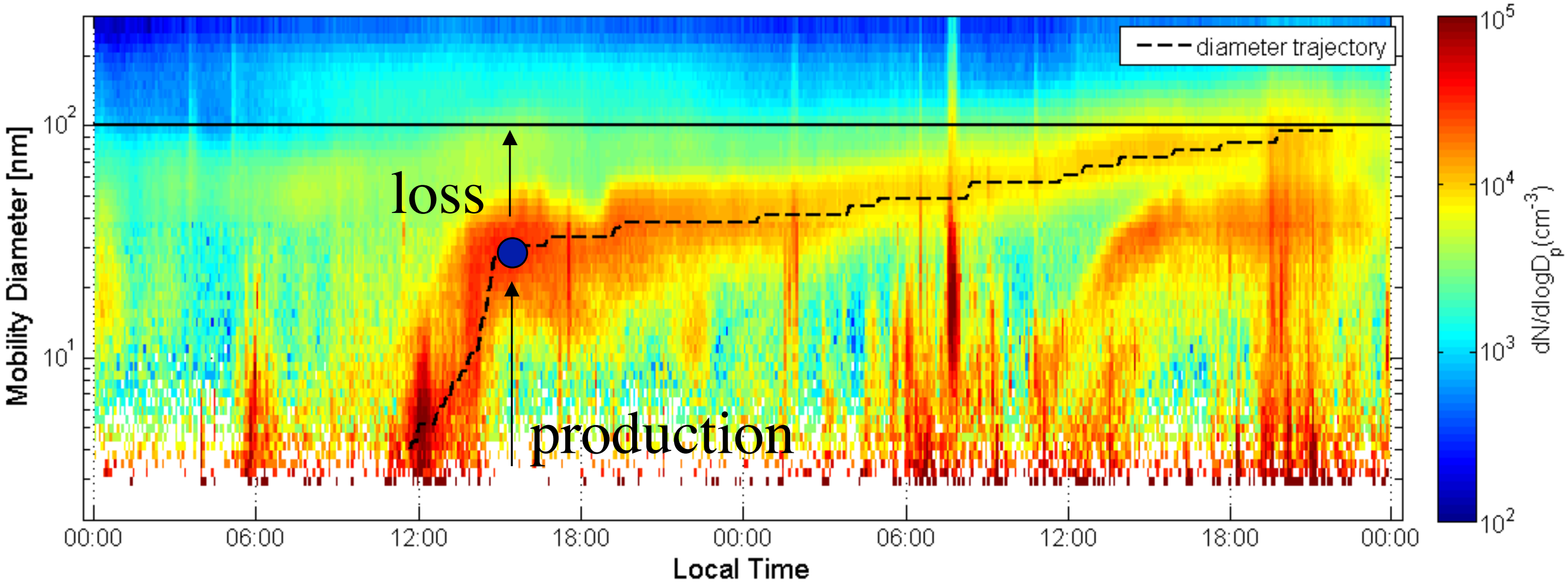


Freshly Nucleated Particles are Hygroscopic and can Serve as CCN: Tecamac, Mexico (16 March, 2006)



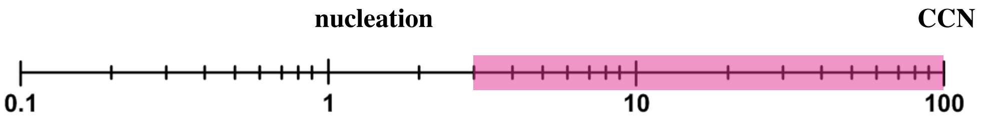
Lance, Smith, Nenes, McMurry et al, *unpublished* 2009

CCN Production Model



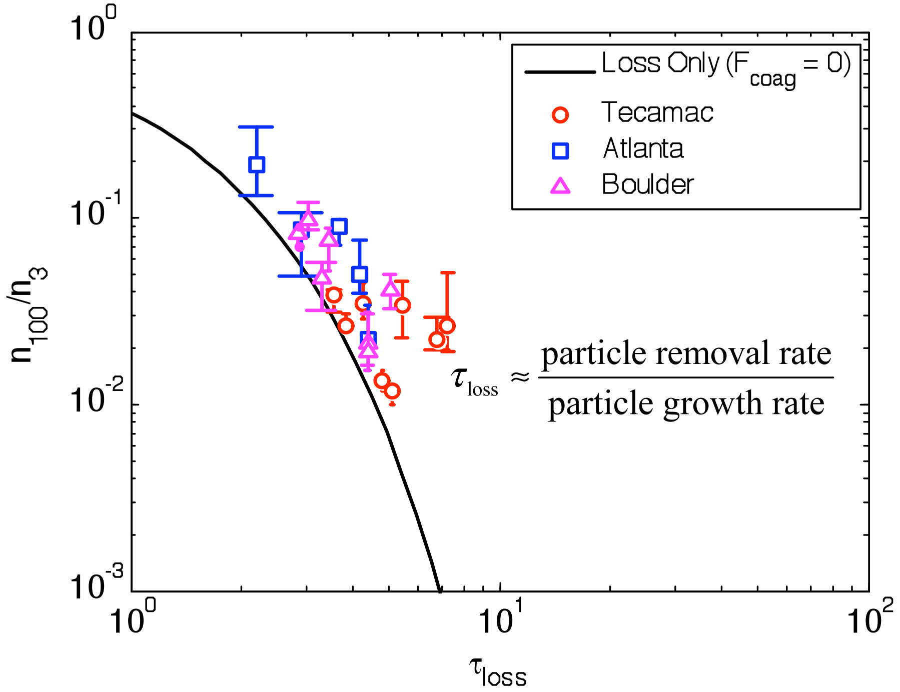
- Aerosol general dynamic equation (GDE) solved along diameter trajectory, constrained by *measured* growth rates and size distributions, to evaluate probability that freshly nucleated 3 nm particle will grow to 100 nm:

$$n_{100}\left(t_{100}\right)=\underbrace{\exp\left[-\tau_{loss}\left(t_{100}\right)\right]}_{\text{Scavenging loss}}\cdot\left[n_3+\underbrace{\int_0^{t_{100}} F_{coag}\left(t\right)\cdot\exp\left[\tau_{loss}\left(t\right)\right]\cdot dt}_{\text{Coagulation production}}\right]$$

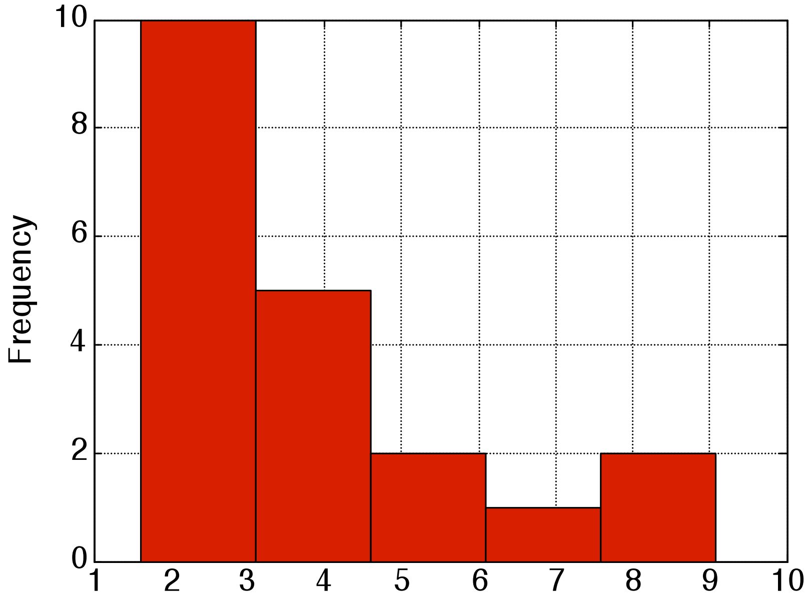


Kuang et al., *GRL* **36**:L09822, 2009

CCN Formation Probability & Effect of NPF on CCN Concentrations

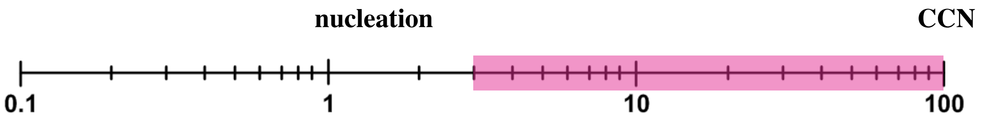


$$\tau_{loss} \approx \frac{\text{particle removal rate}}{\text{particle growth rate}}$$



Enhancement in CCN Number Concentrations due to NPF

- 1 – 10% of 3 nm particles grow to 100 nm
- Pre-existing CCN conc. enhanced by 2 – 9x
- Measured GR: 5 – 22 nm/h (~10x than GR_{H2SO4})



Kuang et al., *GRL* **36**:L09822, 2009

Why is Nucleation an Important Atmospheric Process?

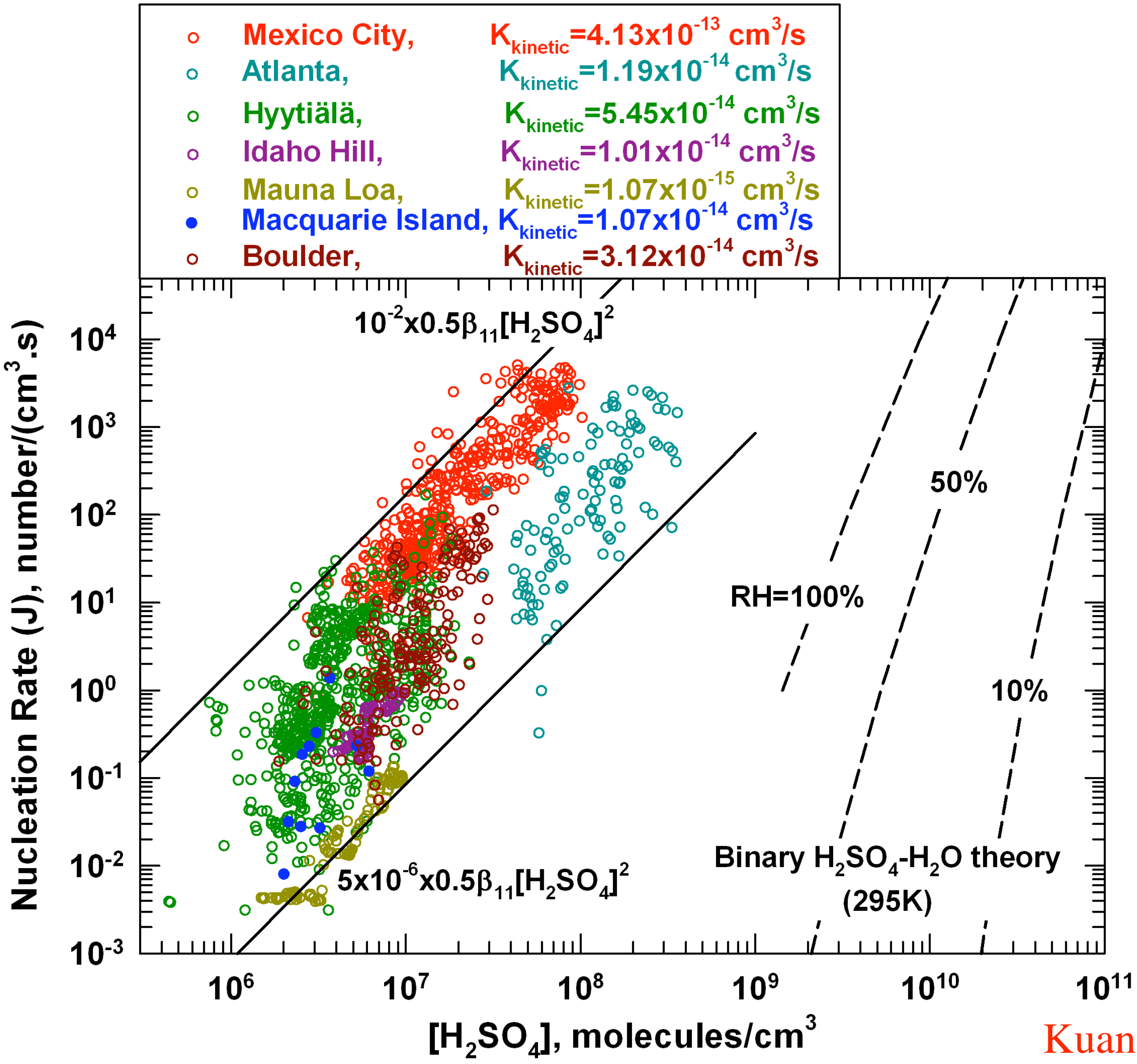
$$\underbrace{J(D_p)}_{\text{NPF Rate}} = \underbrace{J}_{\text{Nucleation Rate } J \approx J_{1\ nm}} \underbrace{\exp\left\{ -\frac{A_{Fuchs}k}{dD_p/dt}\Psi \right\}}_{\text{Survival Probability}}$$

Answer: Both J and dD_p/dt are much higher than we originally thought possible. Our research aims at understanding why.
(**NPF**=New Particle Formation}

Evidence that *J* is Higher than Expected

1. *Boundary Layer Nucleation Rates*, *J*, are very High
   - ~10^6-10^8 X higher than predicted for binary H_2SO_4–H_2O nucleation
   - $J \sim [H_2SO_4]^p$, $1 < p < 2$ rather than $J \sim [H_2SO_4]^p$, $p > 6$-8

Empirical Observation: $J_{1\ \mathrm{nm}} = K[H_2SO_4]^2$
(Applies to measurements in diverse environments)



Note the prefactors: 10^{-2} to 5×10^{-6}

Hyytiälä data courtesy of Kulmala et al.

Kuang et al., *JGR* **113**:D10209, 2008

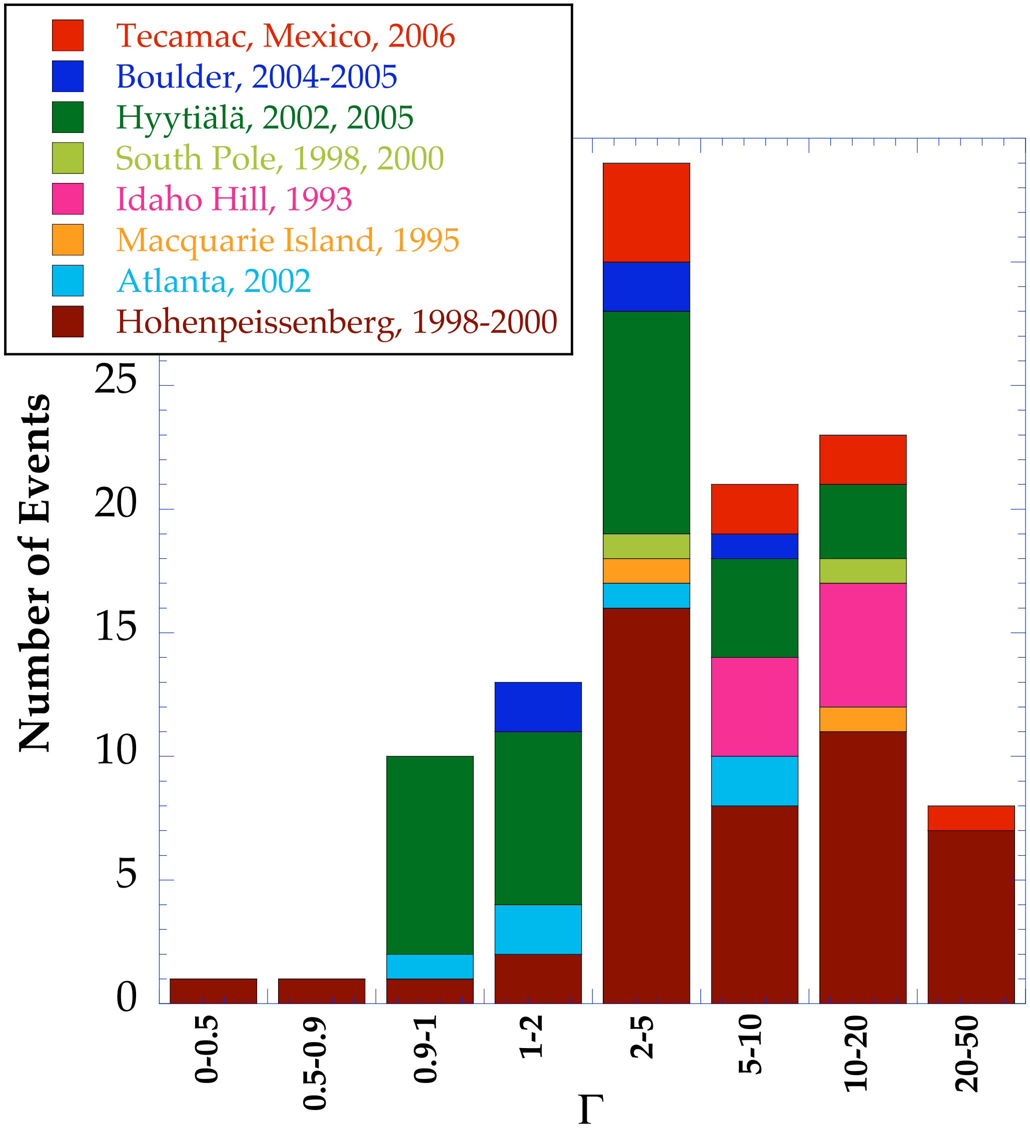
Evidence that $GR=dD_p/dt$ are higher than expected

1. *Boundary Layer Nucleation Rates* are very High
   - ~10^6-10^8 X higher than predicted for binary H_2SO_4–H_2O nucleation
   - $J \sim [H_2SO_4]^p$, $1 < p < 2$ rather than $J \sim [H_2SO_4]^p$, $p > 6$-8

2. *Nanoparticle Growth Rates* are very High.

$$1 < \Gamma < 50; \quad \Gamma = \frac{GR}{GR_{H_sSO_4}}$$

Growth Factors: $\Gamma = GR/GR_{H_2SO_4}$



Stolzenburg et al., 2005; Wehner et al, 2005; Kuang et al, 2010

Relationship between *NPF Rates* and *Nucleation Rates*

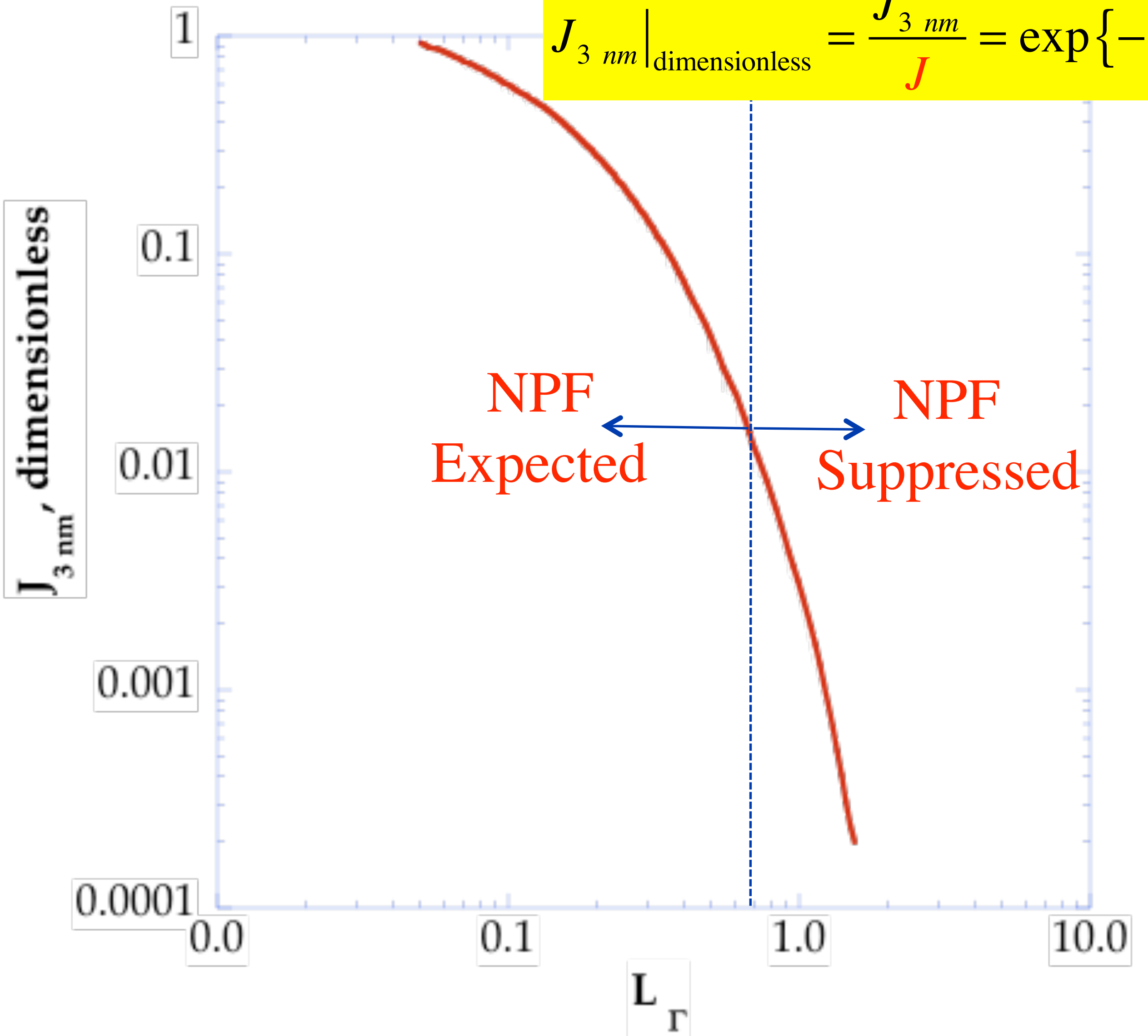
$$\underbrace{J(D_p)}_{\text{NPF Rate}} = \underbrace{J}_{\text{Nucleation Rate } J \approx J_{1\,nm}} \underbrace{\exp\left\{-\frac{A_{Fuchs}k}{dD_p/dt}\Psi\right\}}_{\text{Survival Probability}} = J\exp\{-L_\Gamma\Psi\}$$

$$L_\Gamma = \frac{L_{McMurry\,\&\,Friedlander\,1979}}{\Gamma} = \frac{A_{Fuchs}k/\left(dD_p/dt\right)_{H_2SO_4}}{\Gamma}$$

Kuang et al., *ACPD*, 2010

Probability that a Freshly Nucleated Particle Grows to 3 nm: GDE Solution

$$J_{3\ nm}\Big|_{\text{dimensionless}} = \frac{J_{3\ nm}}{J} = \exp\left\{-L_\Gamma \Psi\right\}$$

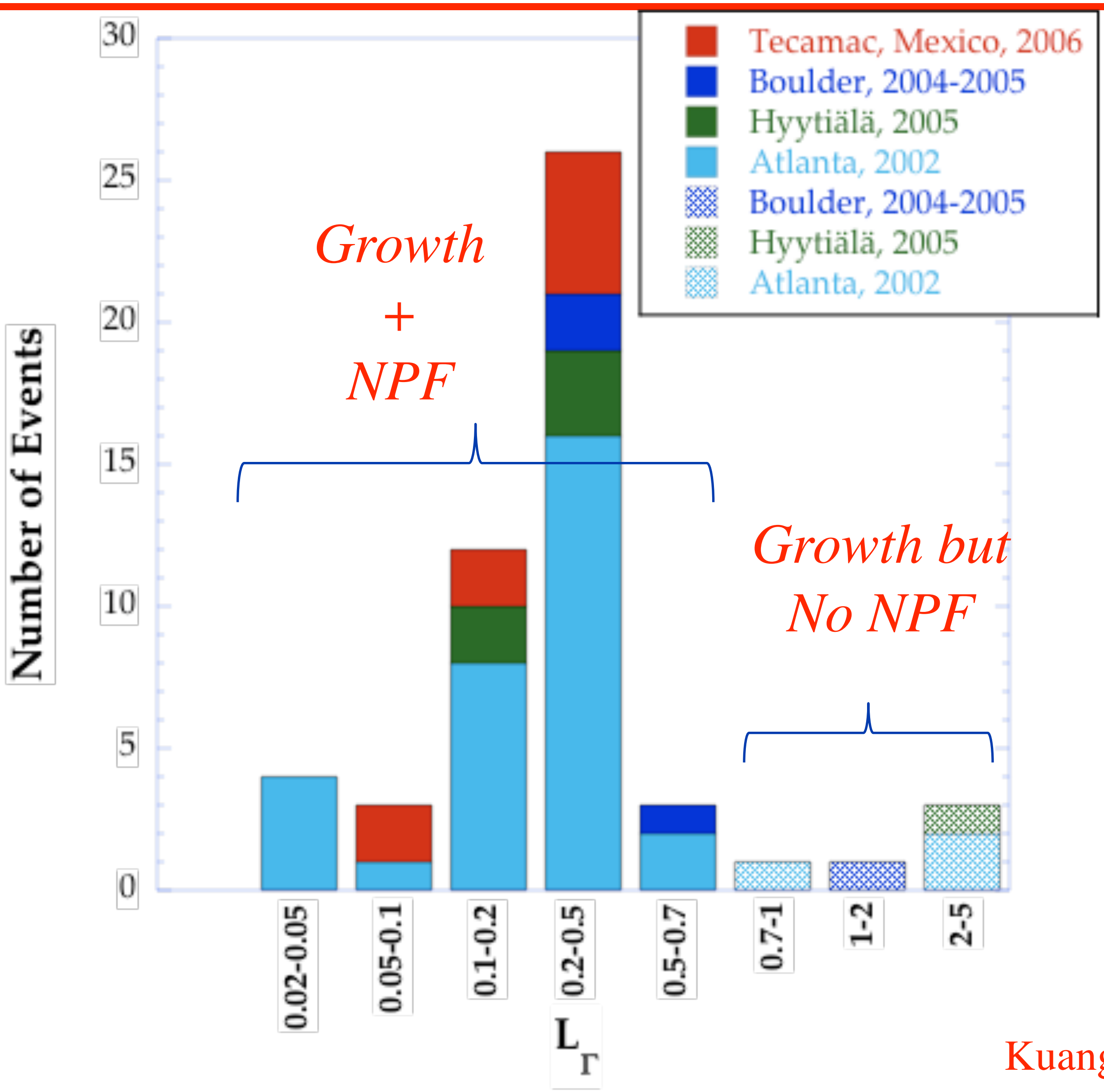


NPF Expected

NPF Suppressed

Kuang et al., *ACPD*, 2010

Values of L_Γ during Nucleation and Growth Events



Growth
+
NPF

Growth but
No NPF

Kuang et al., *ACPD*, 2010

Question 1:

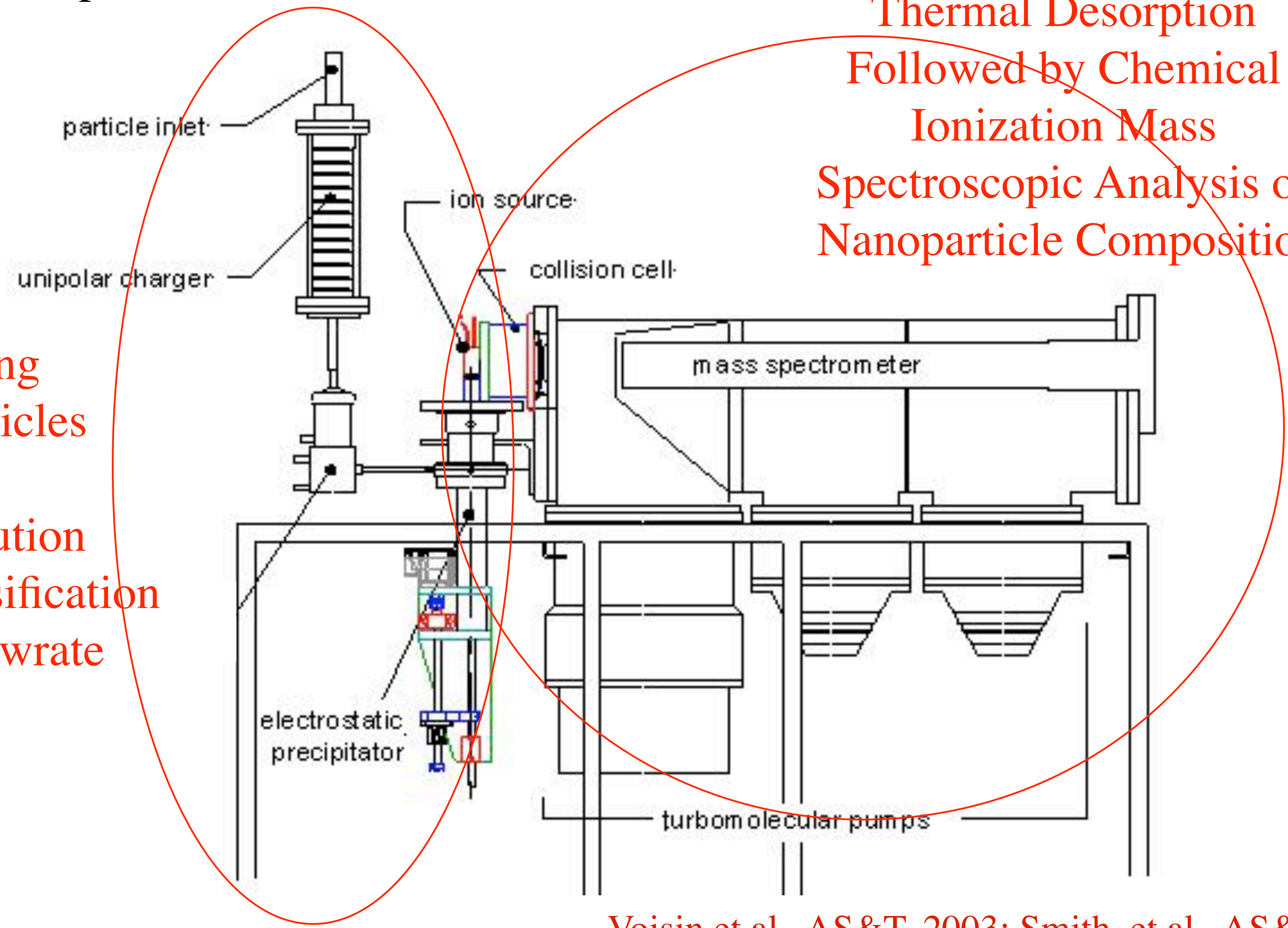
Why are *Growth Rates* of Freshly Nucleated Particles So High?

$$dD_p/dt = \Gamma \bullet dD_p/dt_{H2SO4}$$

(i.e., why is Γ so high, or equivalently, why is L_Γ so low?)

Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS)

an instrument for characterizing the chemical composition of ambient particles from **8 to 50 nm** in diameter

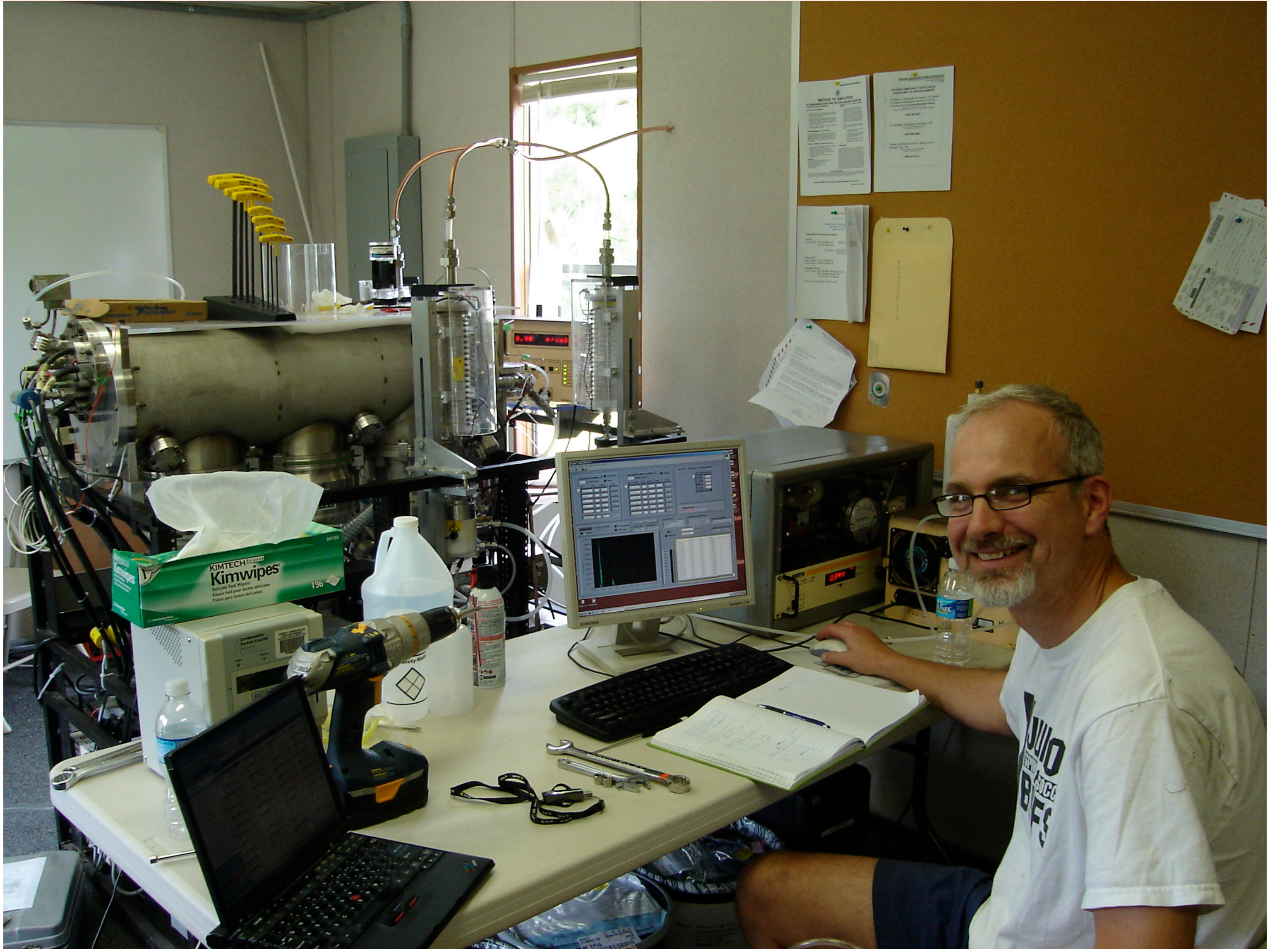


Sampling
Nanoparticles
By
low resolution
mobility classification
at high flowrate

Thermal Desorption
Followed by Chemical
Ionization Mass
Spectroscopic Analysis of
Nanoparticle Composition

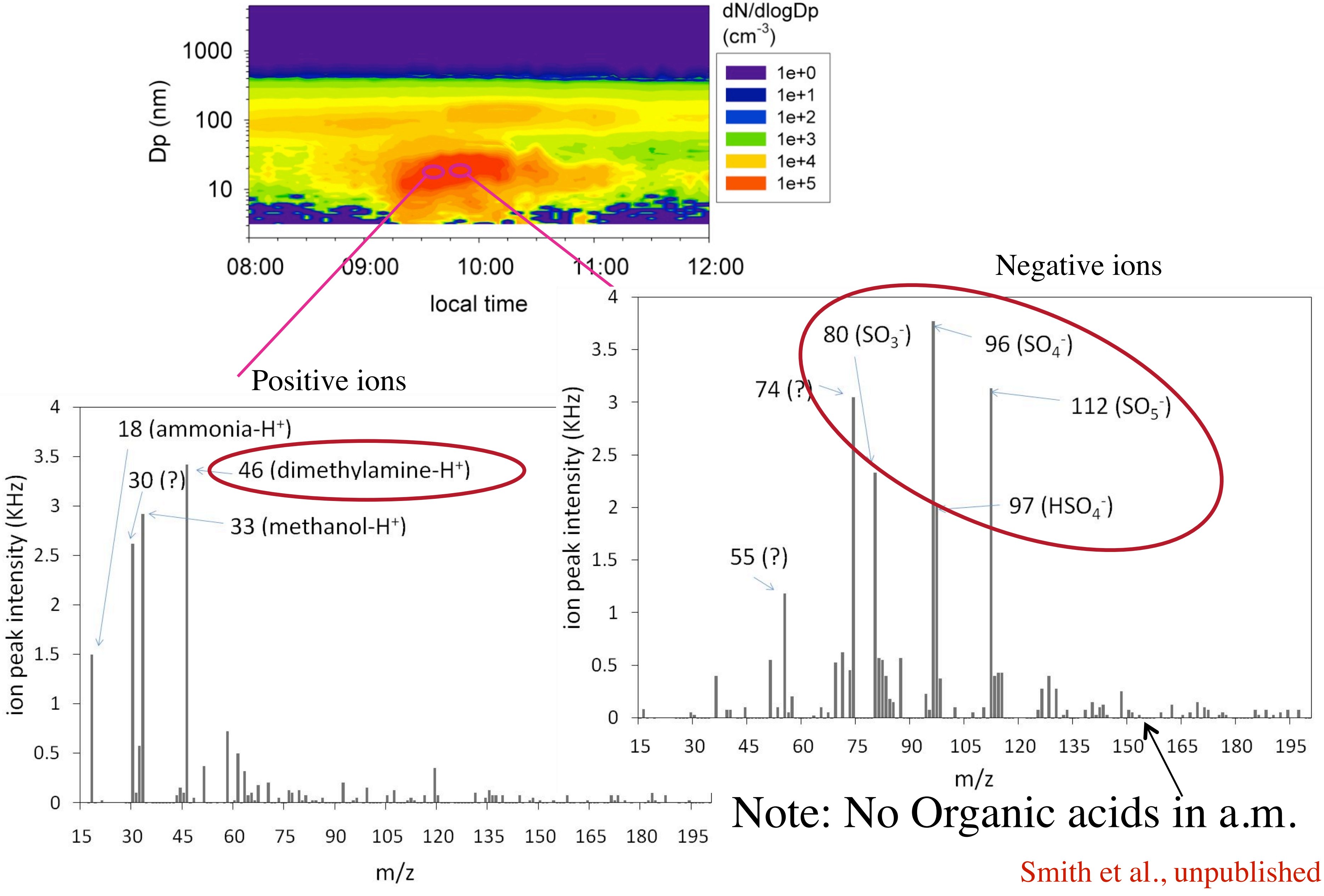
Voisin et al., AS&T, 2003; Smith, et al., AS&T, 2004

The TDCIMS (Atlanta, 7/23/09)



Jim Smith, NCAR & U. Kuopio

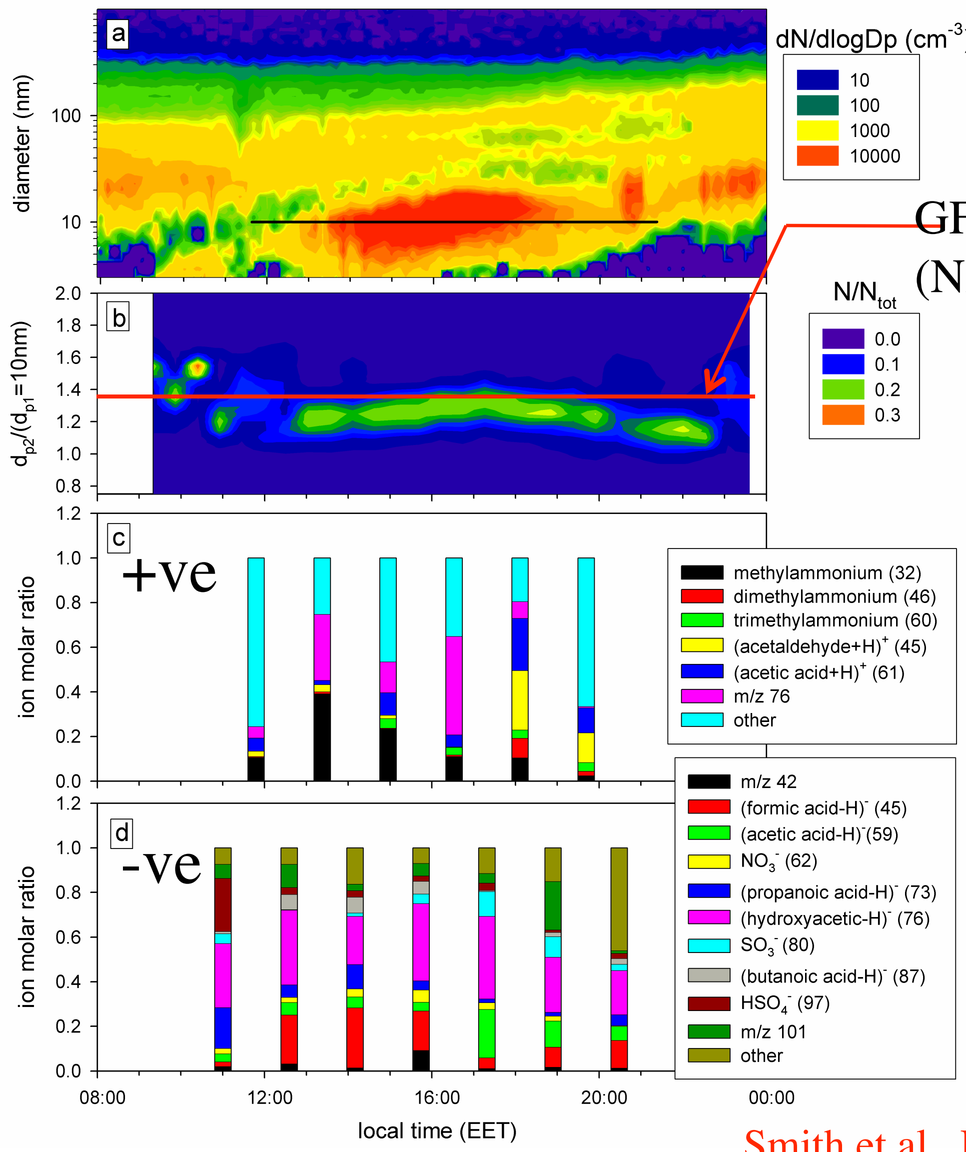
Atlanta, July 25, 2009: Composition of 20nm particles



Note: No Organic acids in a.m.

Smith et al., unpublished

TDCIMS observations at Hyytiälä on 9 April 2007 show aminium ions with deprotonated acids in 10nm particles

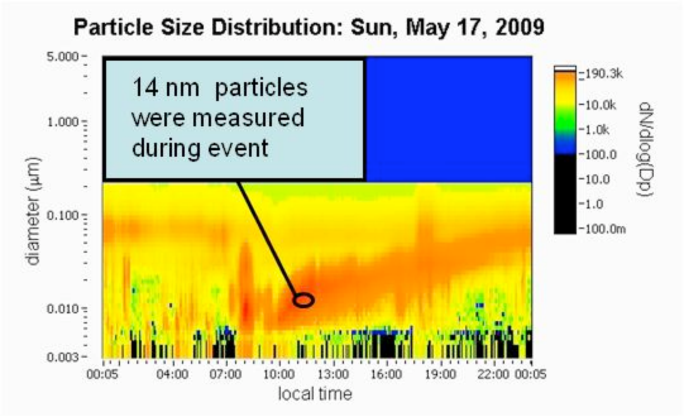


GF for 10nm $(NH_4)_2SO_4$

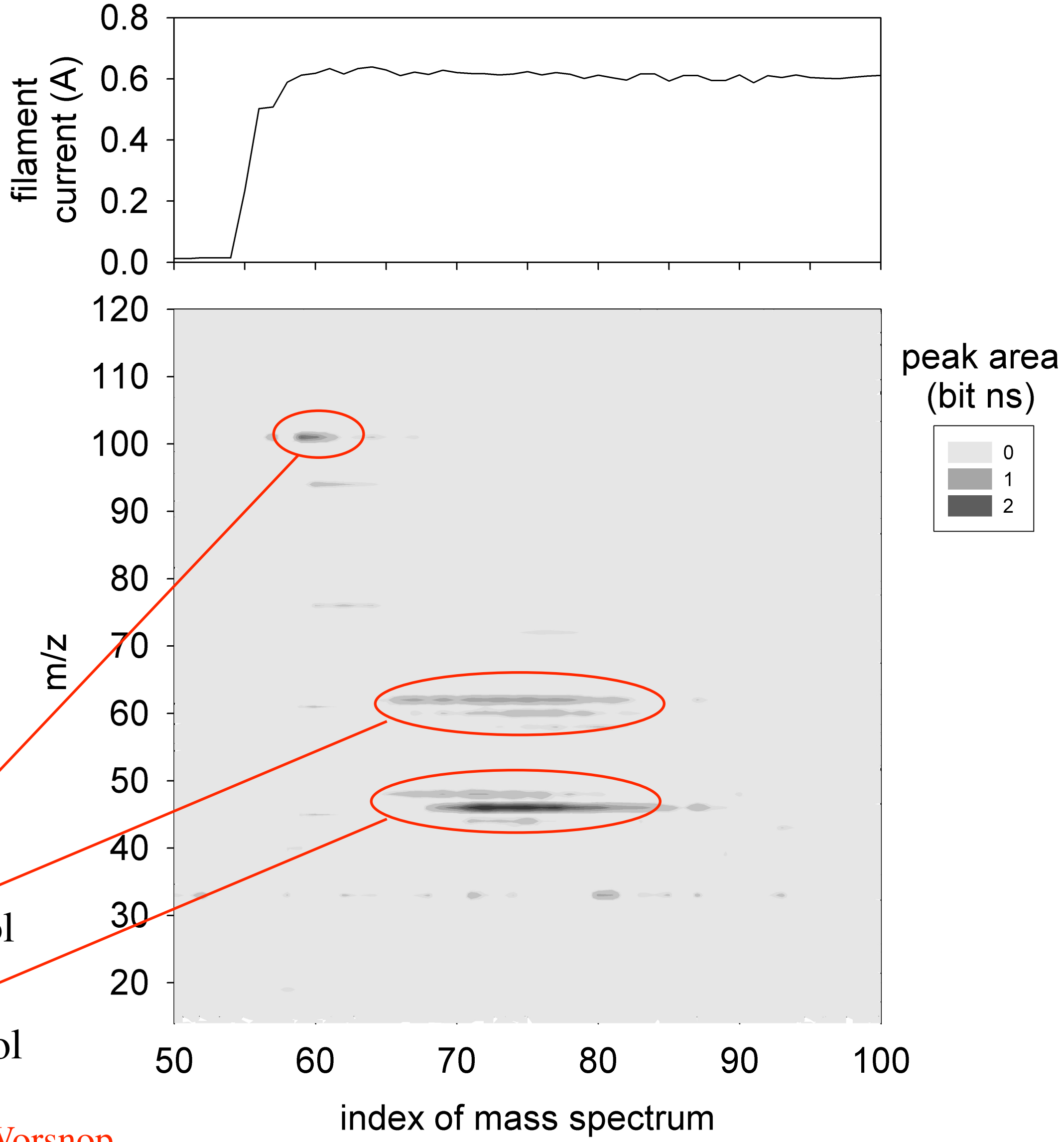
- On average, aminium ions comprise about 23% of positive ion spectrum
- 10 nm particles had an average 90%RH growth factor of 1.27

Smith et al., PNAS, 2010, DOI: 10.1073/pnas.0912127107

TOF-TDCIMS analysis of 14 nm diameter particles collected during a NPF event in Boulder, CO



- As filament is heated, the TOF acquired mass spectra at 5Hz (100x faster than the quadrupole mass spec)
- The peaks appear as streaks in the plot to the right.



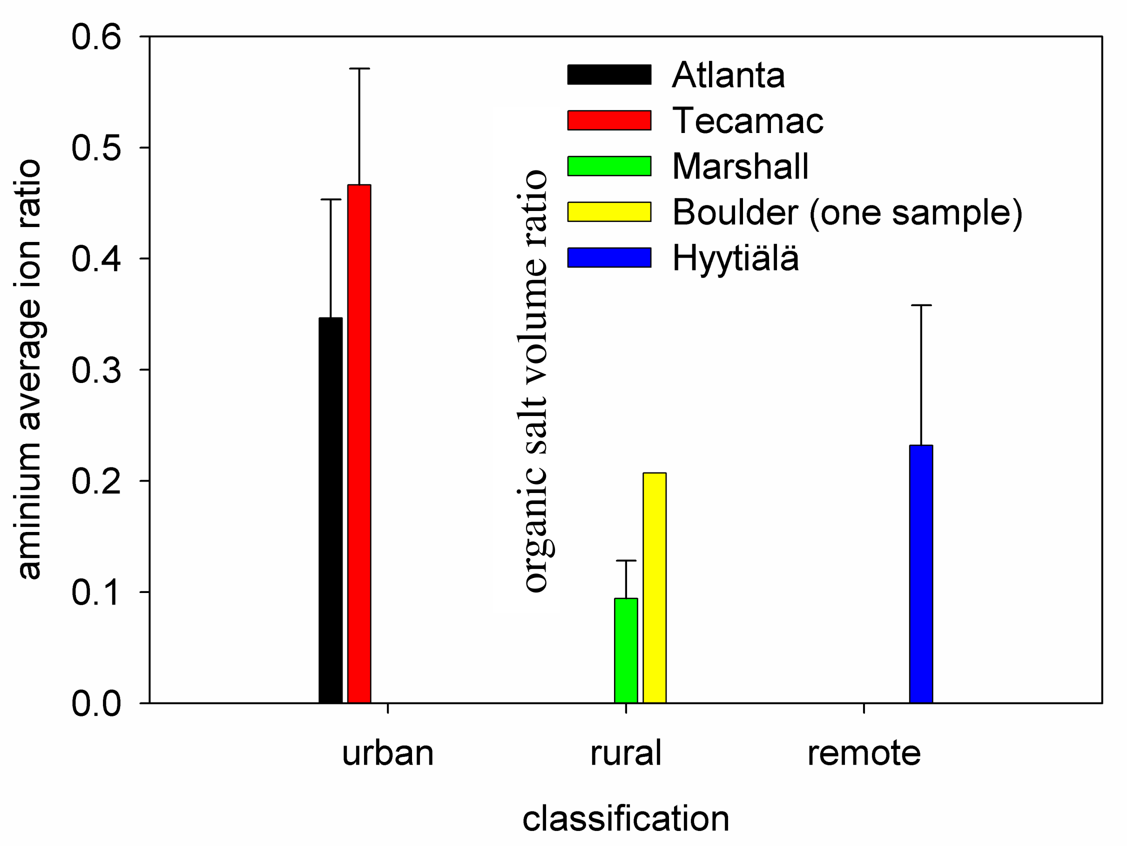
100.17amu ($C_6H_{13}NH^+$), protonated amine

59 & 61amu, protonated C3-ketone & -alcohol

45 & 47amu, protonated C2-aldehyde & -alcohol

Jim Smith, unpublished, 2009. Thanks to Kimmel & Worsnop

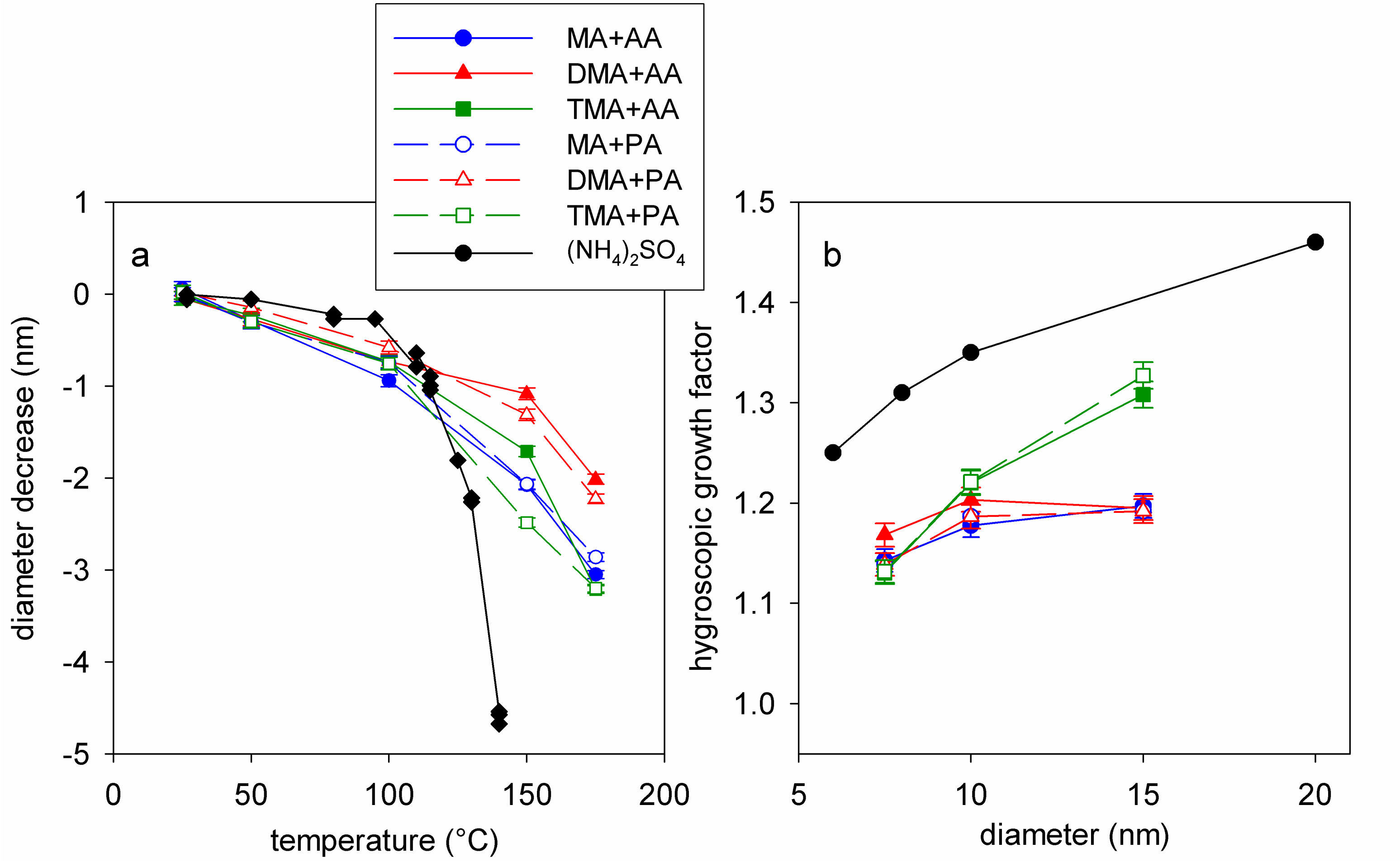
Aminium ion ratios suggest that organic and inorganic salt formation may be a universal, and important, growth process



Conclusion: Aminium salts are largely responsible for high growth rates (i.e., $\Gamma >> 1$)

Smith et al., PNAS, 2010, DOI: 10.1073/pnas.0912127107

What are the physical-chemical properties of organic salts? Results from hygroscopicity and volatility measurements



Smith et al., PNAS, 2010, DOI: 10.1073/pnas.0912127107

Conclusion Regarding High dD_p/dt

Alkylammonium carboxylate salts,
presumably formed by reactions of
amine + carboxylic acid gases,
contribute significantly to high *growth rates* of
freshly nucleated particles everywhere that we
have made TDCIMS measurements.

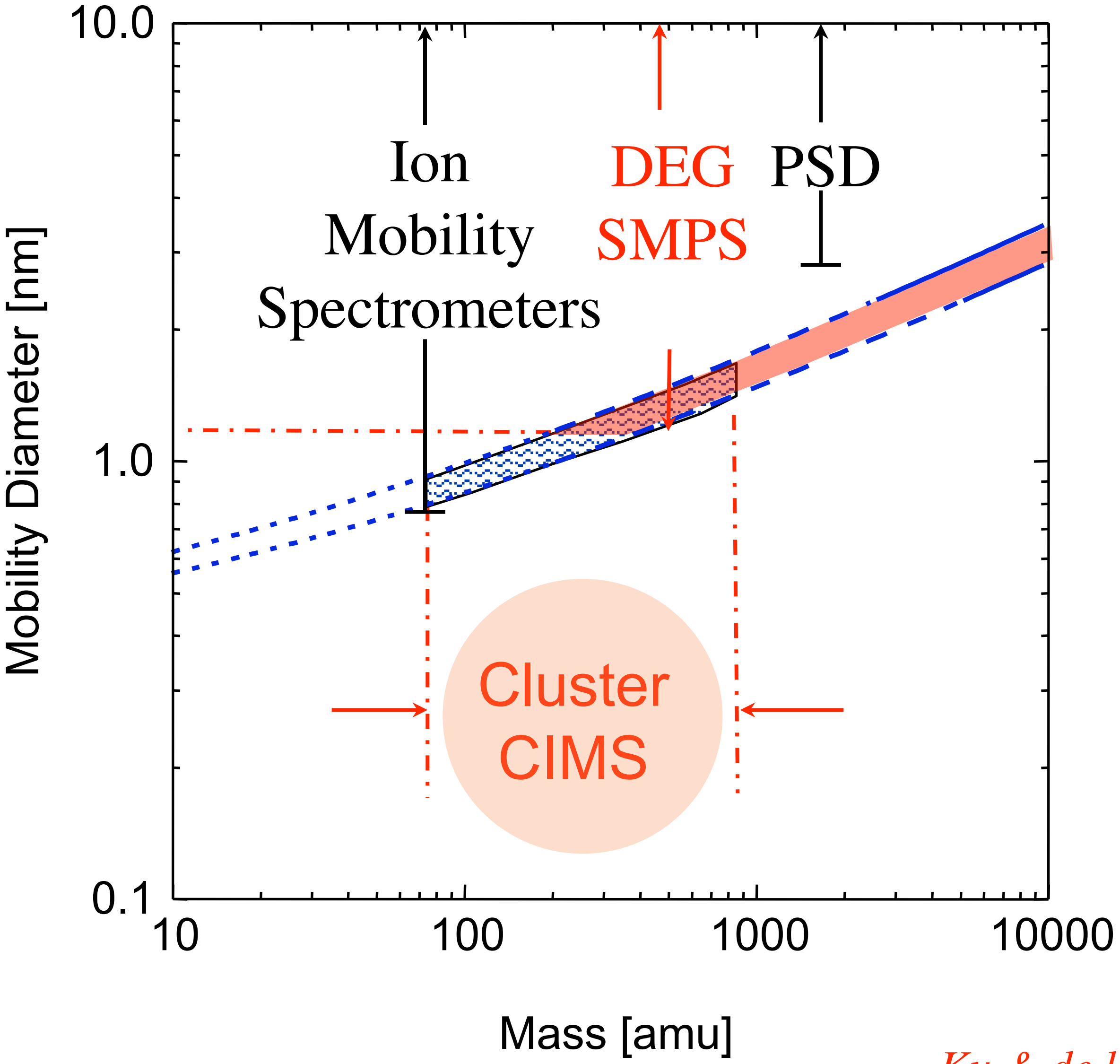
Question 2:

Why are

Boundary Layer Nucleation Rates

so High?

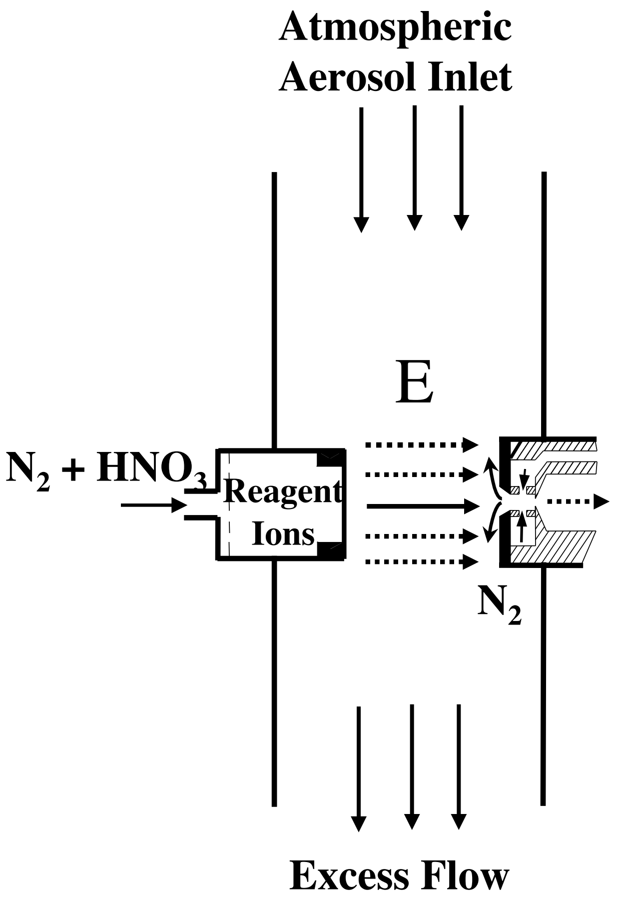
Our Experimental Strategy:
Bridge the gap: Molecules to Clusters to NPs

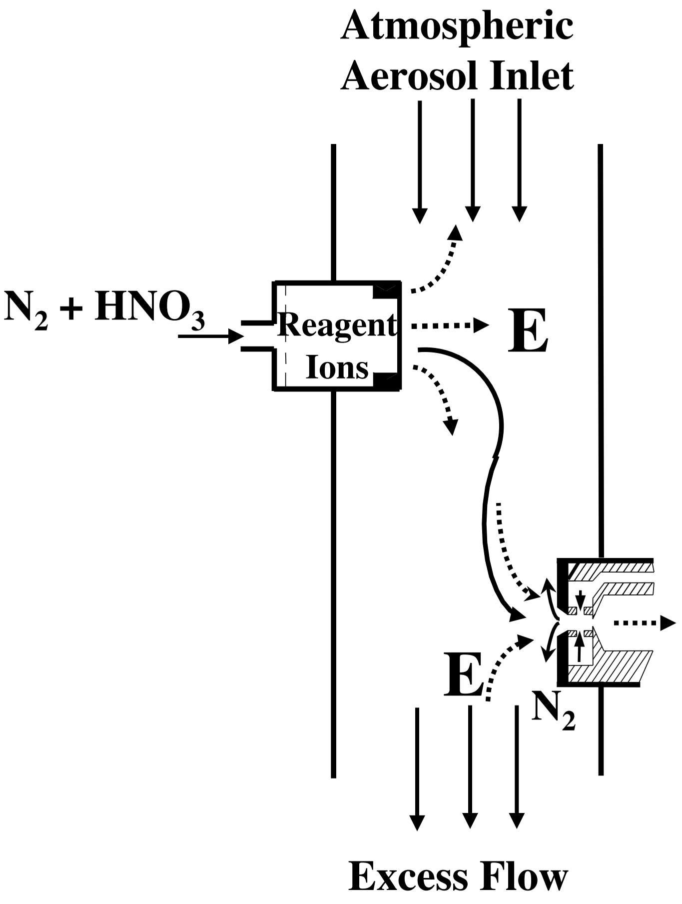


Ku & de la Mora, AST 2009

Chemical Ionization and Ion Transport to MS Inlet In the Cluster-CIMS

Two operation modes

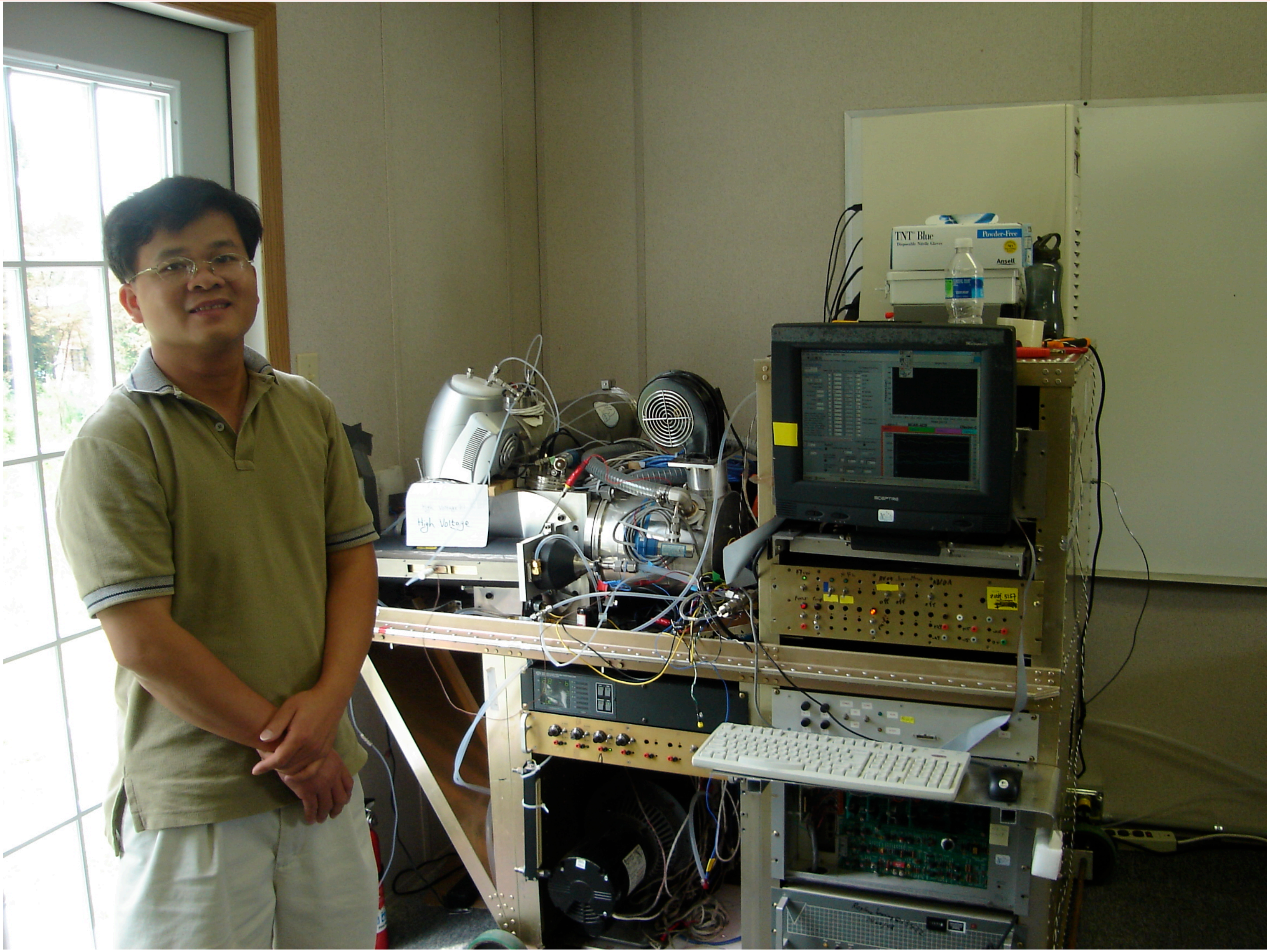




Transverse ion mode *Flow tube mode*

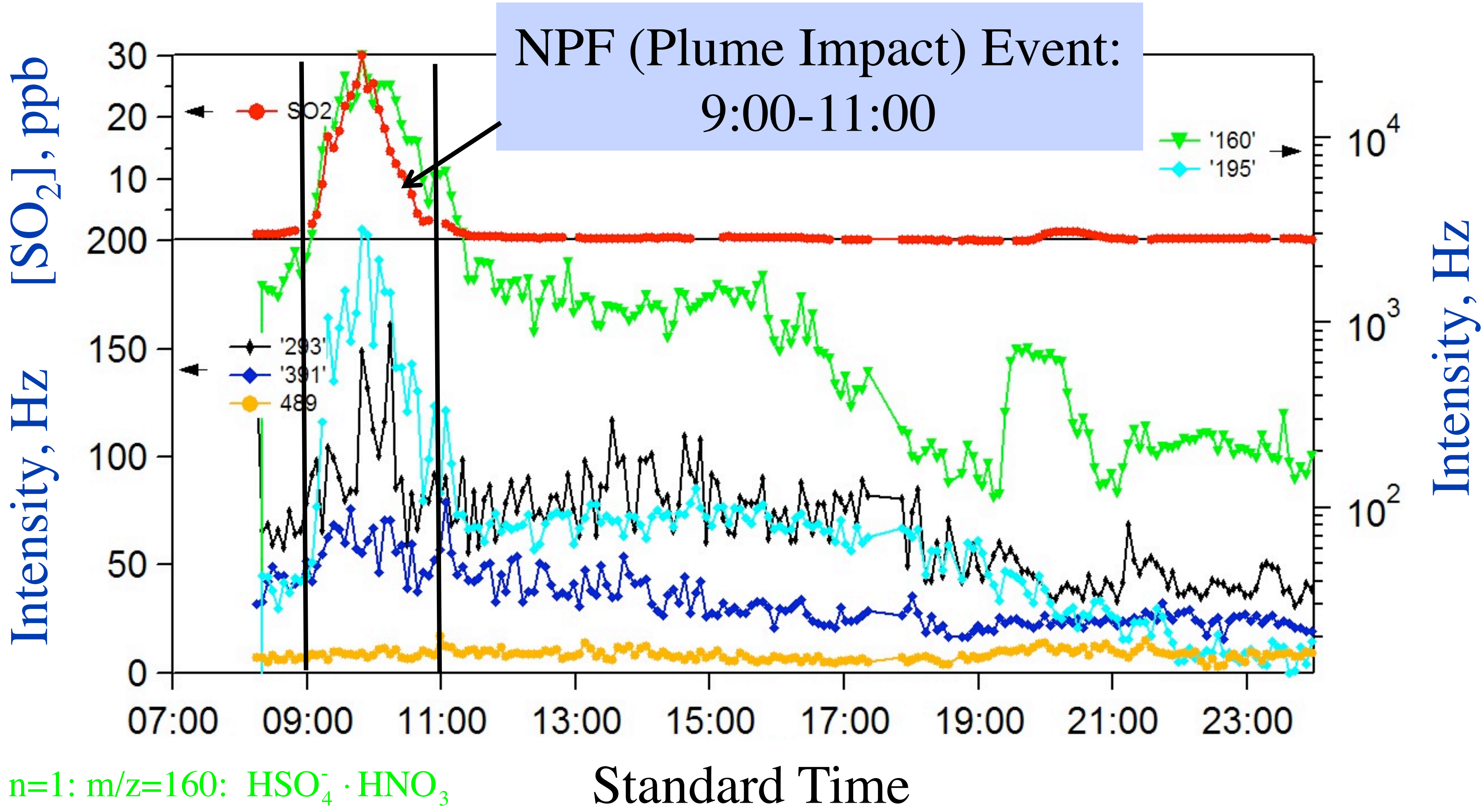
Zhao et al., *JGR*, 2010. DOI: 10.1029/2009JD012606

The Cluster CIMS
(Atlanta, 7/23/09)



Jun Zhao, NCAR

“Raw” Cluster CIMS Data, Atlanta, July 25, 2009



n=1: m/z=160: $HSO_4^- \cdot HNO_3$

n=2: m/z=195: $HSO_4^- \cdot H_2SO_4$

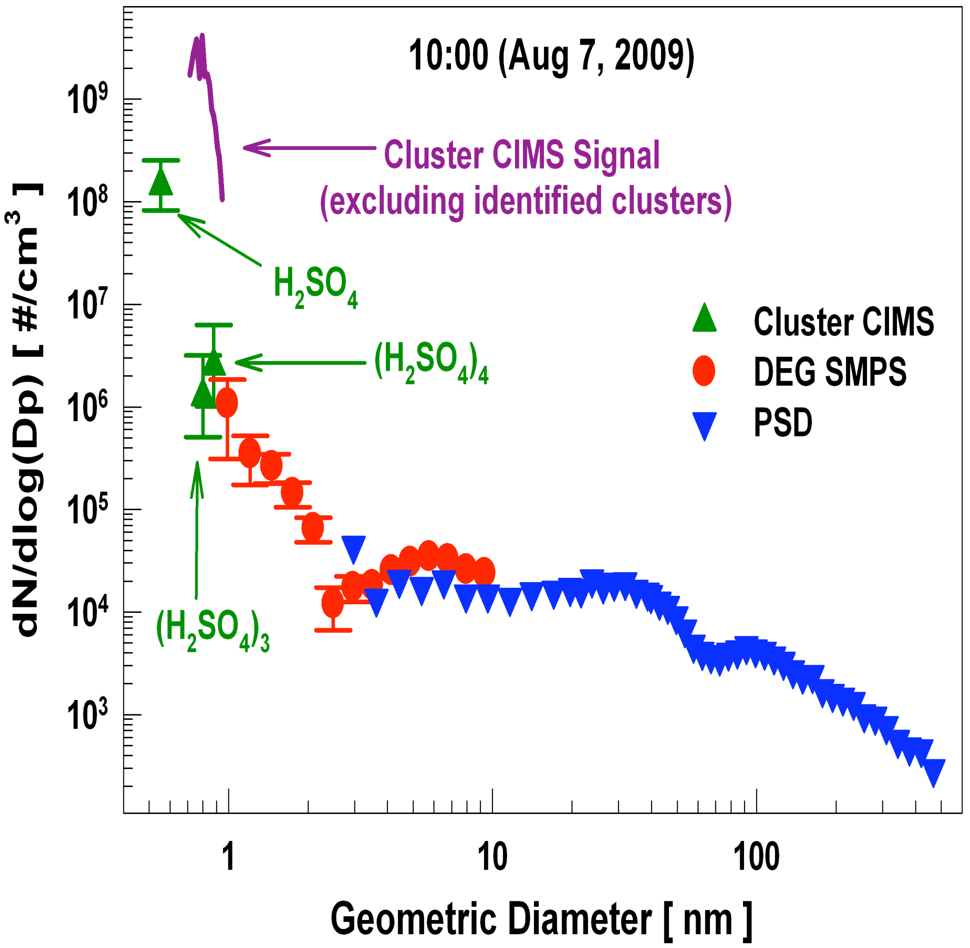
n=3: m/z=293: $HSO_4^- \cdot (H_2SO_4)_2$

n=4: m/z=391: $HSO_4^- \cdot (H_2SO_4)_3$

n=5: m/z=489: $HSO_4^- \cdot (H_2SO_4)_4$

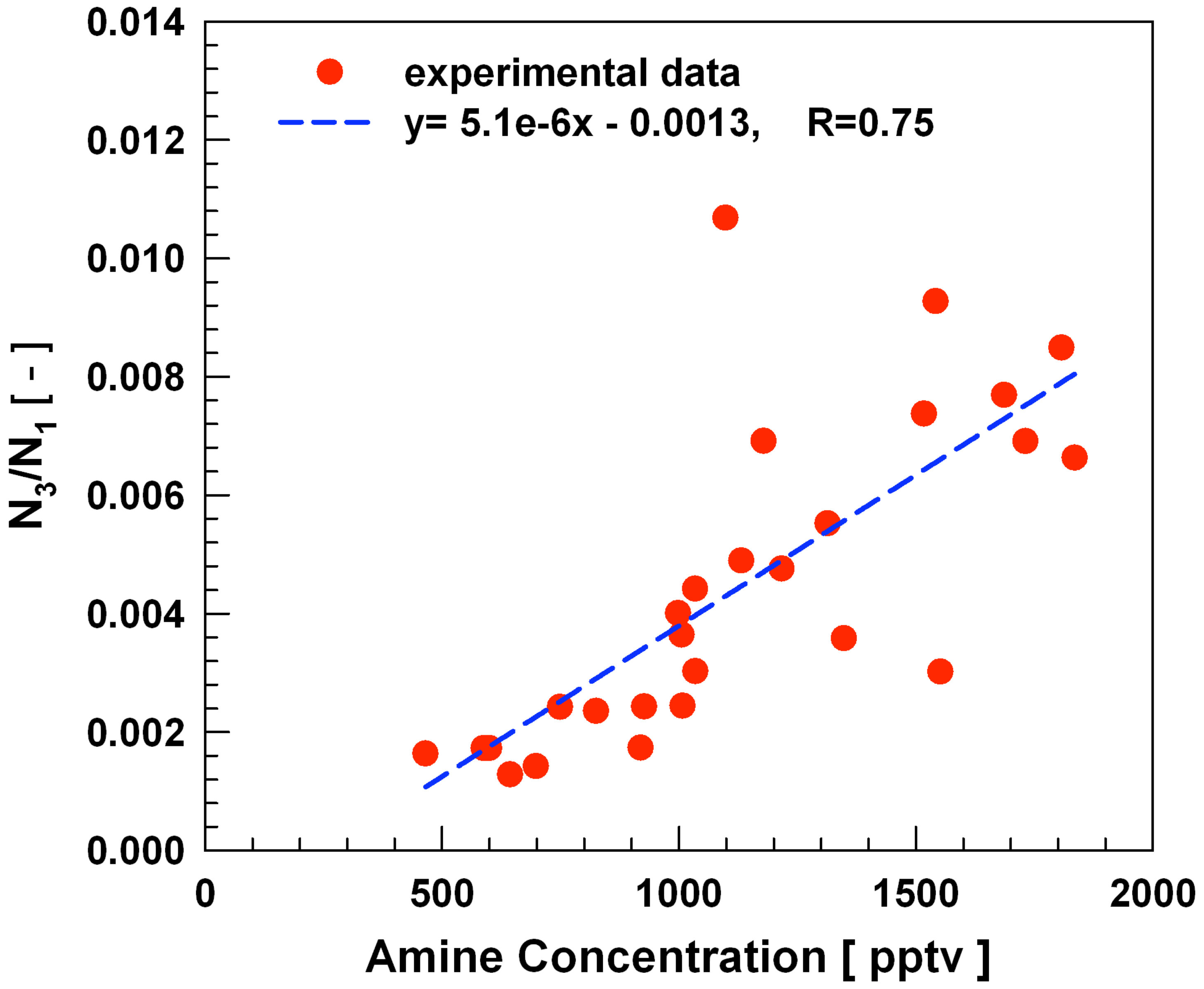
Jun Zhao & Fred Eisele, *unpublished*, 2010

First Complete Measurements of Particle Number Distributions: Nucleating Vapor Molecules, Molecular Clusters, 1 nm Particles & Beyond



UMN & NCAR Team, *Aerosol Sci. Technol. submitted*, 2010

N_3/N_1 Vs Total Amines: Atlanta, 8/7/09



Zhao et al,
and
Hanson,
unpublished
2010

Tentative Conclusion Regarding High Nucleation Rates

Concentrations of neutral, stable molecular clusters formed by nucleation are positively correlated with concentrations of gas phase amines.

We hypothesize that reactions between amines and $(H_2SO_4)_n$ clusters lead to stable clusters that form new particles.

Recent Quotation from Murray Johnston et al APCD article:
“Amine exchange into ammonium bisulfate and ammonium nitrate nuclei”

Uptake coefficients (reaction probabilities) were found to be near unity, implying that complete exchange of ammonia in small salt clusters by amine would be expected to occur within several seconds to minutes in the ambient atmosphere. These results suggest that if salt clusters are a component of the sub-3nm cluster pool, they are likely to be aminium salts rather than ammonium salts, even if they were initially formed as ammonium salts.

Bzdek, Ridge, Johnston, ACPD discuss.net/10/45/2010

Two-Component Nucleation Model: Conceptual Model 2. $SA_2+X\rightarrow SA_2X$.

$$SA \;+\; \mathrm{SA} \xrightleftharpoons[k1b]{k1f} (SA)_2$$

$$(SA)_2 \;+\; X \xrightarrow{k2} (SA)_2 \cdot X$$

$$J = \frac{d\left[(SA)_2 \cdot X\right]}{dt} = k_2\left[(SA)_2\right]\left[X\right] = \frac{k_2\left[X\right]}{k_{1_b} + \kappa_2 + k_2\left[X\right]} \cdot \frac{1}{2} k_{1_f}\left[SA\right]^2$$

NOTE: This Mechanism is consistent with Anderson, Siepmann, McMurry, VandeVondelele, *JACS*, 2008 and uses Hanson & Lovejoy, *JPhysChem* 2006 thermodynamic properties for SA

UMN & NCAR Team, *unpublished*, 2010

Conceptual Two-Component Nucleation Model: $SA_2+X \rightarrow SA_2X$.

$$J = \frac{1}{2}\beta_{11}N_1^2\frac{k_2\left[X\right]}{k_{1b}+\kappa_2+k_2\left[X\right]}$$

$k_{1b} \cong 10^4\ s^{-1}$ to $10^5\ s^{-1}$ (Hanson)

$\kappa_2 = 0.1 \sim 0.01\ s^{-1}$ (integral over size distribution)

$k_2 = 3.4\times10^{-10}\frac{cm^3}{molecule\cdot s}$ (hard sphere collision rate)

$\left[X\right] = 2.34\times10^9$ to $2.34\times10^{10}\ \frac{molecules}{cm^3}$ (10-100 ppt, dimethy amine; Hanson)

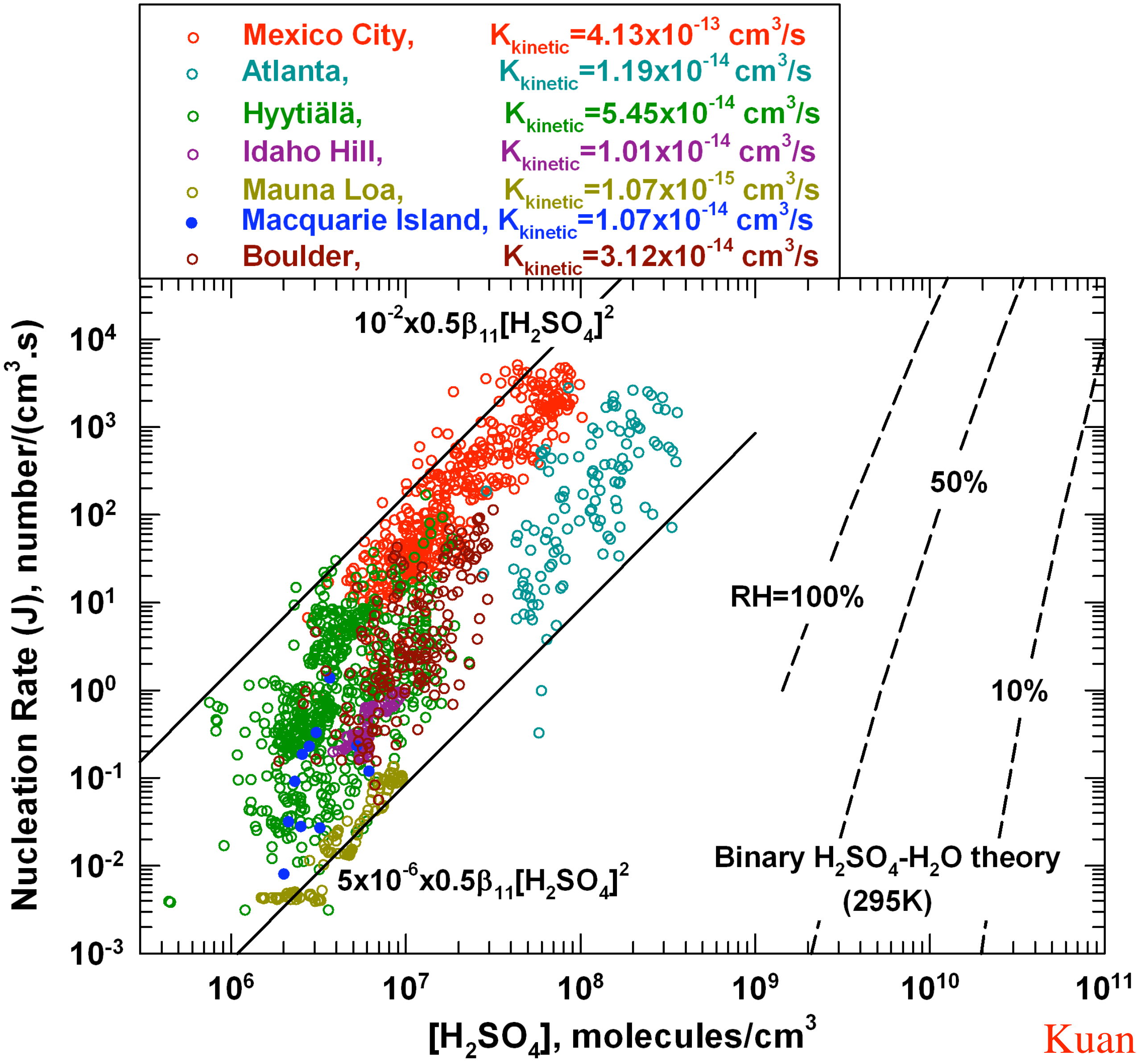
$$10^{-5} < \frac{k_2\left[X\right]}{k_{1b}+\kappa_2+k_2\left[X\right]} < 10^{-3}$$

NOTE: Small critical size (SA_2X) allows using a chemical kinetics framework rather than classical nucleation theory for nucleation rates, J. This may avoid some of the hurdles to earlier treatments of this problem.

UMN & NCAR Team, *unpublished*, 2010

Empirical Observation: $J_{1\ nm} = K[H_2SO_4]^2$

(Applies to measurements in diverse environments)



Note the prefactors:
5×10^{-6} to 10^{-2}
Vs
10^{-5} to 10^{-3}
From the simple theory

Hyytiälä data courtesy of Kulmala et al.

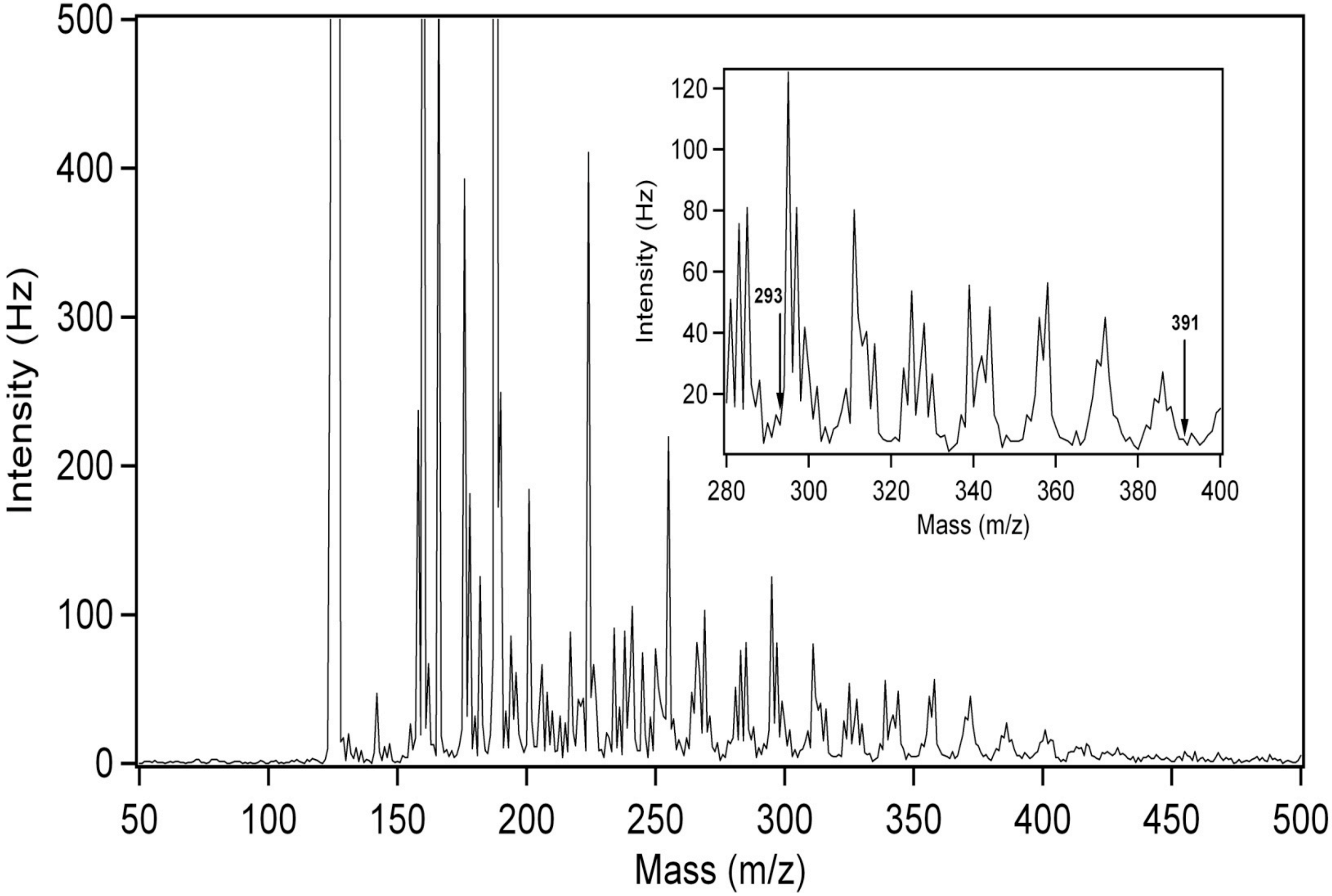
Kuang et al., *JGR* **113**:D10209, 2008

Conclusions

- L_{Γ} determines whether or not Nucleation leads to NPF
  - Nucleation important due to high J and GR (i.e., Γ)
- Organic Salts (e.g., amines + organic acids) responsible, at least in part, for high GR (i.e., for $\Gamma > 1$)
- $[H_2SO_4]_3/[H_2SO_4]=N_3/N_1$ correlated with amines.
- $1\times10^{-4} < [H_2SO_4]_3/[H_2SO_4] < 1\times10^{-2}$
- Small critical size (SA_2X ?) of stable nuclei may allow for a relatively simple theory for nucleation rates, based on chemical kinetics rather than CNT.

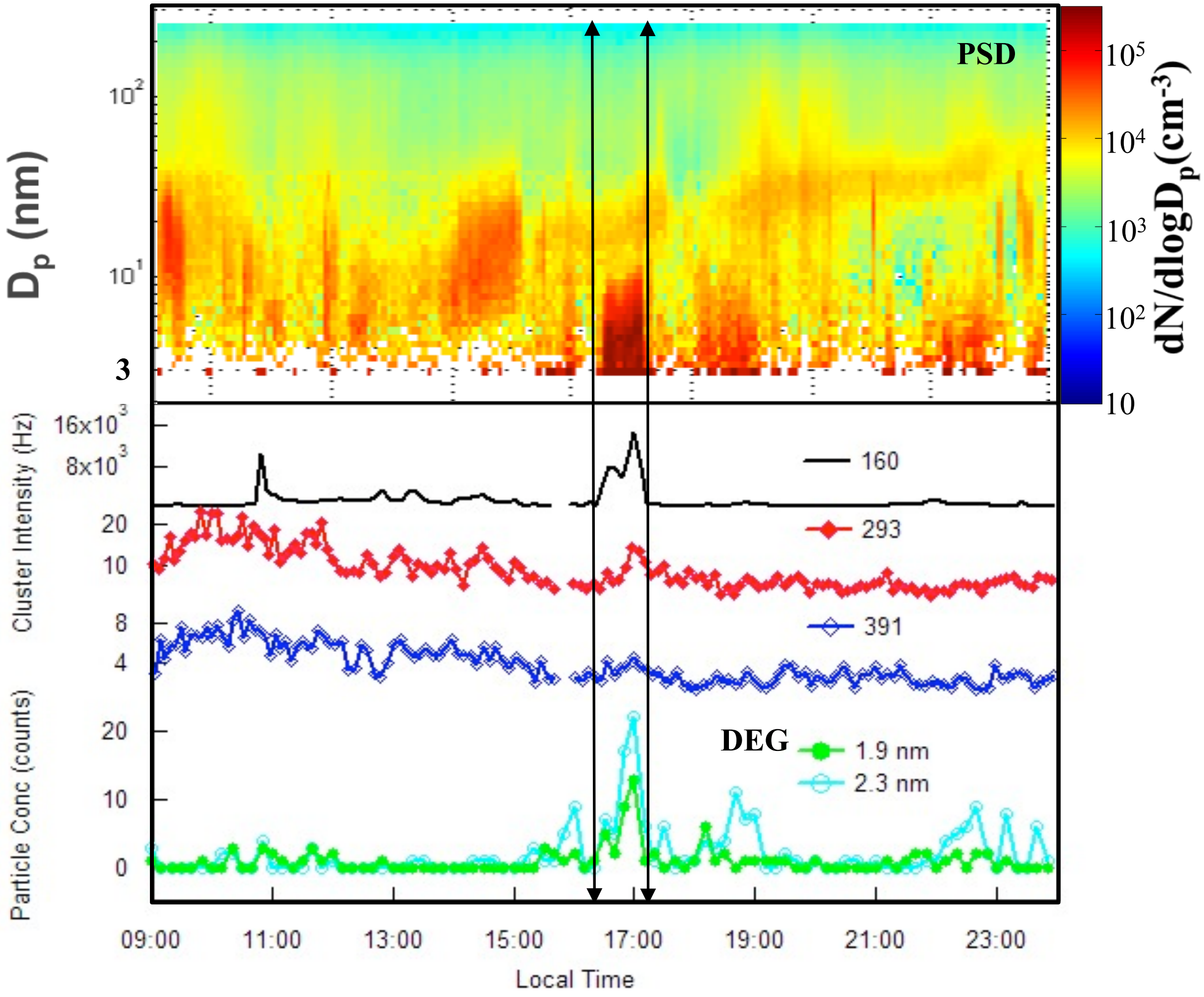
UMN & NCAR Team, *unpublished*, 2010

A Typical Mass Spectrum During Non-Nucleation Periods



Zhao et al., *submitted*, 2009

Nucleation event on 09/26/2008, Boulder



Zhao et al., *submitted*, 2009

Concentrations of Neutral Clusters Containing 3 & 4 Sulfuric Acid Molecules (m/z=293 & 391)

Date	Reaction time (sec)	n=1[a]	n=3[a]	n=4[a]
Boulder, September 26,2008	0.56	9.7×10^7	2.7×10^4	1.3×10^4
	0.37	8.1×10^7	1.2×10^4	6.3×10^3
	0.17	1.2×10^8	9.8×10^4	6.6×10^4
	Average[b]	$8.9(10.0) \times 10^7$	$2.0\ (4.6) \times 10^4$	$9.7\ (26.0) \times 10^3$
Manitou Experimental Forest, August 6,2008	1.42	5.6×10^6	8.3×10^3	1.6×10^4
	0.46	7.5×10^6	1.0×10^4	1.1×10^4
	Average	6.5×10^6	9.3×10^3	1.3×10^4

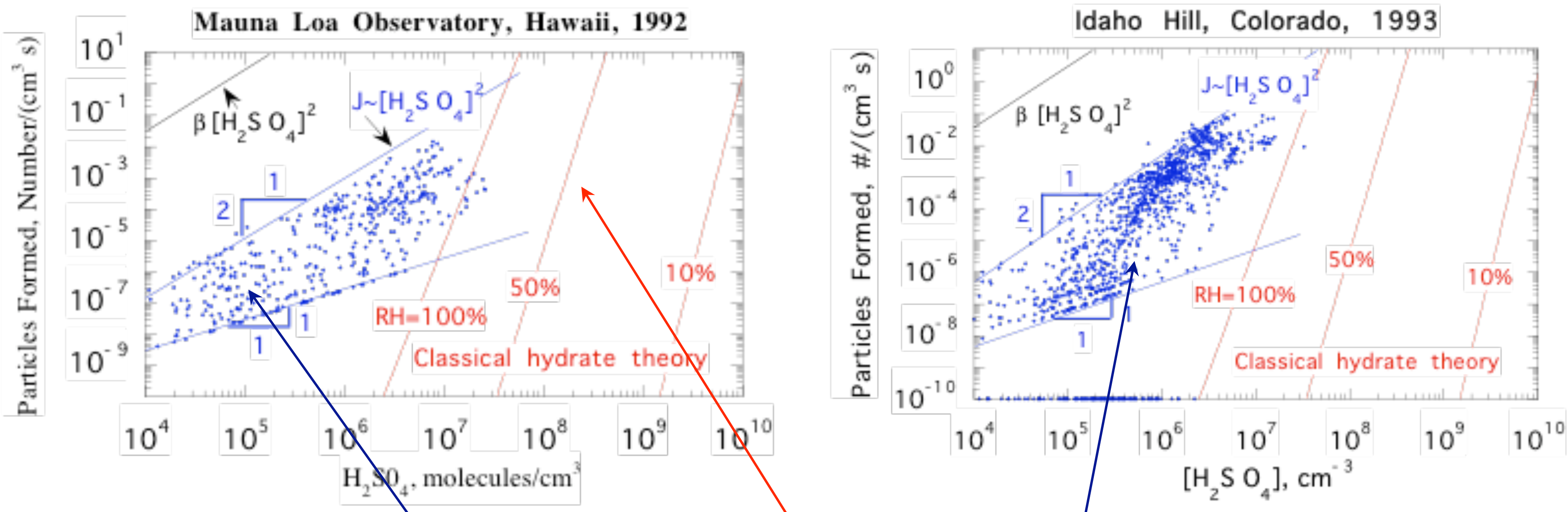
[a] n= 1, 3 and 4 correspond to sulfuric acid monomer, trimer & tetramer.

[b] Averaged values are taken over the two longer reaction times. The values in parenthesis are averaged over all three reaction times.

Zhao et al., *submitted*, 2009

First Atmospheric Observations: Observed & Theoretical NPF Dependence on $[H_2SO_4]$

J_{3nm} vs $[H_2SO_4]$



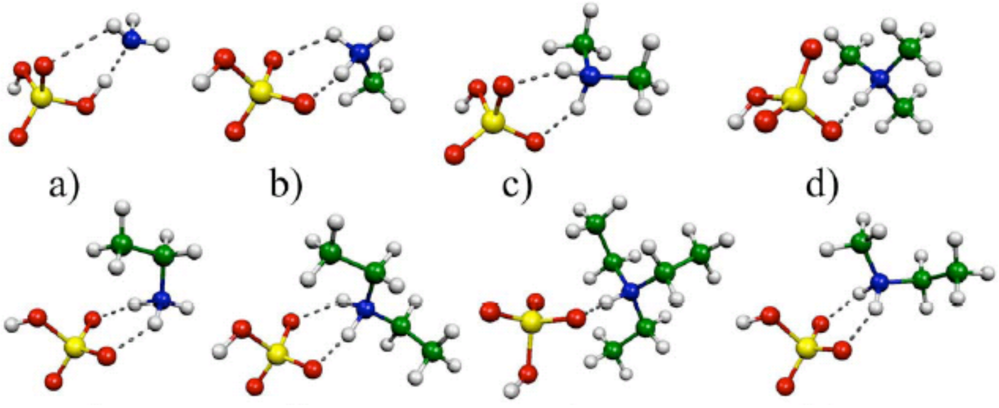
Binary (H_2SO_4-H_20) Nucleation

"Boundary Layer Nucleation" (BLN)

- Actual particle productions rates >> values predicted by binary H_2O H_2SO_4 theory
- Observed functional dependence on $[H_2SO_4]$ is weaker than predicted by nucleation theory

Weber et al., *Chem Eng. Comm.* **151**:53-64, 1996.

What are amines and why are they possibly so important for a particle's first few hours of growth?



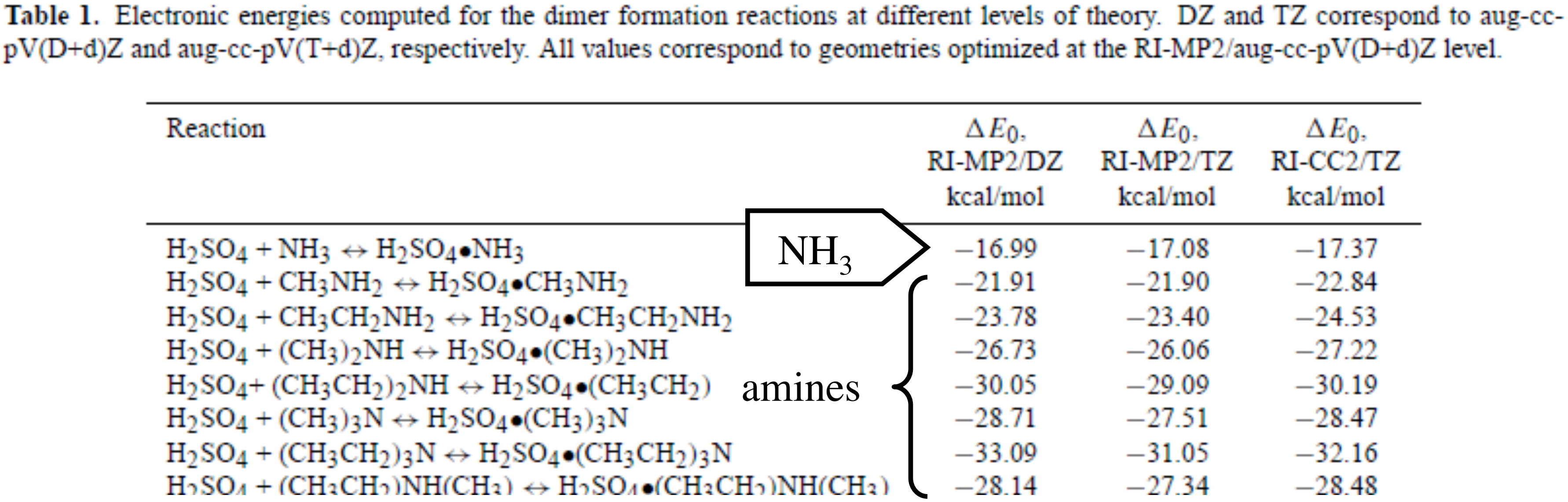


Table 1. Electronic energies computed for the dimer formation reactions at different levels of theory. DZ and TZ correspond to aug-cc-pV(D+d)Z and aug-cc-pV(T+d)Z, respectively. All values correspond to geometries optimized at the RI-MP2/aug-cc-pV(D+d)Z level.

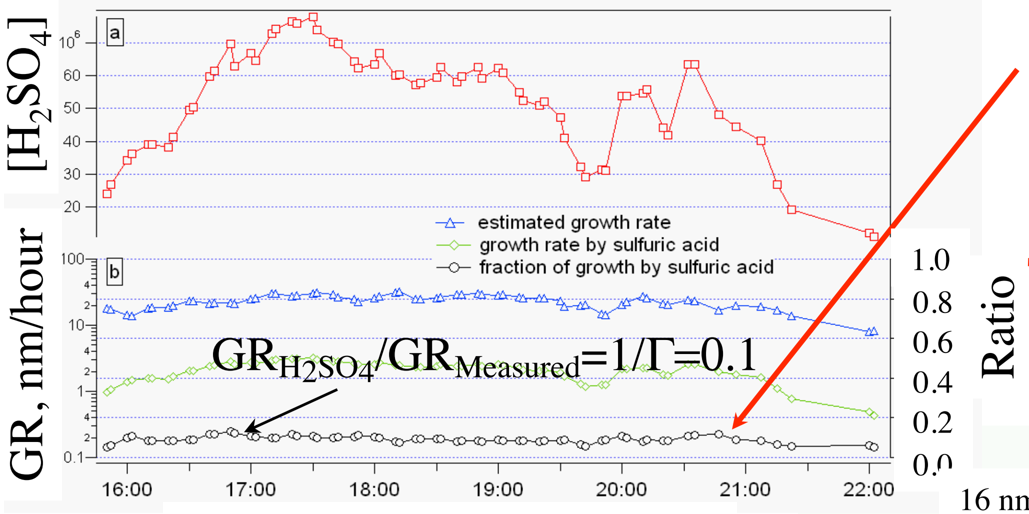
Reaction	ΔE_0, RI-MP2/DZ kcal/mol	ΔE_0, RI-MP2/TZ kcal/mol	ΔE_0, RI-CC2/TZ kcal/mol
$H_2SO_4 + NH_3 \leftrightarrow H_2SO_4 \bullet NH_3$	−16.99	−17.08	−17.37
$H_2SO_4 + CH_3NH_2 \leftrightarrow H_2SO_4 \bullet CH_3NH_2$	−21.91	−21.90	−22.84
$H_2SO_4 + CH_3CH_2NH_2 \leftrightarrow H_2SO_4 \bullet CH_3CH_2NH_2$	−23.78	−23.40	−24.53
$H_2SO_4 + (CH_3)_2NH \leftrightarrow H_2SO_4 \bullet (CH_3)_2NH$	−26.73	−26.06	−27.22
$H_2SO_4 + (CH_3CH_2)_2NH \leftrightarrow H_2SO_4 \bullet (CH_3CH_2)$	−30.05	−29.09	−30.19
$H_2SO_4 + (CH_3)_3N \leftrightarrow H_2SO_4 \bullet (CH_3)_3N$	−28.71	−27.51	−28.47
$H_2SO_4 + (CH_3CH_2)_3N \leftrightarrow H_2SO_4 \bullet (CH_3CH_2)_3N$	−33.09	−31.05	−32.16
$H_2SO_4 + (CH_3CH_2)NH(CH_3) \leftrightarrow H_2SO_4 \bullet (CH_3CH_2)NH(CH_3)$	−28.14	−27.34	−28.48

NH_3

amines

Kurtén et al., ACP, 2008

Species that Contribute to Growth of Freshly Nucleated Particles in Tecamac, Mexico

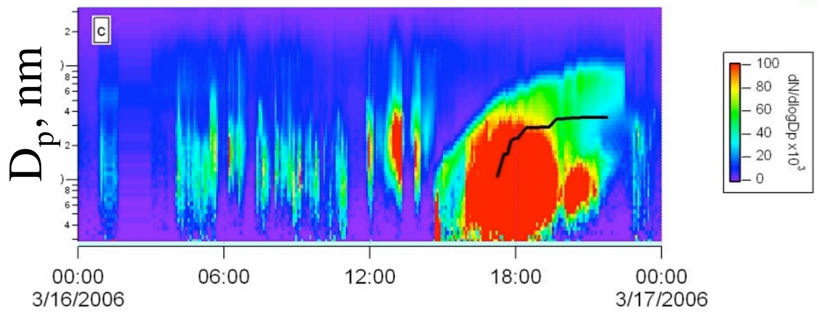


$GR_{H2SO4}/GR_{Measured}=1/\Gamma=0.1$

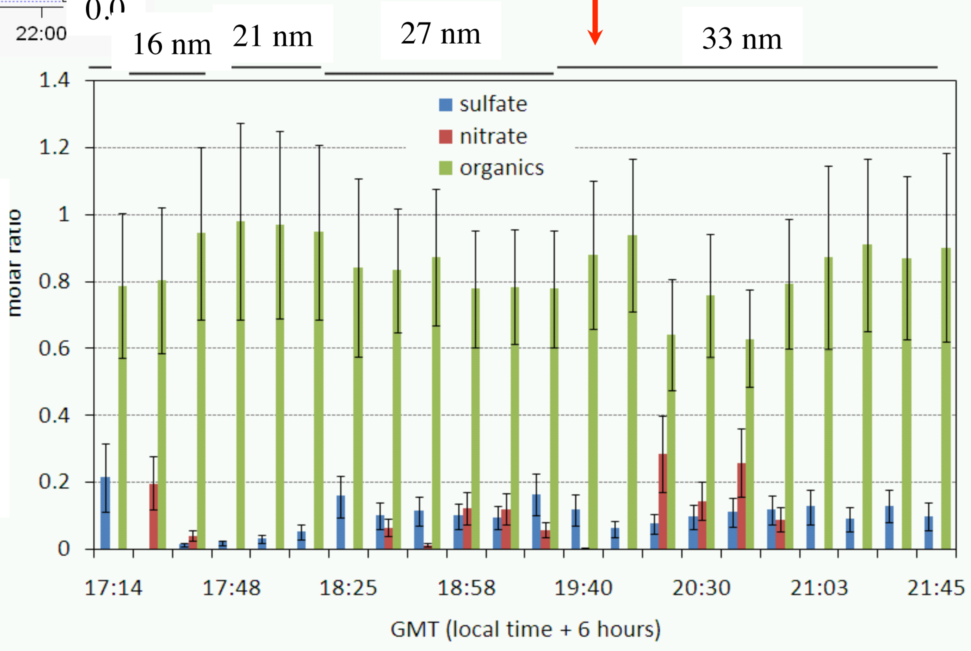
GMT (local time + 6 hours)

Modeled growth due to sulfuric acid shows that sulfuric acid only accounts for 10% of observed growth (Γ=10).

TDCIMS composition measurements are consistent with this, and show that the balance is due to Secondary organics.

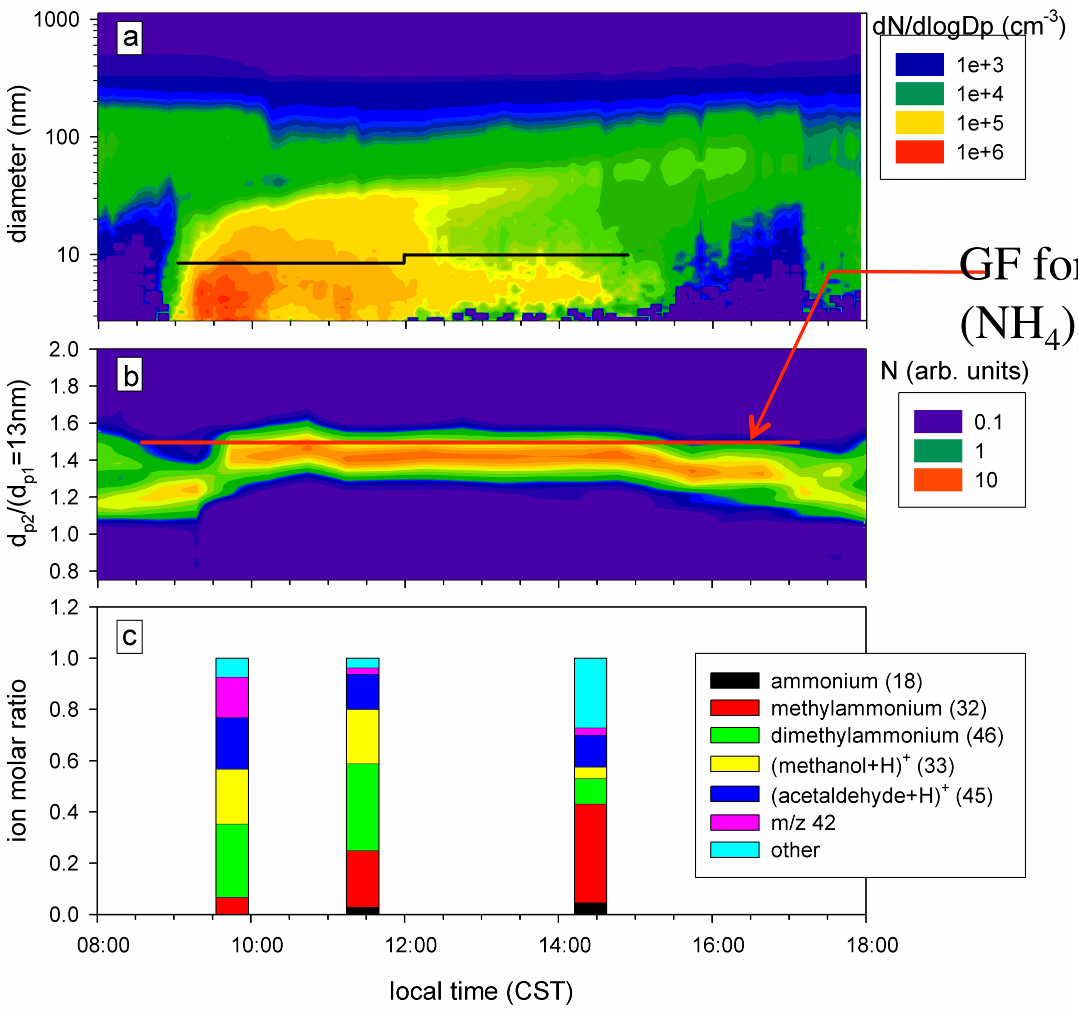


GMT (local time + 6 hours)



Smith et al., *GRL*, doi:10.1029/2007GL032523, 2008

TDCIMS observations at Tecamac (Mexico City) show aminium ions in 8-10 nm diameter particles

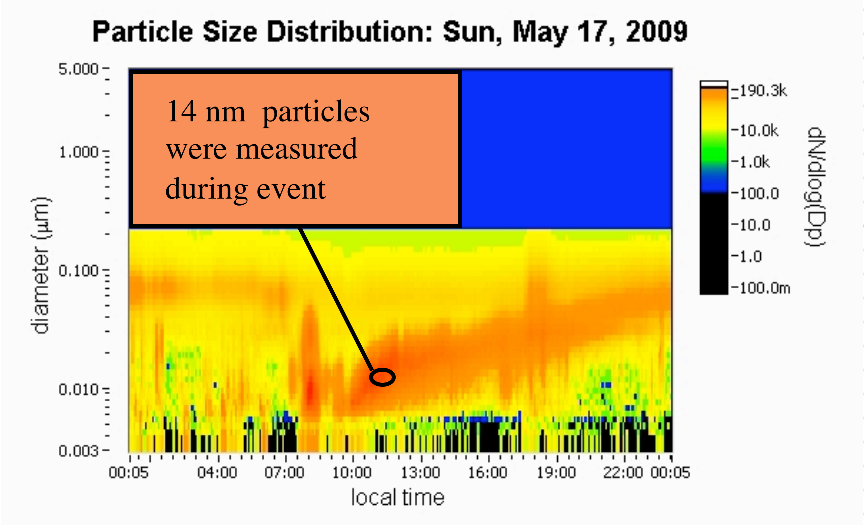


GF for 13nm $(NH_4)_2SO_4$

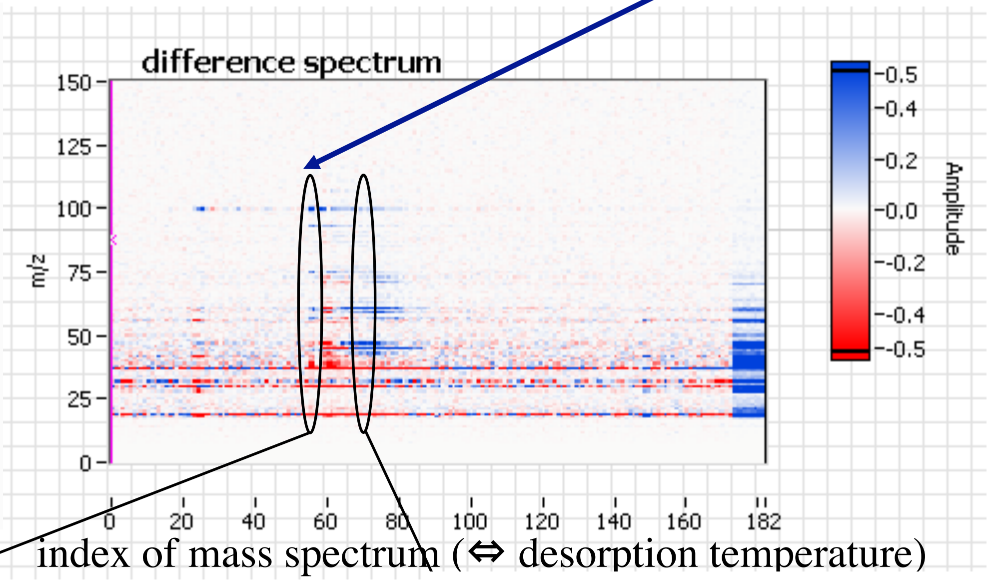
- On average, aminium ions comprise about 45% of positive ion spectrum
- 13 nm particles had an average 90%RH growth factor of 1.42

Smith et al., PNAS, 2010, DOI: 10.1073/pnas.0912127107

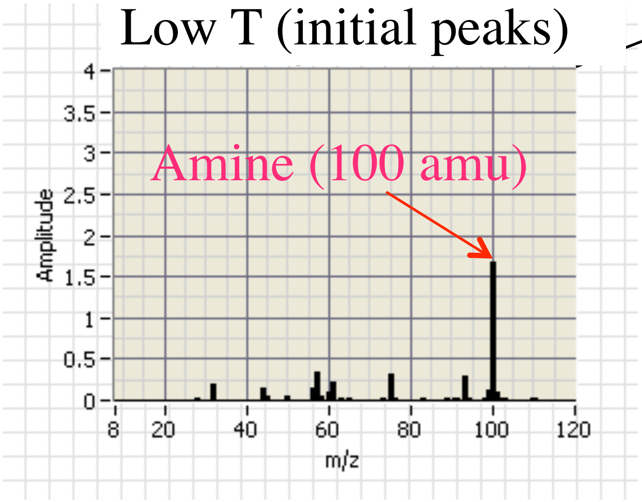
Time of Flight (TOF) Measurements of 14 nm Particles, Boulder, CO (17 May, 2009): TDCIMS



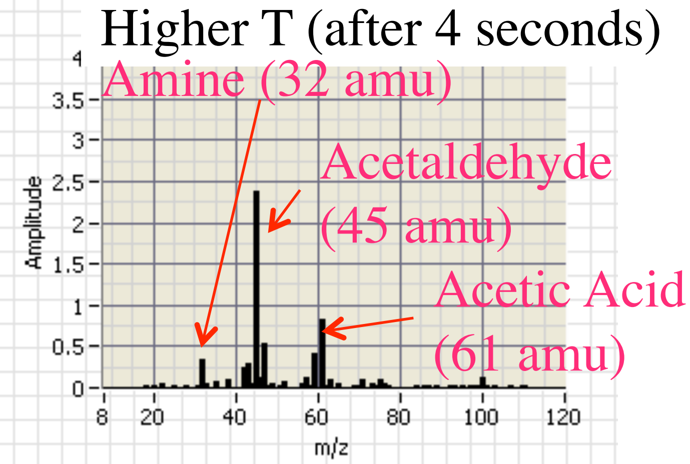
start of desorption current



index of mass spectrum (⇔ desorption temperature)



Positive
Identification
of
Ion Fragments



Jim Smith, unpublished, 2009. Thanks to Kimmel & Worsnop

Minnesota-NCAR Research Strategy

The focus of our research has been to develop methods to measure those "extremely minute quantities."

growth rates: TDCIMS, Nano TDMA, DEG SMPS,
PSD, H_2SO_4 *CIMS*
nucleation rates: Cluster CIMS, AmpMS, DEG SMPS