Acid-Base Chemical Reaction Model for Nucleation Rates in the Polluted Atmospheric Boundary Layer (*PNAS*, 2012, doi: 10.1073/pnas.1210285109)

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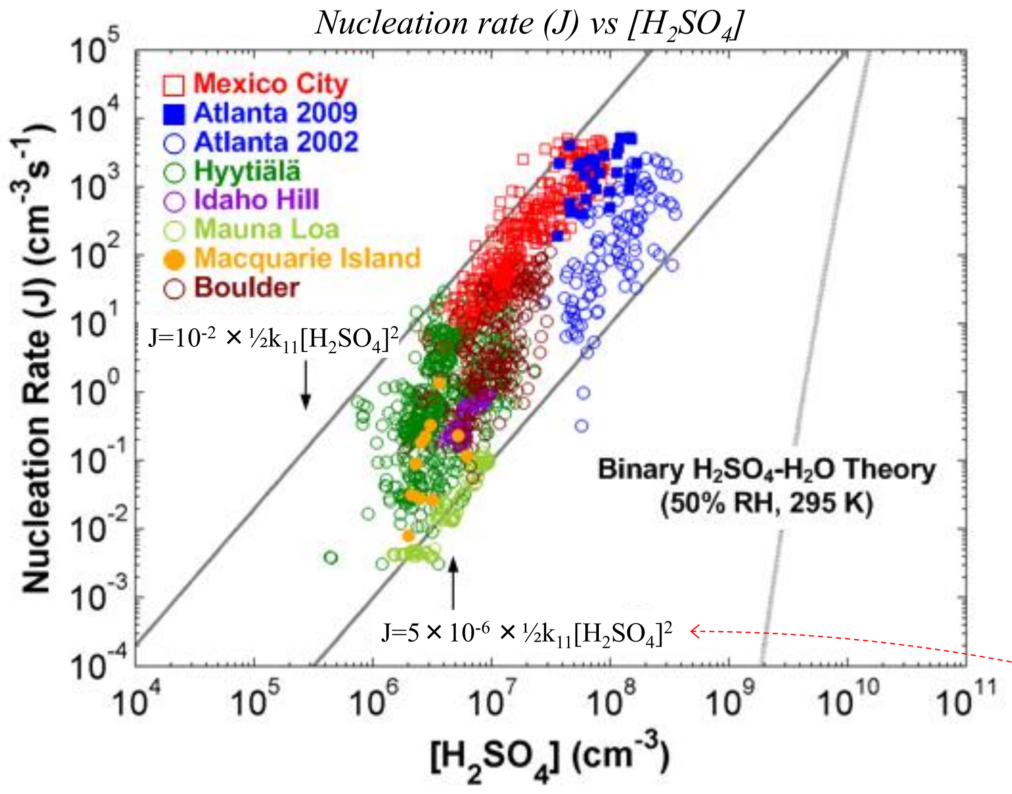
ABSTRACT

Our goal is to understand the physical and chemical processes responsible for new particle formation in the atmosphere. Nucleated particles can grow to sizes that serve as seeds for cloud droplet formation (50-100 nm). New particle formation is an important process for climate modelers because of its effects on cloud cover, which influences albedo. Our strategy involves developing instruments that can measure the trace concentrations (typical mole fractions 10^{-11} to 10^{-15}) of species in the atmosphere that participate in nucleation and growth, and to develop models that are consistent with those measurements.

Summary of Observations over 2 decades: Nucleation rate (J) vs [H_2SO_4]



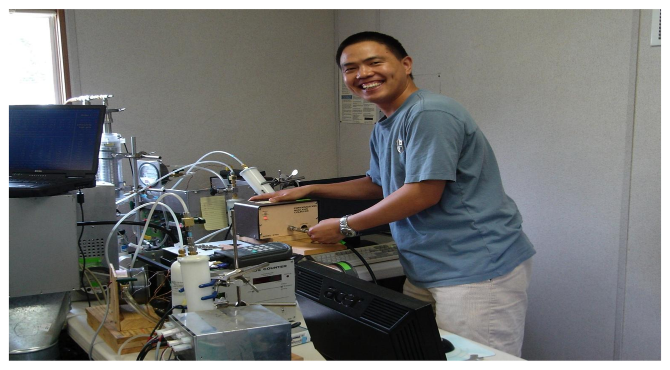
Prototype Instruments for Nucleation Research Developed by Members of Our Research Team

Particle number distributions down to 1 nm

McMurry group
Jingkun Jiang, Modi Chen

Iida et al., *AST*, **43**: 81, 2009;
Jiang et al., *AST* **45**: 510, 2011;
Kuang et al, *AST* **46**:309-315, 2012

DEG SMPS



Cluster CIMS

[H_2SO_4] & [nucleated neutral clusters]

Fred Eisele & Jun Zhao, NCAR
Mari Titcombe, Coty Jen, UMN

1 ppq (10^{-15}) sensitivity

Zhao et al., *JGR*, 2010
Zhao et al., ACP 2011
Titcombe, PhD Thesis 2012
Chen et al., *PNAS*, 2012

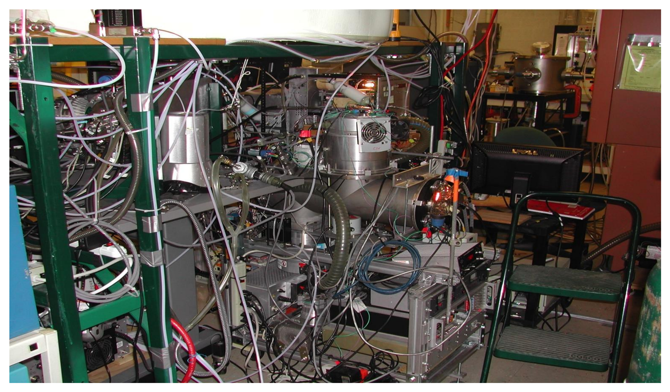
[amines] & [ammonia]

Prof. Dave Hanson and students, Augsburg College

1 ppt (10^{-12}) sensitivity

Hanson et al., *ES&T*, 2011
Zollner et al, *ACP*, 2012

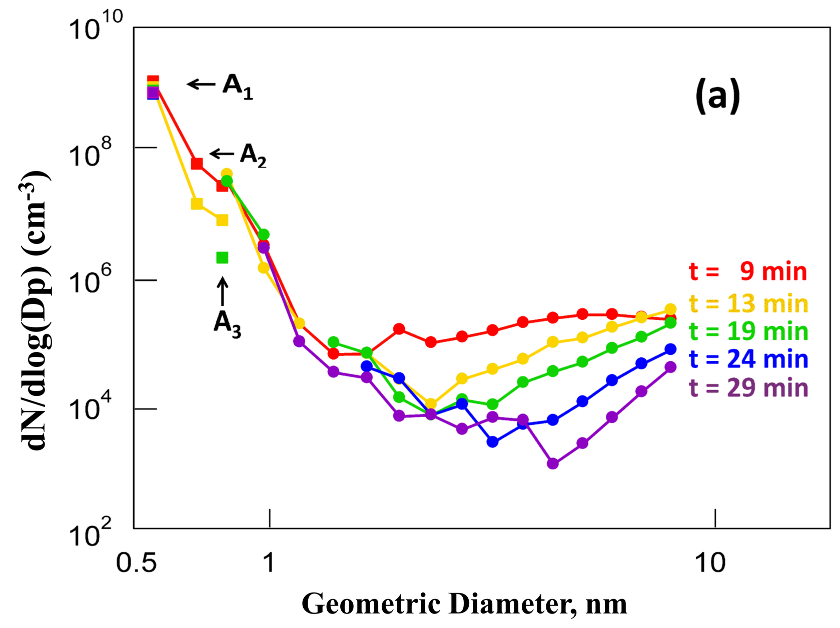
AmPMS



Number Distributions Down to One Molecule From Chamber Experiments at U. Minnesota

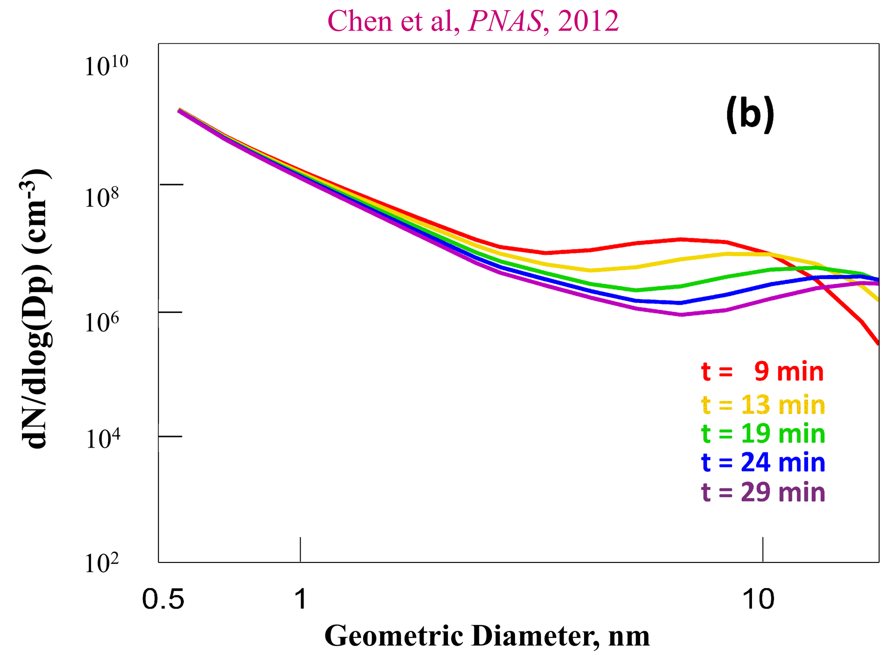
Measured; t=time after lights were turned on

Titcombe, PhD Thesis; Chen et al, *PNAS*, 2012



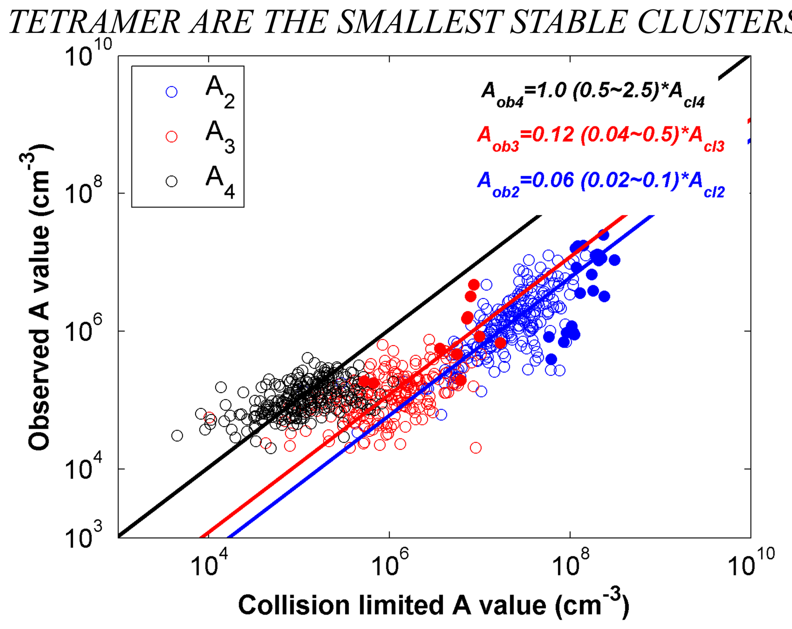
Collision-controlled model corresponding to the above conditions: Note qualitative similarities and quantitative differences

Chen et al, *PNAS*, 2012

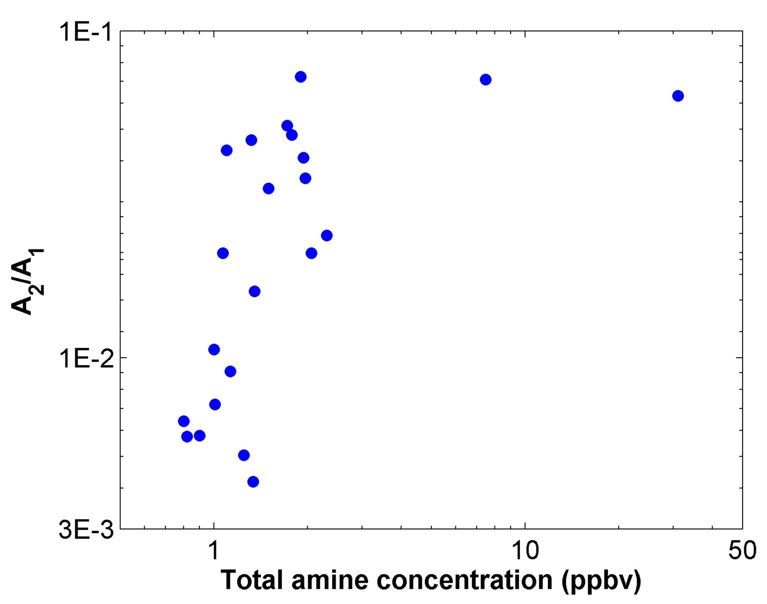


Atmospheric & Lab Measurements of Clusters During Nucleation

Measured Dimer concentrations ≅ 1/16 collision-controlled values
Measured Trimer concentrations ≅ 1/8 collision controlled values
Measured Tetramet concentrations ≅ collision controlled values:
TETRAMER ARE THE SMALLEST STABLE CLUSTERS

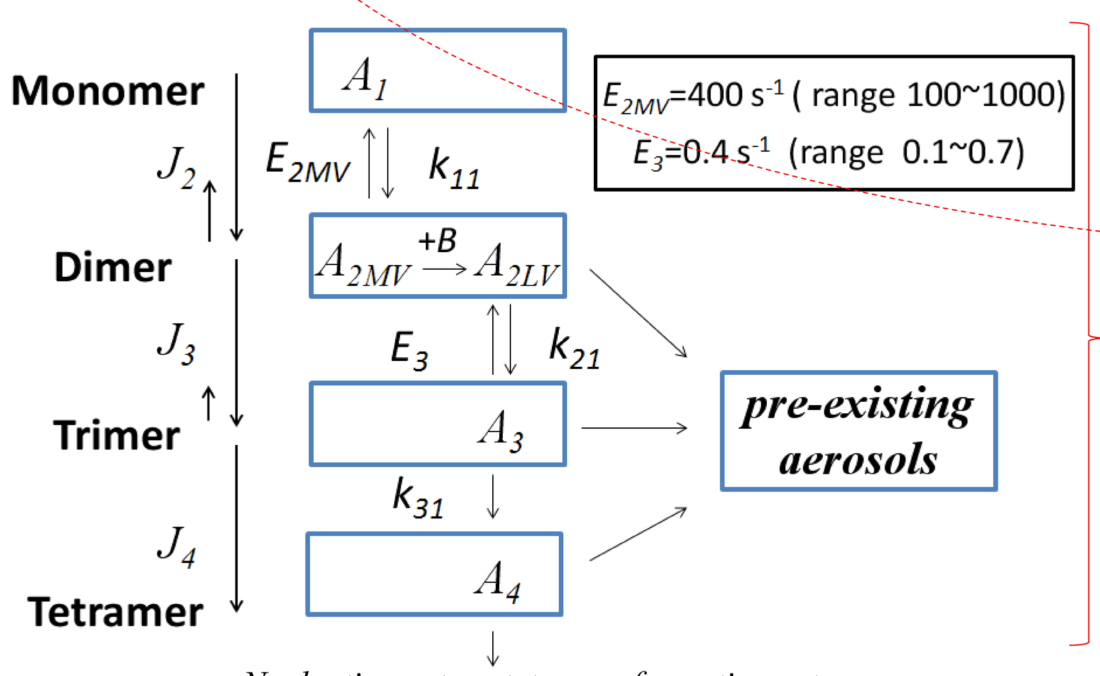


Dimer concentrations increase as concentrations of basic gases increase:
STABILIZATION OF DIMER BY BASIC GASES INCREASES [DIMER]



Acid-Base Reaction Nucleation Model

SIMPLE CONCEPTUAL MODEL FOR CHEMICAL NUCLEATION BASED ON OBSERVATIONS SHOWN IN FIGURES TO THE LEFT



Nucleation rate = tetramer formation rate ($J=J_4$)

- Dimer (A_2), Trimer (A_3), Tetramer (A_4) contain two, three, and four H_2SO_4 molecules plus other compounds (water, ammonia, amines, etc.) that cannot be detected with the cluster CIMS
- Conceptual model treats nucleation as a series of chemical reactions between acidic and basic compounds
- Reaction of More Volatile Dimer (MV) with a basic gaseous compound produces a Less Volatile dimer (LV)
- Tetramer (A_4) is the smallest stable cluster. Therefore, $J=J_4$
- Model does not yet take into account possible dependencies on temperature and relative humidity

Nucleation Rates: Comparison of Observations to Predictions of the Acid-Base Model

Model for nucleation rates ($J=J_4$)

Chen et al, *PNAS*, 2012

$$J_4 = k_{31}\cdot[A_1]\cdot[A_3]$$

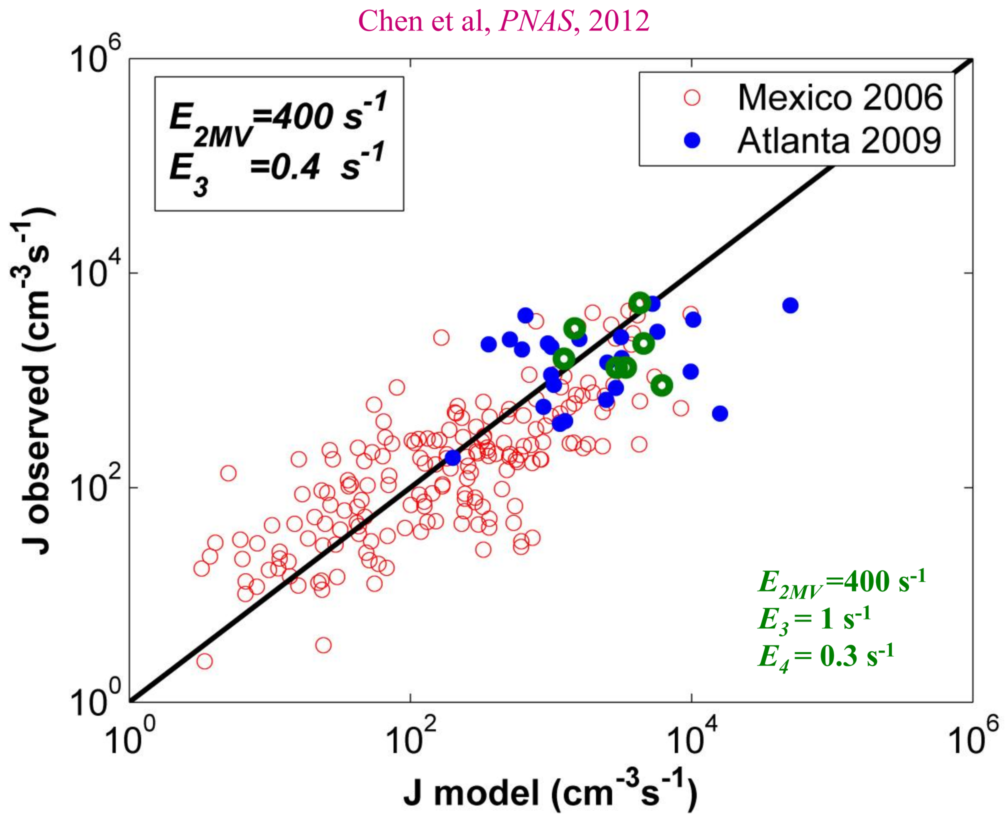
$$= \left\{\frac{k'_{21}\cdot[B]}{E_{2MV}+k'_{21}\cdot[B]+\kappa_2}\cdot\frac{k_{21}\cdot[A_1]}{\kappa_2}\cdot\frac{k_{31}\cdot[A_1]}{E_3+\kappa_3}\right\}\cdot\frac{1}{2}k_{11}\cdot[A_1]\cdot[A_1]$$

$$= P\cdot\frac{1}{2}k_{11}\cdot[H_2SO_4]^2$$

"Monomer" collision rate;
Prefactor P < 1

Acid-Base Chemical Reaction Model Agrees with Direct Observations of Nucleation Rates to within about 10X

Chen et al, *PNAS*, 2012



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