Chemical and Physical Properties of Ammonium Sulfate/Organic Aerosols

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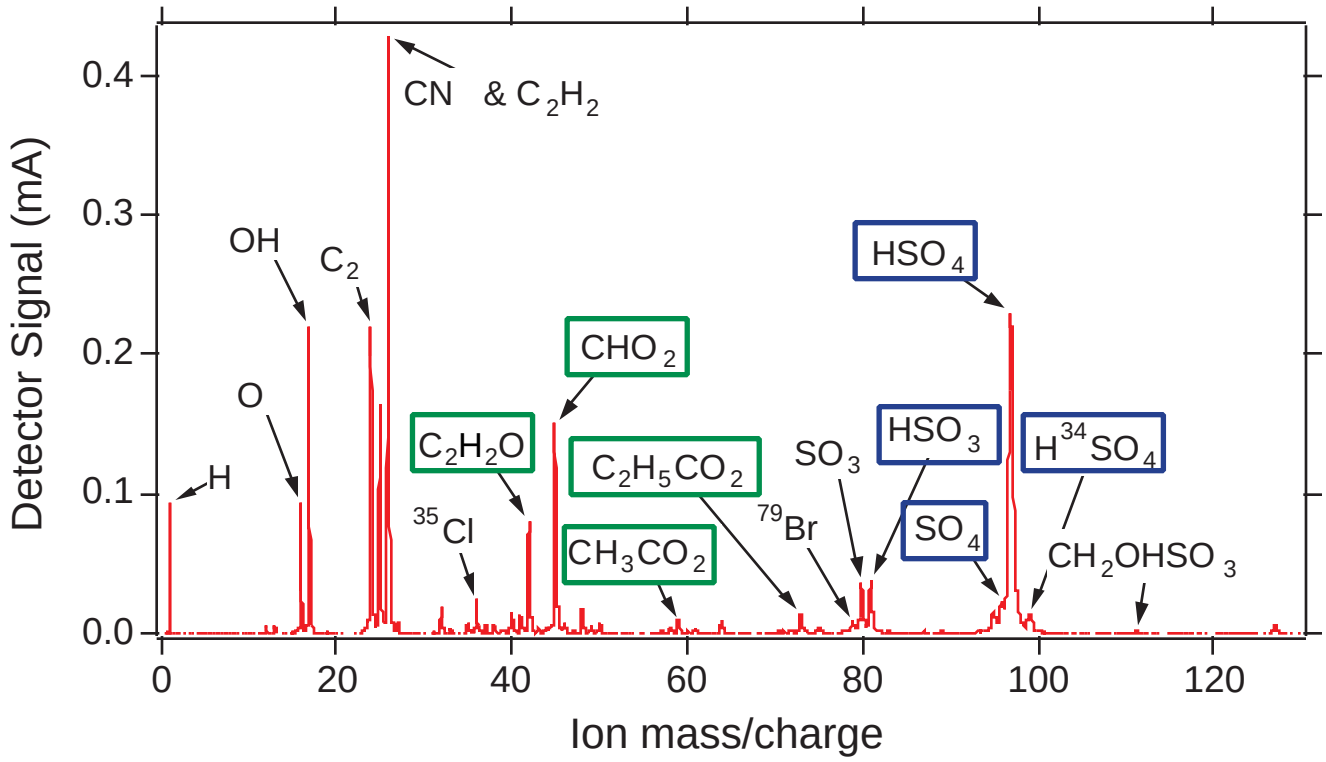
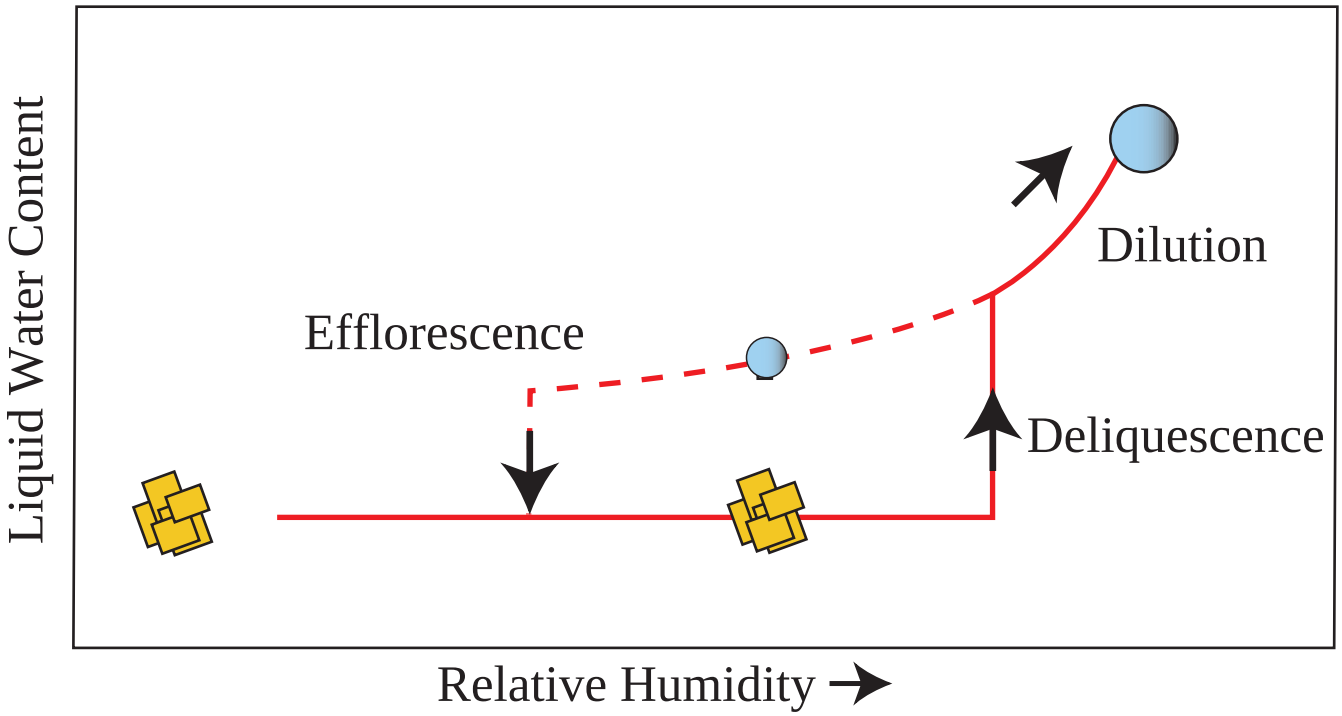


Murphy, Thomson, and Mahoney, Science, 1998

Aerosol Water Content vs RH

Generalized hysteresis curve:



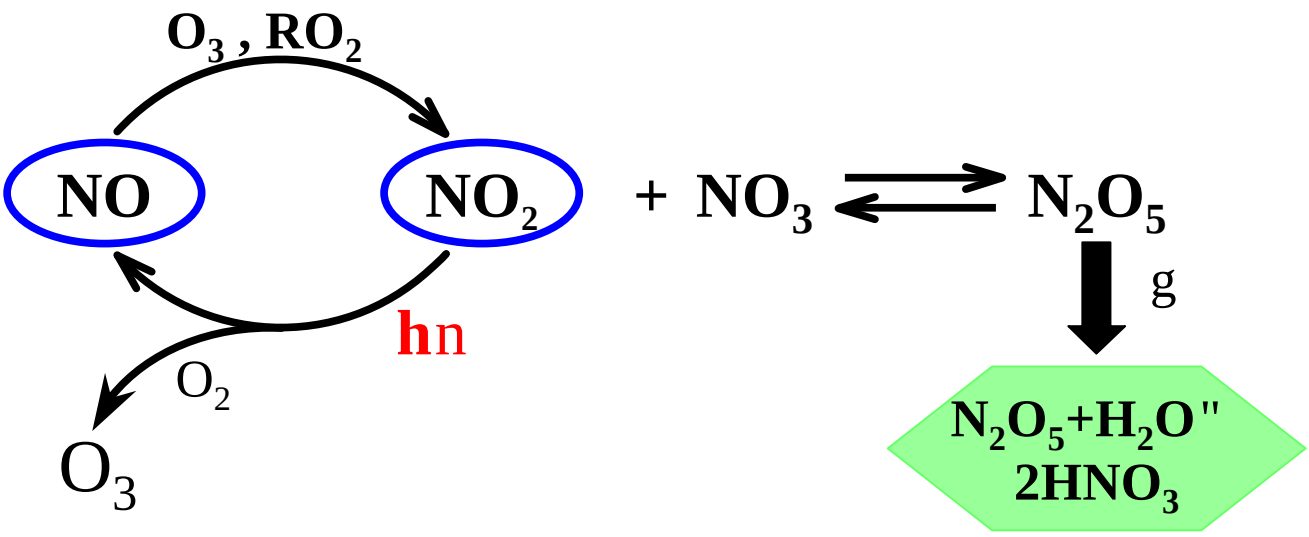
Well known for pure ammonium sulfate

Unknown for ammonium sulfate/organics

This study: impact of organic on ...

- phase change relative humidities
- heterogeneous chemistry

Aerosol Phase Impacts Chemistry



Dentener and Crutzen, '93:

	γ=0.01	γ=0.1
NO_x	$40%	$49%
O_3	$ 4%	$ 9%
OH	$ 3%	$ 9%

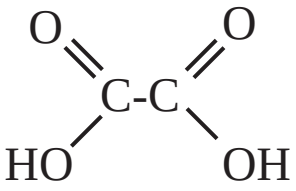
Previous Lab Work on Ammonium Sulfate at RT:

$\gamma_{dry} \sim 10^{-4}$ or $\gamma_{wet} \sim 0.01\text{-}0.05$

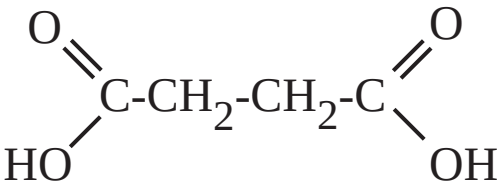
This Study: γ on mixed organic/ammonium sulfate

Organics used in the present study:

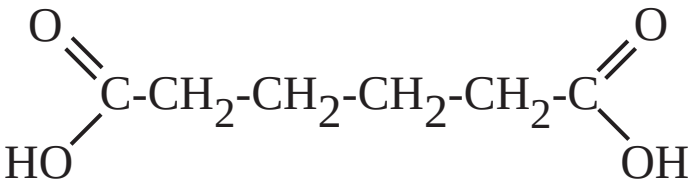
Slightly water soluble



Oxalic acid (C-2)

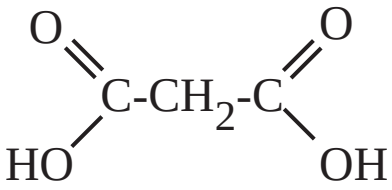


Succinic acid (C-4)

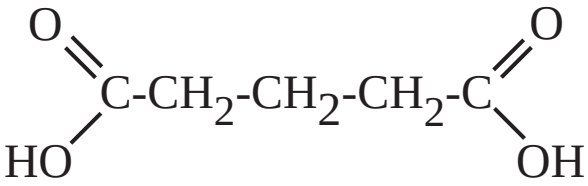


Adipic acid (C-6)

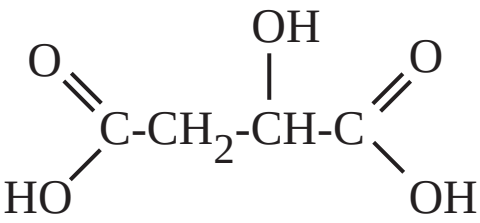
Highly water soluble



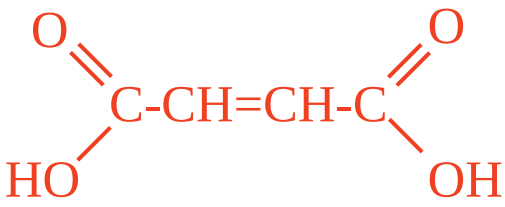
Malonic acid (C-3)



Glutaric acid (C-5)



L-Malic acid (C-4OH)

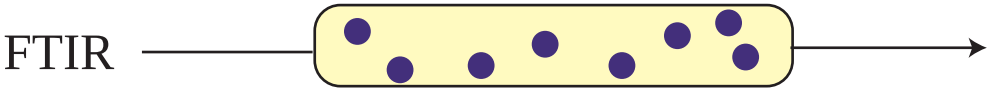


Maleic acid (C-4dbl)

Outline

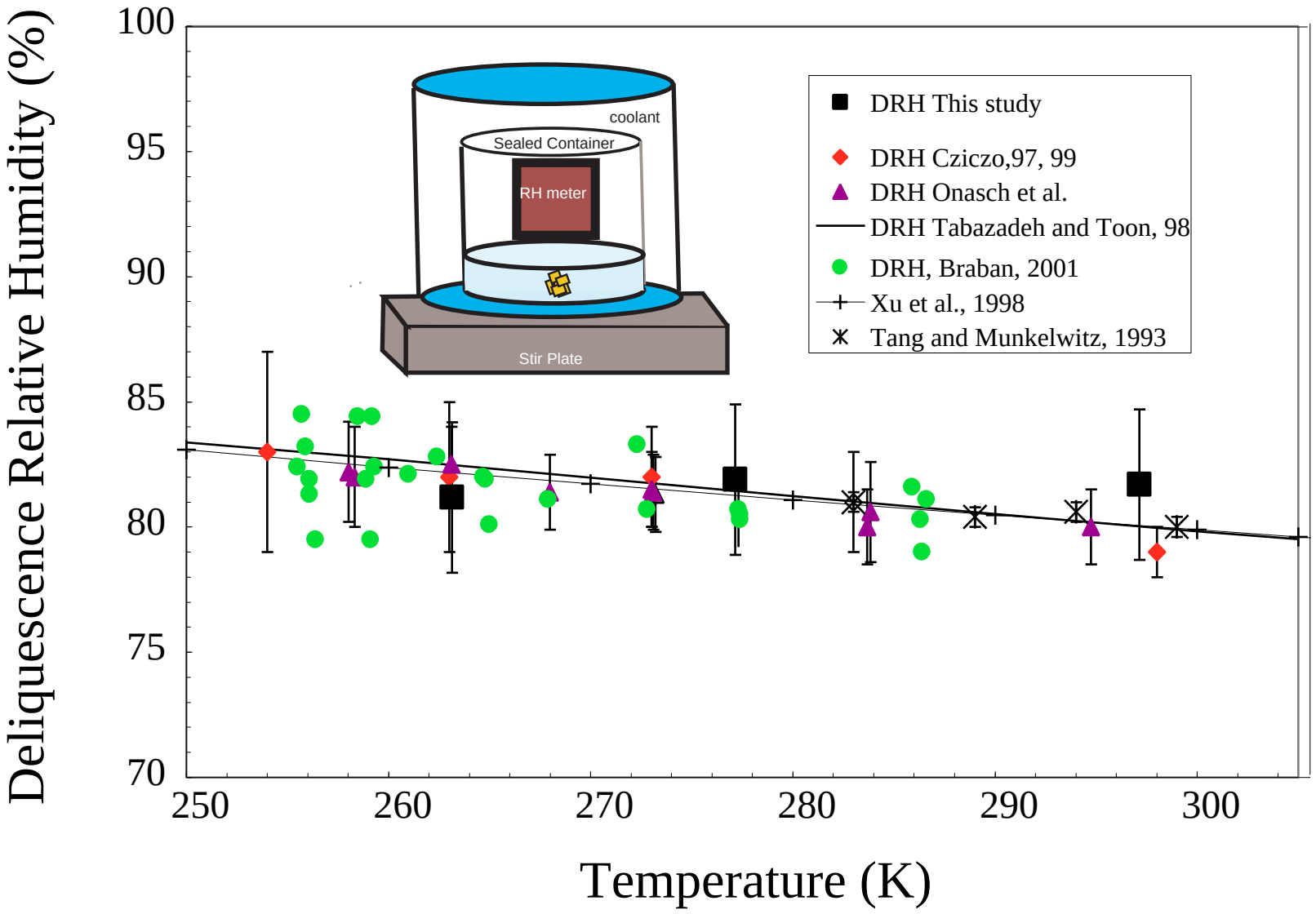
I. Bulk studies of deliquescence of mixed AS/organic diacids - an update

II. Efflorescence studies of mixed AS/maleic acid aerosols

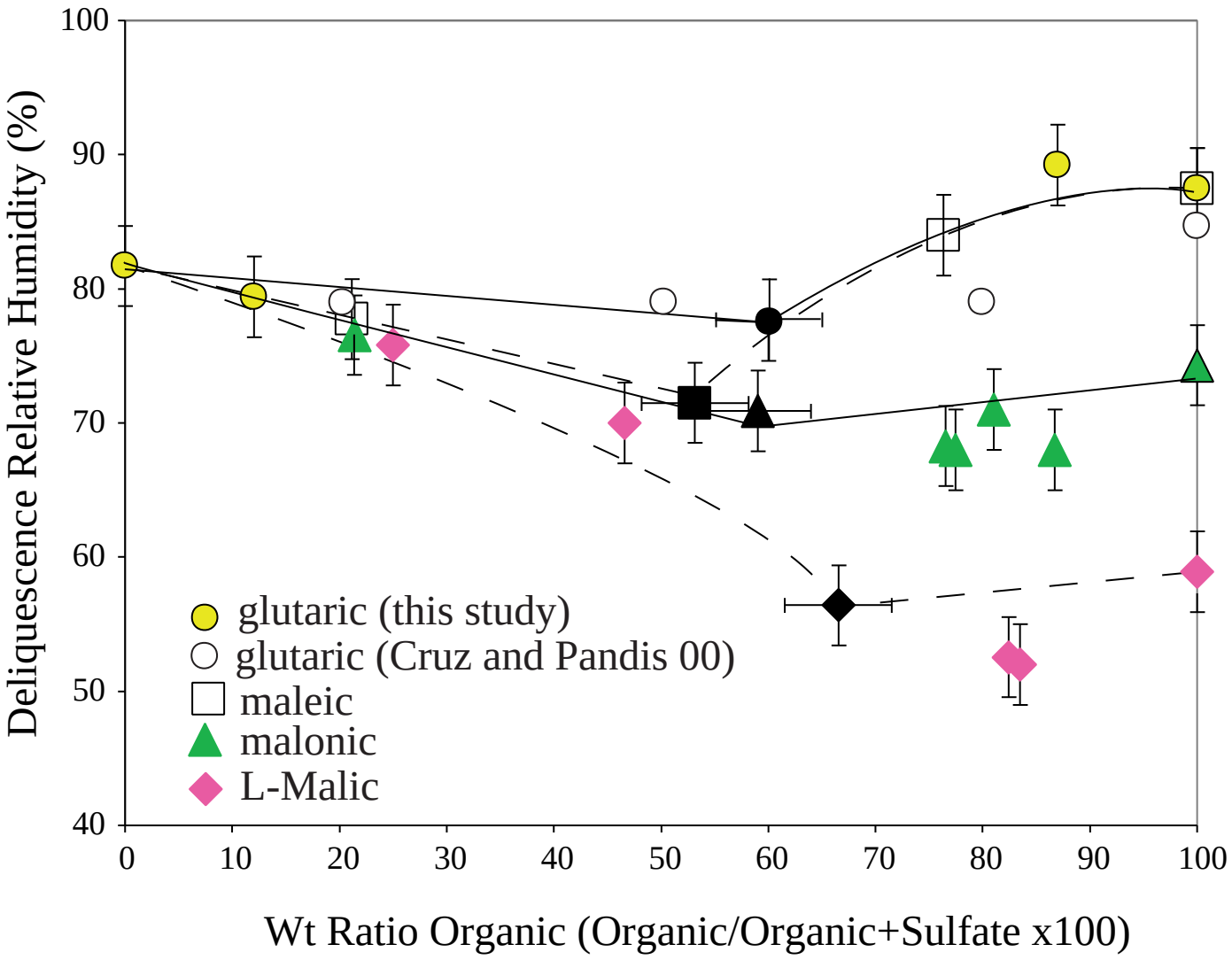


III. Knudsen cell study of N_2O_5 reaction on mixed AS/maleic acid particles on plate

Ammonium Sulfate Deliquescence
Bulk vs Aerosol



Deliquescence RH of Ammonium Sulfate Mixed with Soluble Diacids



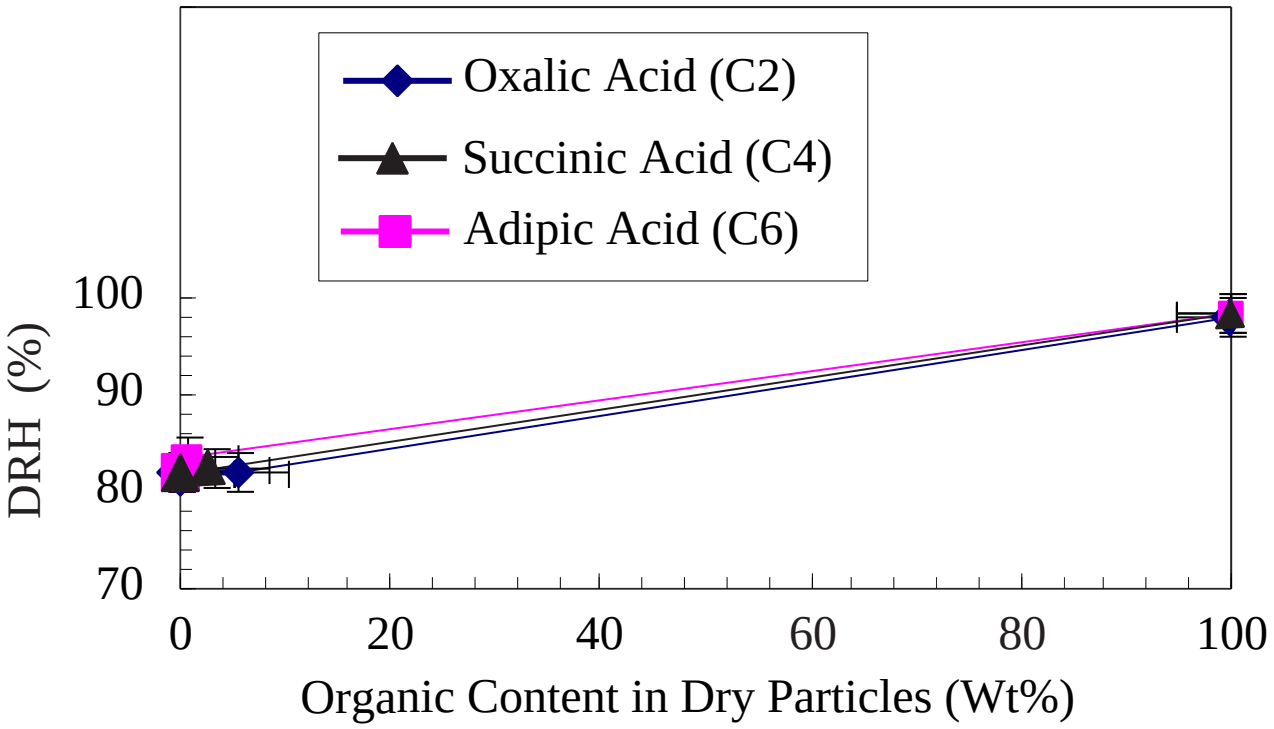
Good agreement with others where data exists

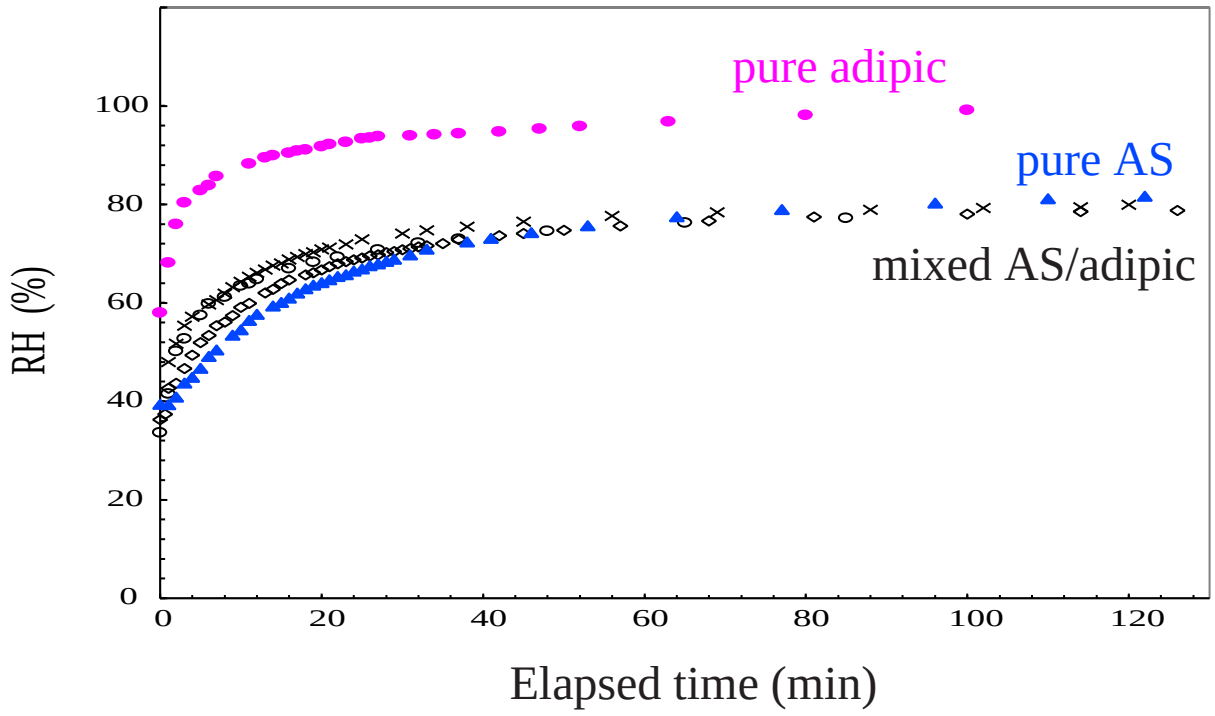
Eutonic AS/organic deliquesces ≤ pures

For all mixes, water uptake will begin at eutonic Del RH

More liquid water at lower RH for mixes!

DRH of Ammonium Sulfate with Low-Solubility Acids

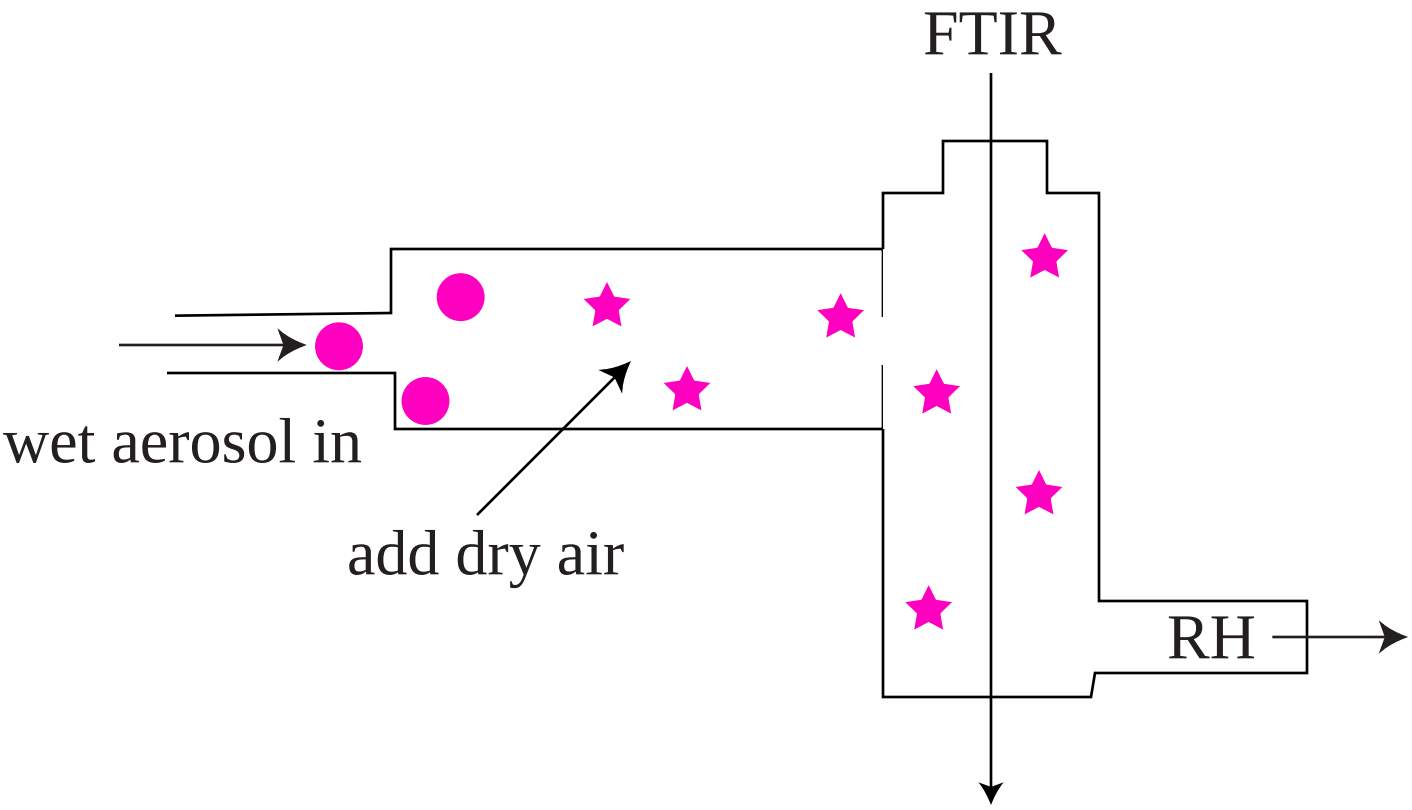


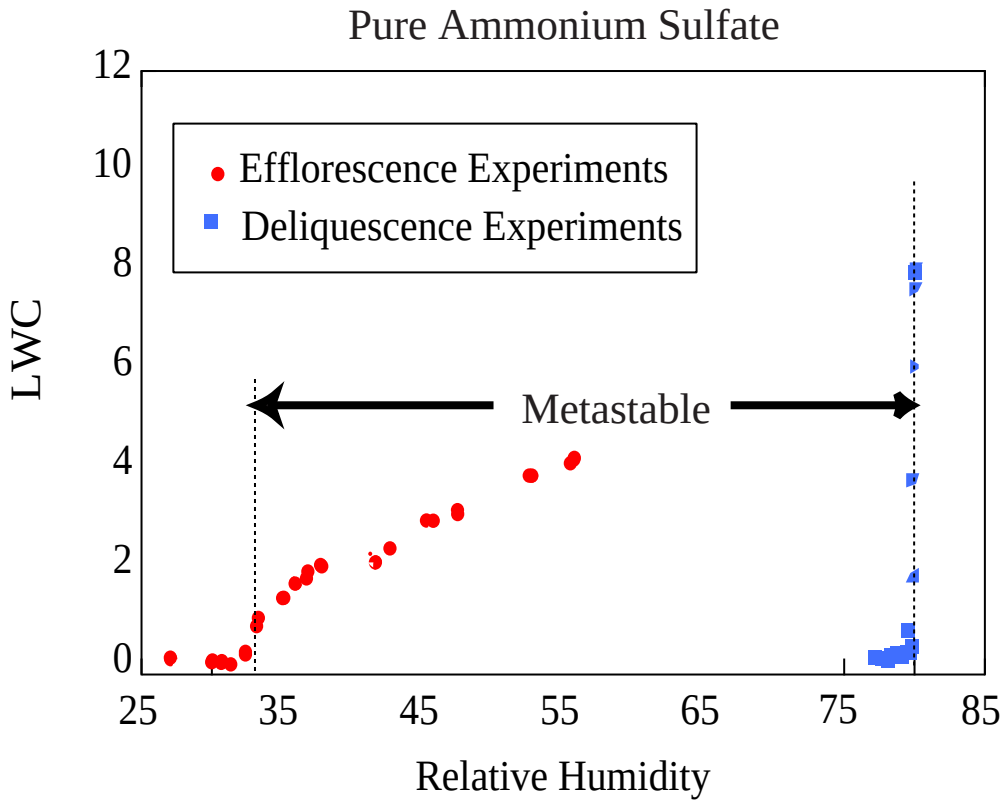


Low solubility organics had no impact on DRH of AS

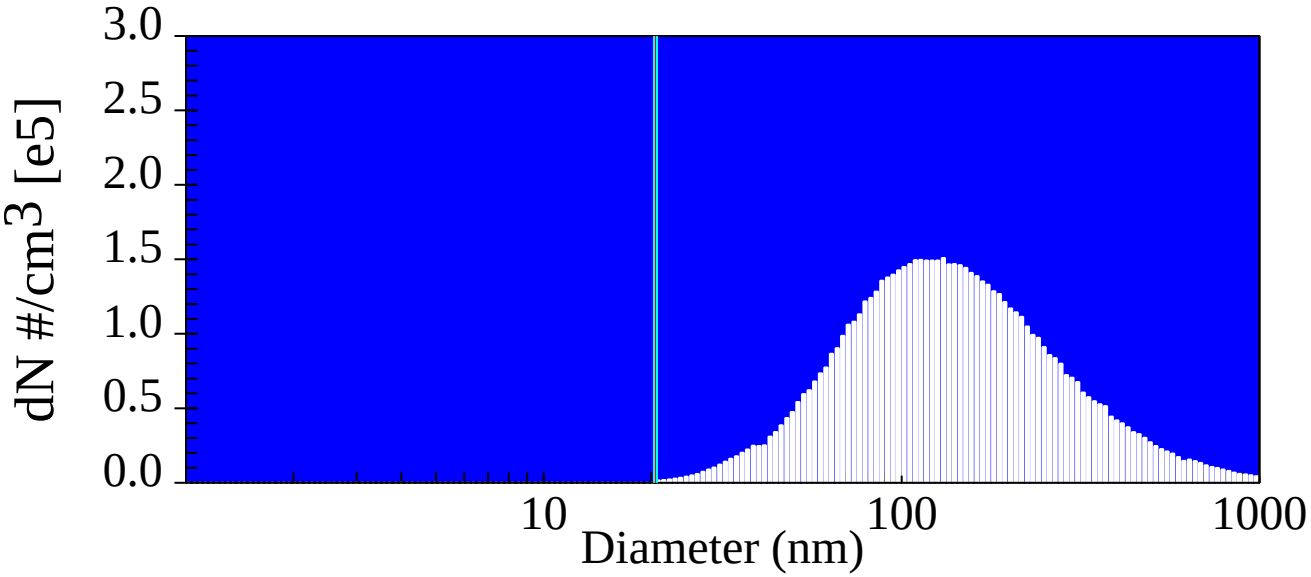
No barrier to water uptake or loss

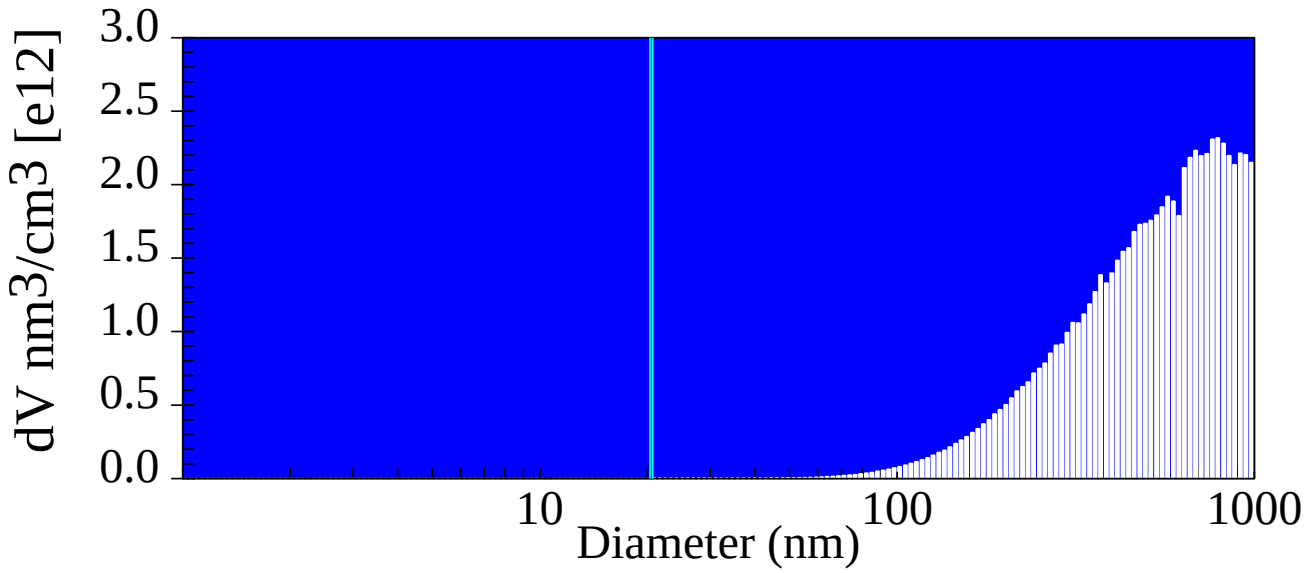
Efflorescence Studies in Flow Tube





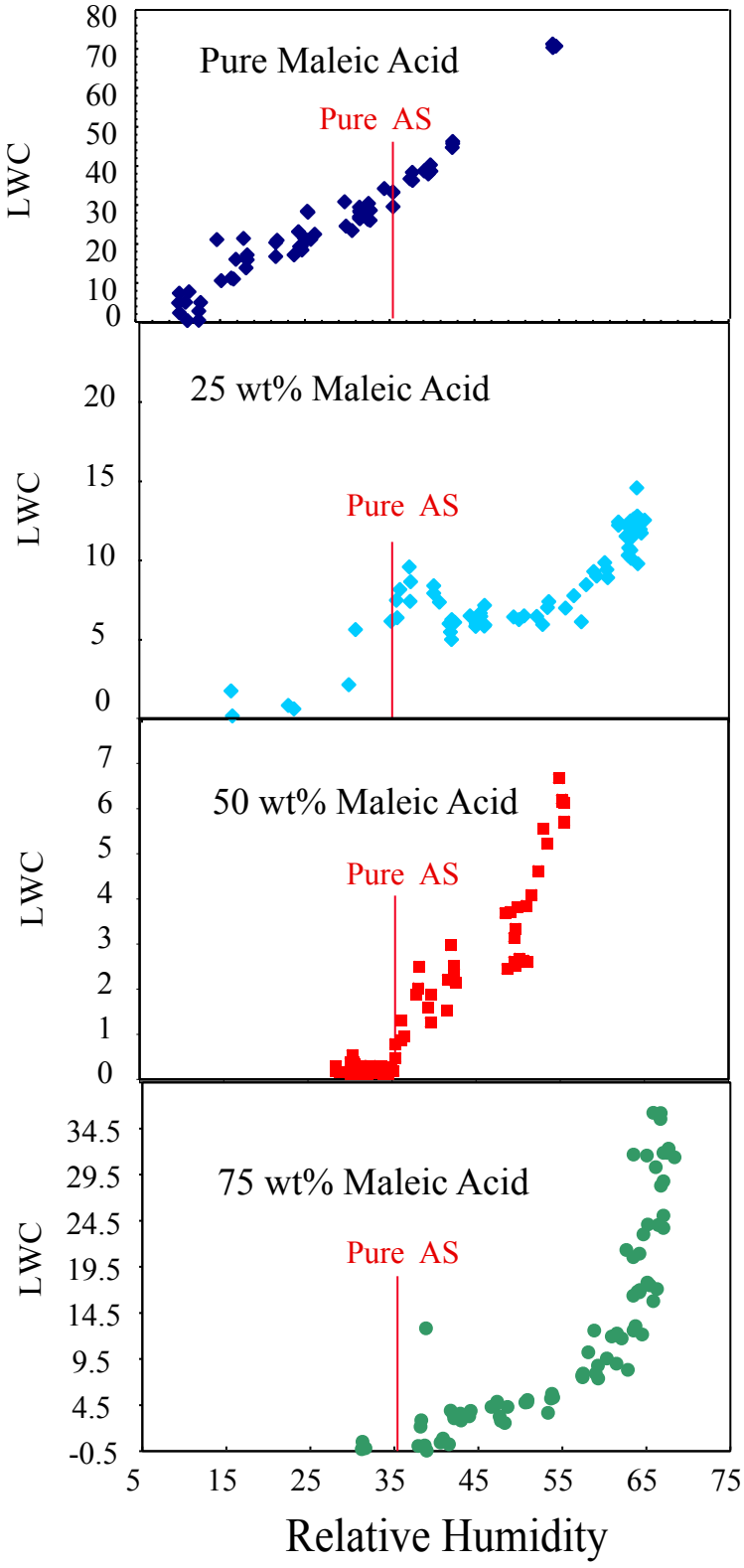
Size Distributions for AS/Maleic acid aerosols





Composition	RH	d(μm)	d_V(μm)
Ammonium sulfate	2%	0.14	0.55
Maleic acid	2%	0.15	0.59
50 wt% MA/AS	2%	0.16	0.55

Efflorescence of Mixed Particles



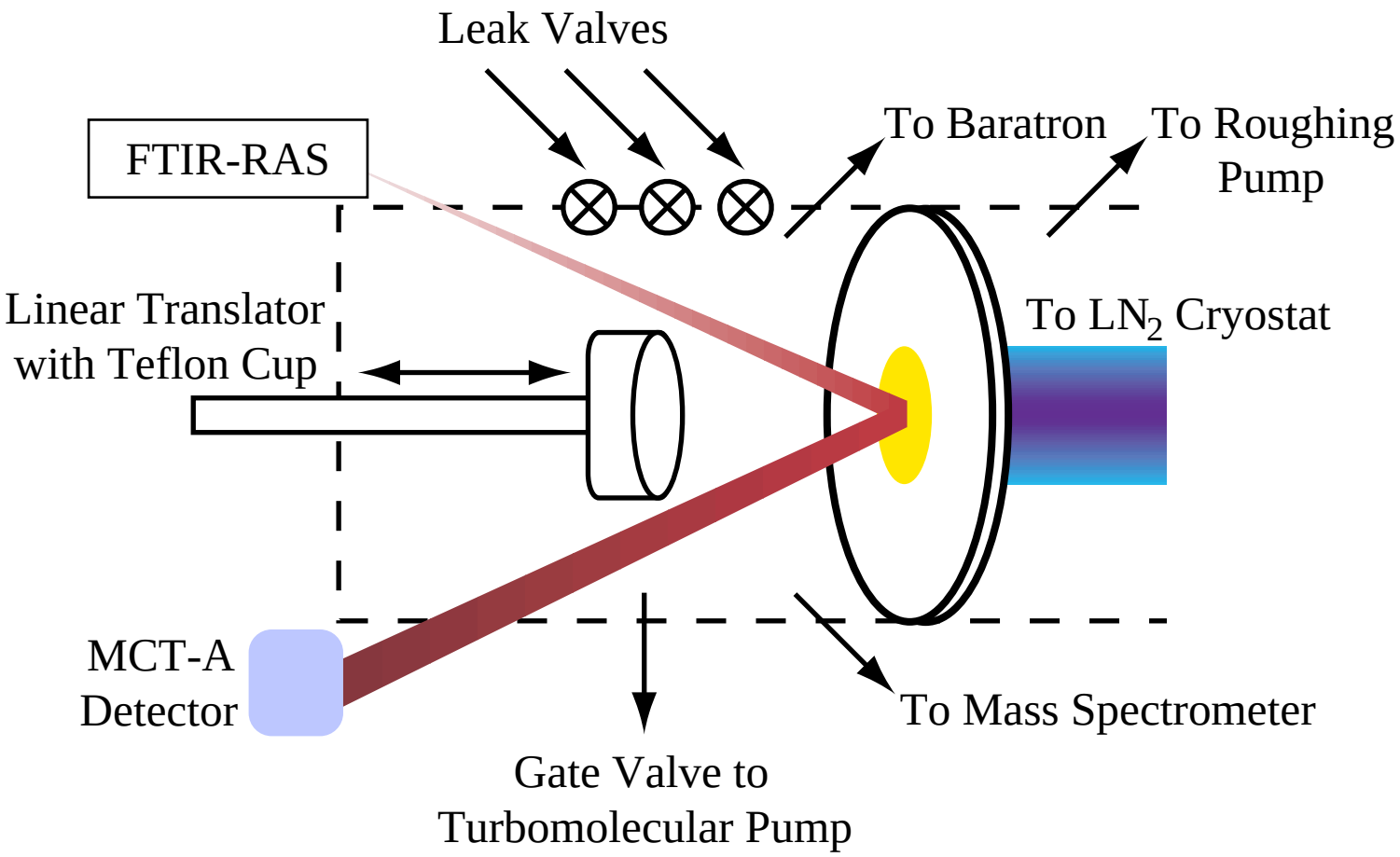
Results

- Maleic Acid effloresces at lower RH than ammonium sulfate.
- Mixtures effloresce at ~same RH as ammonium sulfate.

Possible Explanations

- Ammonium sulfate nucleates first
  → Heterogeneous nucleation of maleic acid.
- Ammonium sulfate increases solubility of maleic acid
  → Loss of dissolved ammonium sulfate makes maleic acid even more supersaturated.

Apparatus



FTIR-RAS

Monitors condensed phase

Knudsen cell

Monitors gas phase

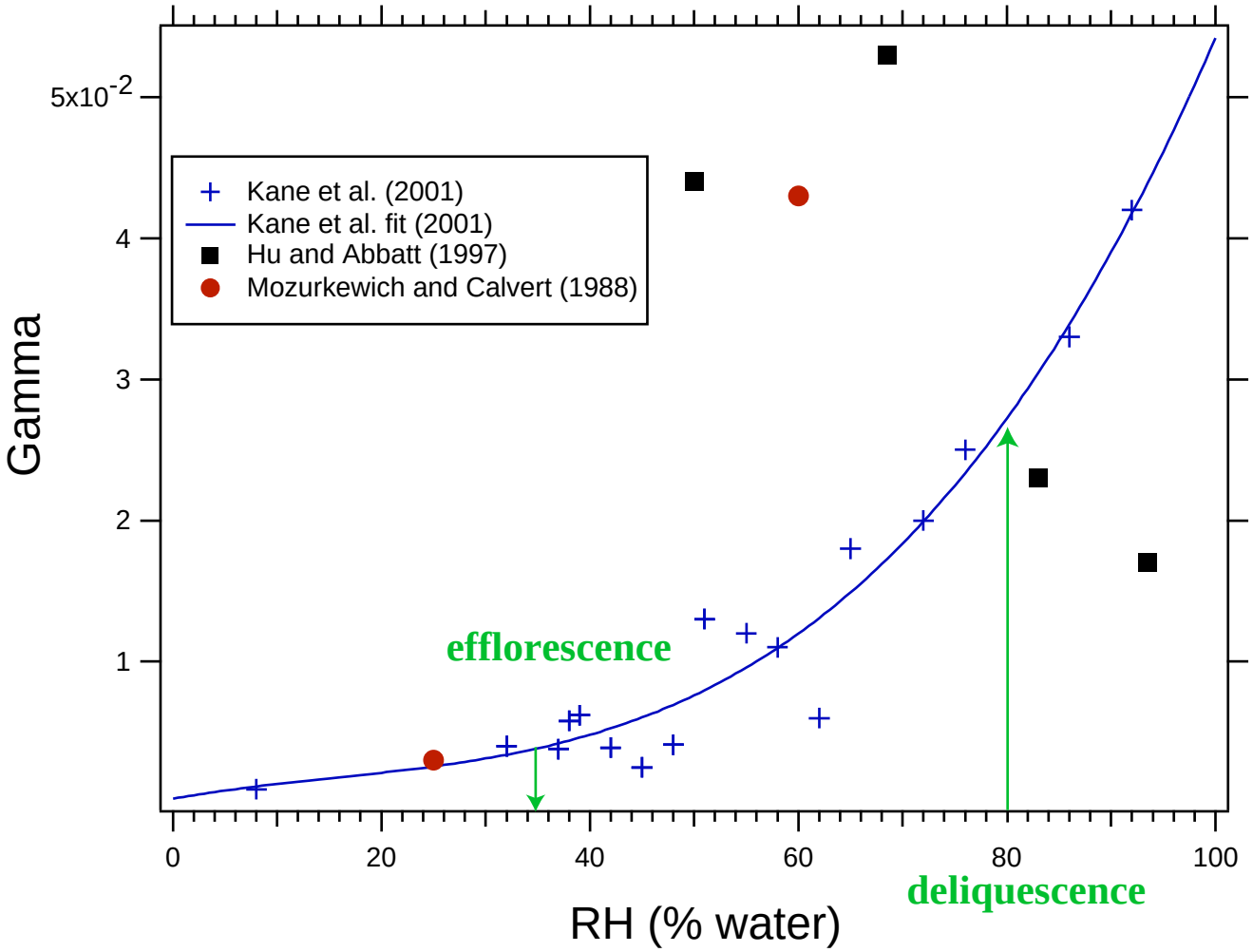
$\gamma = A_h(I^0-I)/A_sI$

This Study: N_2O_5 on ice: $\gamma = 0.017$ at 200 K

Literature Value: $\gamma = 0.02$ on ice at 195 K

Previous Results on Ammonium Sulfate

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$

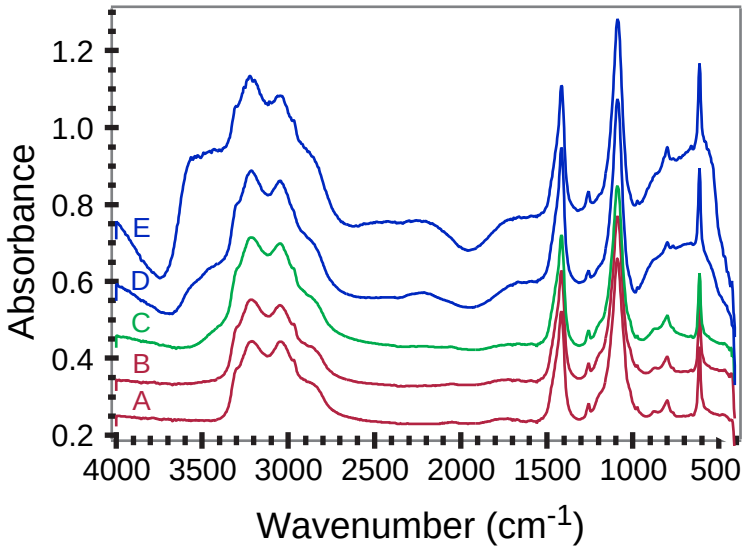


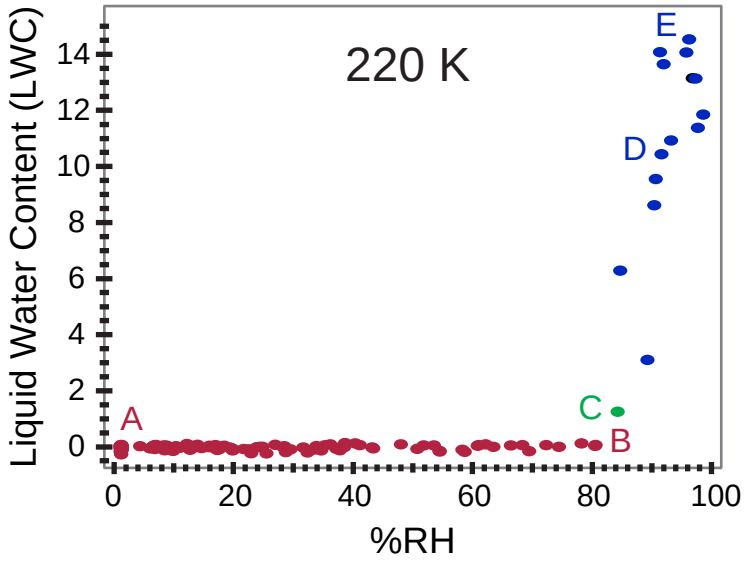
Aerosol phase not always clear!

Below 35 % RH: solid

Above 80 % RH: liquid

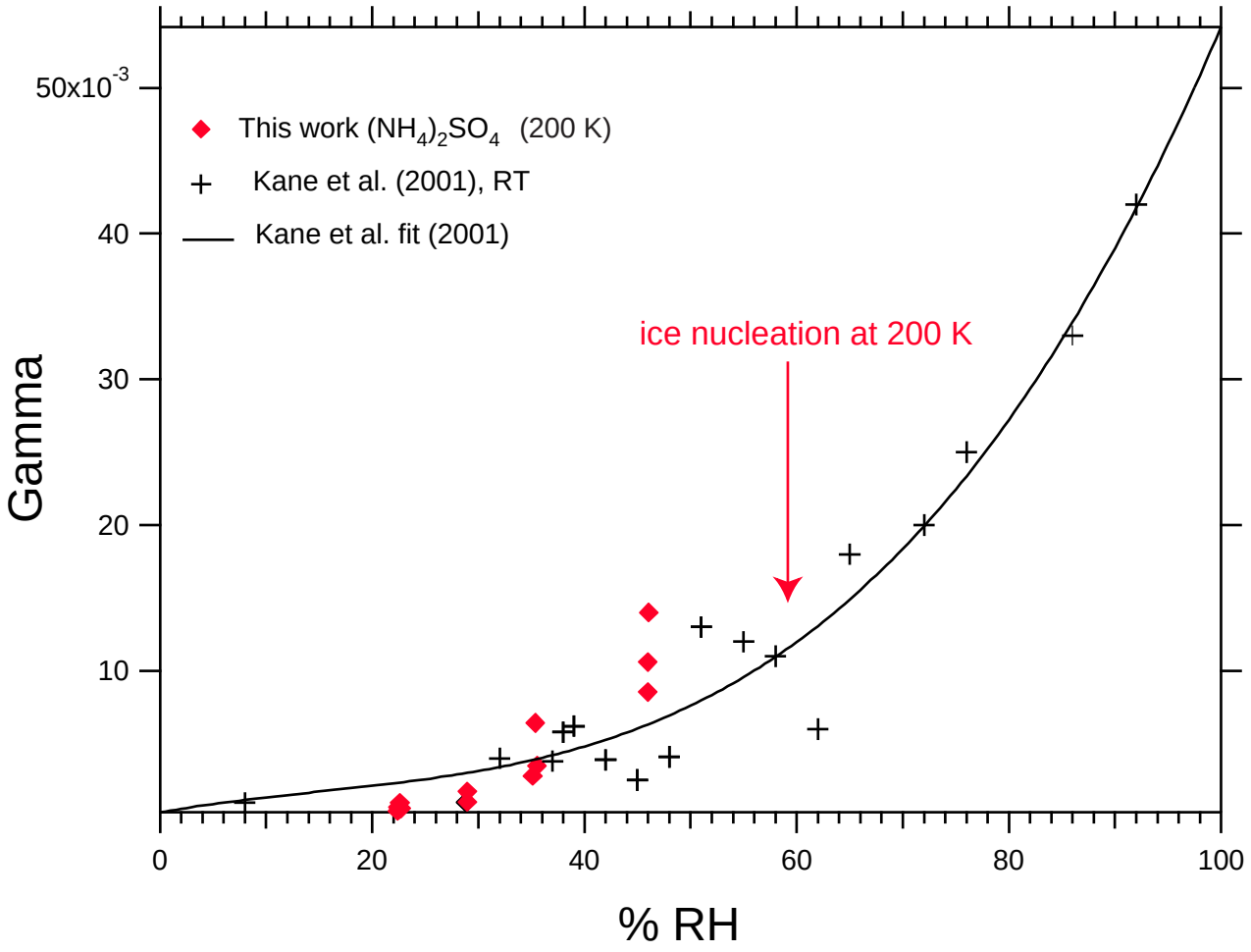
Our Study ⇒ Dry Ammonium Sulfate





No change in spectra until either deliquescence or ice nucleation!

N_2O_5 on Dry Ammonium Sulfate vs. RH



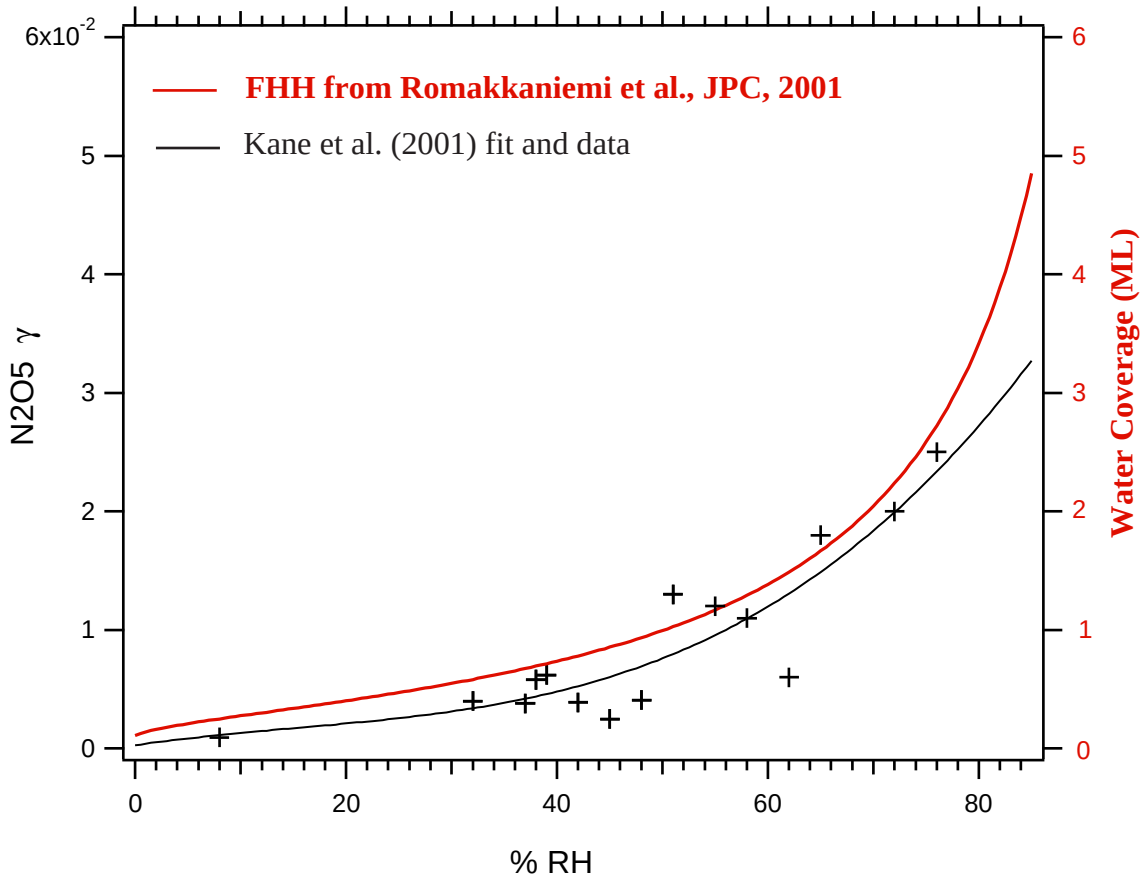
γ increases with increasing RH, even when dry

Kane et al. numbers consistent with dry values

Importance of adsorbed water at RH < deliquescence

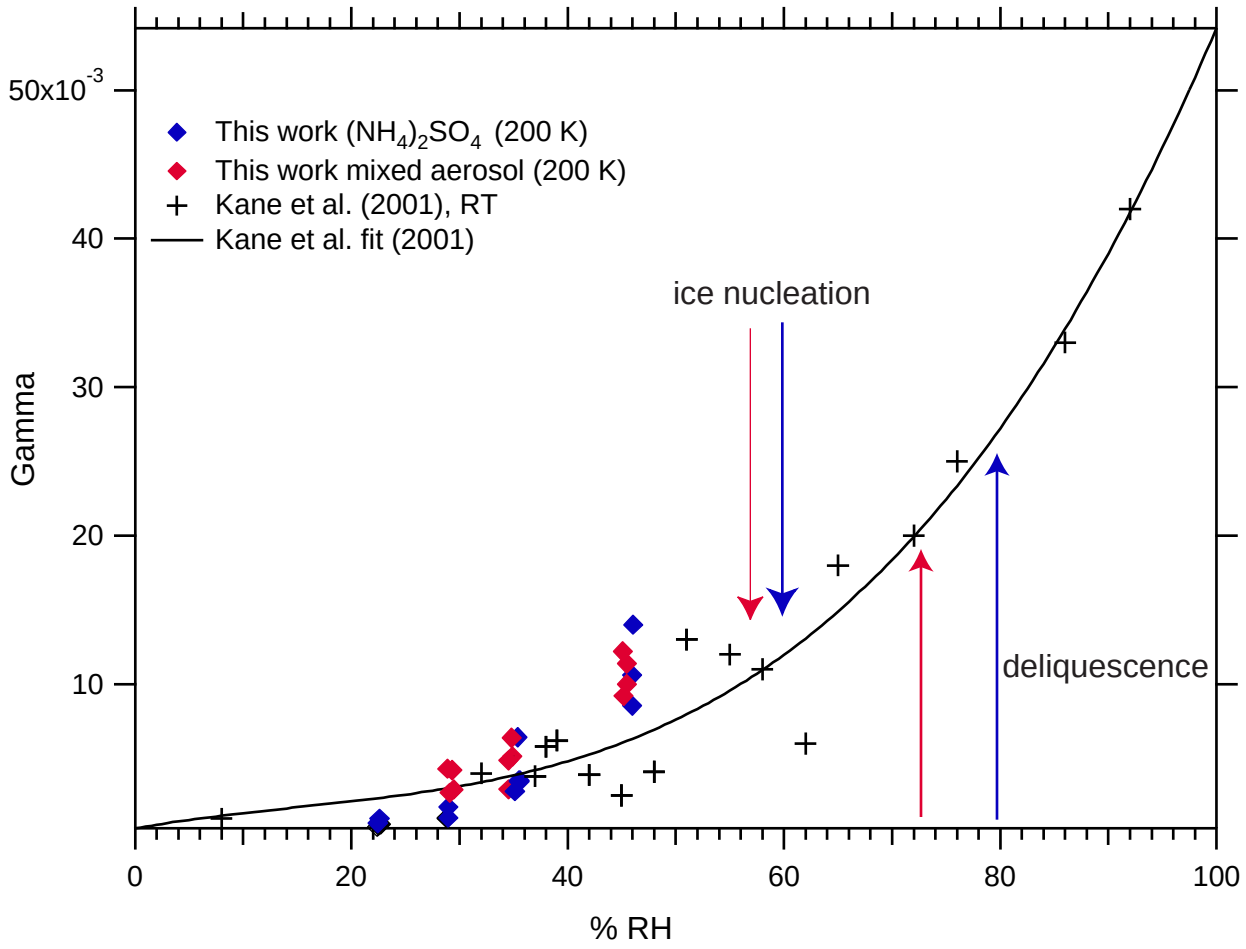
Expected Water Coverage on Ammonium Sulfate

FHH Model for planar surface calculated from particle isotherms at RT



Below deliquescence RH:
N_2O_5 γ scales well with FHH water uptake

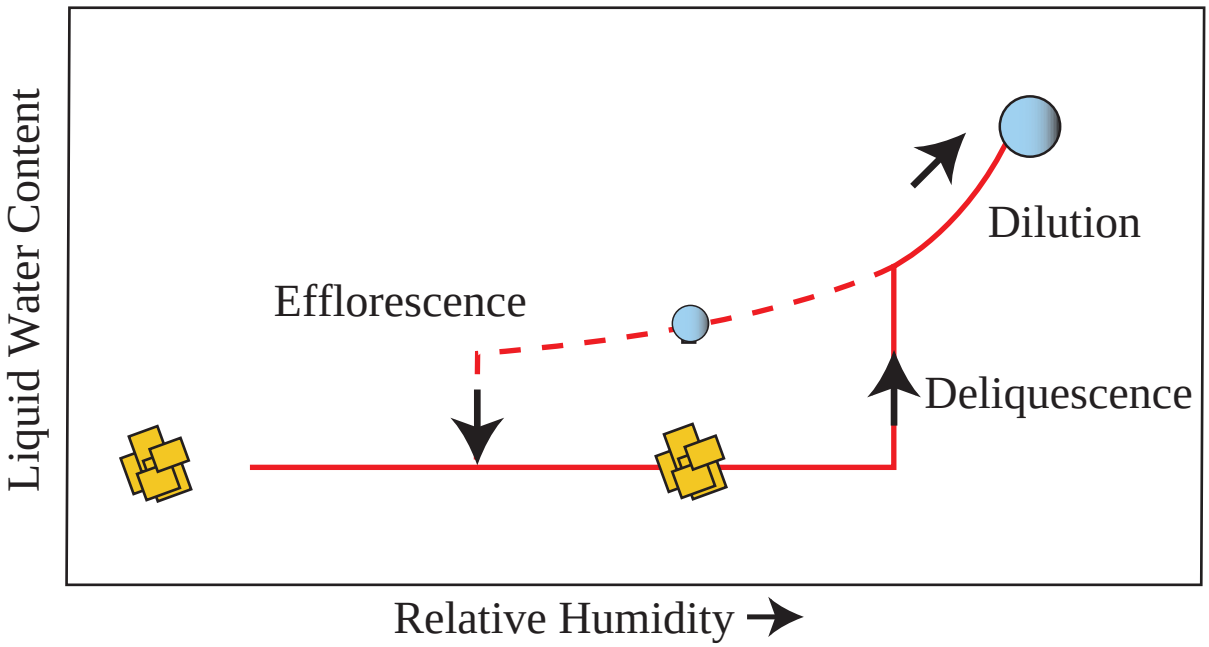
N_2O_5 uptake on 50/50 wt% Ammonium Sulfate/Maleic Acid at 200 K



Very similar uptake on 50 wt% AS/maleic acid vs pure AS

For AS/maleic acid, Eutonic deliquescence RH = 73 % (at -10°C)

Summary and Future Work



I. Phase change RH's:

Deliquescence: AS/insoluble acids = AS
AS/soluble acids ≤ AS

Efflorescence: AS/maleic = AS

Ice Nucleation RH: AS/maleic = AS

II. N_2O_5 Reaction Efficiency:

At low RH on dry: γ is f(RH)

AS/maleic = AS

III. Future:

Measure N_2O_5 at higher RH and wet vs. dry

Measure water uptake on dry and wet

Other organics