Nucleation of Efflorescence by Insoluble Components in Aqueous Inorganic Aerosols in the Troposphere

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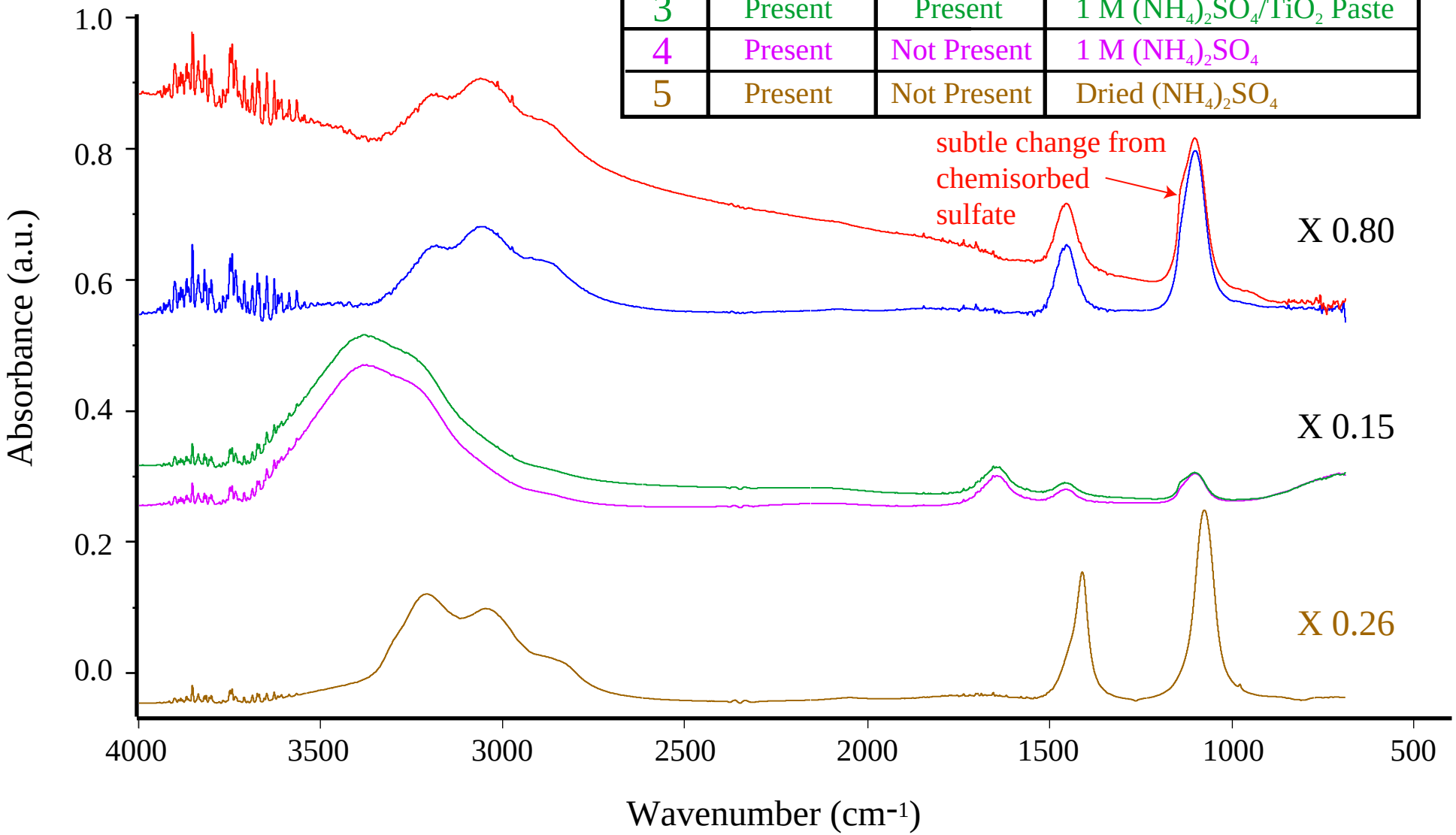
Abstract

Knowledge of the hygroscopic response of aerosols is a fundamental factor for the quantitative modeling of visibility degradation, global warming, PM-10 health issues, cloud microphysics, and the oxidizing capacity of the troposphere. At the present time, however, our current knowledge of the efflorescence properties of hygroscopic aerosols is insufficient to develop accurate quantitative models. Part of the discrepancy between current models and field measurements is accounted for by the kinetic limitations on the rate of solid formation during efflorescence, which arise from homogeneous nucleation. In addition, heterogeneous processes may induce efflorescence and are potentially important in the boundary layer where aqueous aerosols commonly contain many insoluble crustal particles. In the present laboratory work, we have undertaken the generation of $(NH_4)_2SO_4$ particles mixed with TiO_2, Al_2O_3, ZrO_2, and SiO_2 particles. The particles are prepared by condensing gaseous SO_3, H_2O, and NH_3 in the presence of the metal oxide particles. An FTIR spectrophotometer is employed to observe the liquid-to-solid phase changes of $(NH_4)_2SO_4$ particles with decreasing the relative humidity.

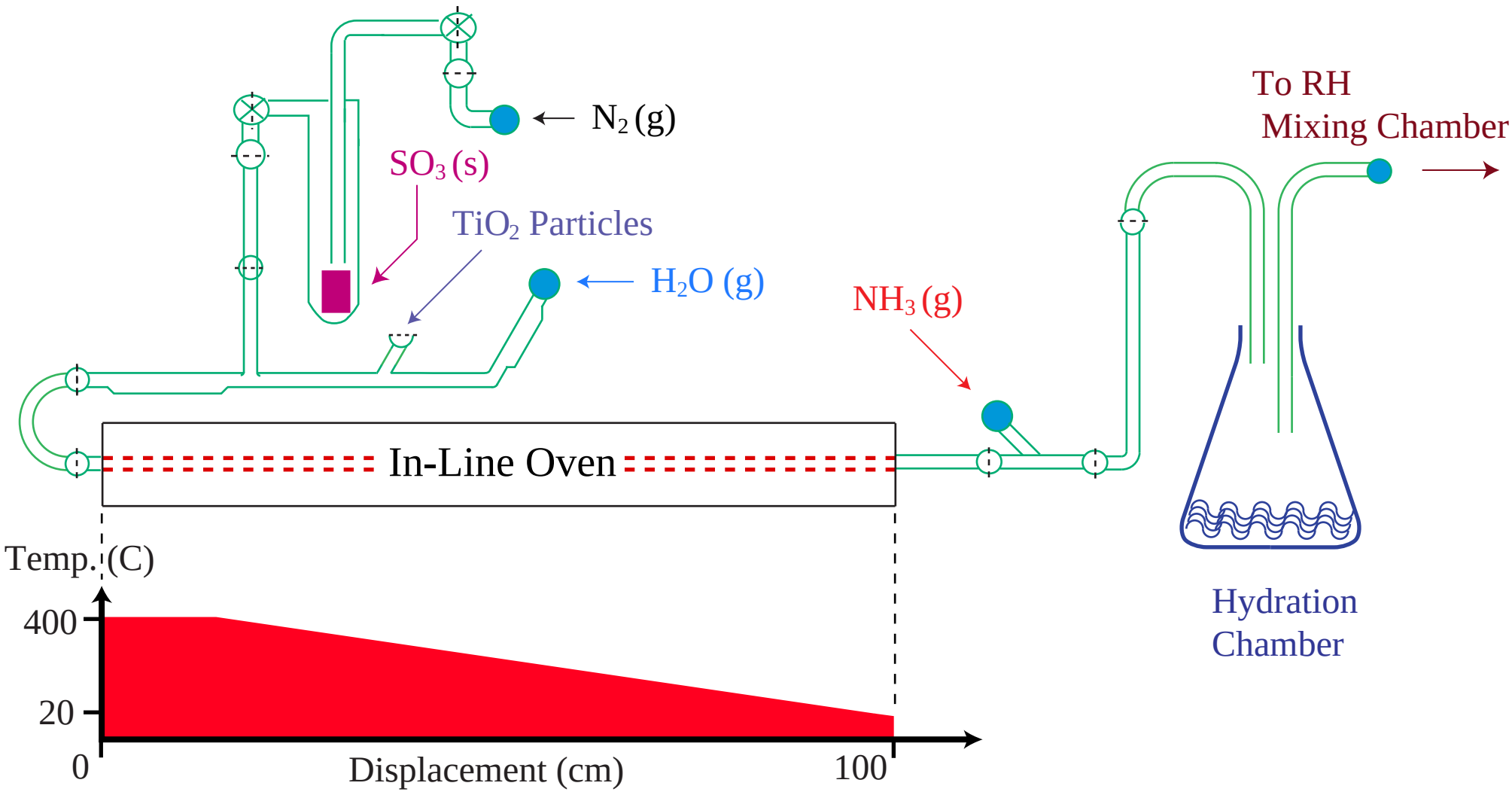
Attenuated Total Reflectance Spectra

($H_2O(g)$ & $CO_2(g)$ subtracted)

No.	$(NH_4)_2SO_4$	TiO_2 Nuclei	Remarks
1	Present	Present	No. 3 minus H_2O (l)
2	Present	Not Present	No. 4 minus H_2O (l)
3	Present	Present	1 M $(NH_4)_2SO_4/TiO_2$ Paste
4	Present	Not Present	1 M $(NH_4)_2SO_4$
5	Present	Not Present	Dried $(NH_4)_2SO_4$



Preparation of Internally Mixed $(NH_4)_2SO_4/TiO_2$ Particles



H_2O (g)	SO_3 (g)	NH_3 (g)	TiO_2 (s)
100% RH = 19.5 g/m^3 365 mL/min (= 8:1 dilution)	1884.3 g/m^3 90.4 mL/min (= 32:1 dilution)	6317 g/m^3 3.1 mL/min (= 2320:1 dilution)	2.9 slpm (N_2 Flow)

indicates an o-ring connector

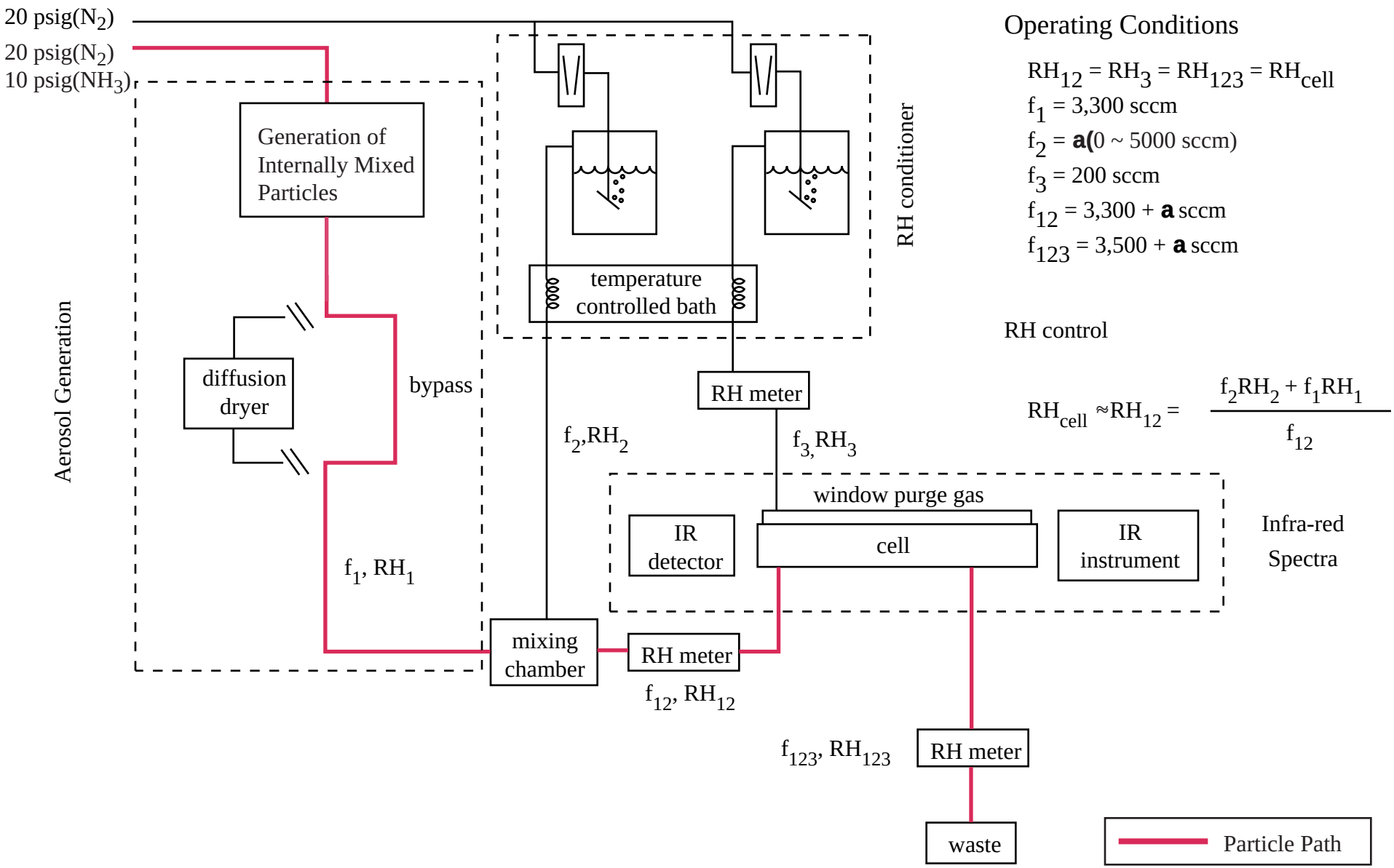
indicates an Schott fitting for tubing

indicates Valves

* 0.5"(i.d.) x 16mm(o.d.) glass tubing

* ALL PYREX.

FTIR measurements



Operating Conditions

$RH_{12} = RH_3 = RH_{123} = RH_{cell}$

f_1 = 3,300 sccm

f_2 = **a(**0 ~ 5000 sccm)

f_3 = 200 sccm

f_{12} = 3,300 + **a** sccm

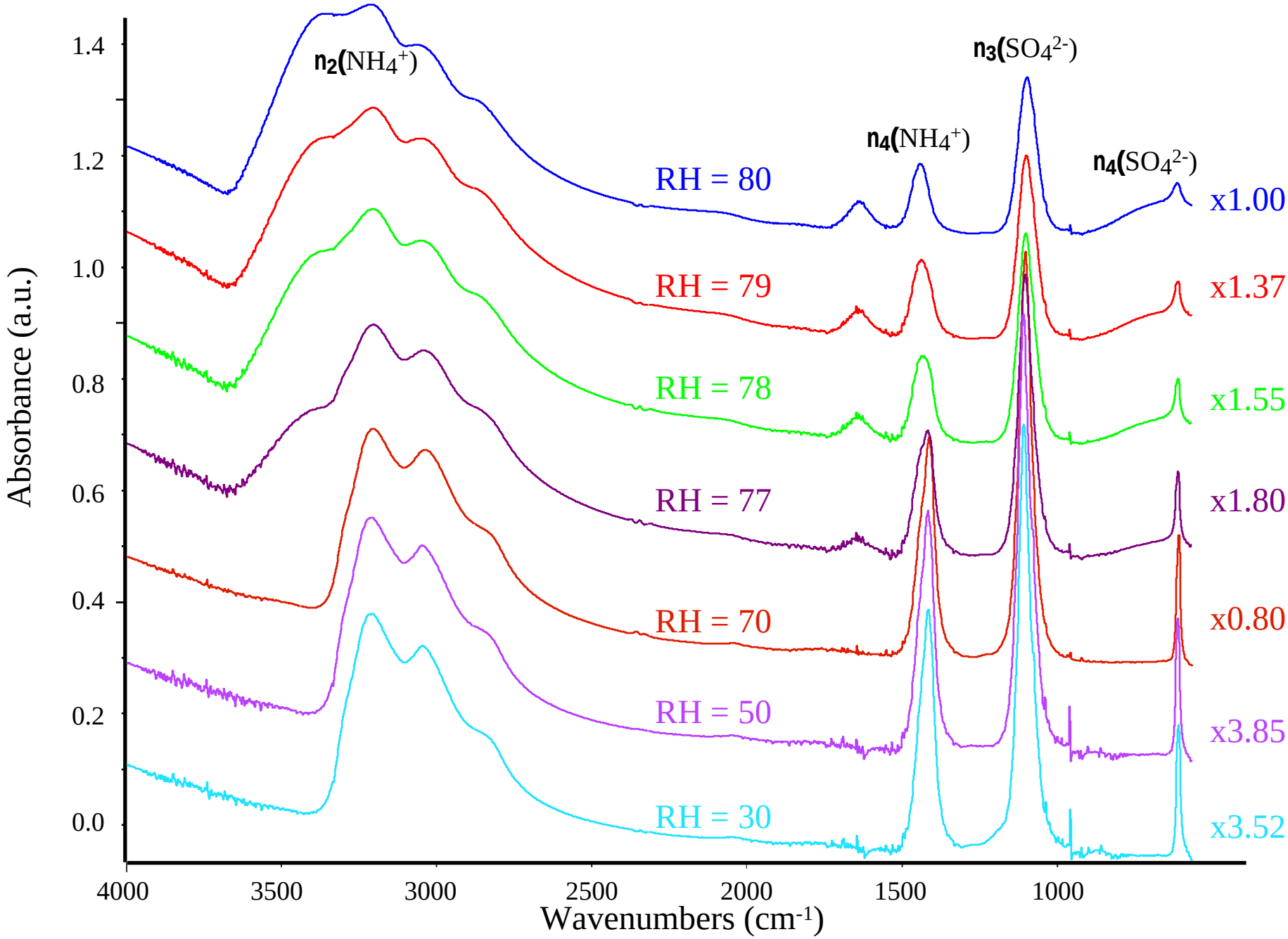
f_{123} = 3,500 + **a** sccm

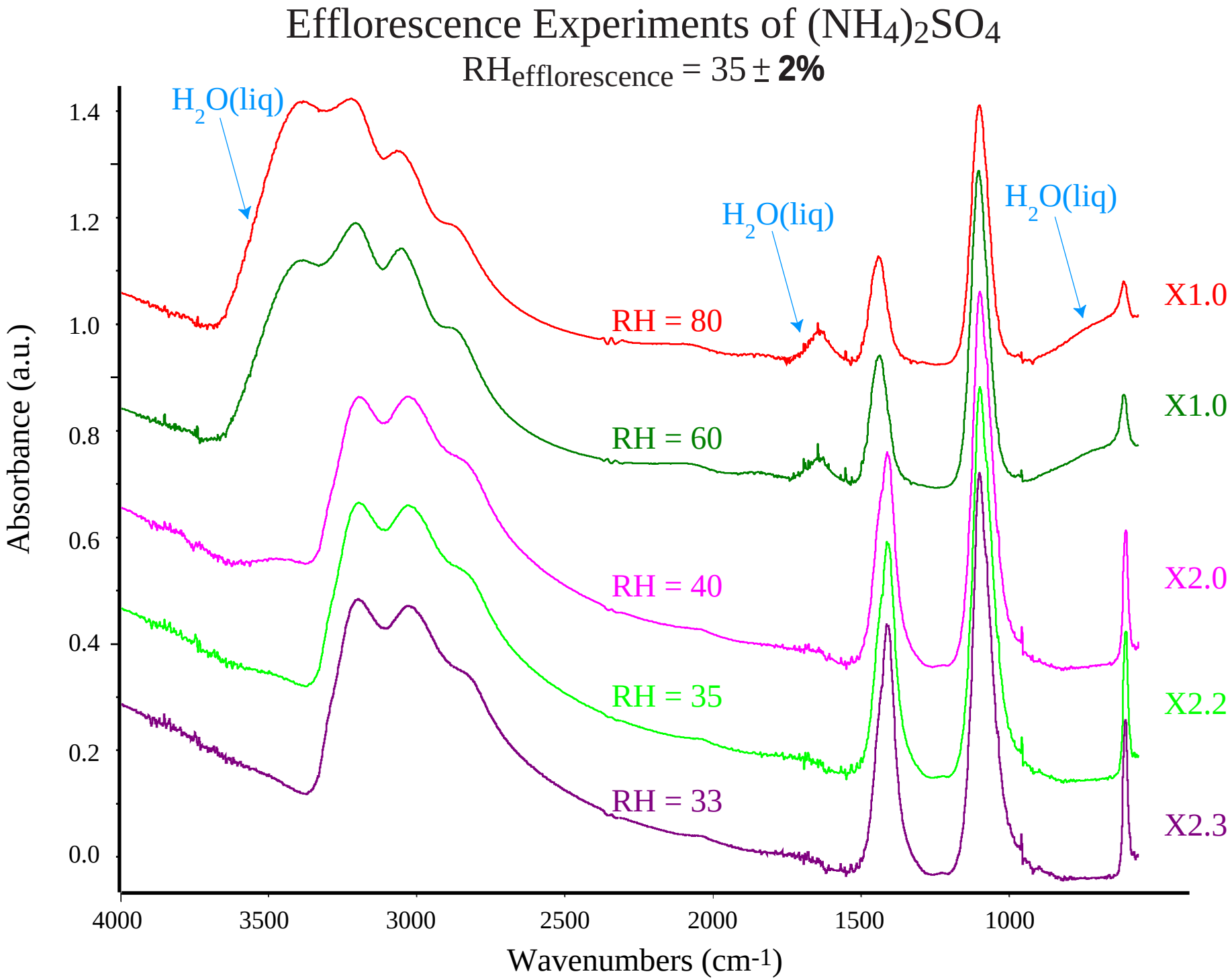
RH control

$$RH_{cell} \approx RH_{12} = \frac{f_2 RH_2 + f_1 RH_1}{f_{12}}$$

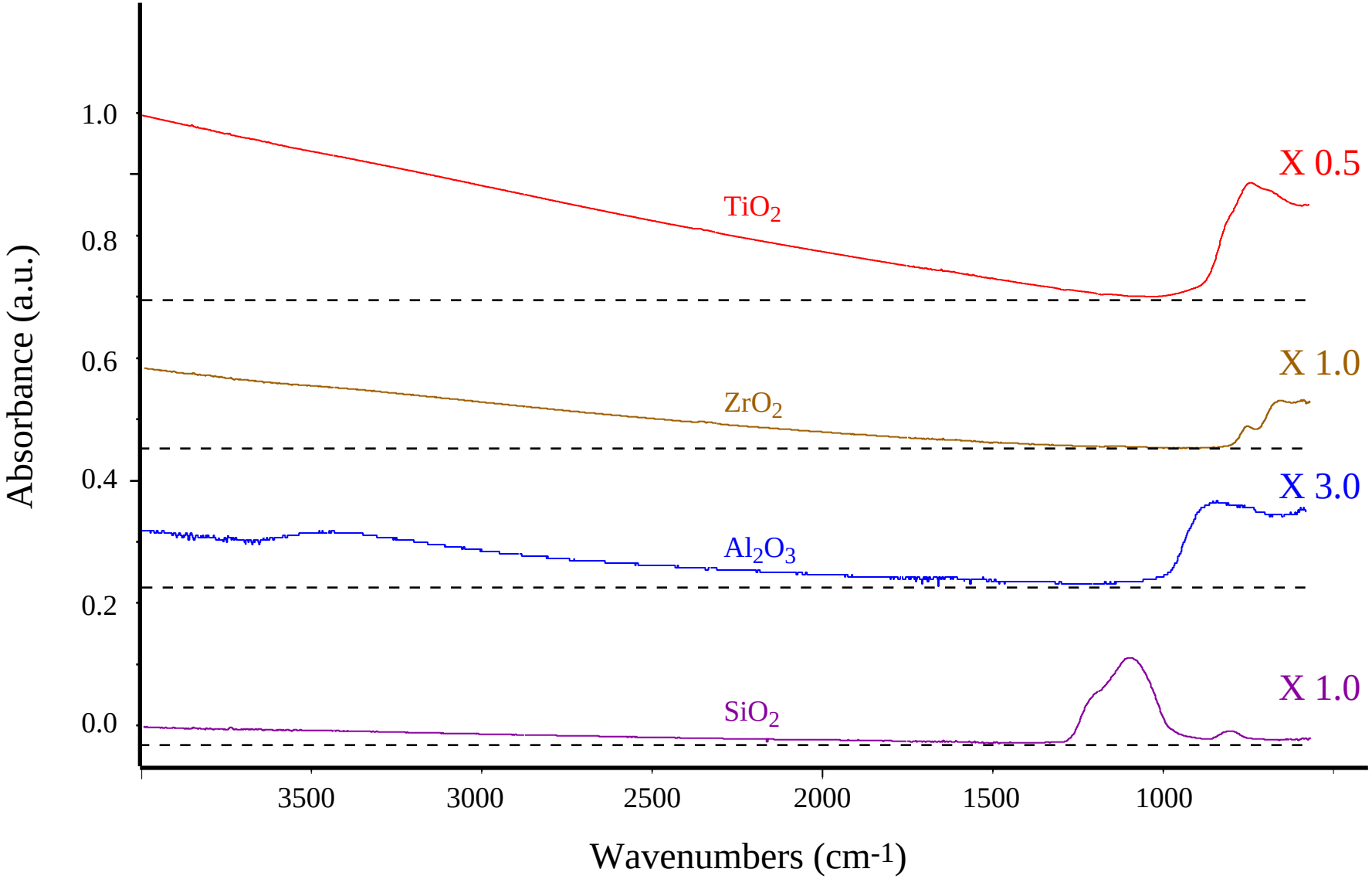
Deliquescence Experiments of $(NH_4)_2SO_4$

$RH_{deliquescence} = 78 \pm 2\%$



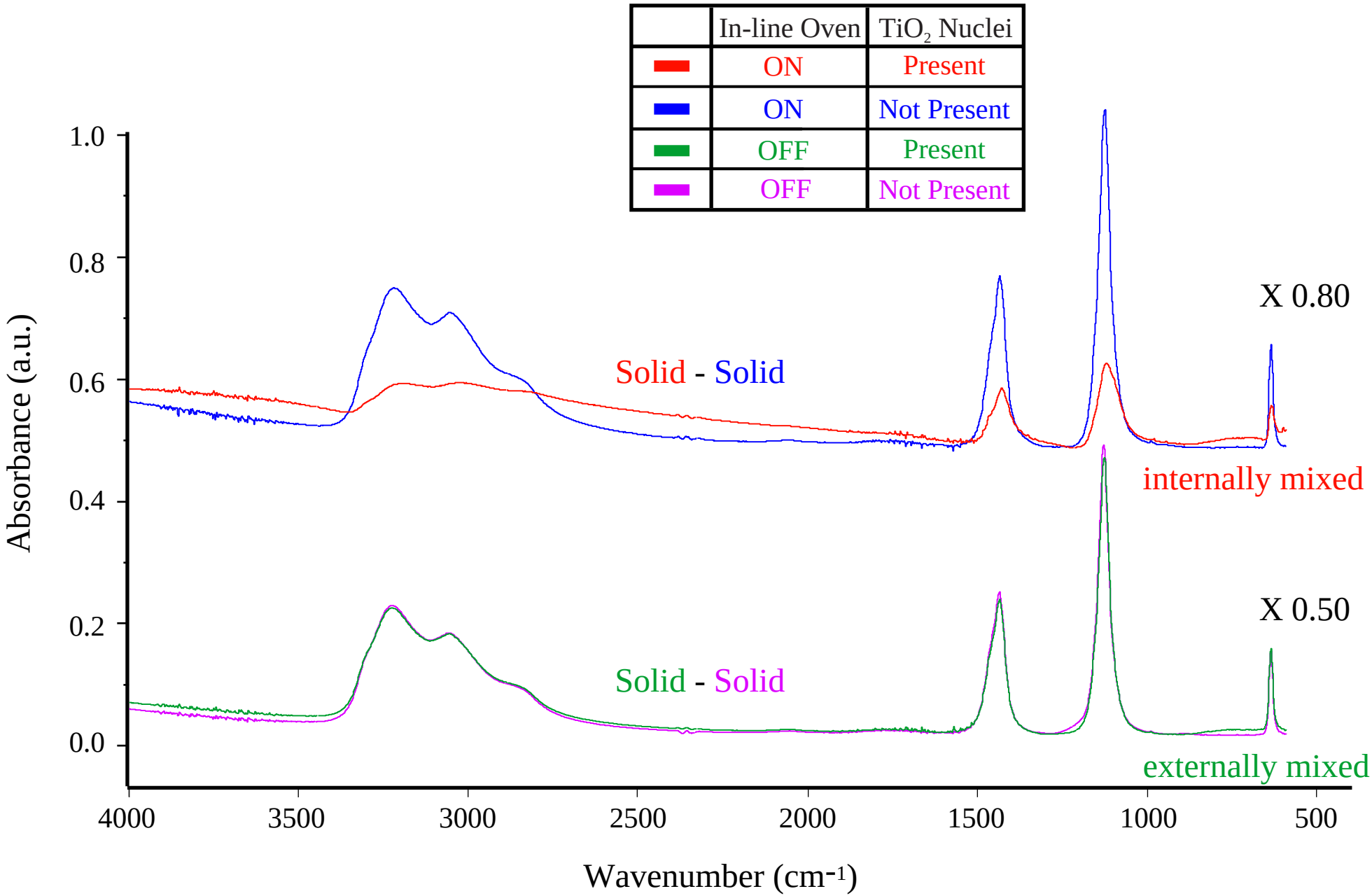

Efflorescence Experiments of $(NH_4)_2SO_4$
$RH_{efflorescence}$ = 35 ± 2%
H_2O(liq)
H_2O(liq)
H_2O(liq)
RH = 80
RH = 60
RH = 40
RH = 35
RH = 33
X1.0
X1.0
X2.0
X2.2
X2.3
Absorbance (a.u.)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm^{-1})

FTIR Spectra of Pure Inorganic Particles



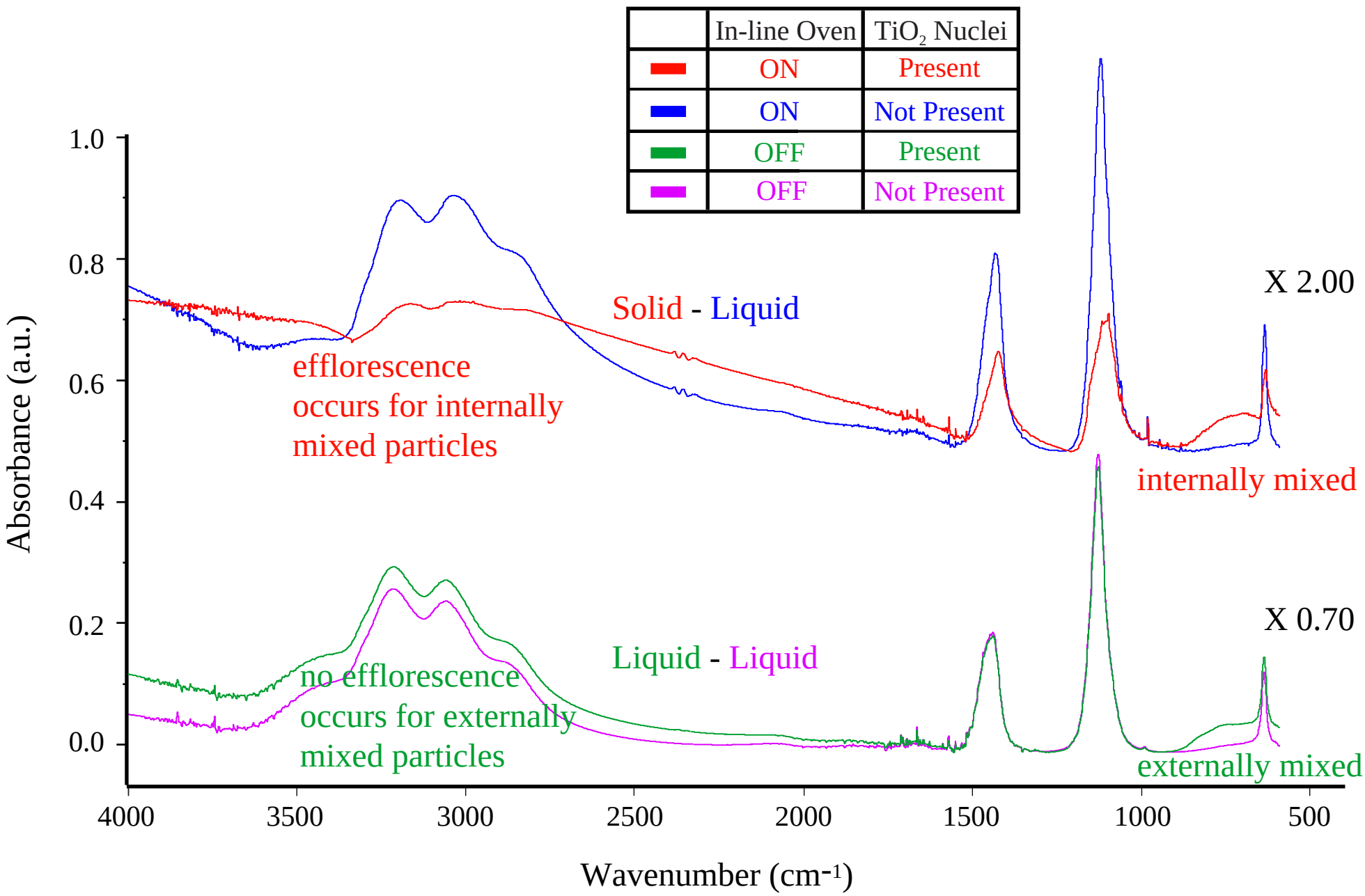
Preparation of Internally & Externally Mixed $TiO_2/(NH_4)_2SO_4$ Particles

(RH = 27 ± **2%**, $H_2O(g)$ & $CO_2(g)$ subtracted)



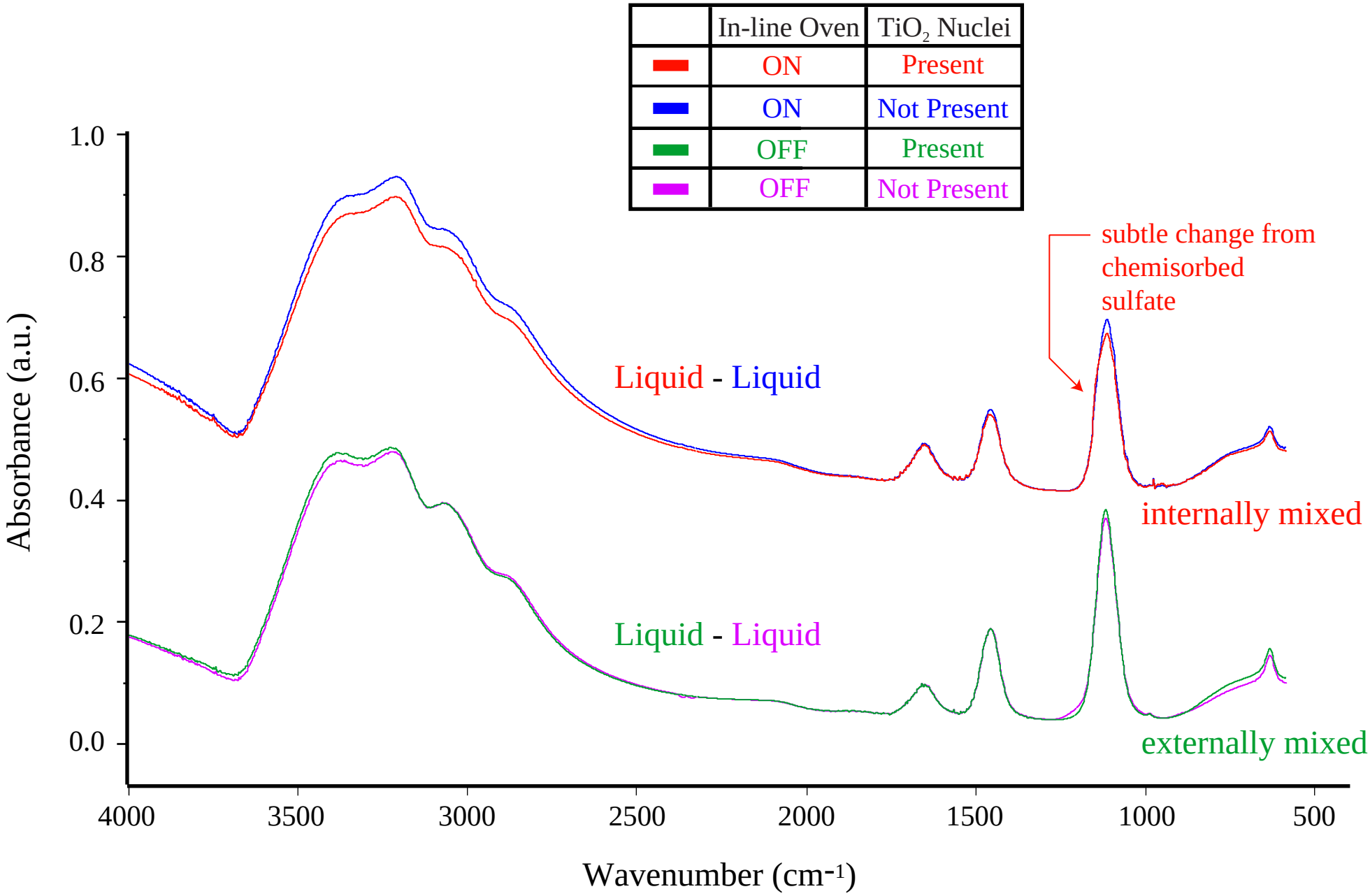
TiO_2 Particles Induce Efflorescence of $(NH_4)_2SO_4$

(RH = 50 ± **2%**, $H_2O(g)$ & $CO_2(g)$ subtracted)



IR Spectra of Internally & Externally Mixed Liquid $(NH_4)_2SO_4/TiO_2$ are Similar

(RH = 80 ± **2%**, $H_2O(g)$ & $CO_2(g)$ subtracted)



Conclusions

- The efflorescence (35 ± 2 % RH) and deliquescence (78 ± 2% RH) values are consistent with homogeneous nucleation of $(NH_4)_2SO_4$ at 20°C.
- Internally mixed $(NH_4)_2SO_4/TiO_2$ particles are prepared by employing a temperature-gradient oven to condense H_2SO_4 onto TiO_2 nuclei, followed by mixing with NH_3(g) at 20°C.
- Whereas $(NH_4)_2SO_4$(aq) particles are shown to effloresce at 35 ± 2 % RH, efflorescence occurs above 50% RH when $(NH_4)_2SO_4$(aq) is internally mixed with TiO_2(s).
- The infrared signature of SO_4^{2-} chemisorbed to TiO_2 is observed.
- The chemical reactor has been employed to generate H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$ particles.
- Experiments are currently underway to determine the efflorescence RH values of $(NH_4)_2SO_4$(aq) particles internally mixed with TiO_2, Al_2O_3, ZrO_2, and SiO_2.

Acknowledgments

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