Detection of Cloud Droplet Activation Through Laser-induced Fluorescence Tagging (LiFT)

Brookhaven National Laboratory
U.S. DEPARTMENT OF ENERGY

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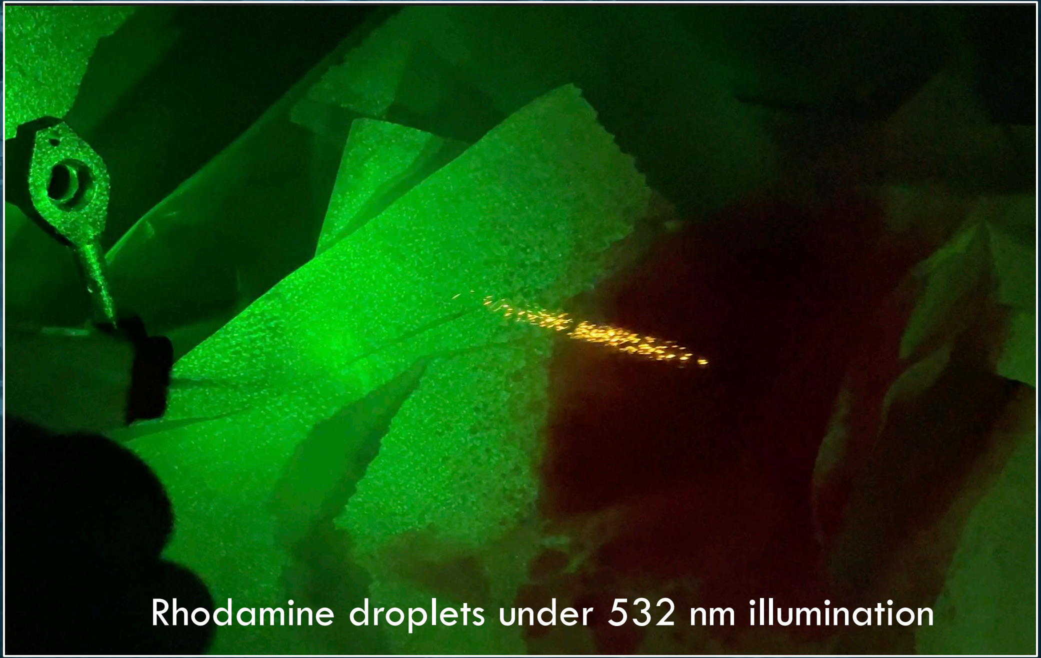
Aerosol-Cloud-Drizzle-Convection Chamber (ACDC2) team

Date: 8/10/23



Rhodamine droplets under 532 nm illumination

A central challenge in reducing indirect radiative forcing uncertainty is quantifying the small-scale spatial distribution of RH in the presence of turbulent fluctuations.

One approach to targeting this challenge is to study small-scale processes within a cloud chamber (e.g., MTU's Pi-chamber)

Point sensors are not optimal:

- They will perturb turbulence properties of the cloud during sampling.
- They will perturb the aerosol properties when drawn into the instrument.

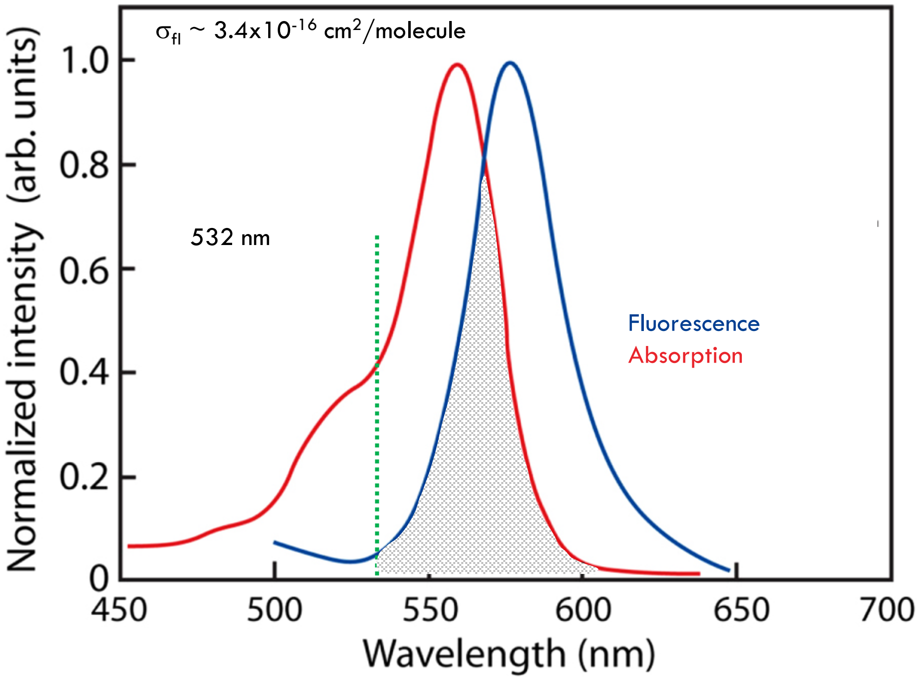
Proposed Solution: Embed fluorescent tags that are sensitive to water uptake, within aerosol particles, and use lidar to remotely identify supersaturation zones.

- **Non-contact**, in-situ detection of supersaturation zones.

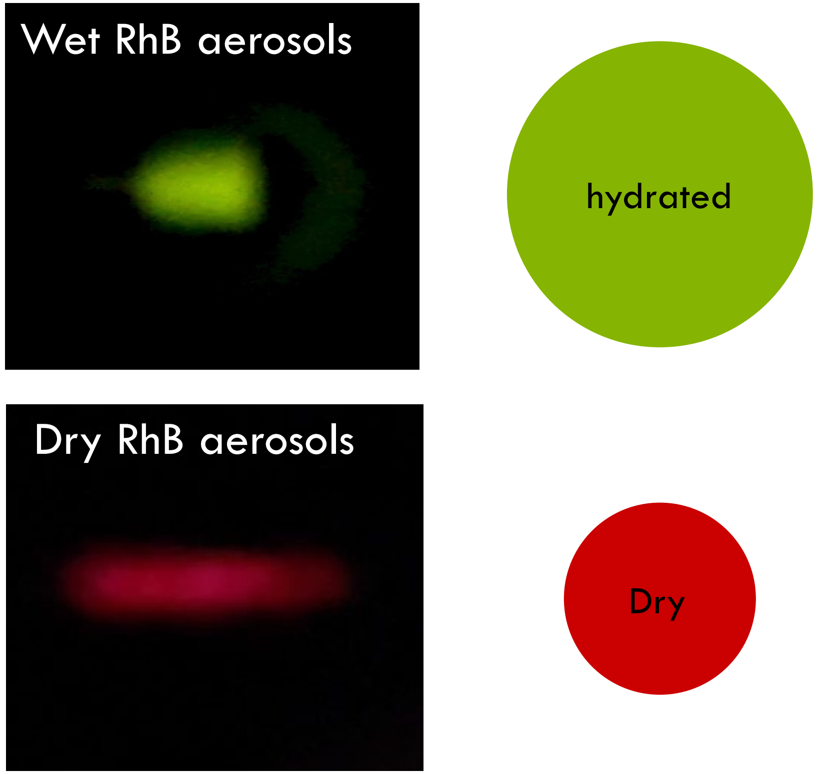
Research Objective: Evaluate efficacy of Rhodamine B (Rh-B) as a fluorescent tag embedded within ammonium sulfate (AS).

Key Taggant Property: Change in Fluorescence with Change in Aerosol Hydration State

Rhodamine B dye

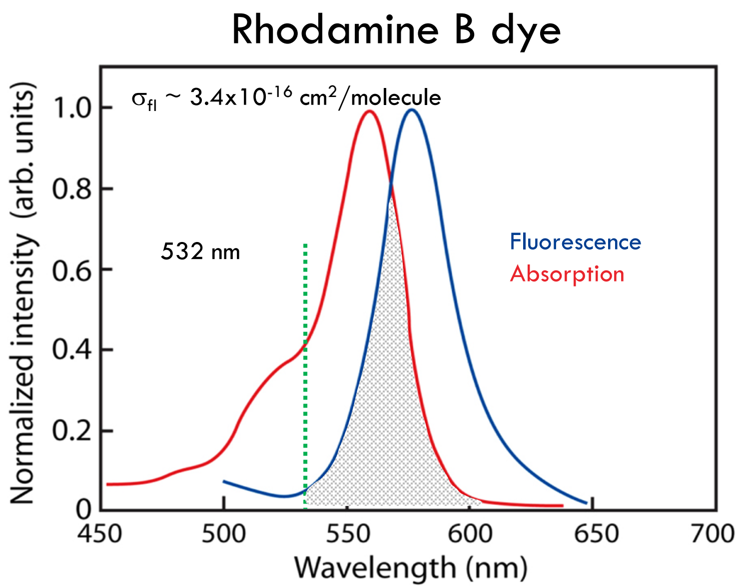


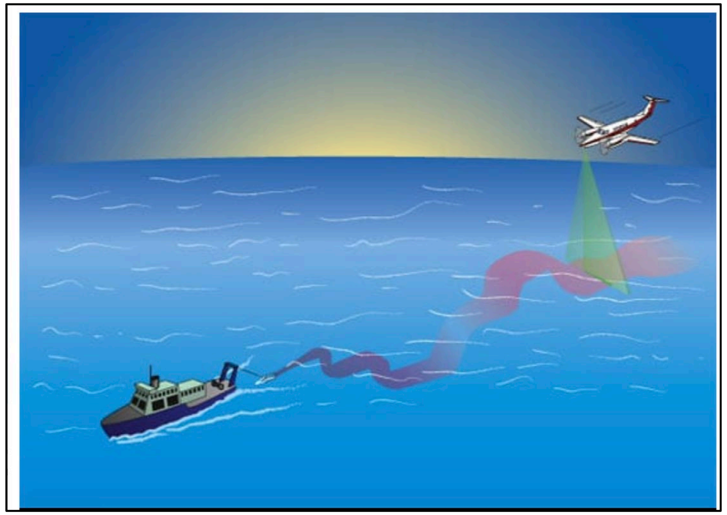
Spectrum shifts to the green with water



Can Rh-B fluorescence provide information on aerosol hydration?

Rh-B Fluorescence Has Many Tracer Applications





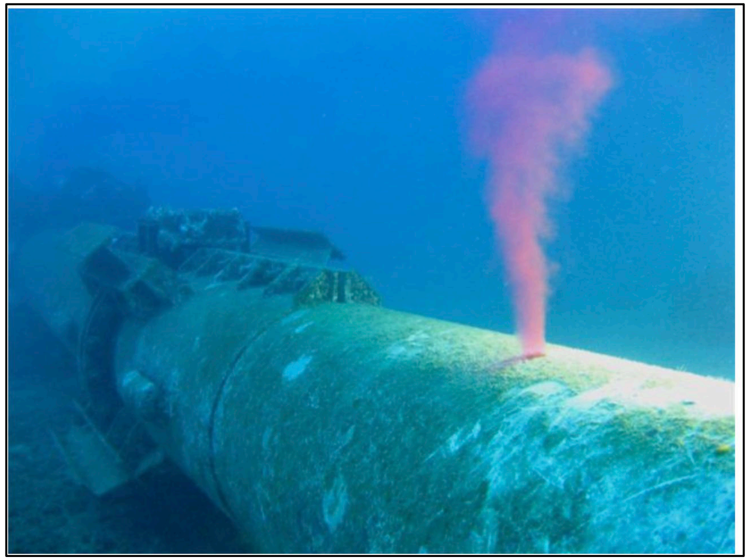
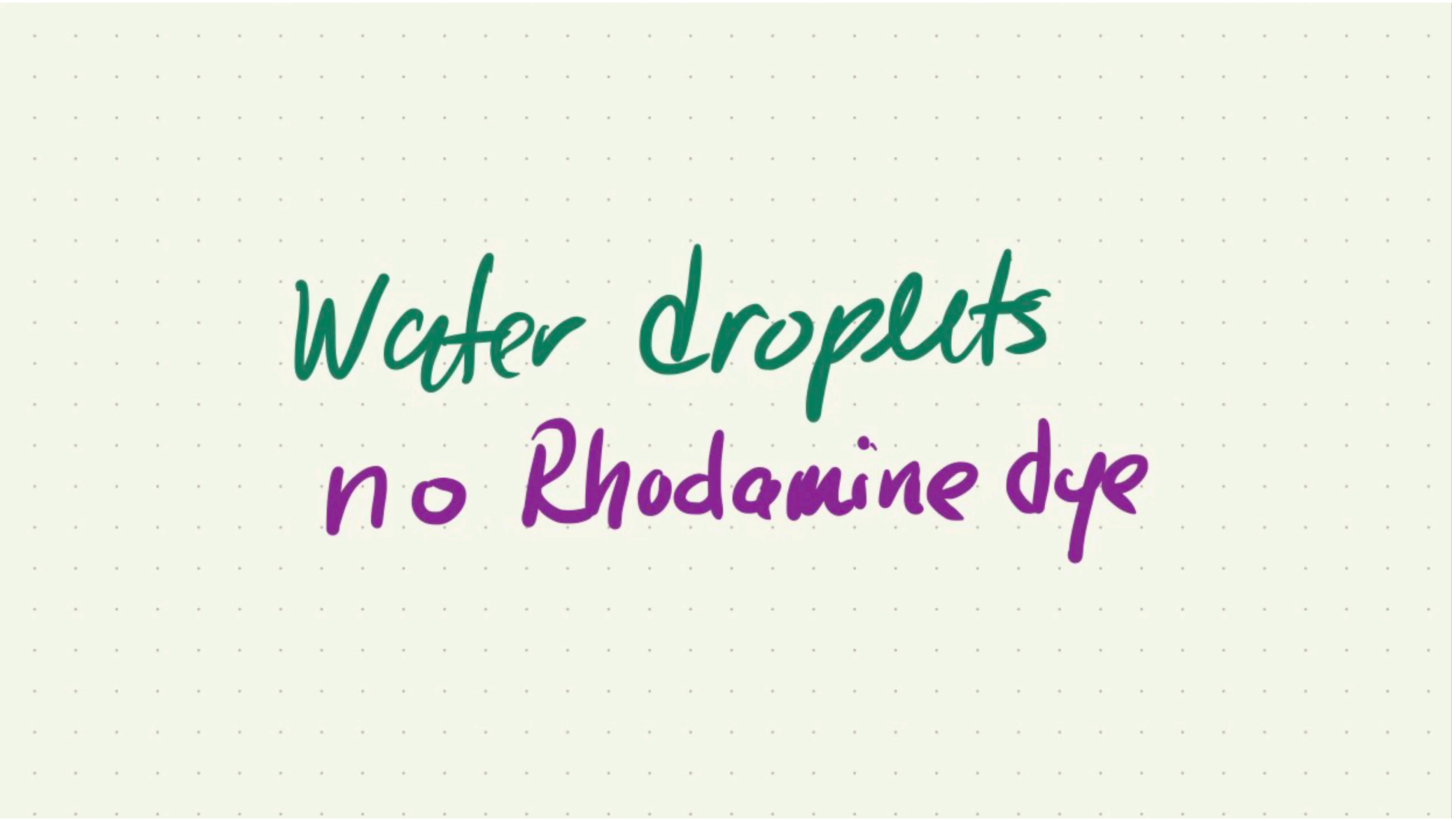
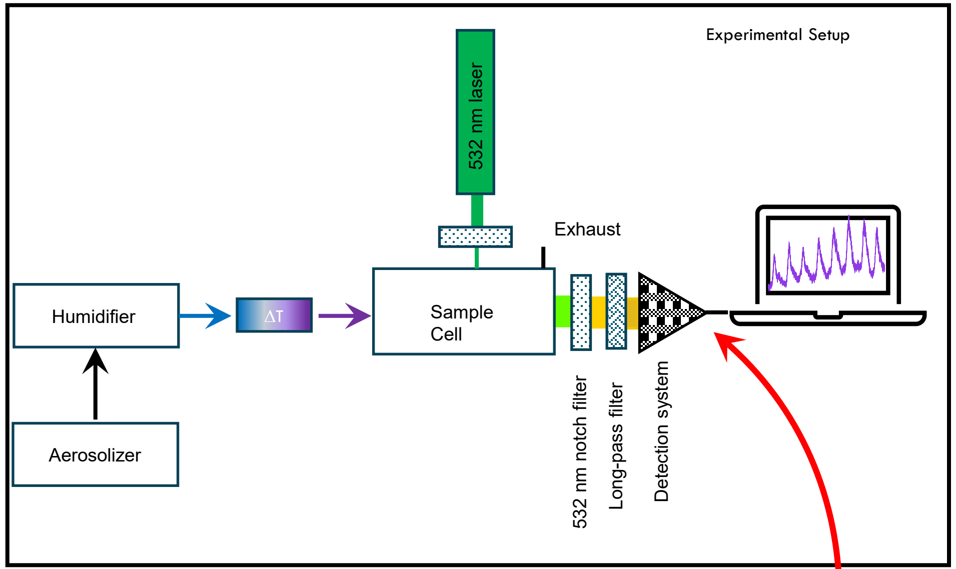


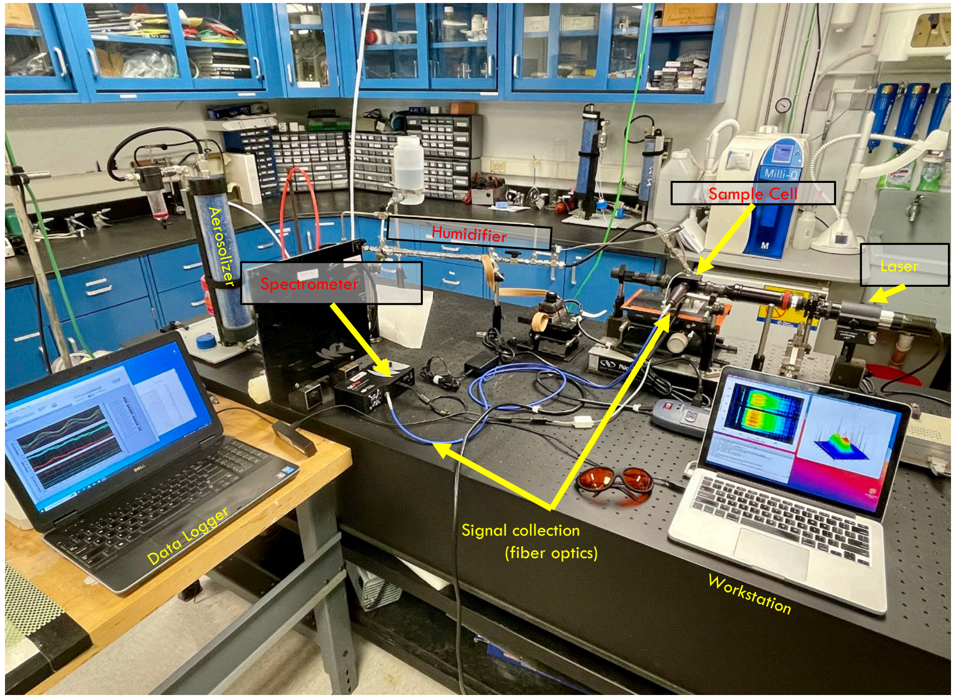
Illustration of Rhodamine-B Fluorescence Magnitude Using Atomized Droplets

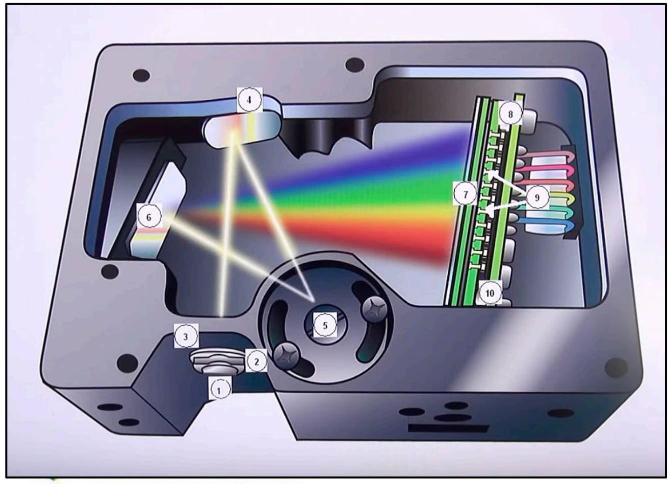
(i) Pure distilled water and
(ii) ~5 ppm of RhB in distilled water



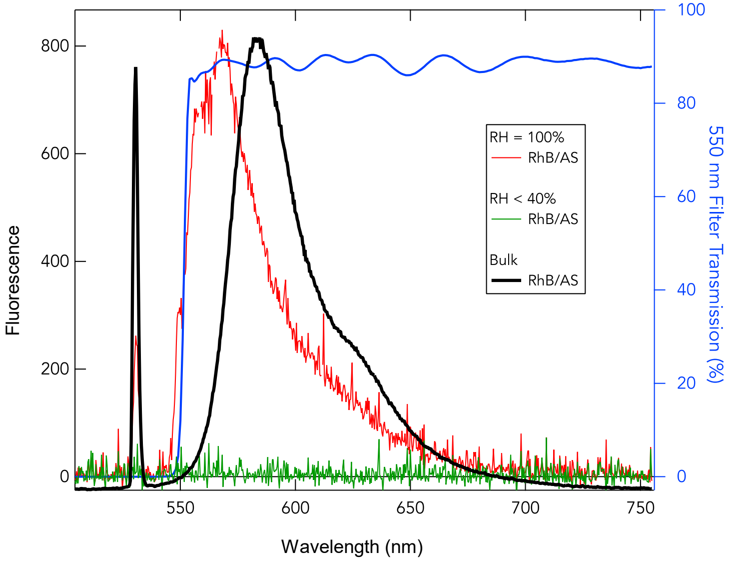
Measuring Spectrally-Resolved Rhodamine-B Fluorescence





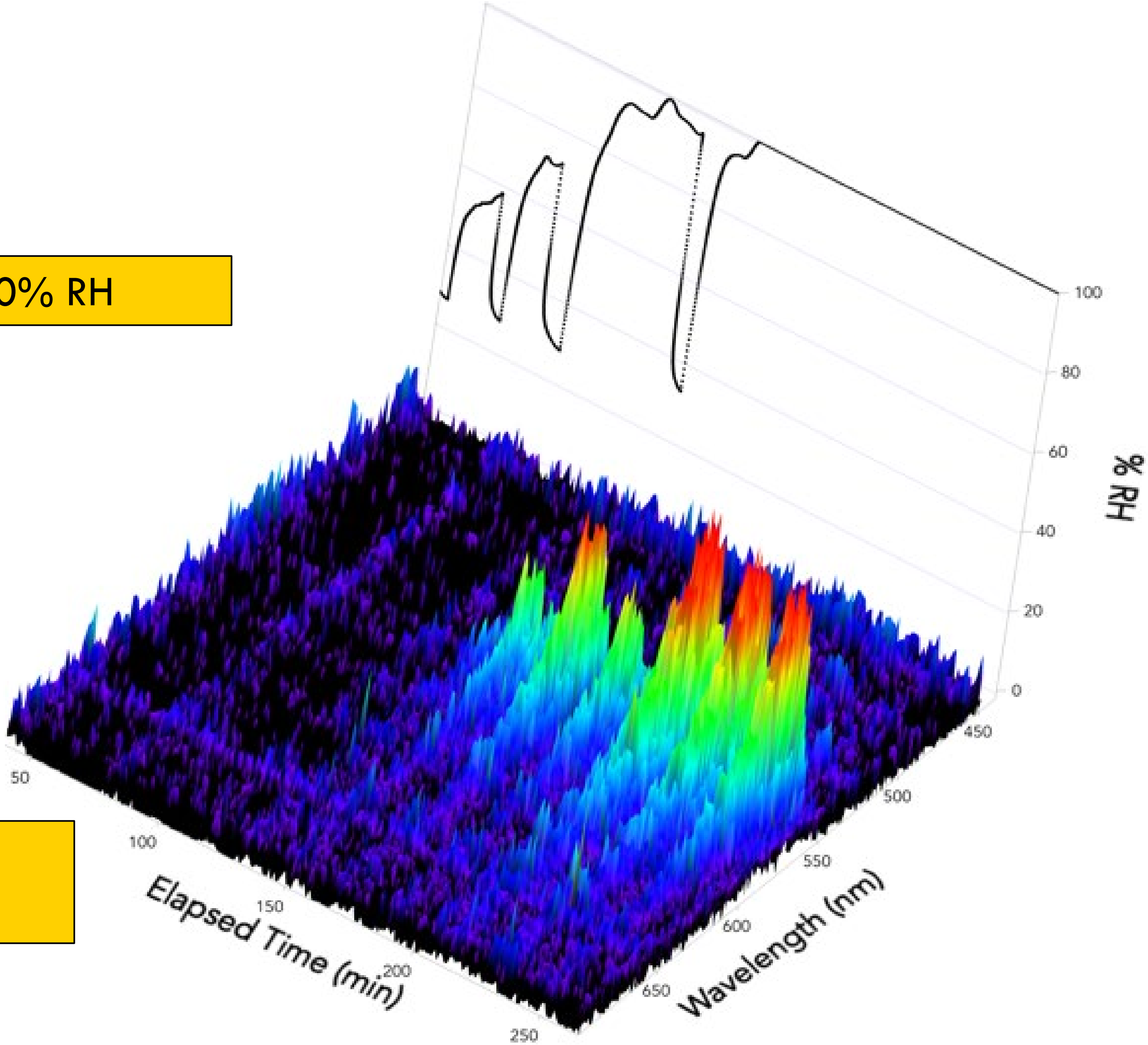


1.2 nm spectral resolution (Ocean Optics)



Spectrally-Resolved Rh-B Fluorescence as Function of RH

No fluorescence is observed below 100% RH



Oscillatory behavior in the fluorescence signal is observed

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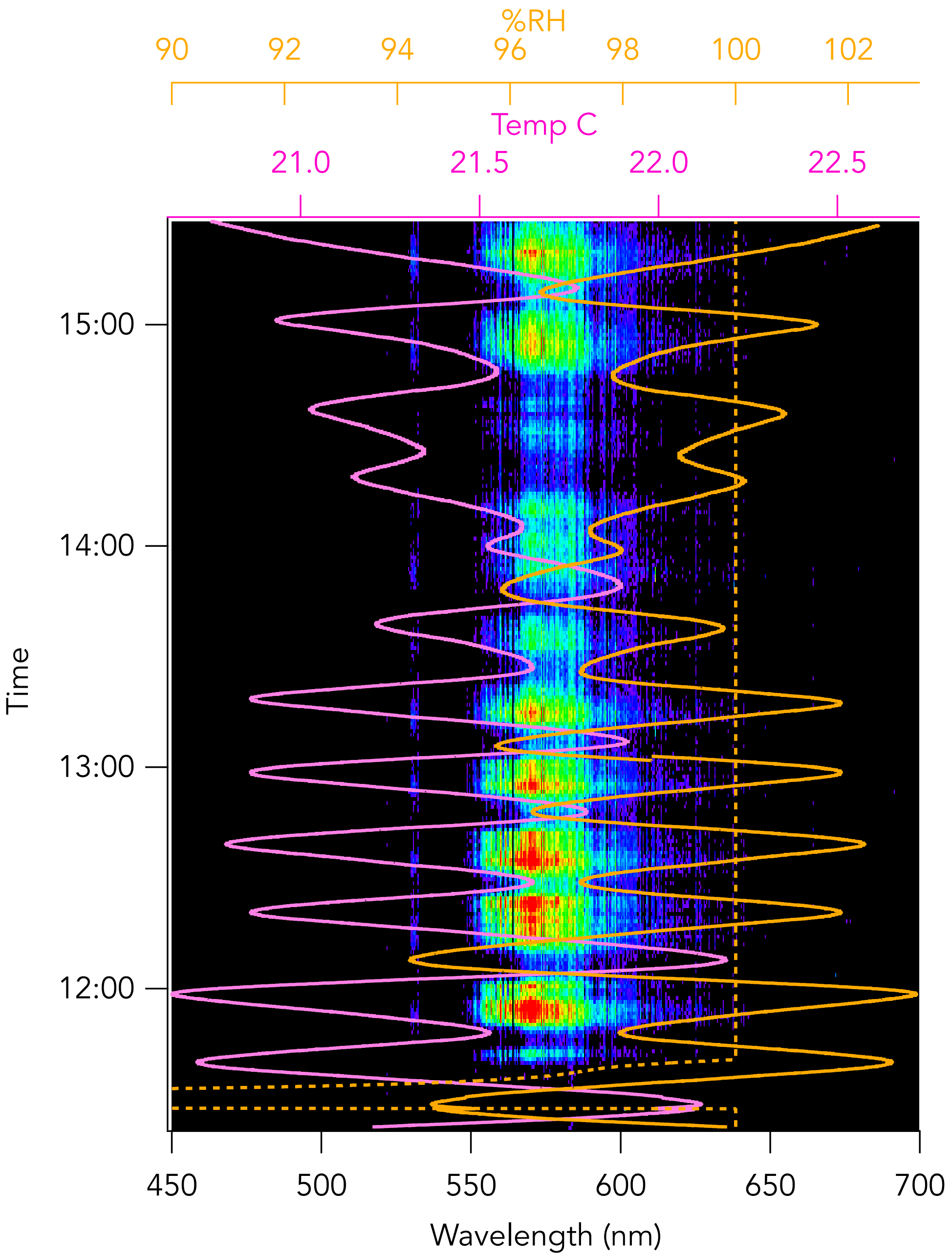
Oscillatory Behavior in Fluorescence at 100% RH

Appearance of fluorescence at 100% RH is expected

Oscillatory behavior of fluorescence at 100% RH is not

Oscillations are correlated with laboratory temperature oscillations

- Fluorescence appears when temperature goes down.
- Fluorescence disappears when temperature goes up.



Estimating RH >100%

- Use derived actual vapor pressure (AVP) from measurements.
- Assume AVP constant and calculate RH from temperature.

Interpretation: Variation in temperature causes the sample to oscillate between saturated and supersaturated conditions.

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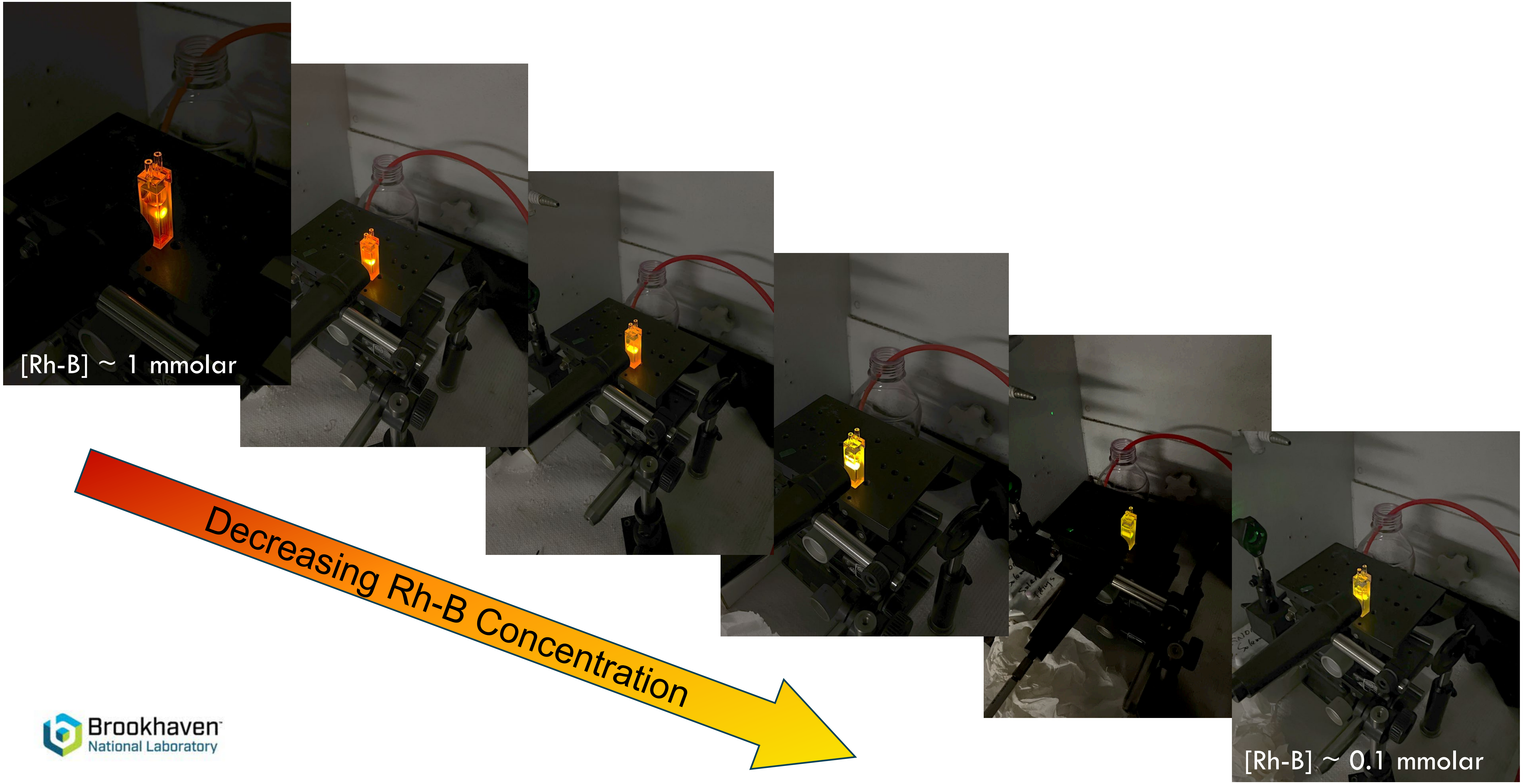
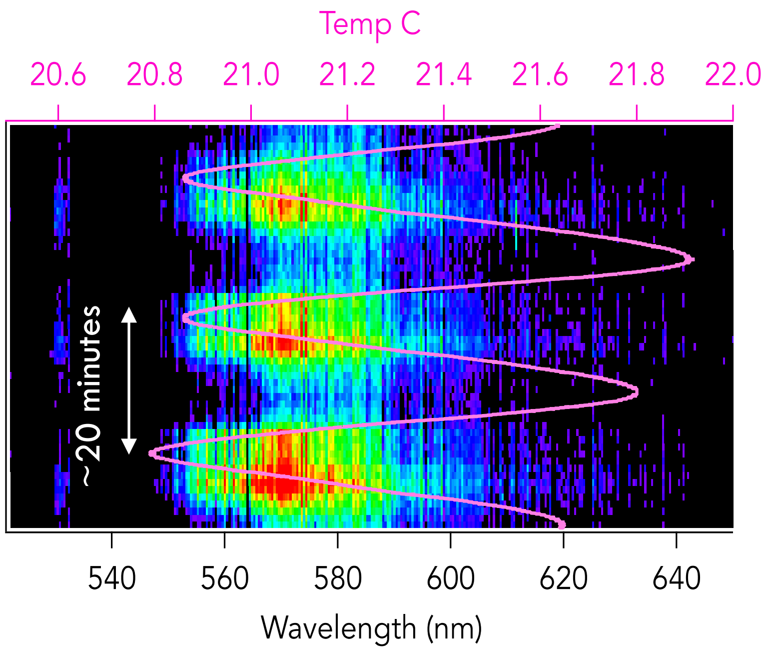
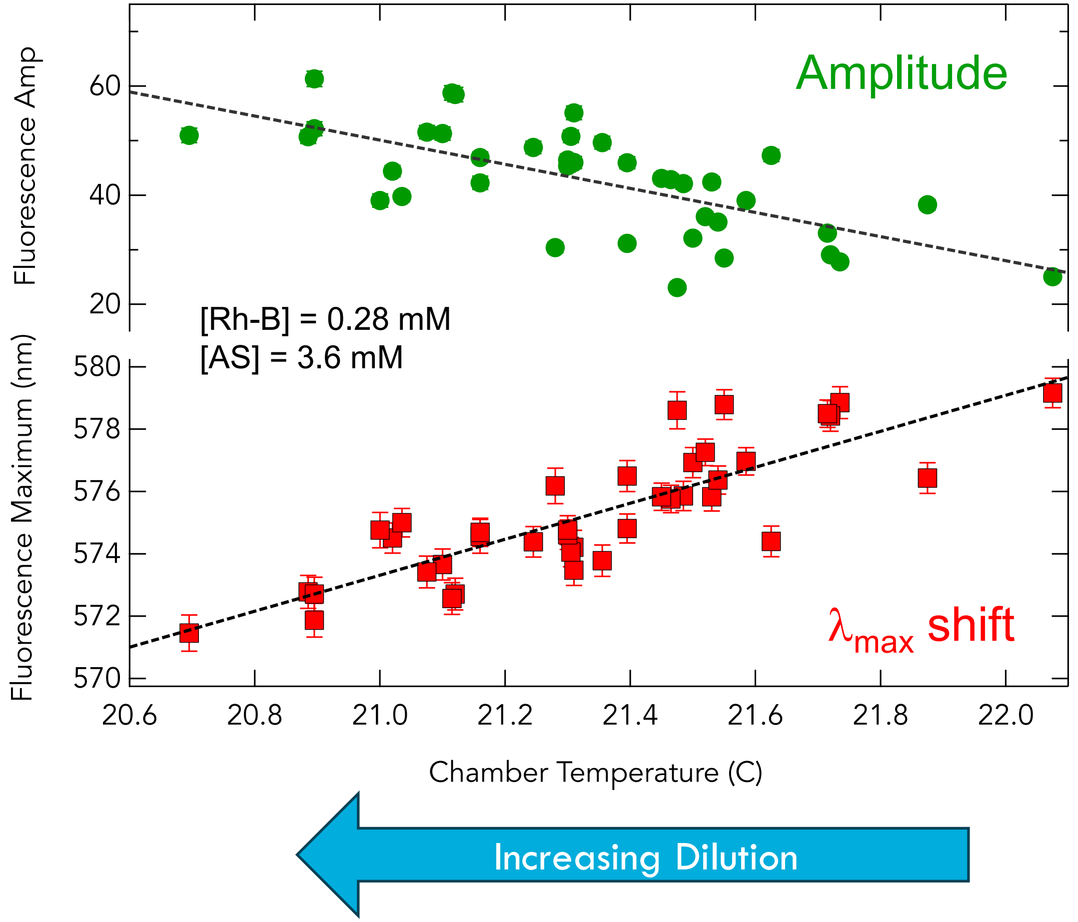
Rh-B Emission Color is Dependent on Concentration



Changes in Rh-B Fluorescence with Sample Temperature





As chamber temperature decreases:

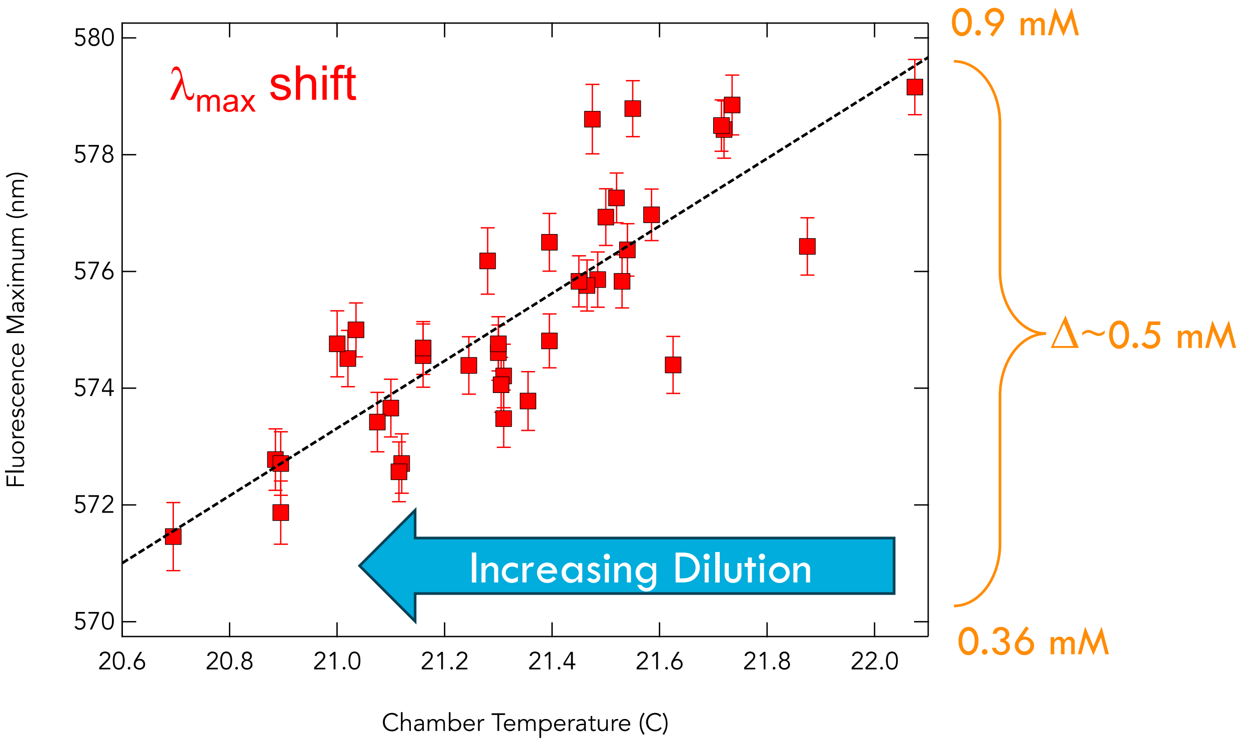
- Location of fluorescence maximum shifts to shorter λs
- Amplitude of fluorescence signal increases

Decrease in temperature brings about condensation growth of Rh-B/AS particle.

Condensational growth → Rh-B dilution → reduction in fluorescence re-absorption.

Using Shift in Fluorescence to Estimate Hydrated Particle Diameter

Use λ_{max} to estimate [Rh-B]



Assume a dry diameter of 80 nm

MW_{AS} = 132 amu; r_{AS} = 1.77 g/cc
MW_{RhB} = 479 amu; r_{RhB} = 0.79 g/cc

Vol_{AS} = 1.24 (-28) m^3/molec
Vol_{RhB} = 10.1 (-28) m^3/molec
} $V_{RhB/AS}$ = 8.2

Estimated hydrated Diameter (0.9 mM) ~ 710 nm
Estimated hydrated Diameter (0.36 mM) 965 nm

D_{100} = 358 nm (Lewis, 2008)

D_{act} = 640 nm (Lewis, 2008)

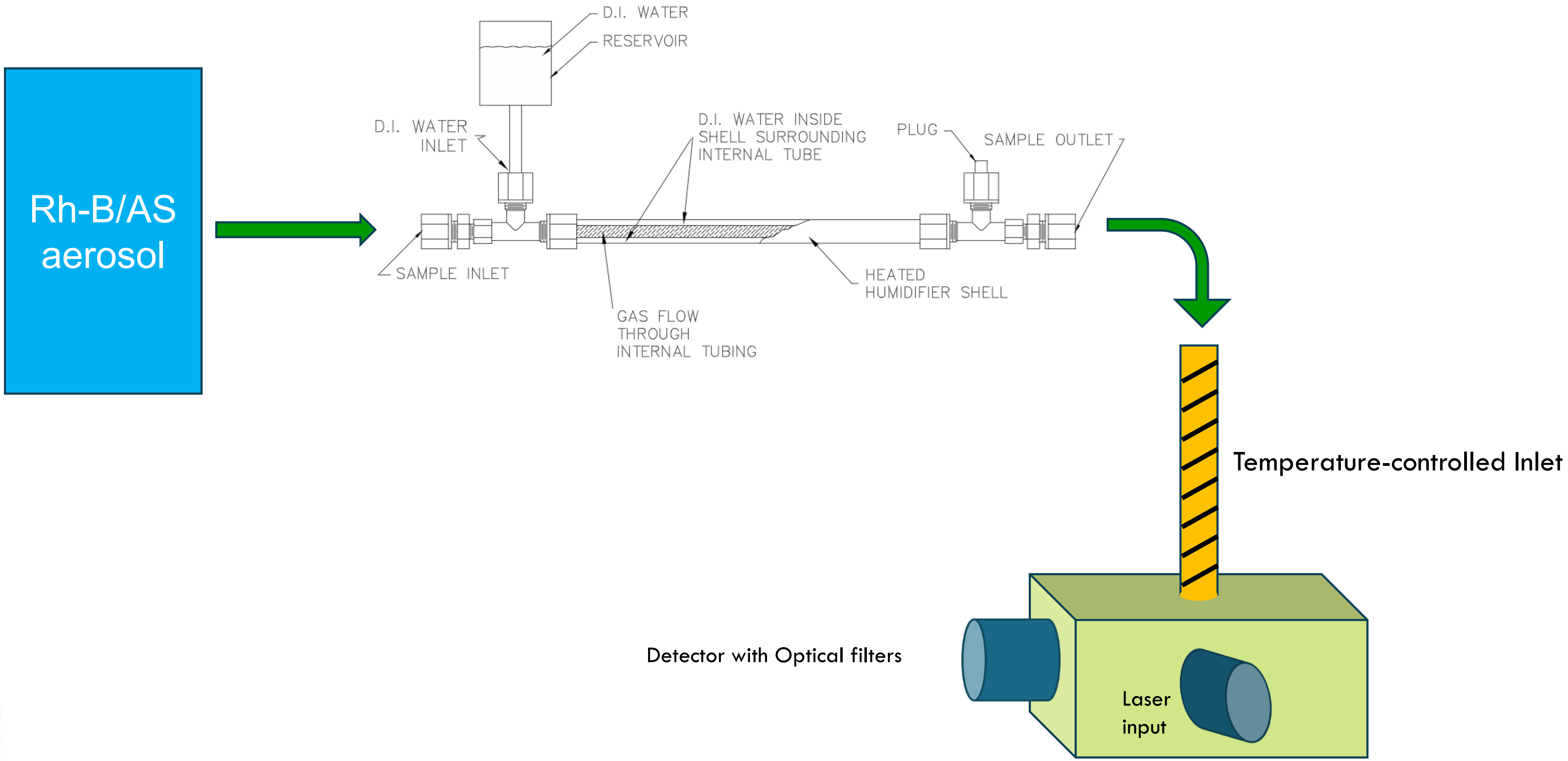
[RhB] > 1 mM – Presence of RhB dimers and reabsorption suppresses fluorescence.

[RhB] < 1 mM – RhB dimers and reabsorption become negligible, and fluorescence turns on.

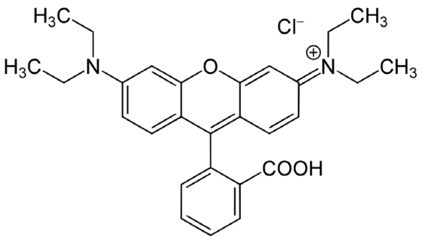
(Setiawan et al., PCCP 2010; Kemnitz et al., JPC 1986)

Higher Precision Measurements Under Supersaturated Conditions

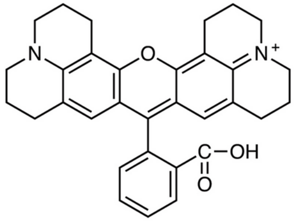
Borrow design ideas from the CCN



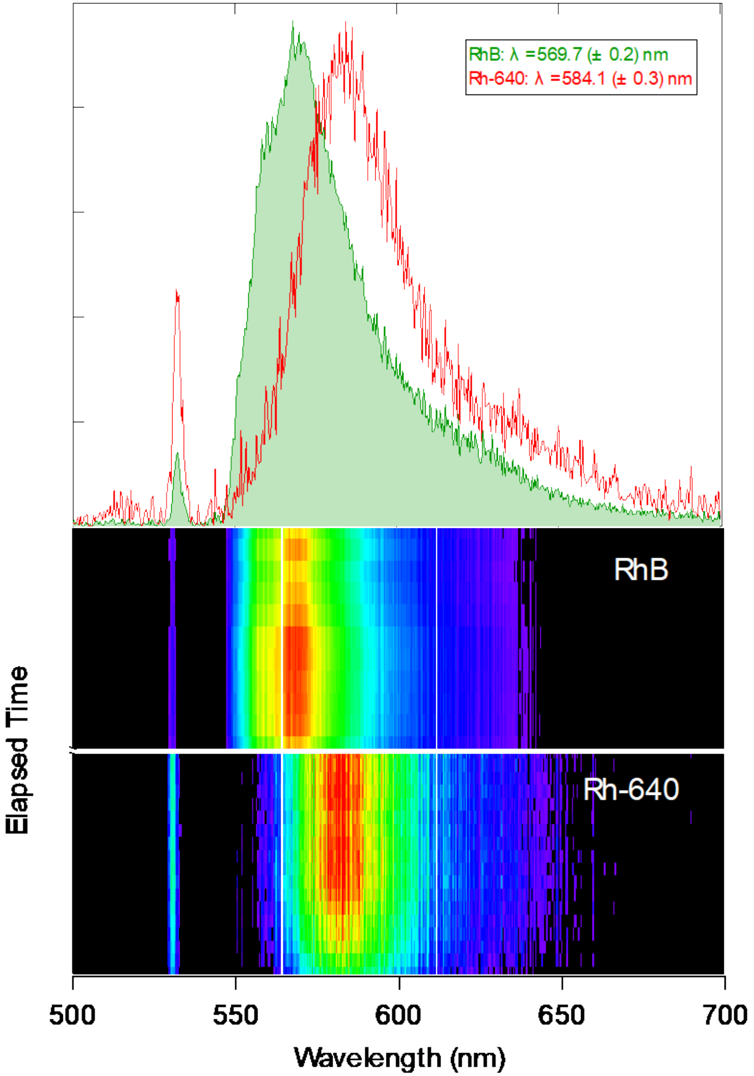
Different Flavors of Rhodamine → Shifted Fluorescence Spectrum



Rhodamine B



Rhodamine 640
(Rh-640)



Aerosol RhB: λ_{max} ~ 570 nm

Aerosol RhB-640: λ_{max} ~ 584 nm

Create two different tagged-AS particles:

Different dopant concentration

→ Different κ

→ Different super saturation for activation

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Summary

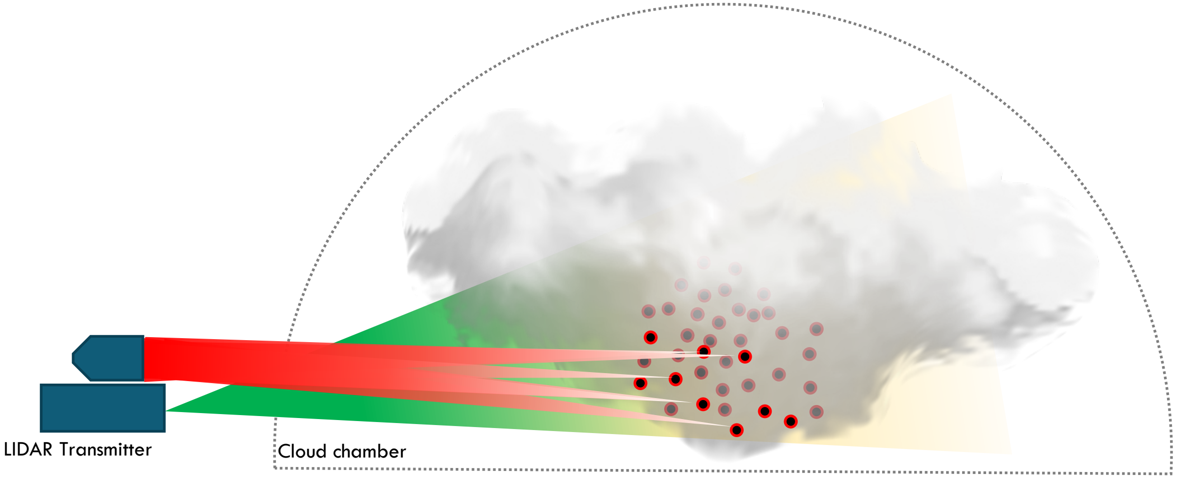
1. Fluorescence tagging of particle types in a cloud chamber offers a novel methodology for the **non-contact**, *in-situ* tracking of particle activation.

2. Rh-B fluorescence signals observed only at RH >100%. Shift in the fluorescence maximum as particle undergoes condensational growth.

3. Estimated Rh-B/AS particle diameter using fluorescence emission suggests aerosol activation.

4. Creation of Rh-B-tagged aerosols with kappa values between 0.6 (pure AS) and 0.2 (pure Rh-B).

5. Use of a second Rhodamine dye (Rh-640) offers the possibility to simultaneously delineate two supersaturation zones via two tagged AS particles types.



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ASR Atmospheric System Research

Extra Slides

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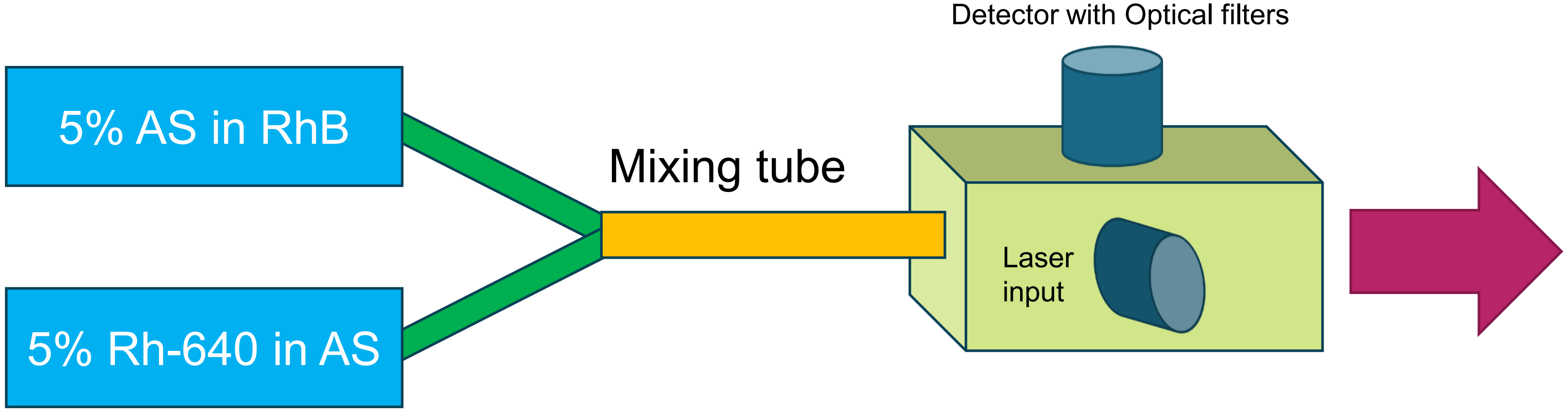
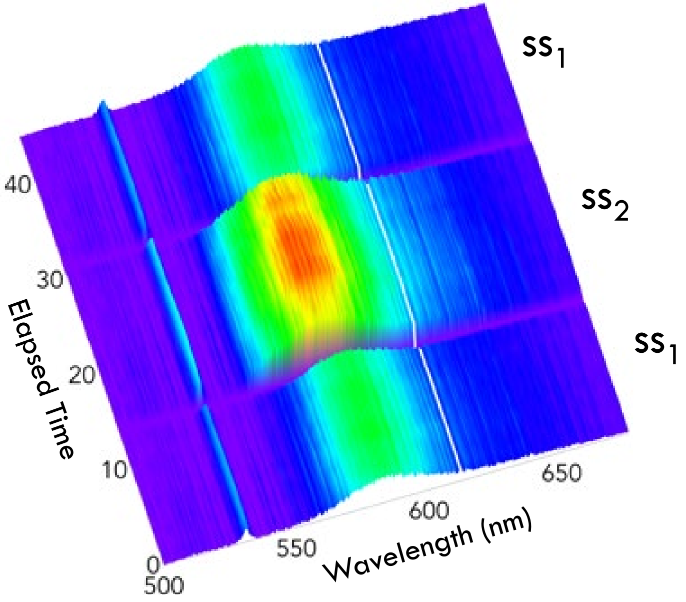
Follow on Experiments

Inject external mixture of two different doped AS particles with differing kappas, and look for differing activation



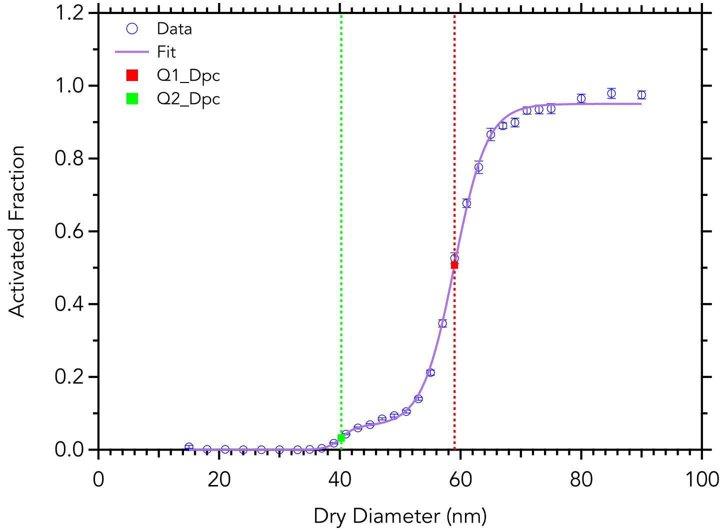


Rhodamine-B Hygroscopic Properties

Rh-B possesses hygroscopic properties typical of organic material

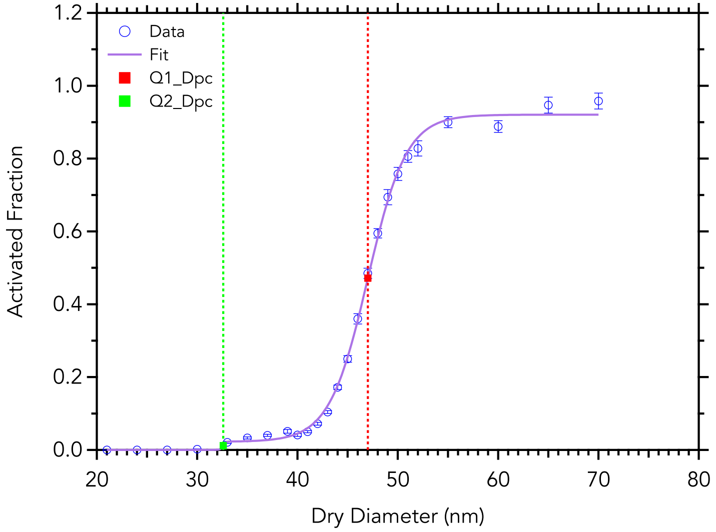
RhB: Rhodamine B
AS: Ammonium Sulphate

Pure Rhodamine B

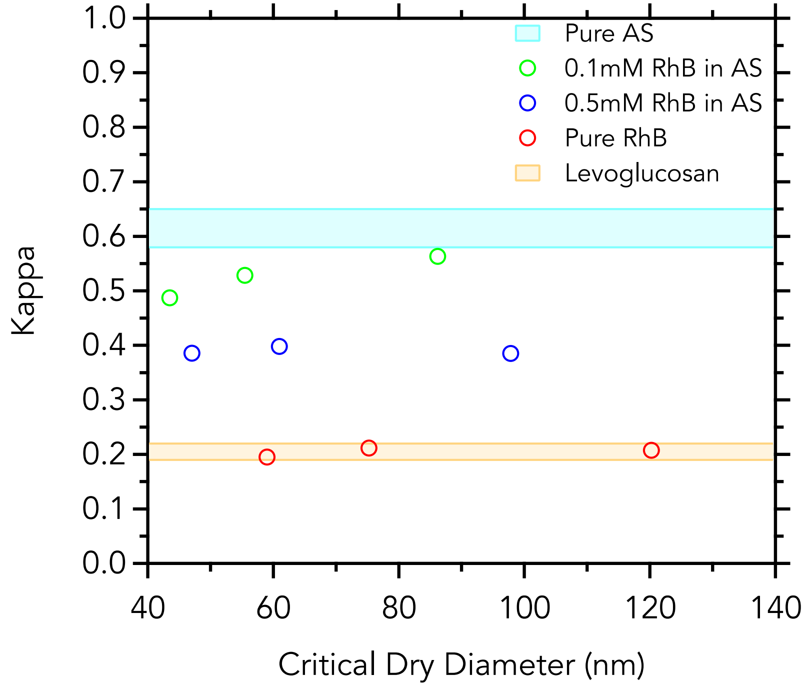


SS = 0.6%, D_{pc}, Q1 = 59 nm

[RhB] = 0.54 mM
[AS] = 4.2 mM



SS = 0.6%, D_{pc}, Q1 = 47 nm



D_{pc_AS} ~ 40 nm for SS = 0.6%

Measurements courtesy of Ogo Enekwizu

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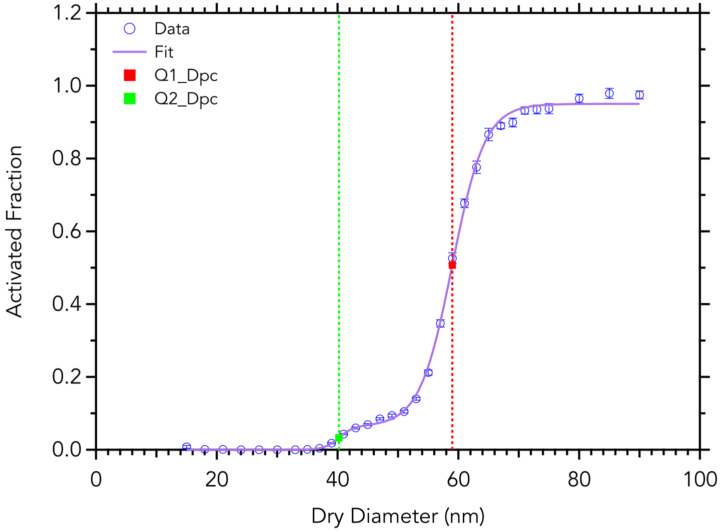

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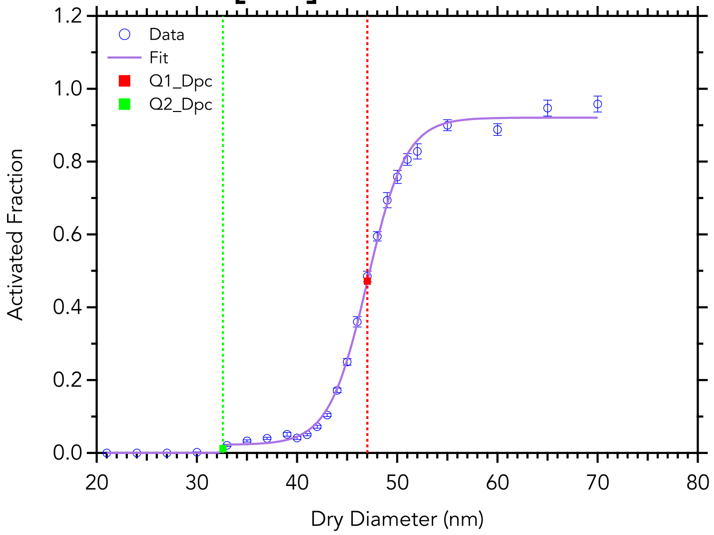
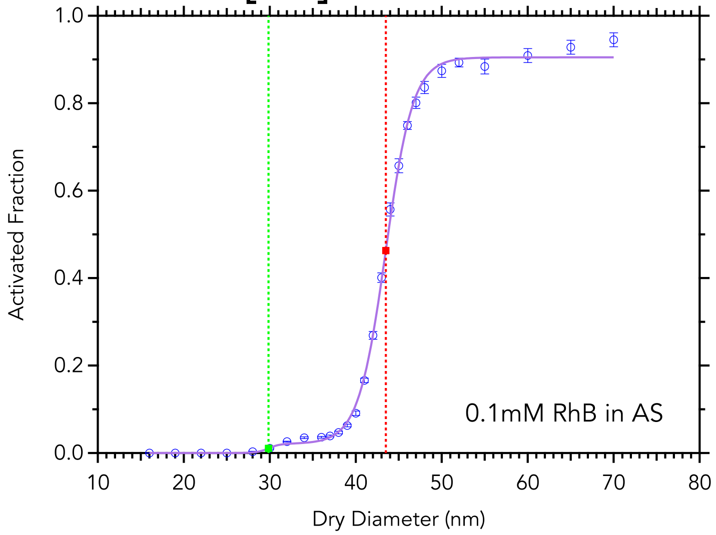


SS = 0.6%, D_{pc}, Q1 = 47 nm

[Rh-B] = 0.99 mM
[AS] = 4.4 mM



SS = 0.6%, D_{pc}, Q1 = 43.5 nm

D_{pc_AS} ~ 40 nm for SS = 0.6%

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Measurements courtesy of Ogo

Rhodamine-B Critical Diameters and Kappa

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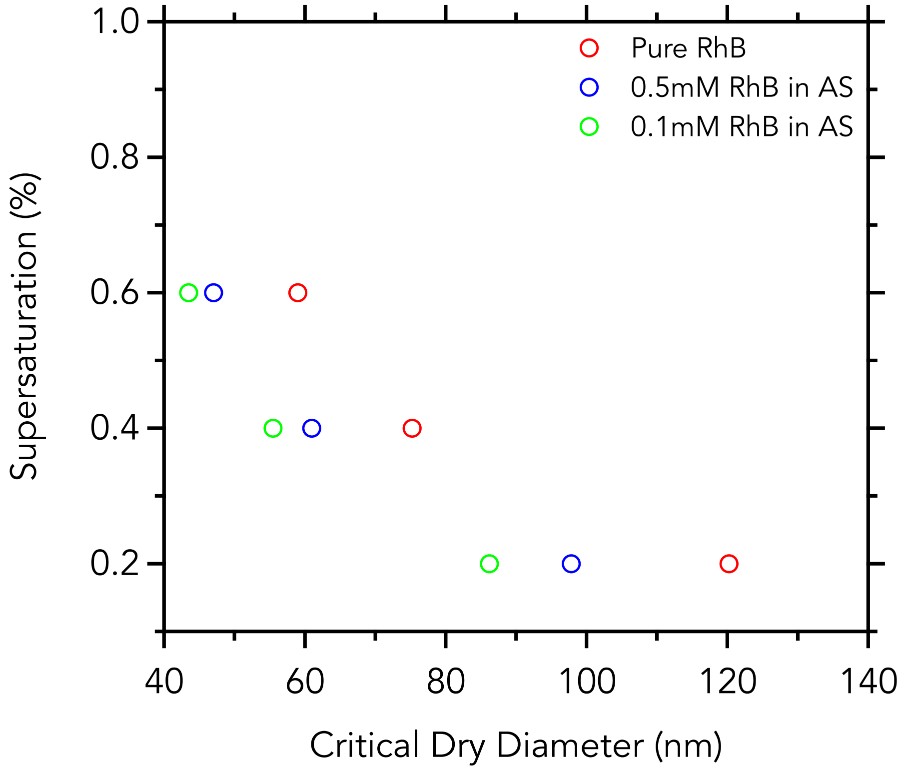

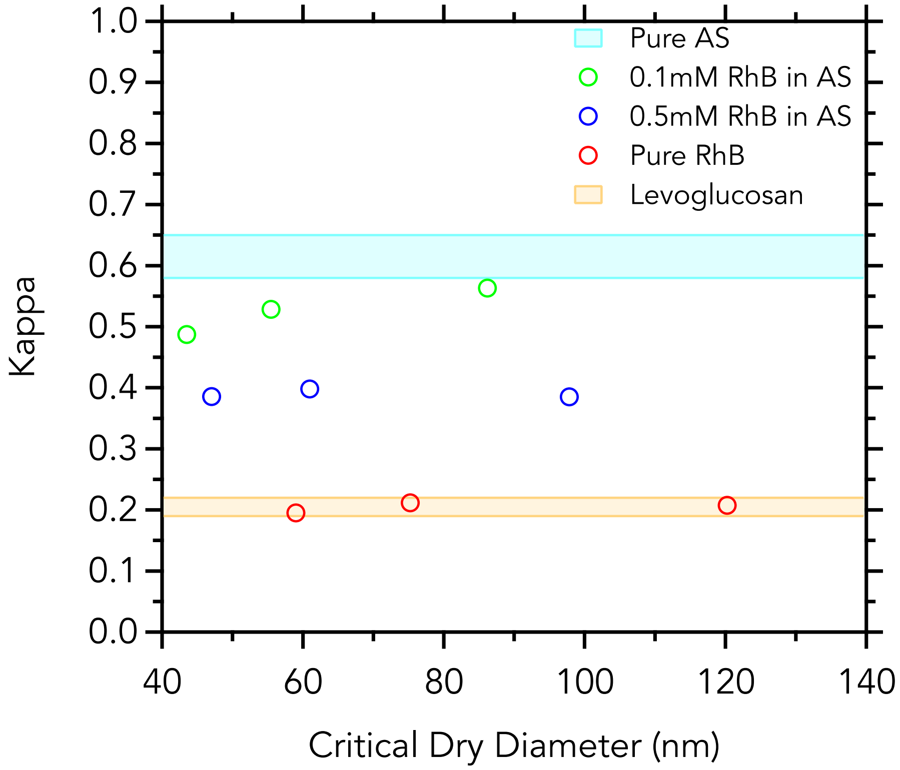

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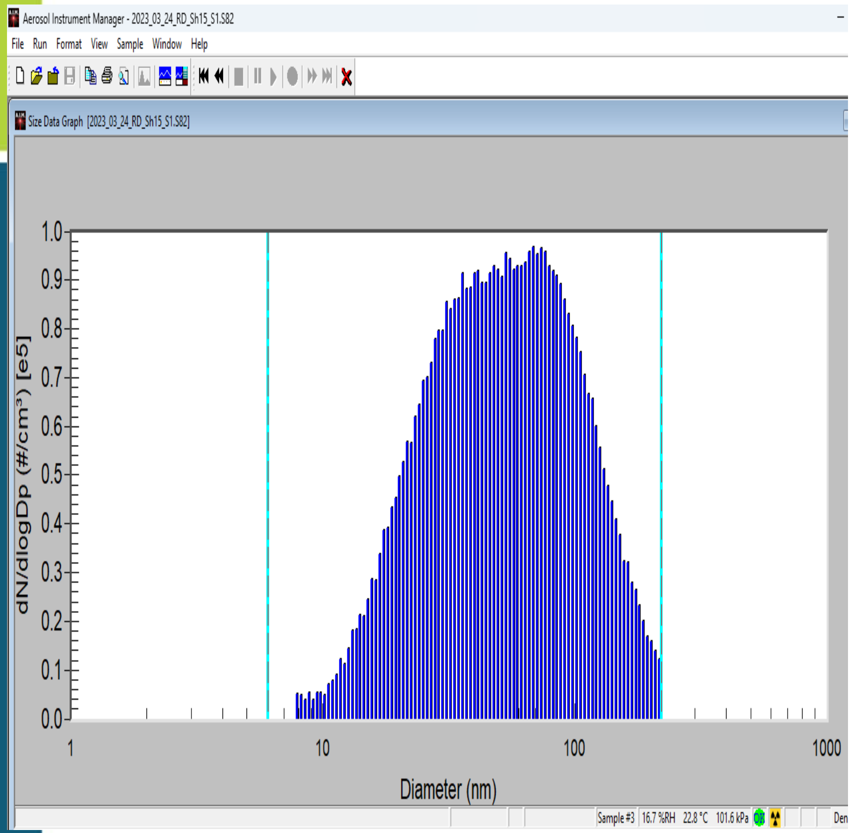
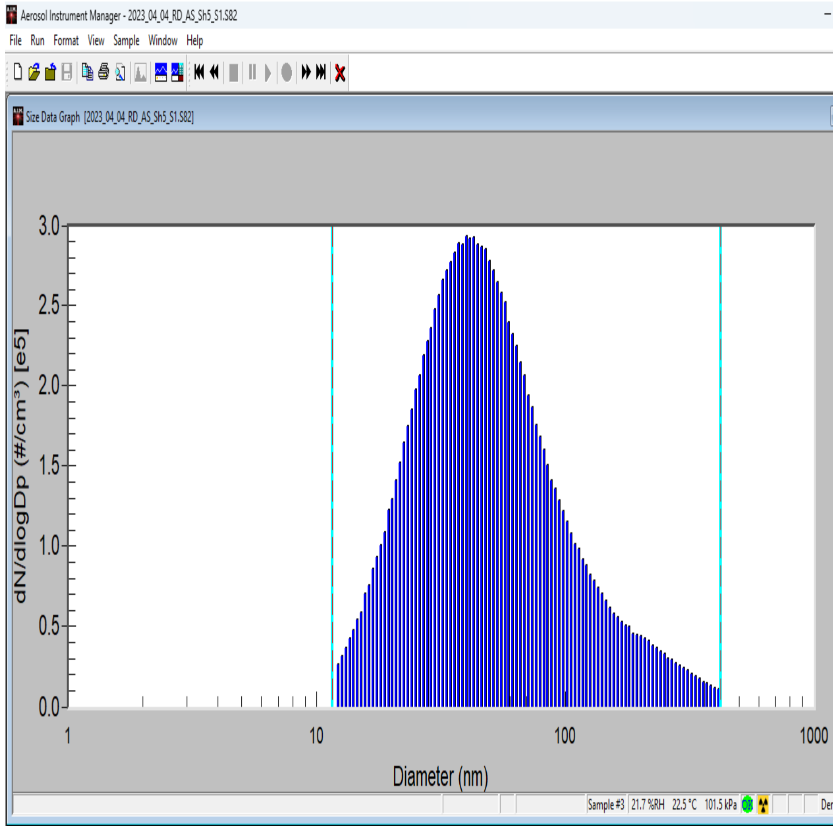
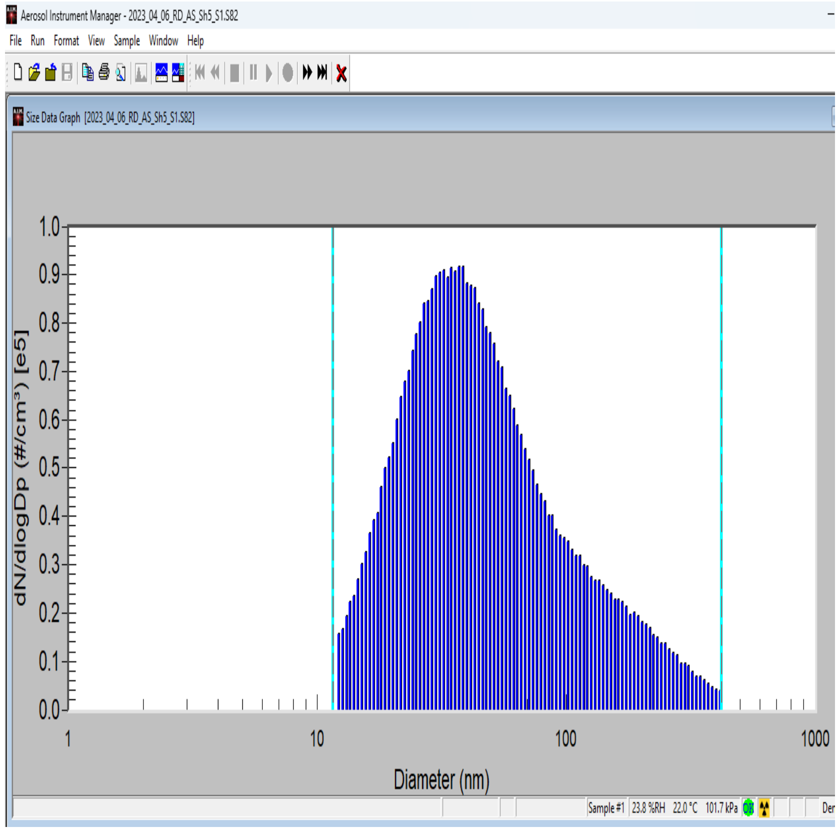
Measurements courtesy of Ogo

Size Distributions







Pure RhB	0.5mM RhB in AS	0.1mM RhB in AS
Mode: 74 nm	Mode: 41 nm	Mode: 38 nm

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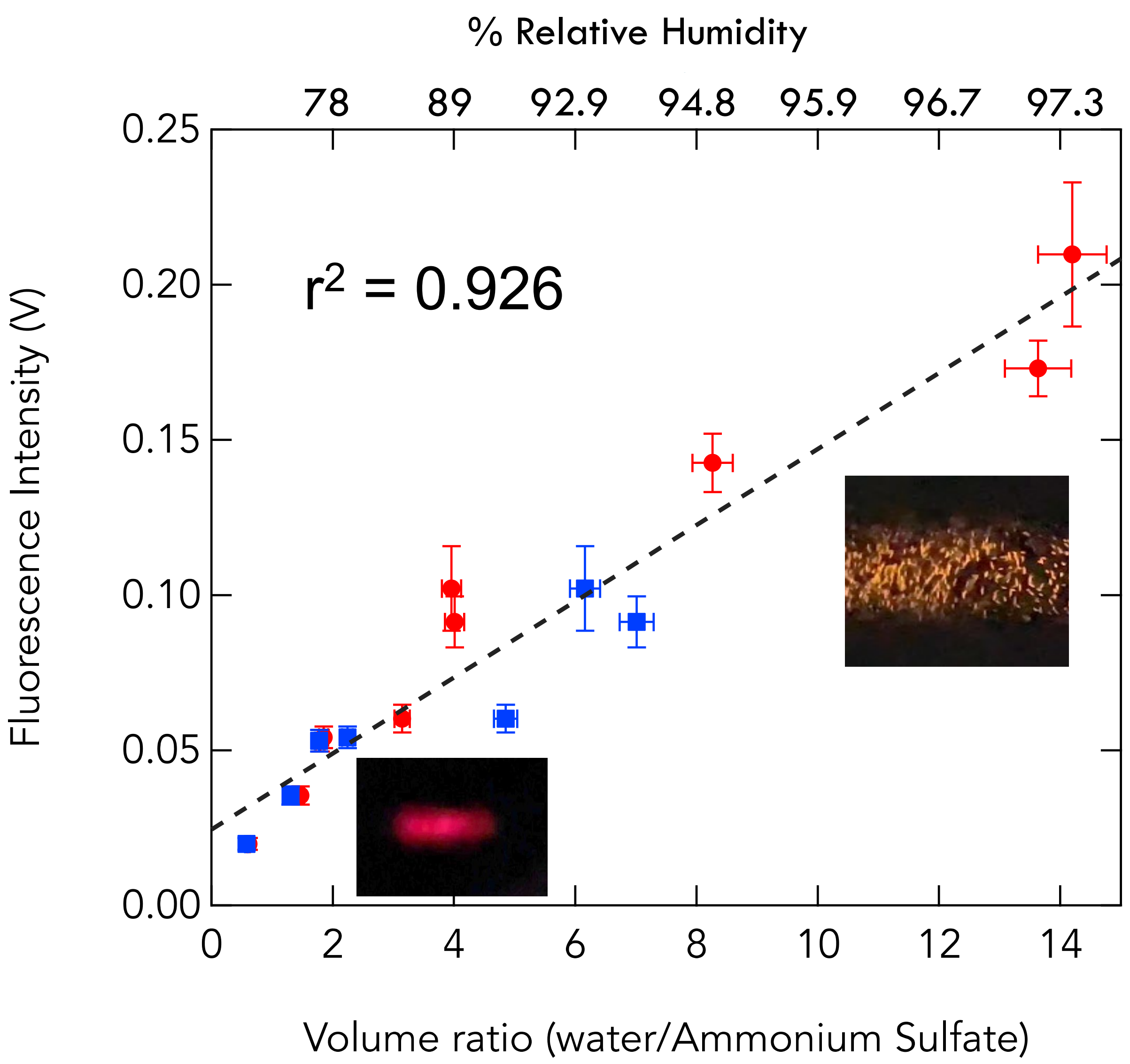
RhB: Rhodamine B
AS: Ammonium Sulphate

Fluorescence as a Function of Water/Ammonium Sulfate Volume Ratio in Particle

Convert RH to volume ratio (water/ ammonium sulfate) Lewis (2008). Valid up to and including 100% RH.

Linearity of fluorescence suggests that this technique could be used as an *in-situ* probe of prevailing RH.



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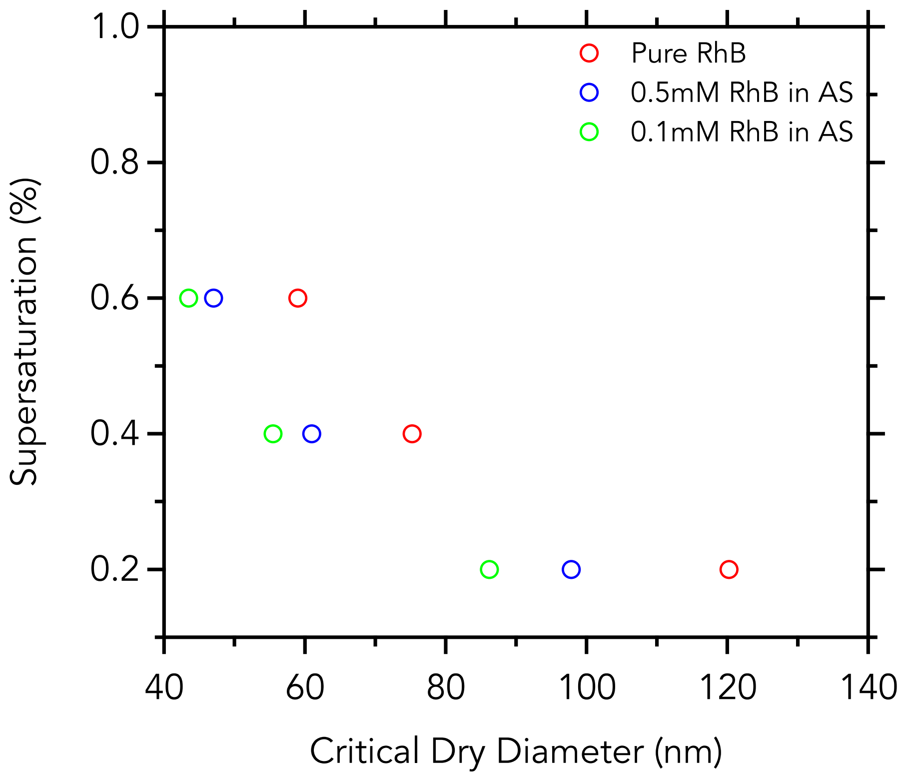

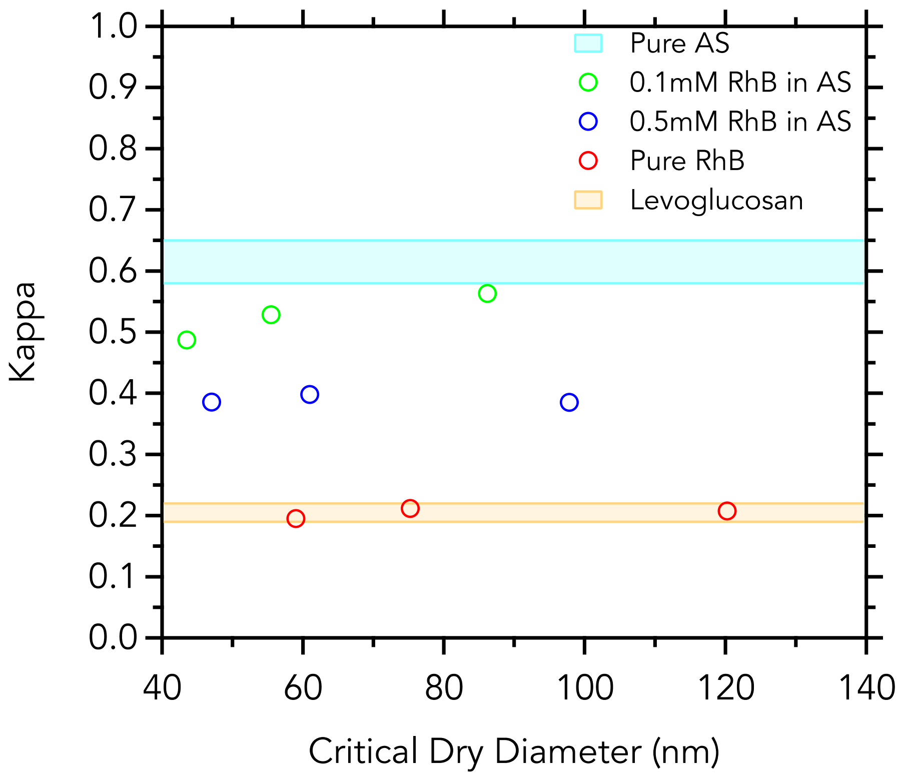

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