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# Optical Properties of Absorbing Aerosols as a Function of Relative Humidity

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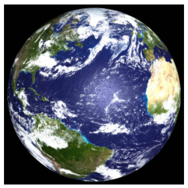
## Background and Introduction

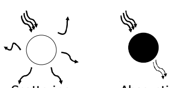
### 1. Motivation and Introduction

- One of the key unknowns for atmospheric aerosols is how water uptake changes the optical properties of absorbing aerosols.
- Changing optical properties as a result of increases in relative humidity (RH) can have significant implications for climate forcing and cloud-aerosol interactions. For example, a model of the global mean aerosol developed by Pilinis *et al.* found radiative forcing increased by a factor of 2.1 when increasing RH from 40% to 80%.



http://www.3dnworld.com/users/1/images/UltimateEarth.jpg

- The quantification of the RH dependence of aerosol light absorption has been mostly limited to theoretical calculations because suitable measurement techniques have not been available. The difference method and filter based instruments, used to measure absorption, can be problematic at elevated RH.



Scattering Absorption
Extinction = Scattering + Absorption

References for 1 and 2: Pilinis *et al., J. Geophys. Res.-Atmos.*, 100(D9), 18739-18754, 1995
Kay and Box, *J. Geophys. Res.-Atmos.*, 105(D10), 12221-12234, 2000
Raspet *et al., J. Atmos. Ocean. Tech.*, 20, 685-695, 2003
and Arnott *et al., J. Geophys. Res.-Atmos.*, 108(D1), 4034, doi:10.1029/2002JD002165, 2003

### 2. Focus

- In this study, photoacoustic spectroscopy is used to measure absorption of aerosols as a function of relative humidity. We need to characterize the photoacoustic response in order to separate changes in absorption due to humidity increases from those due to evaporation or other instrument limitations.
- The need for characterization arises from a lack of other tools to allow comparison of absorption measurements at elevated RH and because a photoacoustic signal decrease at high RH attributed to mass transfer has previously been observed.
- To achieve this goal, novel techniques were used to measure the variation of the growth and water uptake, absorption and extinction of size selected, water-soluble, absorbing nigrosin dye aerosols as a function of relative humidity.
- The particle growth results were used in combination with Mie Theory to model optical properties.
- The modeled and experimentally measured extinction and absorption are compared for consistency and instrument response.

Aerosol Characteristics and Techniques

Aerosol Growth/Water Uptake
Tandem Differential Mobility Analyzer

Aerosol Optical Properties Modeling
Mie Theory and Volume Dilution

Aerosol Extinction
Cavity Ring Down Spectroscopy

Aerosol Absorption
Photoacoustic Spectroscopy

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## Measurement Techniques and Model

### 3. Aerosol Growth

- The first step in this investigation of the RH dependence of aerosol absorption is to measure the change in particle size as RH increases.
- Tandem differential mobility analyzer (TDMA) measurements are used.
  - A charged, mono-disperse aerosol sample is selected according to differential mobility theory.
  - The resulting aerosol is humidified, thus increasing their size through water uptake.
  - Humidified aerosols are then analyzed to determine their size increase.
- A growth factor (GF) for the aerosol is determined as:

$$GF = \frac{D_{RH}}{D_{dry}}$$

$D$ = Particle Diameter

### 4. Model of Aerosol Optical Properties

- For a water soluble aerosol of known refractive index, mixing should be uniform. We can use the volume dilution method to obtain composite refractive index for the mixture and Mie Theory to calculate optical properties as the RH increases.
- We assume the volume fraction of water as the particle is humidified is related to the growth factor (GF):

$$V_{water} = 1 - \frac{1}{GF^3}$$

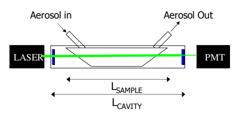
(from Srivastava *et al., J. Geophys. Res.*, 102(D17), 16,605-16,617, 1997).

- A composite complex refractive index ($\tilde{n}_{eff}$) is calculated using volume fractions ($V_i$):

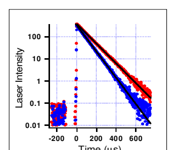
$$\tilde{n}_{eff} = V_{aerosol}\,\tilde{n}_{aerosol} + V_{water}\,\tilde{n}_{water}$$

(from Ouimette and Flagan, *Atm. Envt.*, 16(10), 2405-2419, 1982).

### 5. Aerosol Extinction




- Cavity ring-down (CRD) spectroscopy can be used to measure the extinction (scattering + absorption) of atmospheric aerosols.
- The light in the cavity decays as a result of losses (e.g. aerosol extinction) and appears as an exponential decay. The decay is fit to determine the ring down time constant ($\tau$).




$\tau_0$ = red = no sample
$\tau$ = blue = with sample

$$\sigma_{ep} = \frac{R_L}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \qquad R_L = \frac{L_{CAVITY}}{L_{SAMPLE}}$$

c= speed of light

$\sigma_{ep}$ = aerosol extinction coefficient

- CRD cells at various RH values provide an accurate measure of aerosol extinction as a function of controlled RH.
- The RH dependence of extinction is measured as the ratio:

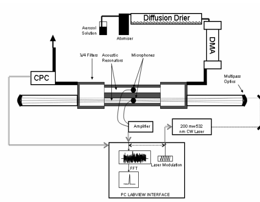
$$fRH(ext) = \frac{\sigma_{ep}(\text{Humidified})}{\sigma_{ep}(\text{Dry})}$$

References: Pettersson *et al., J. Aerosol Sci.*, 35, 995-1011, 2004
and Baynard *et al., Geophys. Res. Lett.*, 33(6), Art. No. L06813, 2006

### 6. Aerosol Absorption

- Resonant photoacoustic spectroscopy (PAS) is an in-situ measurement that avoids scattering artifacts associated with filter based techniques.
- Power modulated diode laser light absorbed by aerosols is released as an acoustic wave. This acoustic signal is directly proportional to the amount of light the aerosol absorbs when other energy pathways are minimized.
- The RH dependence of absorption is measured as the ratio:

$$fRH(abs) = \frac{\sigma_{ap}(\text{Humidified})}{\sigma_{ap}(\text{Dry})}$$

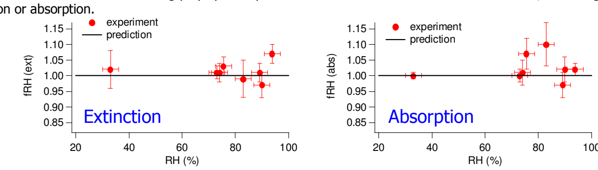



Lack *et al., Aerosol Sci. Tech.*, 40(9), 697-708, 2006

## Results and Discussion

### 7. Internal Check of CRD and PAS as a Function of RH

- Confirm that the measured fRH for extinction and absorption is independent of RH for hydrophobic polystyrene spheres.
- Measurements of 600 nm absorbing polystyrene spheres at various values of RH return values of 1, indicating no change in extinction or absorption.

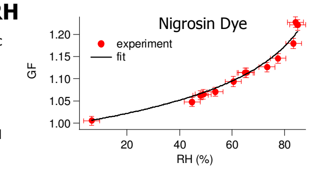



### 8. Aerosol Growth as a Function of RH

- Aerosol GF is related to the relative humidity and a constant specific to the composition of the aerosol ($\gamma$):

$$GF = \frac{D_{RH}}{D_{dry}} = \left(\frac{100}{100 - RH}\right)^{\gamma}$$

- The GF of nigrosin dye at 300 nm dia. was measured for various RH values yielding a fit of $\gamma$ = 0.099.

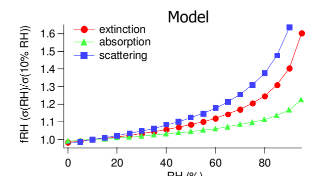



### 9. Aerosol Optical Properties with RH

- Using the volume dilution method, the fRH values are calculated using Mie Theory beginning with 300 nm dry nigrosin having a refractive index of 1.7 + 0.31i.

(refractive index from: Lack *et al., Aerosol Sci. Tech.*, 40(9), 697-708, 2006)

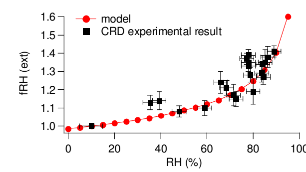
- The fRH for extinction, scattering and absorption each increase with increasing relative humidity.
- We will compare this model with experimental measurements.




## More Results and Conclusions

### 10. Extinction of Nigrosin Dye Aerosol as a Function of RH

- The fRH of extinction for initially dry 300 nm nigrosin dye aerosols was measured with CRD at many different RH values.
- The trend from the model in section 9, matches the experimental results.
- Some scatter is present in the experimental data. This is attributed to small changes in particle size over individual experiments, uncertainties in humidity and corrections for doubly charged particles.
- We expect the model will do a good job predicting the dependence of absorption on RH for nigrosin.




### 11. Absorption of Nigrosin Dye Aerosol as a Function of RH

- The fRH of absorption for initially dry 300 nm nigrosin dye aerosols was measured with PAS at many different RH values.
- The model does a good job matching the experimental results up to 70-80% RH.
- The decrease in signal at high relative humidity indicates possible mass transfer or other limitations of the photoacoustic technique when water is present on aerosols. The cause of this is still under investigation.
- PAS can be used to measure absorption of aerosols having water uptake at elevated humidity. In this limiting case with greater than 30% aerosol water volume above 70% RH, there is some limitation to photoacoustic measurements at relative humidity values above 70%.