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Development of a Nephelometry Camera and Humidity Controlled Cavity Ring-Down
Transmissometer for the Measurement of Aerosol Optical Properties

by

James Gregory Radney

A dissertation submitted in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy
in
Environmental Sciences and Resources: Chemistry

Dissertation Committee:
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Abstract

A Nephelometry camera (NephCam) and Humidity Controlled Cavity Ring-Down Transmissometer (HC-CRDT) were developed for the determination of aerosol optical properties. The NephCams use a reciprocal geometry relative to an integrating nephelometer; a diode laser illuminates a scattering volume orthogonal to a charge coupled device (CCD). The use of a CCD allows for measurement of aerosol scattering in 2 dimensions; scattering coefficients and size information can be extracted.

The NephCam's optics were characterized during a set of imaging experiments to optimize the images collected by the camera. An aperture setting of 1.6 was chosen because it allowed for the most light intensity to reach the CCD - albeit with significant vignetting - and also had a constant modular transfer function (MTF) across the image; approximately 0.3. While this MTF value is approaching the minimum usable MTF of 0.2, other aperture settings did not exhibit constant MTF. While the effects of vignetting can be corrected in image post processing, the effects of non-constant MTF cannot.

An optical response model was constructed to simulate images collected by the NephCams as a function of particle type and size. Good agreement between modeled and measured images was observed after the effects of contrast on image shape were considered. The image shapes generated by the model also pointed towards the use of polynomial calibration for particle sizes less than 400 nm as a result of multiple charge-to-size effects present from the sizing mechanism of the differential mobility analyzer. Initial calibration of the NephCams using size-selected dry Ammonium sulfate (AS) showed that calibration slopes are a function of particle size which is also in agreement

with the model. Calibration slopes decreased as particle size increased to 400 nm; after 400 nm calibration slope oscillated around a common value. This effect is directly related to the forward shift of scattered intensity as particles grow in size and the collection efficiency of the NephCam as particle size increases. The single scattering albedo (SSA) of Nigrosin was calculated using the NephCam; extinction was measured by the HC-CRDT. Good agreement between the SSA and size was noticed for larger particle sizes; particles smaller than 200 nm in diameter over-measured the SSA of Nigrosin because of the multiple charge-to-size effect. In this size regime, light scattering by particles increases much more quickly than absorption; the presence of larger particles causes scattering to be artificially high.

The HC-CRDT is a 4 channel, 3 wavelength instrument capable of measuring the extinction coefficients of aerosols at high ($> 80\%$), low ($< 10\%$) and ambient relative humidity. Extinction coefficients as a function of RH were determined for AS, NaNO_3 , NaCl, and Nigrosin; these particles represent surrogates of the strongly scattering ionic salts and black carbon, respectively. A model was developed to calculate the changes in refractive index and extinction coefficients of these water soluble particles as a function of RH; these particle types were chosen because core-shell morphologies could be avoided. Volume mixing, Maxwell-Garnett and partial molar refraction mixing rules were used to calculate effective refractive indices as a function of water uptake. Particle growth was calculated based upon the Kelvin equation.

Measured and modeled results of $f(\text{RH})$ - relative change in extinction between high or ambient RH and dry RH - agree well for all particle types except Nigrosin. This disagreement is thought to stem directly from an incomplete parameter set for Nigrosin;

growth parameters were assumed to be identical to NaNO_3 , density assumed to be 1 g/mL and molecular weight 202 g/mole, which may not be true in reality (different suppliers of Nigrosin quote different molecular weights). The NephCam was not used during these experiments, so the addition of a scattering measurement to better characterize the growth by Nigrosin is necessary. The $f(\text{RH})$ data for NaNO_3 showed excellent agreement between measured and modeled data; however particle size information collected by an SMPS does not agree with the theory. This stems from the fact that NaNO_3 does not show prompt deliquescence upon drying; instead an amorphous solid forms which exhibits a kinetically limited loss of water.

Dedication

For my family...

Acknowledgements

"Two roads diverged in a wood, and I --

I took the one less traveled by,

And that has made all the difference."

The Road Less Traveled, Robert Frost (Frost 1916)

Graduate school has been my less traveled road, and it has made all the difference. This dissertation represents the more than just my work and schooling at Portland State University, but also quite possibly the greatest adventure of my life. None of this would have been possible without the many people who helped me follow my own road.

I owe a special debt of gratitude to my advisor, Dr. Atkinson; it has been a privilege working in his lab. I couldn't have asked for a better graduate mentor and colleague.

To my friends, thanks for everything both with graduate school and life. Valerie Coffey, thanks for being a great friend and roommate. Ashley Sexton, thanks for your continued support throughout this process. Jon Orleck and Joe Harworth, thanks for all your help with the development of the instruments here-in and many good times to boot. Jeremy Parra, thanks for your help with some of the mathematics and the many sanity checks as we finished our projects and dissertations.

To my family - Mum, Dad and Becky - thanks for your unwavering and unending moral support and love. I wouldn't be here today without you.

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1. Introduction

1.1. Global Climate

Climate is loosely defined as the average weather of a location over long periods of time. According to the IPCC 4th Assessment report, climate is the statistical description of the mean and average variability in surface temperature, precipitation and wind averaged over months to millions of years (Core Writing Team 2007). Classically, the climate period has been defined as 30 years by the World Meteorological Organization (WMO). Climate is generated by interaction between the earth's atmosphere, biosphere, cryosphere, hydrosphere, and land surface.

Humans have impacted climate ever since the discovery of fire through the emission of particulate and greenhouse gases. Initially these effects were small relative to those of the natural system. With the transition from hunter/gatherer societies to agricultural based societies, humans started to have a larger influence on the planet and its climate through the use of fossil fuels and landscape alteration. Post-industrial revolution, the human effect on climate has increased in magnitude almost exponentially due to further increases in fossil fuel use; the emission of elevated levels of greenhouse gases has driven this effect. However, the true magnitude of these effects is still uncertain.

Interactions between earth and human systems affect the entire planet in many inter-related ways with even more feedback mechanisms as shown in figure 1-1 (this is as a vast oversimplification of the problem but serves as a good starting reference). Emissions of greenhouse gases and aerosol particles by humans have been identified as climatic process drivers (left box). These drivers affect both the earth system through climate change (top box) and human systems by affecting socio-economic development

(bottom box). Both climate change and socio-economic development are vulnerable systems that can be impacted (right box). Societies can then respond to both the climatic drivers and impacts by mitigation and adaptation, respectively.

Figure 1-1: Simplified view of the link between human systems and earth systems and the effects of climatic drivers on climate and communities. From Contribution of working groups I, II and III to the fourth assessment report of the intergovernmental panel on climate change, IPCC, page26, figure I.1 (Core Writing Team 2007).

Climate change can be identified by changes in global mean temperature and precipitation caused by climatic drivers such as anthropogenic emissions of greenhouse gases and aerosols. Solar irradiance also plays into climate change, but is outside the

realm of human control. These changes are linked to an array of effects: glaciers melting, sea levels rising, changing ocean circulation patterns, increases in the number of extreme weather events, etc.

As a result of these climatic changes, ecosystems and resources are impacted and can become vulnerable and drive further climate change. Societies also become vulnerable; issues concerning food and water supply, security and human health can result. When societies become vulnerable, socio-economic development is also impacted. Societies can then either adapt to or mitigate the climatic changes.

The importance of the research presented here-in is multifold. The occurrence of global warming and cooling stems from changes in the earth's radiation budget. When the amount of solar radiation retained by the planet is larger than the amount re-emitted, warming occurs. Conversely, when the amount of solar radiation re-emitted by the planet is larger than the amount absorbed, a cooling occurs. This warming and cooling represent a delicate interplay between solar irradiance, planetary albedo, greenhouse gases and aerosols. Changes in the intensity of solar irradiance can drive earth's climate; increases/decreases in intensity lead to increases/decreases in planetary temperature, respectively. However, the relative magnitude of solar irradiance effects over recent years is minimal as the intensity of the sun has remained relatively constant. Changes in planetary albedo also affects the radiation budget of the earth; increases in the reflectivity of the earth's surface can cause either a warming or cooling influence depending upon the presence of aerosols aloft. Since a majority of the earth is covered by ocean, which has a low albedo, the change in surface albedo is minimal relative to other climatic drivers present like the greenhouse gases and aerosols.

The main focus of the work presented here is developing instrumentation for the better understanding of aerosols. Aerosols mostly oppose the warming influence of greenhouse gases. However, spatio-temporal variability of aerosols is very high due to short atmospheric lifetimes (less than 1 week) and the modification of physical and chemical properties from aging mechanisms. While the instrumentation developed here is only capable of measuring at a single ground location, it is capable of better characterizing aerosol optical properties as function of relative humidity. By developing a better understanding of aerosol optical properties through physical measurement, we are able to improve the predictions of global climate models (GCM's) through improved ground truthing.

1.1.1. Greenhouse gases

The warming effects of greenhouse gases have been well documented and are relatively well understood; it is *very likely* that the increase in greenhouse gas concentrations since the industrial revolution are the primary cause of increased planetary temperatures over what would be predicted with omission of the human influence (Core Writing Team 2007). Greenhouse gases are comprised of non-reactive and long-lived gas phase species; CO₂, CH₄, N₂O and halocarbons. The average atmospheric lifetime of the greenhouse gases is greater than 10 years, so their concentrations are globally distributed. Greenhouse gases affect climate because they absorb strongly in the IR wavelengths. Incoming solar radiation at these wavelengths is absorbed, while visible light is allowed through the atmosphere to warm the planet's surface. The earth then re-emits the absorbed visible energy as IR radiation that can be absorbed by greenhouse

gases. The earth retains this energy as heat causing the earth to re-radiate this energy as a slightly warmer black body.

1.1.2. Aerosols

Aerosol particles represent the "wild card" in the radiative budget of the earth and are not as well understood as any other climatic drivers. This can be seen visually in the IPCC's figure on climate change (figure 1-2) in that the total magnitude of the radiative forcing is approximately that from CO₂ but the error bars are approximately that from aerosol effects. The impact of aerosols can be either a cooling or warming influence depending ultimately upon the optical properties – scattering and absorption – of the aerosol and the underlying surface albedo; although cooling is expected to dominate globally. The optical properties of aerosols can be modified by relative humidity and atmospheric processing. Further, the lifetime of aerosol particles is short relative to the greenhouse gases; on the order of minutes to weeks versus years. The end result is that the radiative affect of aerosols varies strongly both spatially and temporally as a function of many different parameters.

Figure 1-2: Contributions of different components to radiative forcing effects. From Contribution of working groups I, II and III to the fourth assessment report of the intergovernmental panel on climate change, IPCC, page 26, figure I.1 (Core Writing Team 2007).

1.1.3. Global Climate Models

Many climate models require aerosol chemical and optical properties as input parameters; model results can vary widely depending upon the exact parameters used (Bond and Bergstrom 2006). Thus, the improvement of climate models requires a better understanding of the optical properties of aerosols and their variation both in space and time as a function of composition. The instruments developed here – a Humidity Controlled Cavity Ring-Down Transmissometer (HC-CRDT) and Nephelometry Camera (NephCam) – are both stationary instruments that are either laboratory or field deployable. While we could gain some information about the temporal evolution of

aerosol from these instruments, my focus is on the better understanding of the optics of aerosol properties as a function of relative humidity.

1.2. Focus and questions to answer

The ultimate focus of my work can be divided into 2 primary components. One that focuses on the development and characterization of the NephCam as a measurement and another that focuses on the development of the HC-CRDT and using it to measure the effects of RH on extinction. My primary research goals are to address the following questions:

1. Can a CCD be used in place of a PMT as a detector for a better determination of scattering coefficients?
2. Can image shape be linked to scattering phase functions and ultimately particle size?
3. What is the effect of relative humidity on the measured optical properties of aerosol particles?
4. How does the refractive index and size change of the particles as a function of RH?
5. What is the ultimate effect of RH on the measurements?

1.3. Aerosols and climate

1.3.1. Direct effects

Aerosols affect climate directly through the scattering and absorption of radiation.

The magnitude of these effects is highly dependent on the refractive index and size of the particles. The refractive index (n) of a material can be represented by

$$n = m + ik \quad (\text{eq 1-1})$$

where m and k are the real and imaginary parts, roughly corresponding to the scattering and absorption efficiency of a material, respectively. Note that n , m , and k are all functions of wavelength, containing both the classical scattering response and quantum mechanical connections (i.e., molecular spectra). (A more complete treatment of how the refractive index, wavelength and scattering and absorption efficiency are related will

be presented later.) This allows for a simple classification of aerosol particles into "white" ($k = 0$) and "black" ($k \neq 0$) types. White particles absorb negligibly in the visible part of the spectrum but depending upon size can scatter radiation effectively. White particles are commonly composed of Ionic salts – Na^+ , NH_4^+ , Cl^- , NO_3^- and SO_4^{2-} ions – and non-absorbing organics. Black particles absorb light strongly across the spectrum, are primarily composed of carbon (elemental carbon) and are formed from combustion processes. Brown carbon particles absorb light strongly in the ultraviolet but more weakly in the visible and are also formed in combustion processes. For now, only the distinction between white and black aerosol (absorbing vs. non-absorbing) will be considered to elucidate how these aerosols can affect climate. Brown carbon aerosols will be discussed further in the aerosol optical properties section (Section 2.5.2.1).

Increased loading of white aerosol particles leads to an increase in the reflectivity of the earth and a cooling or warming effect can result upon the underlying surface albedo. Increased loading of white aerosols over dark surfaces – low surface albedo – will result in the "whitehouse effect" (Schwartz 1996); an overall cooling influence due to an increase in planetary albedo. More solar radiation is reflected back into space. Over light surfaces like snow and ice – high surface albedo – a warming influence is expected. Here, solar radiation reflected by the surface can be redirected back towards the planet by aerosols. The net effect is an increase in the absorption of solar radiation since planetary reflectance has been decreased by multiple scattering events (Finlayson-Pitts and James N. Pitts 2000). A majority of earth's surface ($\sim 75\%$) is covered by water which has a low surface albedo of 0.06 – 0.08 so the cooling influence is expected to dominate globally (Eck 1987).

An increase in the loading of black (strongly absorbing) aerosols leads to an increase in the absorption of solar radiation. This absorbed light is converted into heat and re-emitted. The result is warming of the local atmosphere.

The magnitude of the direct optical effects is highly size dependent. Aerosols are commonly grouped into 3 bins by size: the nucleation, accumulation, and coarse modes: smaller than 100 nm, between 100 nm and 2.5 μm , and larger than 2.5 μm , respectively. The nucleation and accumulation modes can be collectively referred to as the *fine* mode. As a general trend, scattering and absorption of light by an aerosol increases with size as a function of particle diameter; $(D_p)^6$ and $(D_p)^3$, respectively.

1.3.2. Indirect effects

Indirectly, aerosols affect clouds and atmospheric circulation patterns. Aerosols can act as "seeds" or centers for droplet or ice crystal formation in clouds; a.k.a., cloud condensation nuclei (CCN) and ice nuclei (IN), respectively. As CCN or IN number concentration increases, cloud droplet size and precipitation efficiency decrease and cloud albedo and lifetime increase (Lohmann and Feichter 2005). Atmospheric cooling or warming can occur as a result of increased reflection of solar or planetary thermal radiation by clouds, respectively (Schwartz 1996).

The activation of an aerosol particle to become a CCN or IN particle is ultimately controlled by the composition of the particle and the RH of the air mass in which it is present. As air rises in the atmosphere, it cools. As a result, the RH of the air mass increases from the decreased temperature. If temperature decreases enough, the air can become supersaturated in water vapor.

Aerosol particles grow with increasing RH. When water vapor is supersaturated in air, aerosols can reach a "tipping point" - as predicted by the Köhler equation - at which the particles will continuously grow as a byproduct of Raoult's law; vapor pressure of an inhomogeneous liquid is lower than that of the pure liquid. Depending upon aloft temperature, condensing water can be present in either the liquid or solid phase and the particle is now considered a CCN or IN particle, respectively.

1.3.3. Semi-direct effects

Strongly absorbing aerosol affects climate semi-directly by changing cloud formation and atmospheric circulation. Absorption can lead to a local negative climatic forcing by reducing the amount of radiation reaching earth's surface: *surface dimming*. The local atmosphere becomes warmer, drier and more stable preventing further cloud formation and water evaporation (Koren, Kaufman et al. 2004). Cloud evaporation is also possible (Lohmann and Feichter 2005).

1.3.4. Summary of climate effects

While the direct, indirect and semi-direct effects of aerosols on climate have been well documented, determination of the globally averaged effect remains elusive due to the spatio-temporal variability of aerosols. Thus the absolute magnitude of each of these effects is uncertain on global and regional scales. Many climate models require the use of generalized aerosol data as input parameters, large variation in model results occurs. Model improvement and uncertainty reduction requires a similar level of improvement and uncertainty reduction in the measured aerosol optical properties that are used to refine and ground-truth model predictions.

1.4. Optical properties of aerosols

Aerosol particles can either scatter or absorb incident radiation; morphology, composition and size drives these effects. The sum of scattering and absorption is referred to as extinction. The exact magnitude of scattering and absorption are a function of particle refractive index, size and shape. Exact solutions for the optical properties of any particle can be calculated using Maxwell's equations, however in many cases the application of Maxwell's equations are computationally prohibitive. One of the best known approximations to Maxwell's equations is the Lorenz-Debye-Mie Theory (or just Mie Theory for short). Mie theory includes the constraints that particles are spherically symmetric and homogeneous. While not all particles in the atmosphere are spherically symmetric (in reality most are not) Mie theory does provide a good first order approximation to the optics of all aerosol particles. Other methods, such as the T-Matrix and discrete dipoles, do exist for the determination of particle optical properties when the assumptions of particle sphericity and homogeneity are not applicable. However, these methods are computationally intensive.

1.4.1. Extinction measurement

The removal of light intensity by aerosol particles in the atmosphere, aka extinction, follows the Beer-Lambert law:

$$\frac{I}{I_0} = e^{-b_{ext}L} \quad (\text{eq 1-2})$$

Where I_0 is initial intensity, I is the intensity at distance L and b_{ext} is the extinction coefficient. Since both scattering and absorption participate in extinction, the extinction coefficient can be rewritten as:

$$b_{ext} = b_{abs} + b_{scat} \quad (\text{eq 1-3})$$

where b_{abs} and b_{scat} are the absorption and scattering coefficients. The extinction, scattering and absorption coefficients are typically given in units of inverse distance; inverse megameters (Mm^{-1}) are our preferred unit, which corresponds to a loss of 1 part per million of the light per meter of air traversed. For bulk aerosols, the extinction, scattering and absorption coefficients represent the cumulative contribution from all particles and sizes present. For a single size bin of particles, the extinction is a function of the extinction cross-section and the number density of particles:

$$b_{\text{ext}} = N_i \sigma_i \quad (\text{eq 1-4})$$

Where N_i and σ_i are the particle number concentration and extinction cross-section of a particle of size i . The extinction cross-section is a measure of the effective cross-sectional area a particle has available for interaction with photons. It is not necessarily the same size as the actual geometric cross-section. Similar relationships exist for the absorption and scattering coefficients. To derive the extinction coefficient for bulk aerosols with multiple sizes present, the summation over all particle sizes as a function of concentration and cross-section is needed:

$$b_{\text{ext}} = \sum_0^i N_i \sigma_i \quad (\text{eq 1-5})$$

1.4.2. Theoretical relationship between extinction and size

The extinction efficiency (Q_{ext}) of a particle is the ratio of the extinction cross-section to the geometric cross-section:

$$Q_{\text{ext}} = \frac{\sigma_{\text{ext}}}{\sigma_{\text{geometric}}} \quad (\text{eq 1-6})$$

Where σ_{ext} and $\sigma_{\text{geometric}}$ are the extinction and geometric cross-sections, respectively. An identical relationship can be written for scattering and absorption. The geometric cross-section is related to particle radius through:

$$\sigma_{geometric} = \pi r^2 \quad (\text{eq 1-7})$$

The size parameter (χ) relates the particle radius to the wavelength of light:

$$\chi = \frac{2\pi r}{\lambda} \quad (\text{eq 1-8})$$

where r is the particle radius and λ is the wavelength of light. Mie theory ultimately relies on the size parameter for the calculation of optical coefficients. This induces a scale invariance in the calculation; i.e. nm size particles interact with nm wavelengths the same as mm size particles with mm wavelengths assuming the different sizes have the same refractive index at their respective wavelengths.

The extinction, scattering and absorption efficiency of a particle displays 3 regimes relative to particle size as seen in figure 1-3 and 1-4 for a Nigrosin ($n = 1.70 + 0.31i$) and NaCl ($n = 1.55$) particle at 532 nm, respectively. In the Rayleigh limit ($\chi \ll 1$), the extinction, scattering, and absorption efficiency goes towards 0 as particle size decreases; the optical effects decrease faster than the particle size; scattering decreases as r^6 and absorption as r^3 . In the visible portion of the spectrum, this corresponds to particles with radii less than approximately 30 nm; roughly the nucleation mode.

In the geometric limit ($\chi \gg 10$) the extinction efficiency goes towards 2 as particle size increases. The absorption and scattering by large particles does increase with particle size, but does so at a smaller rate. For large particles, absorption shifts from a volume effect to a surface area effect; it increases as r^2 instead of r^3 . The geometric limit roughly corresponds to coarse mode aerosols in the visible; particles with radii larger than approximately 5 μm fall into this category.

Figure 1-3: Extinction (solid black), scattering (blue dash) and absorption (red dash dot) efficiency for Nigrosin ($n = 1.70 + 0.31i$ at 532 nm) particles as a function of diameter.

Figure 1-4: Extinction efficiency for NaCl ($n = 1.55$ at 532 nm) particles as a function of diameter.

The Mie paradox is one caveat to the extinction efficiency of coarse mode aerosols. Under Mie theory, the extinction efficiency approaches 2 as size increases. But when the same calculations are done using geometric optics instead, the extinction efficiency approaches 1. This phenomenon is justified because of the shift in scattering intensity towards the forward direction as particle size increases. Under Mie theory, all scattered photons are included in the efficiency calculation. Under geometric optics, photons scattered in the forward direction are not treated as being scattered.

In the Mie regime ($1 < \chi < 10$), the extinction, scattering and absorption efficiency hit a maximum; here particle diameter and wavelength are approximately equal.

Interaction of photons and particles increases because of non-linear size effects. The Mie regime roughly corresponds to the accumulation mode in the visible portion of the solar spectrum.

1.4.3. Particles with size near visible wavelengths

Solar radiation in the IR and UV wavelengths are strongly absorbed by the atmosphere. In the vacuum UV (< 200 nm) all radiation is absorbed; molecular O_2 , H_2O , CO_2 , N_2 and H_2 all strongly. In the near-UV, photochemically active species dominate absorption (O_3 , O_2 , CO_2 , SO_2 , H_2O and Halocarbons) (Horvath 1993). In the IR, the greenhouse gases dominate (CO_2 , CH_4 , N_2O and Halocarbons) with water vapor also playing a significant role (Wayne 1996). However, the visible spectrum strongly transmitted by the atmosphere; NO_2 and O_3 absorb weakly.

The accumulation mode particles are especially important players in the radiative balance of the earth because their size is close to the visible wavelengths; light scattering efficiency reaches maximum as seen in figures 1-3 and 1-4. Accumulation mode particles also have long atmospheric lifetimes and high number concentrations further adding to this effect.

Absorption is dominated by fine mode particles, but the nucleation mode particles play a stronger role than the accumulation mode. Most absorbing particles are carbonaceous in nature and the result of combustion processes. They are composed of fractal agglomerates consisting of primary particles with diameters between 20 and 50 nm (Lee, Cole et al. 2002; Mathis, Mohr et al. 2005). Total particle diameters are

typically less than 100 nm, but due to their high number concentration play a strong role in absorption. These particles can be atmospherically processed and grow to accumulation mode size, but absorption typically decreases relative to the increases in scattering.

1.4.4. Scattering phase functions

Light scattering as a function of angle by an aerosol can be represented by the scattering phase function. This represents the normalized plot of intensity as a function of angle (Integral over all angles equals 1). As particles grow in size, fraction of scattered light shifts towards the forward direction as evidenced by the 10 nm (black), 100 nm (red), 250 nm (green) and 500 nm (blue) NaCl particle phase functions shown in figure 1-5. In the Rayleigh limit, scattering is isotropic (equal in forward and backward directions).

Figure 1-5: Plot of scattering phase function for NaCl particles with diameters of 10 nm (black), 100 nm (red), 250 nm (green) and 500 nm (blue). Designations of 0° and 180° represent forward and backward scattering, respectively.

1.4.5. Asymmetry parameter

The asymmetry parameter (g) represents the intensity weighted average as a function of scattering angle:

$$g \equiv \langle \cos \theta \rangle \quad (\text{eq 1-9})$$

In the limits where $g = 1$ or $g = -1$ purely forward or backward scattering is present, respectively. These limits are never obtained for aerosols. Particles in the Rayleigh limit can have g values approaching 0 due to isotropic scattering. Particles in the coarse mode can have g values approaching 1, but 0.9 is a more realistic value. Asymmetry parameters of an NaCl aerosol as a function of particle diameter can be seen in figure 1-6. The asymmetry parameter is an important parameter in GCM's; smaller values of g imply that a larger fraction of scattering is in the backwards direction; an asymmetry parameter of 0 translates to 50% of scattering being backscatter. Smaller values of g correspond to a larger fraction of incoming solar radiation being scattered directly back into space or energy reflected by the planet being scattered back towards earth's surface.

Figure 1-6: Asymmetry parameter (g) of NaCl aerosol as a function of particle diameter.

1.4.6. Ångström exponents (α)

Scattering Ångström exponents (α_{scat}) represent the power law dependence of scattering on wavelength:

$$\frac{b_{scat,\lambda}}{b_{scat,\lambda_0}} = \left(\frac{\lambda}{\lambda_0}\right)^{-\alpha_{scat}} \quad (\text{eq 1-10})$$

where $b_{scat,\lambda}$ is the scattering coefficient at wavelength λ and b_{scat,λ_0} is the scattering coefficient at a reference wavelength λ_0 . The differential form of α_{scat} is the more common form:

$$\alpha = \frac{-d \ln b_{scat}}{d \ln \lambda} \quad (\text{eq 1-11})$$

Similar equations can be derived for absorption and extinction. The scattering Ångström exponent is inversely related to particle size; smaller particles have larger values up to a maximum of 4, while larger particles have values tending toward 0 (Taubman, Marufu et al. 2004; Bergstrom, Pilewskie et al. 2007; Moosmüller, Chakrabarty et al. 2009).

Absorption Ångström exponents greater than 0 imply the presence of absorbing material. Black carbon has been shown to have an absorption Ångström exponent near 1 because spectral absorption (governed by the imaginary part of the refractive index k) is nearly independent of wavelength (Bergstrom, Russell et al. 2002; Schnaiter, Horvath et al. 2003; Bergstrom, Pilewskie et al. 2007). Other forms of light absorbing carbon, such as brown carbon and humic-like substances (HULIS), have absorption Ångström exponents significantly greater than 1; values as high as 6-7 have been reported (Hoffer, Gelencser et al. 2005; Yang, Howell et al. 2008). This reflects the fact that k only begins to become significant in the short-wave visible and UV, but then increases dramatically with decreasing wavelength.

1.4.7. Single scattering albedo

The single scattering albedo (SSA or ω_0) represents the fraction of extinction that is scattering:

$$\omega_0 = \frac{b_{scat}}{b_{ext}} \quad (\text{eq 1-12})$$

The SSA is a measure of aerosol "whiteness": for strongly scattering aerosol, $\omega_0 \approx 1$. For strongly absorbing aerosol it can approach 0 as particle size decreases. The SSA of light absorbing carbon in the visible is approximately 0.2 (Bergstrom, Pilewskie et al. 2007). In general, aerosols will be more likely to exert a cooling influence if they have a high single scattering albedo.

1.5. Particle types and classifications

Aerosol particles exhibit a wide array of chemical compositions that depend upon both the source and atmospheric processing. The two primary chemical groups or aerosols are inorganic and carbonaceous particles. However, these two classes are rarely present as one form or the other but typically as a mixture of both.

Beyond the division of particles into inorganic and carbonaceous; they are also divided upon formation mechanisms. Primary particles are those particles that are directly emitted into the atmosphere while secondary particles are formed by chemical reactions in the atmosphere. Primary particles can be converted into secondary particles through atmospheric processing.

1.5.1. Inorganic particles

Inorganic particles are typically formed by mechanical processes (primary aerosol) or gas to liquid condensation or reaction (secondary aerosol). These particles are primarily composed of the water soluble cations and anions: Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , and SO_4^{2-} . However, this is not an exhaustive list as a majority of the elements have been observed depending upon formation mechanism: crustal elements in natural processes and heavy elements associated with engines and boilers in anthropogenic

emissions (Milford and Davidson 1985; Toscano, Moret et al. 2011). The vast majority of inorganic particles strongly scatter radiation and absorption is minimal. However, some types of inorganic particles, such as those containing iron oxides (i.e. hematite) and clay minerals (kaolinite, illite and montmorillonite), can absorb radiation but the total absorption is small compared to that by carbonaceous aerosols (Finlayson-Pitts and James N. Pitts 2000).

The lifetime of inorganic particles depends strongly upon formation mechanism. Mechanically generated particles typically have diameters larger than $3\mu\text{m}$ and quickly settle out of the atmosphere. However, sometimes the particles can be re-entrained in the atmosphere due to surface winds. Saharan dusts have been observed at the Jungfraujoch site - a free tropospheric site in the Swiss Alps at 3580 m altitude - and in the Caribbean (Reid, Kinney et al. 2003). Particles produced from gas to liquid condensation or reaction can have diameters in the accumulation or nucleation range depending upon the species involved. Lifetimes of these particles are days to weeks depending upon meteorology; rain tends to scavenge aerosols from the atmosphere.

Many inorganic particles are involatile and relatively inert compared to other particle types. However, the sulfates and nitrates are not inert and represent a significant formation pathway for secondary aerosols. $\text{SO}_{2(\text{g})}$ can be oxidized to form H_2SO_4 which can then further react with or adsorb to particles. $\text{NH}_{3(\text{g})}$ can titrate acidic particles; the NH_4^+ then remains adsorbed to the particle. Reaction of NH_3 with H_2SO_4 is the primary production mechanism of ammonium sulfate aerosols. Both of these species are in relatively high concentrations in the atmosphere due to emission of SO_2 from fuels (coal and diesel) and NH_3 from agricultural processes (fertilizers and manure). NO_2 can be

oxidized to form HNO_3 which, like H_2SO_4 , readily reacts with and adsorbs to particles. In fact, a large number of the oxides of nitrogen have been shown to react with particles containing chloride and bromide to produce gas phase chlorine and bromine species (De Haan, Brauers et al. 1999).

1.5.2. Carbonaceous aerosols

Carbonaceous aerosols represents a large class of aerosols that are related on the basis that they contain carbon. Depending upon composition, morphology and size, these particles can strongly absorb and/or scatter radiation. They are produced from anthropogenic and biogenic emissions as both primary and secondary aerosols. Many naming conventions have been adopted for these particles that can mean similar or different things depending upon the context.

1.5.2.1. BC vs. BrC

Depending upon the measurement method - thermochemical or optical - similar classes of carbonaceous aerosols have different names as shown in table 1-1. The total carbon (TC) content of an aerosol is the sum of all forms of carbon present in the aerosol minus the contribution from inorganic carbonates. If thermochemical methods are being employed, TC can be further split into elemental carbon (EC), organic carbon (OC) and refractory organic carbon. In optical methods, TC is split into black carbon (BC), brown carbon (BrC) and organic carbon (OC). Both EC and BC are used to describe carbonaceous aerosols that have properties similar to soot; graphitic layers of carbon arranged in an sp^2 hybridized array. Elemental carbon is typically unreactive – except at surface sites where reactive species may be present – stable up to very high temperatures and composed of primary particles that cluster to form fractal like agglomerates. BC refers to any aerosol with a strong absorption character that is essentially independent of

wavelength. Absorption typically shows a λ^{-1} dependence, *i.e.*, α_{abs} near 1, and mass absorption coefficient near $10 \text{ m}^2\mu\text{g}^{-1}$ have been observed (Kirchstetter, Novakov et al. 2004; Bond and Bergstrom 2006). Scattering for BC aerosols is usually minimal except at large particle sizes. While there are not many other components that behave like EC in terms of the optical properties, it is not guaranteed that a BC aerosol is EC; Nigrosin dye is a primary example.

Table 1-1: Distinction between carbonaceous aerosols by measurement method (adapted from (Poschl 2005))

Thermochemical	Molecular Structure	Optical
Elemental Carbon (EC)	Graphene Layers (Graphitic or turbostratic)	Black Carbon (BC)
Refractory Organic Carbon	Polycyclic Aromatics, Conjugated Organics, HULIS, Biopolymers, etc.	Brown Carbon (BrC)
Organic Carbon (OC)	Low Molecular Mass Hydrocarbons and Derivatives	Organic Carbon (OC)

Thermochemically, the OC component of an aerosol is the difference between the TC and EC. In thermochemical classifications, the temperature dependence and oxidation reactivity of an aerosol plays a key role in how it is defined. OC consists of those compounds that are not stable at high temperatures or towards oxidation. Refractory organic carbon can be misclassified as EC as a result of this temperature and oxidation stability (Gelencser, Hoffer et al. 2000; Mayol-Bracero, Guyon et al. 2002). This includes polycyclic aromatics hydrocarbons, Humic-like substances (HULIS), low molecular weight hydrocarbons, etc.

When particle optics are being measured, OC refers to those compounds that have optical signatures different than BC. This includes colorless organics that do not absorb or scatter visible radiation like low molecular weight hydrocarbons and their derivatives. Recently, the classification of brown carbon (BrC) has been added. BrC aerosols do not absorb appreciably in the visible and NIR, but do absorb strongly in the UV; as a result BrC particles appear yellow to brown in color. BrC mass absorption efficiencies of $0.03 \text{ l m}^2 \text{ g}^{-1}$ at 532 nm and $2\text{-}3 \text{ m}^2 \text{ g}^{-1}$ at 300 nm and α_{abs} as high as 6 - 7 have been reported (Hoffer, Gelencser et al. 2005). BrC aerosols are commonly composed of polycyclic aromatic hydrocarbons, HULIS and other polyfunctional groups; the presence of oxygen, nitrogen, conjugated aromatic systems or multifunctional groups on the aerosol are thought to drive this enhanced UV absorption (Sun, Biedermann et al. 2007). BrC possesses a polar character, although it may or may not be water soluble. In fact, the methanol soluble fraction, versus water or hexane soluble fractions, has been linked to the increased UV absorption by BrC (Chen and Bond 2009).

BC and BrC are typically the result of combustion processes and originate from anthropogenic emissions or biomass burning (of which a sizable fraction are still anthropogenically influenced). The split between BC and BrC depends on combustion conditions and except for a few distinct cases, such as diesel soot production, a clear link between conditions and the type of aerosol formed has not yet been elucidated (Andreae and Gelencser 2006; Chen and Bond 2009). In the case of a diesel engine, BC is formed in the fuel rich zones inside the piston due to incomplete mixing of fuel and air. This

lack of oxygen results in the production of black carbon from the organic backbone, but a non-negligible organic fraction is also emitted.

Brown carbon possesses significantly more organic carbon character than black carbon (Chen and Bond 2009). In the case of biomass burning aerosols, BrC emission has been linked to biomass pyrolysis but actual emissions can vary depending upon fuel type, amount and conditions (Andreae and Gelencser 2006; Chen and Bond 2009; Levin, McMeeking et al. 2010). These BrC emissions from biomass burning have come to be termed Humic-Like Substances (HULIS) for their similarities to Humic acids found in biomass (Pöschl 2003). BrC has also been shown to be produced from the combustion of some types of coal, specifically lignite and from the oxidation and polymerization products of geogenic aerosol (Bond, Bussemer et al. 1999; Andreae and Gelencser 2006).

Because the focus of my dissertation work is on the optical properties of aerosol and not their thermochemical properties, the terms TC, BC, BrC and OC will be used as such: TC is the total carbon component present in an aerosol minus that found from inorganic carbonates. BC represents aerosol components that show optical signatures similar to that of graphitic carbon; i.e. λ^{-1} dependence. BrC refers to those aerosol components that have a stronger wavelength dependence on absorption than BC; i.e. greater than λ^{-2} dependence. OC will then refer to any organic components present in an aerosol that do not optically behave as either BC or BrC.

1.5.3. Primary vs. secondary aerosols

Primary organic aerosols (POA) consist of directly emitted organic aerosols, semivolatile organic compounds (SVOC) or non-volatile organic compounds (NVOC) that are condensable under atmospheric conditions. POA is not limited to BrC, but can

also include particles generated from wind or traffic-driven re-suspension of organic particles, biological materials, and sea spray droplets containing organics (Poschl 2005).

Secondary organic aerosols (SOA) are the result of new particle formation from gas phase or heterogeneous reactions or atmospheric processing of POA. Volatile organic compounds (VOC's), SVOC's or NVOC's react with oxidant species in the atmosphere - O_3 , OH, NO_x , Cl and $h\nu$ to name a few - and results in a many different product types. Typically, a more oxidized, lower-volatility organic compound (SVOC or NVOC) is obtained such as carbonyls, carboxylic acids or peroxides. However, sometimes these products can undergo further oxidation, re-arrangement, isomerization or decomposition to form more volatile products.

In the event that SVOC or NVOC's are produced by oxidation, these compounds can then condense onto pre-existing particles or molecular clusters of H_2SO_4 - H_2O - NH_3 or form H_2SO_4 -SVOC complexes (Kulmala, Laakso et al. 2004; Zhang, Suh et al. 2004). In the case of molecular clusters, adsorption or absorption rates of additional SVOC's or NVOC's is increased as particles grow (Anttila, Kerminen et al. 2004; Kulmala, Laakso et al. 2004).

1.6. Relative humidity and particles

Relative humidity influences the physical properties of aerosols in a variety of ways. Water uptake by an aerosol with increasing humidity causes a change in chemical composition and size; the water content of the particle increases and so must the diameter. An increase in water content can also trigger a change in particle morphology. Ultimately, aerosol optical properties are changed as a result of water uptake.

Depending upon the type of particle, 3 general classes of aerosol growth as a function of RH are possible. Aerosols can exhibit hygroscopic growth with hysteresis or continuous hygroscopic growth or be hygrophobic and exhibit minimal growth as a function of relative humidity. These growth factors can be represented as hygroscopic growth factors based upon either particle diameter or optical properties ($\beta(RH)$ or $f(RH)$, respectively):

$$\beta(RH) = \frac{D(RH)}{D(dry)} \quad (\text{eq 1-13})$$

$$f_{ext}(RH) = \frac{b_{ext}(RH)}{b_{ext}(dry)} \quad (\text{eq 1-14})$$

Where $D(RH)$ and $D(dry)$ are the particle diameters at high and low RH, respectively, and $b_{ext}(RH)$ and $b_{ext}(dry)$ are the extinction coefficients at high and low RH, respectively. Similar relationships can be constructed for absorption ($f_{abs}(RH)$) and scattering coefficients ($f_{scat}(RH)$); $f_{scat}(RH)$ is the most commonly used $f(RH)$ form since scattering tends to be more strongly affected by RH than absorption and extinction tends to be driven by changes in scattering (Kotchenruther, Hobbs et al. 1999; Andrews, Sheridan et al. 2004). In both of these equations, the dry RH is taken to be less than 40%, however this value is not always low enough for a dry measurement of some particle types (Baltensperger, Barrie et al. 2003). The parameters $\beta(RH)$ and $f(RH)$ are inherently linked because the optical properties are dependent upon particle size, but they are not directly related. As particles take up water, the refractive index of the particle is diluted towards that of water. This results in the actual $f(RH)$ of a given particle being lower than expected as defined by $\beta(RH)$.

Strongly hygrophobic particles do not take up appreciable amounts of water and $f(RH) \sim 1$ until very high RH, as seen by the blue dot-dash line in Figure 1-7.

Extinction, scattering and absorption are effectively independent of RH for this type.

Many organic aerosols are hygrophobic. When many particles of this class take up water, a core-shell structure is observed instead of complete mixing within the particle.

Strongly hygroscopic aerosols continuously absorb water at almost all humidities: prime examples are volcanic ash, H_2SO_4 , NaOH, and soluble organic aerosols (Carrico, Kus et al. 2003). This is illustrated by the red dashed line in Figure 1-7. Increasing relative humidity causes these aerosols to grow monotonically (Tang 1976).

Figure 1-7: Plot of $f(RH)$ for hygrophobic aerosol (blue dot-dash), hygroscopic (red dash) aerosol and hygroscopic aerosol with deliquescence/efflorescence behavior (black line).

Deliquescent and efflorescent aerosols also take up water from the atmosphere, but exhibit hysteretic RH dependence. These aerosols can exist as either solid or liquid particles at the same RH depending on their RH history (which form were they previously in or which extreme of RH were they last exposed to). Most inorganic salts exhibit this behavior (Tang 1976). Starting from a low RH – crystalline aerosol – in

figure 1-7, these aerosols remain as a crystalline solid until the Deliquescence Relative Humidity (DRH) is reached. Above the DRH, the aerosol spontaneously absorbs water and phase transition to a hydrated particle as shown by the upward arrow. As RH increases beyond the DRH, the aerosol will continue to grow like a hygroscopic aerosol. From a high RH – starting with hydrated aerosol – the aerosol will remain in a metastable supersaturated state until the Efflorescent Relative Humidity (ERH) is reached. Below the ERH, the aerosol spontaneously phase transitions back to a crystalline state, as shown by the downward arrow. The lifetime of these phase transitions is relatively short, and has been shown to be less than 10 seconds for sea salt aerosols smaller than 10 μm in diameter (Lewis and Schwartz 2004). Hysteresis is caused by the fact that $\text{ERH} < \text{DRH}$, sometimes as much as 35% (Freney, Martin et al. 2009).

1.6.1. RH and particle thermodynamics

The effect of water vapor on particle growth is ultimately controlled by physics but can be described using the Kelvin and Köhler equations. The Kelvin and Köhler effects are essentially competing terms on particle growth; one (Kelvin) opposes growth at small particle diameters and the other (Köhler) increases growth at larger particle diameters. Both equations are based upon the thermodynamics of the aerosol in question.

1.6.1.1. Kelvin effect

The change in free energy of the environment (dG_{en}) containing an aerosol particle taking up water from the air is the total contribution from both terms:

$$dG_{\text{en}} = dG_{\text{a}} + dG_{\text{w}} \quad (\text{eq 1-15})$$

where dG_{a} and dG_{w} are the changes in free energy of the aerosol and the air (from water loss), respectively. The change in free energy of the water vapor is a function in the

change in the number of moles water (dn_w), the temperature and the initial and final vapor pressures (p_0 and p , respectively):

$$dG_w = dn_w RT \ln\left(\frac{p}{p_0}\right) \quad (\text{eq 1-16})$$

The change in free energy of the particle by water uptake is equal to the change in the surface area (dA) of a particle with surface tension (γ):

$$dG_a = \gamma dA \quad (\text{eq 1-17})$$

This can be rewritten in terms of particle radius (r):

$$dG_a = \gamma(8\pi r dr) \quad (\text{eq 1-18})$$

since surface area equals $4\pi r^2$. If the density and molecular weight of the aerosol are ρ and MW, respectively:

$$\rho = \frac{(MW)dn}{4\pi r^2 dr} \quad (\text{eq 1-19})$$

Then dG_a can be rewritten as:

$$dG_a = \gamma \frac{(MW)dn_a}{D\rho} \quad (\text{eq 1-20})$$

where D is the particle diameter and dn_a is the change in the number of moles in the particle. Combining equations 1-14, 1-15, and 1-19 yields:

$$dG_{en} = dn_w RT \ln\left(\frac{p}{p_0}\right) + \gamma \frac{(MW)dn_a}{D\rho} \quad (\text{eq 1-21})$$

Following the conservation of mass, loss by water vapor is gain by the aerosol:

$$-dn_w = dn_a \quad (\text{eq 1-22})$$

And equation 1-20 becomes:

$$dG_{en} = -dn_a RT \ln\left(\frac{p}{p_0}\right) + \gamma \frac{(MW)dn_a}{D\rho} \quad (\text{eq 1-23})$$

the value p and p_0 can be replaced by RH:

$$\left(\frac{p}{p_0}\right) = \left(\frac{RH}{100a_w}\right) \quad (\text{eq 1-24})$$

where a_w is water activity since RH is a measure of water activity relative to saturation.

Thus, equation 1-22 can be rewritten as:

$$dG_{en} = -dn_a RT \ln\left(\frac{RH}{100a_w}\right) + \gamma \frac{(MW)dn_a}{D\rho} \quad (\text{eq 1-25})$$

In the limit where a particle is at equilibrium with the water vapor in air ($dG_{en} = 0$), the

Kelvin equation can be obtained:

$$\left(\frac{RH}{100a_w}\right) = \exp\left[\frac{\gamma(MW)}{D\rho RT}\right] \quad (\text{eq 1-26})$$

For larger particles (diameters larger than ~ 100 nm), the Kelvin effect is negligible because of the diameter weighting in the denominator of the exponential term. For smaller hydrated particles, growth is significantly depressed due to surface tension effects. The Kelvin effect implies that water vapor in the atmosphere may spontaneously condense into liquid droplets at high enough RH. However, the vapor pressure over the newly formed droplets is so great that the droplets immediately re-evaporate. Instead, a seed particle must be present as a center for particle growth to initiate water adhesion.

If the free energy of crystallization becomes less (more negative) than the change in free energy due to water loss, the particle will effloresce. For crystalline particles, when the free energy of hydration becomes less than the free energy change as a result of changes in surface tension and size, the particle will deliquesce. Depending upon the magnitude of the crystallization and hydration free energies, deliquescence and efflorescence may or may not occur.

1.6.1.2. Köhler effect

The Köhler effect is essentially the opposite of the Kelvin effect. The Kelvin effect results in a decrease in particle diameter at a given RH due to surface curvature. The Köhler effect results in activation of an aerosols to form a CCN or IN near or above supersaturation ($RH > 100\%$). In equation 1-25, if the air is supersaturated with water, the dG_{en} contribution from water vapor will always be negative. Particles can still grow to an equilibrium drop size. But, if particle diameter is large enough, then the free energy contribution by the aerosol will always be less in an absolute sense than the water vapor's contribution. Thus, dG_{en} will always be negative and will become more negative with increasing drop size; density and surface tension will become essentially constant due to droplet size and the composition approaching that of pure water, respectively. When this occurs, the particle is said to be activated and is now a CCN or IN depending upon whether water or ice is being taken up by the particle.

Raoult's law also ties into the Köhler effect because it decreases the vapor pressure of an ideal solution due to other components in the system:

$$\frac{p_a}{p_{a,0}} = 1 - x_b \quad (\text{eq 1-27})$$

Where p_a and $p_{a,0}$ and x_b are the vapor pressure of pure solvent a, vapor pressure a and the mole fraction of solute b present, respectively. This has the effect of lowering the supersaturation ratio required for a droplet to become activated and turn into a CCN/IN.

The Köhler effect is the primary driver of cloud formation in the upper atmosphere. As air masses rise, they cool. This has the effect of increasing the RH of the air mass to values typically above supersaturation. Many of the particles present in that air mass can then become activated to CCN or IN because of this increase in RH.

The end result of aerosol uptake of any gas phase species is dependent upon the initial characteristics of the aerosol under investigation. Many water soluble aerosols will readily uptake water and form a homogeneous mixture. In some instances, surface water adsorption and structural rearrangement occurs before a hydrated particle is formed; this effect has been observed in NaCl particles (Krämer, Pöschl et al. 2000; Hämeri, Laaksonen et al. 2001).

BC and OC aerosols can show different growth properties when gas phase species condense onto a particle and externally mixed, internally mixed or core-shell particles result. In externally mixed particles, the carbonaceous particles and the condensing species are present in separate phases on the same particle. Internally mixed particles result in a near homogenous particle. With core-shell mixing, the condensing species forms a shell around the original aerosol which serves as a core. For BC with a fractal structure, uptake of any coating can induce collapse of the fractal structure (Slowik, Cross et al. 2007; Zhang, Khalizov et al. 2008).

The core-shell morphology is very common among BC and sparingly soluble OC when water or H₂SO₄ condenses onto a particle. The end result is that absorption of light by the particle is increased due to lensing (Bond, Habib et al. 2006; Bueno, Havey et al. 2011). The exact magnitude of the increase is dependent upon the refractive index of the coating. Clear coatings such as H₂O, H₂SO₄ or clear OC result in a much larger increase in absorption than absorbing coatings such as BrC (Lack and Cappa 2010). Absorption increase is inversely related to the absorption strength of the coating. Regardless of what type of coating is present, the increase in particle size results in an increase in light scattering by the particle.

Coating thickness dictates the extent to which absorption increases. For small particles, any coating will increase absorption, but thicker coatings result in larger absorption increases. For cores larger than about 150 nm, absorption increase is essentially constant regardless of shell size (Bond, Habib et al. 2006). The same trends are true for absorbing coatings, but the extent of increase is smaller (Lack and Cappa 2010).

1.7. Measurement aerosol optical properties

Many measurement techniques exist for the determination of aerosol optical properties. These techniques are categorically divided between filter versus in-situ measurements and single particle versus bulk measurements. All sub-categories have their own inherent advantages and disadvantages. These sub-categories can be further split depending upon the property under investigation: extinction, scattering or absorption.

1.7.1. Filter vs. *in-situ* measurements

Filter measurements of aerosol optical properties require the deposition of particles onto a membrane or fiber filter for measurement, whereas in-situ measurements measure the optical properties of the aerosol as it flows through the instrument. Filter measurements are easily implemented and relatively inexpensive compared to many of the in-situ measurements. Filter measurements can also offer greater spectral coverage than their in-situ counterparts; the Aethalometer operates at 7 wavelengths across the solar spectrum.

Depending upon the exact filter characteristics and type, overestimation of absorption coefficients can occur due to multiple scattering effects by the filter and

deposited particles. Typically, whenever more than a monolayer of particles is deposited on the filter, a correction must be made and can be significant (Campbell, Copeland et al. 1995). Further, particle collection on a filter can alter particle morphology; BrC particles have been observed to form beads on filter fibers instead of maintain their natural shape like BC particles (Subramanian, Roden et al. 2007). It is also possible for volatile compounds to evaporate off of the filter surface during collection resulting in an incomplete measurement of particles present (Subramanian, Roden et al. 2007).

1.7.2. Single particle vs. bulk measurements

In-situ measurements operate by passing particles through a flow tube or cell where a measurement of particle optics can be made. Many different types of in-situ measurements exist, and they are commonly split between whether a single particle or bulk measurement is being made. The single particle measurements can provide significant amounts of information about the particle under investigation but can miss much of the information contained within bulk aerosol. The reverse is true of bulk measurements in that less information about specific particles is collected, but ensemble effects are quantifiable.

1.7.3. Absorption

1.7.3.1. Single particle soot photometer

Laser induced incandescence (LII) can characterize thermally refractory particles such as elemental carbon. LII does not do well with organic carbon or non-absorbing particles due to a lack of thermal incandescence. In LII, a particle is heated to its boiling point by an intense laser and subsequently incandesces. The total amount of incandescence is proportional to the mass of elemental carbon present. While LII is based upon particle absorption, LII does directly measure absorption; incandescence is a

function of mass. With an approximation of the mass absorption coefficient, absorption coefficients can be obtained. The Single-Particle Soot Photometer (SP2) is a commercially available instrument based upon the LII technique. The SP2 is also equipped with multiple photodetectors allowing for the determination of light scattering from which particle size can be inferred.

1.7.3.2. Photoacoustic Spectrometer

The photo-acoustic spectrometer (PAS) is capable of directly measuring absorption coefficients by aerosol particles. Unlike the SP2, the PAS measures the bulk absorption coefficient. It operates on a similar principle to the SP2, but has some fundamental differences. A pulsed laser is used to heat an aerosol sample. Upon absorption, the particles will transfer heat to the surrounding air and a pressure (sound) wave is created that can be detected by a microphone. The PAS suffers from non-idealities in mass transfer effects by the particle. If surface coatings, such as water or volatile organics, are present on the surface of an absorbing aerosol, these coatings can be evaporated when the particle is heated. This results in less of a pressure wave being emitted by the particle and an under-measurement of the absorption coefficient.

1.7.4. Scattering

Light scattering by aerosols is commonly measured by a Nephelometer; the integrating and polar nephelometer are the most common. In an integrating nephelometer, a flash lamp illuminates a scattering volume containing aerosol particles. The light scattered by the particles is then directed to a photomultiplier tube through a series of baffles. The amount of light reaching the PMT is directly proportional to the total scattering by the aerosol particles. Integrating nephelometers suffer from truncation angle effects; the total range of collected scattering is less than the ideal 0° to 180° . As

particle size increases, the truncation angle effect worsens because scattering shifts more toward the forward direction.

Polar nephelometers operate by illuminating a scattering volume using a laser beam. The light scattered by the particles is then measured by multiple photo-detectors placed at various angles between 0° and 180° . Polar nephelometers offer a couple distinct advantages over integrating nephelometers. Size effects can be corrected, because scattering intensity is collected as a function of angle. The elucidation of scattering phase function and asymmetry parameter is also possible from this angular information.

1.7.5. Extinction

Many measurements for extinction by aerosol particles exist, but the single-pass cell, multi-pass cell and cavity ring-down spectroscopy are the most common. In a single-pass or multi-pass extinction cell, light is directed into a large flow cell typically larger than 100 L and longer than 20 m in size. The extinction by aerosols is then measured by comparing the difference in light transmission through the cell when aerosols are present and absent. The single and multi-pass cells suffer from high limits of detection (typically greater than 20 Mm^{-1}) and physical size constraints.

To improve on the detection limits and sensitivity of the single and multi-pass cells, cavity ring-down (CRD) has been implemented for the measurement of extinction coefficients. A laser pulse is directed into an optical cavity consisting of a pair of highly reflective mirrors. As the laser pulse traverse the cavity, light intensity decays exponentially due to absorption and scattering by aerosols, the mirrors and any gases

present in the cavity. Extinction coefficients are obtained by taking the difference between decay constants when aerosols are present and absent.

1.8. Present developments & modifications

Presently, a nephelometry camera (NephCam) and a humidity-controlled cavity ring-down transmissometer (HC-CRDT) have been developed for the determination of scattering and extinction coefficients, respectively, of aerosols. The NephCam is different than either an integrating or polar nephelometer in that it uses a charge coupled device (CCD) to measure the intensity of light scattered by aerosols instead of a PMT. Like other nephelometers, the NephCam suffers from truncation angle effects, however because area based detection is being used (by virtue of the CCD), these effects can be corrected. A model simulating the physical construction of the NephCam was developed for the comparison of actual image shapes to modeled image shapes to test agreement between reality and theory.

The HC-CRDT is a 4 channel CRD that is capable of measuring the extinction coefficients of aerosols at 3 wavelengths (355 nm, 532 nm, and 1064 nm) at high (> 80%), low (< 10%) and ambient humidity simultaneously. This type of instrumental setup allows for the determination of humidity effects on the optics of aerosol particles in real time. A model to link the observed changes in extinction to theory was developed for comparison.

2. Materials & Methods

2.1. Aerosol generation system for laboratory studies

The measurement of aerosol optical properties in a laboratory setting requires a stable aerosol source capable of producing many aerosol types at different concentrations with known physical and chemical properties. Strongly scattering aerosol can be produced from solutions of ionic salts (NaCl, $(\text{NH}_4)_2\text{SO}_4$, etc.) dissolved in water. Similarly, strongly absorbing black carbon and brown carbon surrogates can be produced from Nigrosin dye and Humic acid solutions, respectively. A block diagram of the setup used is shown in figure 2-1, below.

Figure 2-1: Block diagram of the aerosol generation system used in laboratory studies.

Aerosol is generated using a modified concentric-tube nebulizer from an Atomic Absorption Spectrophotometer. A 4 L sidearm flask is sealed at the top using a rubber stopper with the nebulizer hanging suspended inside by an air inlet line. The sample eductor tube is immersed in the solution that is to be aerosolized. As dry, HEPA filtered air is passed through the nebulizer, the solution is atomized and polydisperse wet aerosol (droplets) is produced. Delivery pressure to the nebulizer was controlled using a step-down delivery system; house air at 50 psi was delivered to a 3 gallon ballast. Air from the ballast was then delivered to the nebulizer at 25 psi. A step down system was necessary since small fluctuations in delivery line pressure to the nebulizer can cause significant changes in the particle size distribution. Increased pressure increases the

aerosol number concentration, but decreases geometric mean size of the droplets and thus the dried particles. Increasing solute concentration in the aerosol solution results in an increase in both aerosol number concentration and geometric mean size. A major advantage of this strategy is that the copious amount of water droplets that are produced by the nebulizer get recaptured and recycled within the flask, so the solutions can be used continuously for days.

The flask used in the aerosol generation is connected directly to a 20 L aluminum pot (turkey deep fryer) using a short (~ 1") piece of rubber tubing that seals the sidearm outlet to a hole in the side of the pot. HEPA filtered dilution air at 30 Lpm enters the mixing pot from the opposite side of the aerosol stream. This results in a swirling air pattern within the mixing pot that encourages mixing and drying of the aerosol droplets. The perforated poultry rack (from the turkey deep fryer) is inverted so that aerosol must pass upwards through the holes in the rack to enter the 4" PVC exit tube, ensuring that the aerosol is well mixed before leaving the mixing pot. During size-selected experiments, the dilution air stream is dried by passing it through a silica gel dryer. During the non-size selected experiments, the RH of the dilution air was controlled by splitting the dilution air and passing it through a silica gel dryer to lower RH and/or a bubbler to increase RH. By controlling the flow rates through each side of the split, the ambient RH could be raised or lowered from near 50% to less than 10% depending upon ambient temperature.

Aerosol exits the mixing pot through a 4" O.D. piece of PVC pipe connected to a 4" O.D. aluminum HVAC duct for transport to a modified and combined pair of Aluminum registers that form a 4" x 4" x 8" box with diagonal inlet and outlets. In the

non-size selected experiments, an aerosol cyclone (URG 2000-30EQ, Teflon coated aluminum cyclones with a nominal 1.0 μm cutoff at 6 Lpm flow) is placed in this box and connected to 1/2" Cu tubing for transport to the instruments using modified wide-bore Swagelok fittings. For the size-selected experiments, only the 1/2" Cu tubing is present as aerosols are directly transported to the DMA (the DMA has a 1.0 μm impactor so the cyclone was not necessary). The register box sits in line with the Aluminum HVAC tube and a squirrel cage blower that controls the aerosol flow and exhaust to the fume hood.

2.2. NephCam

2.2.1. Theory of operation

Bulk aerosol scattering coefficients are commonly measured using a nephelometer. In a traditional integrating nephelometer, such as the Radiance Research M903 (figure 2-2) a flash lamp is pulsed inside of a sample chamber, illuminating aerosol particles with broadband incoherent light. Scattered light is directed through a series of baffles and a bandpass filter (not shown) to a photomultiplier. The baffles are arranged so that the light scattered toward the photomultiplier is almost directly proportional to the scattering coefficient. This type of integrating nephelometer suffers from truncation errors that cause negative bias in the measurement of the aerosol scattering coefficient for larger particles.

Figure 2-2: Schematic of a Radiance Research M903 integrating nephelometer.

The Radiance Research M903 integrating nephelometer is particularly prone to truncation errors. Because of the instrument orientation, the PMT can only collect light scattered between 10° and 170° relative to the direction of light propagation (Heintzenberg, Wiedensohler et al. 2006). As aerosols grow in size, the scattering intensity shifts towards the forward direction (0° - along the original light path); the fraction of light not detected by the PMT will also increase as the aerosols grow in size, and total scattered light intensity is under-measured. This truncation error by the Radiance Research nephelometer has been shown to grow monotonically with aerosol size and be about 5% for 200 nm aerosol and 23% for $1\ \mu\text{m}$ geometric mean diameter aerosol (Müller, Nowak et al. 2009).

The nephelometer that is incorporated into our instrument uses a different strategy, based on the *reciprocal* geometry. Digital charge coupled device (CCD) cameras are positioned orthogonally to an incident laser beam, as shown in figure 2-3. As an aerosol passes through the laser beam, light is scattered upwards towards the camera after being focused by multiple lenses. Unlike photomultipliers, CCDs are area sensitive detectors allowing a 2-dimensional representation of the aerosol scattering intensity AND thus a spatial distribution.

Figure 2-3: Schematic of NephCam.

2.2.2. Optimization of optical system

A green LED light box was created for optimization of the NephCam's physical setup. Green LED's were chosen to mimic the green diode laser used during experimentation. Images of different types of calibration images were taken to investigate the presence and effects of image distortions: targets for astigmatism, dot matrices for coma and distortion, a white background for vignetting and a checkerboard for contrast and Modular Transfer Functions (MTF's). The aperture settings were optimized to obtain the best possible contrast and image quality. Images at aperture settings of $f = 1.6$, 4 and 8 were collected.

2.2.3. Physical Construction

In theory, the scattering of a bulk aerosol could be measured by placing a detector at a 90° angle in a CRD experiment. In practice, the pulsed laser does not provide enough intensity to measure scattering. However, a continuous laser source can be used to generate enough scattered laser power to be measurable. We designed and built a new type of scattering instrument that we call nephelometry cameras (NephCams) that use a CCD detector to measure aerosol light scattering. This scattering measurement is complementary to the extinction measurement produced by the HC-CRDT. A schematic diagram of the NephCams can be seen in figure 2-4.

Figure 2-4: Block diagram of the NephCam aerosol scattering instrument.

Images of light scattering by aerosols are taken using one CCD camera (ThorLabs DCU224M USB – 1.3 MPixel monochrome CCD, 1280x1024 pixels) per channel. The NephCam instrument body was constructed from a 6" x 4" x 1.5" (L x W x H) aluminum block. Two 1/2" Al rods and a 90-degree rod mount were used to form a rigid scaffold which was affixed to the NephCam body using JB-Weld to serve as a camera mounting arm. The camera is aligned orthogonally above the aerosol flow and laser beam. Cameras are aligned such that laser beam propagates along the long (x-axis) such that image pixels 0 and 1279 are forward and backward, respectively. NephCams view light scattering through a 1.0" glass window.

A green laser diode (Information Unlimited LM532-20, 20 mW, $\lambda = 532$ nm) was mounted in an Al mount using thermally conductive epoxy (Arctic Silver). This laser mount was attached to the camera mount using a 1" section of straight copper tubing to ensure proper alignment. The laser beam passes through a 7/16" diameter hole cut through the length of the NephCam body (as shown in figure 2-4, Top View). A single laser baffle is present before the laser enters the scattering volume to reduce diffractive spreading. Without the inclusion of a laser baffle, diffractive spreading leads to significant wall scattering interference. Laser light that is not scattered is optically removed using a beam dump at the far end of the camera mount.

Aerosol flow propagates through a 1" hole cut corner to corner of the Al block and crosses the laser beam axis at an acute ($\sim 16^\circ$) angle. Light scattering takes place in the center of the flow axis, minimizing wall interference. Two 1/2" to 3/4" Cu pipe unions provide the step up/down from the 1" aerosol flow channel to 1/2" sections of straight Cu pipe. The 1/2" straight pipe is then further reduced to 1/2" Cu tube using Swagelok fittings. This 1/2" Cu tube connects the NephCams to the valving system and input of the HC-CRDT. Scattering images are focused onto the CCD using a plano-convex lens (ThorLabs, focal length = 25.4 mm, diameter = 1") and a CCTV lens system (Tamaron MVL25, focal length = 0.25 m, aperture = 1.6).

2.2.4. Computer system and data collection

Data collection for all 4 cameras was controlled using LabView 8.6 vi's and the uc480 drivers supplied by ThorLabs. Prior to data collection, all cameras were initialized to use a digital trigger, 10 second exposure length, and a master gain of 1. Image settings

were initialized to a Y8 Monochrome color scheme (8-bit, black and white) and an image size of 1280 by 1024 pixels (full sensor area).

Semaphore control of the ThorLabs uc480 drivers and image buffer required that image triggering and transfer be done sequentially for each channel. Image collection was initiated by a digital trigger that takes approximately 10 msec to complete. After image exposure, image data was read from the camera to the uc480 buffer; approximately 25 msec. Immediately after transfer the image data was written into an IMAQ buffer in LabView so that the uc480 buffer could be reused for other channels. Because of this semaphore control scheme, the camera triggering and data transfer processes were spaced 50 msec apart between channels to ensure that both processes had enough time to complete with extra overhead in case of computer lag.

Images collected by the cameras were stored directly as .jpeg files with no compression. The images are converted to data arrays during the analysis. Time stamps, image number and valve state of the HC-CRDT were written to a separate Excel comma separated values (.CSV) file. Valve states were read from the PXI box on the HC-CRDT computer using a local area network connection.

2.2.5. Data processing and analysis

Raw images taken by the NephCams require significant processing for the extraction of aerosol size and aerosol scattering coefficients. As with the HC-CRDT, the NephCams require that the difference between clean and aerosol laden air be calculated to determine aerosol contribution. From the resulting difference images, information about aerosol size and aerosol scattering coefficients can be extracted by using image information along the horizontal and vertical axes, respectively. While this background

subtraction method is the basis for image processing, there are other image components that must be accounted for to extract the desired information; i.e. hotpixel effects, laser intensity fluctuations and the statistical distribution of aerosols within the images.

The ThorLabs DCU224M cameras are known to suffer from hot pixels; these are pixels with significantly higher intensity than the surrounding pixels, even though increased intensity is not actually present at that pixel location. Hot pixels locations do not change location in time for a given experiment, but do fluctuate in intensity. Between experiments, the hot pixels can shift in location. To remove the effect of hot pixels, a LabView code was written to screen for hot pixels. Image pixels are compared to all neighboring pixels and if current pixel intensity has more than a 40% deviation from the average value of the surrounding pixels, the current pixel is assigned the average value of the surrounding pixels. LabView does provide built in capabilities to screen for hot pixels, however the LabView algorithm averages all of the pixels and assigns all the average value to all pixels instead of just the single hot pixel. A comparison of the hot pixel removal algorithms can be seen diagrammatically in figure 2-5.

50	52	50
51	255	54
53	52	51

Image

50	52	50
51	52	54
53	52	51

Our Algorithm

74	74	74
74	74	74
74	74	74

LabView Algorithm

Figure 2-5: Image processing for hot pixel removal. Left, original image; center, our algorithm; right, LabView's algorithm.

The 1.6 aperture setting used for results in significant vignetting; image intensity falls off from center as $\cos^4$ due to non-normal intersection of the CCD and scattered radiation. This $\cos^4$ weighting was applied to the NephCam images to flatten the image and correct for the effect of vignetting.

The diode lasers used in the NephCams are quoted to have a power stability of 10%. This implies that fluctuations in laser intensity directly impact NephCam images since the intensity of scattered light by aerosols is dependent upon both the aerosol scattering cross-section and the intensity of incident radiation. To correct for this effect, the average gray level was used; this is a measure of the average image intensity across the entire image. Average gray level directly correlates with laser power during clean cycles. By applying the assumption that laser power does not change drastically at any given moment in time, i.e. it doesn't jump up or down but rather follows a smooth curve, a 3rd order polynomial fit of gray level versus time for clean cycles was applied. This polynomial fit was then extended to apply a laser power correction term during ambient cycles. The average gray level during ambient cycles does not correlate directly with laser intensity since the ambient cycle intensity is also influenced by aerosol light scattering.

2.2.6. Scattering coefficients and size information

For the extraction of scattering coefficients and particle size information, all clean images were averaged (after gray weighting and hot pixel removal). Ambient images were averaged to 240 sec. Any image taken during a valve transition was dropped from analysis along with the subsequent 5 images (approximately 1 minute). The resulting clean images were then subtracted from the ambient images. This difference image was then row averaged and the resulting image shape fit using a Lorentzian with a linear offset:

$$z = \frac{A}{1 + \frac{(x-\mu)^2}{g^2}} + mx + b \quad (\text{eq 2-2})$$

Where x is pixel location (0 to 1024), z is pixel intensity, μ is the center, g is the scale parameter to specify half-width half-maximum, m is the slope of the background and b is the offset. The calculated amplitude term directly relates to b_{scat} . To determine particle size, the central 100 rows were removed from the difference image and column averaged. The resulting shape function correlates to aerosol size.

2.3. NephCam size selected experiments

Monodisperse ammonium sulfate (AS) aerosols were measured for NephCam calibration and elucidation of size to image shape correlation. A block diagram of the flow system setup during these experiments can be seen in figure 2-6. Aerosol particles were generated in the system described above and mixed with dry dilution air before sampling through the AI HVAC register. Immediately after sampling, the particles were size selected using a TSI 3081 long DMA (aerosol flow 0.33 Lpm, sheath flow 2.2 Lpm). This set of flow conditions results in geometric standard deviation of 1.25 about mobility diameter set by the DMA.

Figure 2-6: Block diagram of instrumental setup during size-selected experiments.

A second stream of dry dilution air was pulled into the 20L mixing pot (this is a secondary mixing pot after the one in the aerosol generation system) from excess flow

caused by the HC-CRDT pumps and the CPC. While this secondary dilution was not desirable because it greatly reduced monodisperse particle concentration it was necessary to minimize ambient air leakage into the HC-CRDT from pressures significantly below ambient.

AS was used as the test aerosol because absorption is negligible - ring-down and NephCam measurements equivalent - has a moderate ERH between 37 and 40% (Tang and Munkelwitz 1994) and crystallizes to a near spherical shape so Mie theory can be applied. Prior to size selection, it was necessary to dry the aerosol to below the ERH. This ensured that the particle sizes selected by the DMA were equivalent to the particle sizes reaching the NephCams and HC-CRDT; had particles been non-effloresced prior to sizing, particle diameter can change due to fluctuations in RH. The humidifier and dryer were removed from the HC-CRDT for these experiments for similar reasons.

2.3.1. "Drift-down" experiments

The size-selected experiments were done as "drift down" experiments; particle concentration (and extinction/scattering) was started high and allowed to slowly decrease in time; the impactor on the DMA became clogged with salt from the high concentrations of AS solution required (1500 - 16000 ppm). Depending upon salt solution concentration, experiments would last between 2 and 8 hours; higher salt solution concentrations had shorter experiment lengths. In very high salt limit, multiple data sets were run. Data collection was stopped when there was not enough aerosol reaching the HC-CRDT for detection.

2.4. HC-CRDT

2.4.1. Theory of operation

The use of cavity ring-down has been well documented, so only a brief review will be presented here (Bulatov, Fisher et al. 2002; Atkinson 2003; Moosmuller, Varma et al. 2005). A conceptual diagram of a cavity ring-down transmissometer (CRDT) can be seen in Figure 2-7 below:

Figure 2-7: Conceptual diagram of a cavity ring-down instrument.

Nanosecond laser pulses are injected into an optical cavity formed from two highly reflective ($R > 99\%$) mirrors. The intra-cavity intensity decays exponentially due to absorption, scattering and mirror transmission as the beam traverses the cavity

$$I = I_0 e^{-\beta t} \quad (\text{eq 2-3})$$

where I_0 and I are the initial beam intensity and the intensity at time t , and β is the decay constant (s^{-1}). Decay constants in units of inverse length Mm^{-1} are obtained using the speed of light

$$\beta(\text{Mm}^{-1}) = \frac{\beta(\text{s}^{-1})}{c \left(\frac{\text{m}}{\text{s}} \right)} \times \frac{10^6 \text{m}}{\text{Mm}} \quad (\text{eq 2-4})$$

Our preferred unit of measurement is the inverse megameter (Mm^{-1}) which corresponds to a loss of 1 part per million of the light per meter of air traversed. In practice, the intra-mirror cavity length and the length of the aerosol sample inside the cavity are not equivalent. To account for this difference, a correction of the ratio of lengths is applied

$$\beta(Mm^{-1}) = \frac{\beta(s^{-1})}{c(m/s)} \times \frac{10^6 m}{Mm} \times \frac{l_{cavity}}{l_{aerosol}} \quad (\text{eq 2-5})$$

where l_{cavity} and $l_{aerosol}$ are the cavity and aerosol length. Extinction coefficients (b_{ext}) for aerosols can be determined by calculating the difference in decay constants between the aerosol sample and a clean air background. Mathematically:

$$b_{ext}(Mm^{-1}) = (\beta_{aerosol} - \beta_{clean}) \quad (\text{eq 2-6})$$

Clean air is generated by passing the aerosol sample through a HEPA filter to remove all radiatively significant particles.

2.4.2. Physical construction

A Humidity Controlled – Cavity Ring-Down Transmissometer (HC-CRDT) was developed in our lab. A detailed block diagram of the HC-CRDT can be seen in figure 2-8. A system of 4 aerosol flow lines and ring-down cavities each incorporating 3 laser wavelengths ($\lambda = 355, 532, 1064$ nm) was constructed for the measurement of extinction by aerosol particles as a function of relative humidity. These 4 independent aerosol flow/CRD systems will be referred to as channels. Depending upon the type of experiment being conducted – intra-cavity comparison, humidity control investigation, or ambient measurements/field work – the HC-CRDT can be operated in different flow modes. Since only laboratory experiments were performed, the 4 channels will be referred to as Ambient-A, Ambient-B, Dry and Humidified. In the field, a slightly different flow setup is used.

Nanosecond laser pulses are generated by an Nd:YAG laser (Big Sky Laser CFR200, 15 Hz) at the fundamental and 2nd and 3rd harmonics; 1064 nm, 532 nm and 355 nm, respectively. These laser pulses are transferred to the instrument via fiber optic bundles. A separate fiber optic bundle is used for each wavelength. A single fiber optic

Figure 2-8: Schematic of the HC-CRDT instrument.

bundle is split in quadrature to deliver each given wavelength to all 4 channels simultaneously.

Prior to cavity delivery, laser pulses are shaped by 2 lenses; a 3 mm diameter x 3 mm focal length plano-convex mounted to the end of the fiber bundle and a 10 mm diameter x 500 mm focal length plano-convex in a focusing block ~1" from the cavity mirror. This results in a scrambling of the "spotty" image produced by the individual fibers in the bundle and a rough (~ 0.5 cm diameter) focusing of the laser intensity at the opposite mirror. The 355 nm and 532 nm laser pulses also pass through a corresponding bandpass filter to remove residual contributions of other wavelengths (1064 and 532 nm in the 355 nm, and 1064 nm and 355 nm in the 532 nm).

Each wavelength is contained within the optical cavity by a pair of highly reflective mirrors: 1064 nm (Layertec, LLC., $r = 1000$ mm, $R > 99.98\%$), 532 nm (Layertec, $r = 1000$ mm, $R > 99.98\%$), and 355 nm (Layertec, $r = 1000$ mm, $R > 99.9\%$). The 3 mirrors are positioned in a triangular pattern so that the optical path of each wavelength is parallel to the cavity axis and aerosol flow.

Light exiting the cavity for each wavelength is passed through a corresponding Schott glass cutoff filter and a 10 mm diameter 100 mm focal length plano-convex lens before reaching a detector. Detector signals are carried by 3 m long SMB co-axial cables to a pair of National Instruments PXI-5150 high speed 8 channel digitizers mounted in a National Instruments PXI-8105 (2.0 GHz Intel Core Duo T2500 dual core-processor, 512 MB dual channel 667 MHz DDR2 RAM, Windows XP) chassis. This design allows for the rapid and real-time collection of the decay signals because the fast A/D conversion is directly present on the PCI bus, allowing signals to be collected and processed at high

speed and overall high throughput. All 12 data streams – 4 channels with 3 wavelengths each – can be digitized, processed and stored simultaneously at the operating speed of the laser (15 Hz). Data collection and processing is controlled by custom LabView 2010 vi's.

Data collection is initiated by triggering data acquisitions off the laser's Q-switch synch line. Analog voltages from all 12 detectors are sampled for approximately 68 μsec corresponding to a data string of 4096 points. From the full 4096 data points, a portion is dropped on the front end to remove the non-exponential portion of the signal. Exact magnitude of truncation varies slightly by channel depending upon total light intensity transmitted by the individual fibers, but is in the range of 200, 400 and 0 points for the IR, Vis and UV, respectively. The exponential decay constant of each ring-down signal is then calculated using the direct sums algorithm (Everest and Atkinson 2008). Data array lengths are further truncated to a number of samples that corresponds to 6 times the $1/e$ time from the previous decay ($5 - 7 \tau$ was determined to be the best compromise for relevant noise levels) (Everest and Atkinson 2008). After calculation of the exponential decay constants, this data is logged to an Excel comma separated values (CSV) file and the raw ring-down data is discarded. Thus 12 ring-down decay constants are recorded from a single laser pulse 15 times per second (180 Hz real-time measurement rate).

Separate but identical optical cavities exist for each of the 4 channels. Aerosols enter and exit a 1 m long 34 mm square extruded aluminum tube (ThorLabs XT34 system, 29 mm ID) at either end through 3/4" tube ports at 45° angles to minimize flow disturbances (figure 2-8). To prevent mirror contamination, a filtered air back-flush flow is generated. A double-headed peristaltic pump (Stenner Pump Company 170DM5)

circulates air through a HEPA filter and the dead space between the mirrors and aerosol flow ports on all 4 channels. Since only a single double-headed peristaltic pump is used, a single head must be used as the backflush for both ends of a pair of channels. This translates to the backflush air flow being split end-to-end and then between a pair of cavities. Flow lines are recombined for return to the peristaltic pump. Total backflush flow to one end of a single channel is 50 cc/min. To minimize "cross-talk" between the backflush streams, air enters between two cavities and exits on the periphery.

The main aerosol flow through the HC-CRDT is controlled by a pair of linear pumps (EMS MegaLite IAQ Pump, Model # 6025SE-V) at 2.0 Lpm; 1.0 Lpm flow per channel. Since a single head of the peristaltic pump is split between a pair of channels, it was also necessary to pull aerosol flow using a single pump split between the same pairs of channels. This prevents "cross-talk" between the channels from the common backflush connection and small variations in aerosol flow. The Ambient-A and Dry channels form one flow pair while the Ambient-B and Humidified channels form another flow pair.

All aerosol containing parts were constructed from metal (Cu or Al) to minimize static charging or water adsorption effects and consequent loss of particles. All metal pieces were grounded at various locations throughout the system using wire to eliminate local static charging.

The determination of aerosol extinction coefficients requires that the extinction of both particle-laden and particle-free air be measured separately, as mentioned in the discussion of eq. 2-6. Particle-laden air is directly sampled; while particle-free air is obtained by passing the same aerosol through a HEPA filter (Whatman Hepa-Cap) using

a pair of electrically actuated 3-way valves (Assured Automation 31DXV4). Separate valves and HEPA filters were installed for each channel (see figure 2-8) and are computer controlled by a Measurement Computing relay board (USB-ERB08, 8-channel electromechanical) and custom LabView 2010 vi's.

2.4.3. RH sensors and location

Relative humidity and temperature are also measured every second at various points in the instrument (figure 2-8) using six Vaisala HMP50 RH/T sensors. (A seventh RH/T sensor is present on the Dry Valve, however the temperature measurement has malfunctioned.) These sensors are connected in line with the flow system using Ultra-Torr vacuum fittings. Digitization and archival of the 1 Hz relative humidity and temperature measurements is accomplished using a high speed 8 channel 16 bit A/D converter (Measurement Computing USB-1616FS) controlled by custom LabView 2010 vi's.

2.4.4. Humidifier/Dryer

The relative humidity of the Humidified and Dry channels is controlled using a humidifier and dryer, respectively, fashioned after the commercially available TSI 3062 Diffusion Dryer. Aerosols traverse the humidifier and dryer through a 2 foot section of 1" diameter stainless steel perforated tube (La Choppers, 1/8" diameter holes, 3/8" staggered centers) surrounded by a stainless steel mesh. Dryer and humidifier are connected to HC-CRDT flow lines using 1/2" Swagelok fittings. The external casing of the dryer was made from a 3" OD, 2 3/4" ID acrylic tube with properly sized end caps. The void between the stainless tube and acrylic tube was filled with Silica gel desiccant (Fisher Scientific, indicating, 4-8 mesh). The acrylic tube diameter of the dryer is larger than that of the humidifier to allow for easier desiccant exchange through 1/4" NPT

plugs. The external casing of the humidifier was made from a 1 3/4" OD, 1 1/4" ID acrylic tube with properly sized end caps. The stainless steel tube in the humidifier was wrapped using water wick (Wickstore.com #756). An external water reservoir supplies a constant water flow through the wick to the humidifier. Excess water from the wick drains to a reservoir to avoid entrapment in flow lines. Stainless steel mesh surrounding stainless perforated tube was included to prevent desiccant and water wick from entering the aerosol particle flow line and scavenging aerosol. End to end electrical conductivity ($< 10 \Omega$) of the humidifier and dryer (across Swagelok fittings and stainless steel tube) was checked periodically for the prevention of particle loss to static charging.

2.4.5. Data processing and analysis

The HC-CRDT measures the total extinction coefficients of a bulk aerosol sample ($b_{ext,TOT}$). This total extinction includes losses from aerosol ($b_{ext,aerosol}$), background air ($b_{ext,bkg}$), mirror transmission ($b_{ext,mirrors}$) and any other non-aerosol extinction loss (b_{other}):

$$b_{ext,TOT} = b_{ext,aerosol} + b_{ext,bkg} + b_{ext,mirrors} + b_{ext,other} \quad (\text{eq 2-7})$$

The measurement of aerosol extinction coefficients requires the separation of extinction due to the presence of aerosol ($b_{ext,aerosol}$) and all other losses. Experimentally, this is accomplished by passing the aerosol flow through a HEPA filter to remove the aerosol particles. These "clean air" cycles allow for the measurement of a single extinction coefficient that represents the extinction caused by all non-aerosol loss mechanisms (background, mirrors, other). The clean air background signal changes slowly in time, so a linear regression of background extinction versus time is performed on the clean cycles on either side of an aerosol cycle. These background subtractions are performed using LabView 2010 vi's on all ring-down data.

2.5. Allan Variance

An Allan Variance analysis was performed on the HC-CRDT to determine instrument stability as a function of random noise and drift. It also serves as a measure for the minimum variance in a measurement as a function of integration time. To perform the Allan Variance, dry, filtered air was sampled by the HC-CRDT for 24 hours. Valve control on the HC-CRDT was disabled and all valves were left in the clean state. Data analysis was done using an Igor Pro (Wave Metrics, v. 1.6.2.1) script obtained from Andrew Freedman at Aerodyne, Inc (Freedman 2009).

2.6. Humidification experiments

2.6.1. Flow system setup

For the humidification experiments, a slightly different flow setup was used to allow for the measuring of extinction coefficients of a polydisperse aerosol. A block diagram of the flow system can be seen in figure 2-9.

Figure 2-9: Block diagram of flow system setup for Humidification experiments.

Aerosols produced in the aerosol generation system were mixed with dilution air. of varying humidities ranging between approximately 50% and 10% RH. RH of the dilution air was controlled by a split line on the dilution air stream that allowed the air stream to pass through a dryer and/or bubbler to lower or raise the humidity, respectively.

The RH of the system was allowed to stabilize at either dry ($\sim 10\%$) or wet ($\sim 50\%$) prior to starting data collection. After a couple of data cycles, the dilution air flow was changed slightly to raise or lower the ambient RH, respectively. In the experiments where RH was increased from dry to wet, some of the data in the transition region had to be removed due to the presence of water droplets getting into the flow lines. During the RH decreasing experiments, this was not a problem since the system was allowed to equilibrate and remove all water droplets before data collection began.

Aerosols were directly sampled into the secondary 20L mixing pot through a URG-2000-30EQ cyclone. Total flow of all instruments was approximately 6.0 Lpm corresponding to a cut-point of $1.0\ \mu\text{m}$ at the cyclone. A secondary dilution was not implemented to maintain a consistent RH within the second mixing pot. Also, sufficient flow from aerosol generation was available so sampling through the cyclone did not induce ambient air leakage into the HC-CRDT (sampling very near ambient pressure).

The DMA was operated in scanning mode with a TSI CPC3776 downstream for the measurement of size distributions. Sheath and aerosol flows were set to 1.15 and 2.2 Lpm, respectively. Scan time was 180 sec up with a 15 sec retrace. The ratio of sheath to aerosol flows results in a tradeoff between the sharpness of cutoff for a given size bin and total width of the size distribution. We chose to maximize the width of the collected size distributions (16.8 nm to 982.2 nm) to most closely mimic the particle sizes passing through the cyclone. A TSI CPC 3007 was operated in parallel to measure total particle concentration in addition to the size distribution measurement.

Correction factors for particle transmission through the HC-CRDT were calculated for this flow system using AS aerosols. Humidity controls were not used for

the generation of these correction factors as they were measured separately. A schematic for the setup to measure particle transmission by the Humidifier and Dryer can be seen in figure 2-10.

Figure 2-10: Block diagram of the flow system used to measure particle transmission through the Humidifier and Dryer.

To measure particle transmission by the Humidifier and Dryer, 20 ppm AS and Nigrosin solutions were aerosolized. These particles were then sampled at the HVAC register through the URG-2000-30EQ. This line was split to allow aerosol particles to travel through the Humidifier, Dryer or a 1/2" Cu tube or to a TSI CPC 3007 for the determination of number concentration. Tube leaving the Humidifier, Dryer or Cu tube was split again to allow for a second count by a TSI CPC 3776 (0.3 Lpm flow). Flow going to the EMS pump was set to 0.7 Lpm to mimic the typical flow and particles losses through the humidifier and dryer (1.0 Lpm).

2.6.2. Aerosols used

Humidification experiments were performed on solutions of AS, NaNO₃, NaCl and Nigrosin. The Nigrosin represents a black carbon surrogate. All species were chosen because of water solubility; core-shell type morphologies were assumed to not be

occurring for modeling of the water uptake and change in optical properties by these aerosols.

3. Results & Discussion - NephCam experiments

3.1. NephCam characterization and getting good image results

The NephCams were constructed using a CCD so both shape and intensity information could be obtained for scattering measurements. As with any camera or imaging system, characterization of the physical design (optics and image collection surface at the CCD) is necessary to produce images of optimal quality so the most information can be extracted from an image.

The quality of an image generated in any photographic system is ultimately a function of the lens system employed. The aberrations, or imperfections, in an image can be classified into 6 primary types: spherical aberration, coma, astigmatism and field curvature, oblique spherical aberration, distortion and chromatic effects (Cox 1966). For the NephCam setup employed, oblique spherical aberration and chromatic effects do not need to be considered; these are only present when multiple wavelengths are used. The diode laser employed in the NephCams operates at 532 nm. Each aberration has its own effect on image quality and the resulting image; however, the complete removal of all aberrations is impossible due to the opposing nature of many aberrations.

3.1.1. Targets

Lens curvature results in spherical aberrations; not all rays passing through a spherical surface are imaged to the same point. It arises from light entering at the edge of the optic being focused to slightly different location than light entering near the center of the optic as shown in figure 3-1. The presence of spherical aberrations can result in radial blur and astigmatism; images appear to blur towards the edges and different lines of focus in an image are obtained. This effect worsens as the aperture is stopped down (closing of the aperture, higher f-stop) and is directly linked to light diffraction by the

aperture. The easiest way to correct this problem is to stop up (open the aperture, lower f-stop).

Figure 3-1: Physical representation of spherical aberrations being caused by lens curvature.

If only radial blur was present, then the camera sensor surface could be curved to remove the effect. In most cameras the sensor surfaces are flat, not curved. Thus, rays imaged by a lens system need to be focused both radially (sagittal focus) and tangentially (tangential focus) for the best possible image. If both types of focus are not obtained, astigmatism results. The effects of astigmatism can be seen in figure 3-2. When sagittal focus, but not tangential focus, is obtained, lines going around the radial direction of the lens are not in focus while those crossing through the center of the image are focused. When tangential focus, but not sagittal focus, is obtained, the reverse is true. If astigmatism and radial blur are minimized concurrently, a focused image in all directions is obtained.

Figure 3-2: Physical representation of astigmatism in the sagittal (middle) and tangential (right) focus. The left image represents an image where astigmatism is not present.

Figure 3-3: Image of target by digital Nikon D40, 9 MPixel SLR camera backlit with ambient lighting. Target has been white balanced and corrected to give maximum contrast and highlight shape.

Figure 3-4: Normalized NephCam images of the target in the figure 3-3 with aperture settings of 1.6 (left), 4 (center) and 8 (right).

Maximum image intensity for all targets is slightly off center. This resulted from the 1" light-harvesting lens not being perfectly centered over the CCTV lens. This effect was corrected during actual NephCam operation, but the effects of astigmatism are still evident. The 1.6 aperture setting does a very good job of reproducing the original target image. As the aperture is stopped down, signs of sagittal blur are evident and worsen

with decreasing aperture size (higher f number). The tangential focus in all of the images is good; vertical and horizontal crossing lines are recreated well at all aperture settings.

3.1.2. Calibration matrix

Distortions are classified as either pincushion or barrel types; straight lines on an image appear to bow inward or outward, respectively, like the shape of a pincushion or barrel. Figure 3-5, shows the general shape of barrel versus pincushion distortions; left and right, respectively.

Figure 3-5: Square grid without distortion (left), barrel distortion (center) and pincushion distortion (right).

Coma can arise from distortions. When imaged rays do not originate on the optical axis, but somewhere off axis, images exhibit a "comet" like shape with intensity diffusing away or towards the center of the image as shown in figure 3-6.

Figure 3-6: Physical representation of image coma; dots not located at image center show comet-like tails extending away from center.

Calibration dot matrices are useful for determining the presence of coma, pincushion and barrel distortions. Points are arranged along a grid in both the horizontal and vertical directions with regular spacing. If either pincushion or barrel distortions are

present, then the horizontal and vertical lines will appear bowed either inward or outward at image edges. Figure 3-7 shows the NephCam images of the calibration dot matrix. (For these images, the 1" light focusing lens was re-centered to remove the lens decentralization effect seen above.)

Figure 3-7: Normalized NephCam images of a dot-calibration matrix with 1.6 (left), 4 (center) and 8 (right) aperture.

As with the targets, closing the aperture causes radial blur to worsen. In the 1.6 aperture settings, the rows and columns of dots are straight. As the aperture was closed to 4 and 8 the rows of dots at the edges bow inward near the center; a pincushion distortion is present. The aperture 1.6 setting also does a good job of recreating dot matrix as a matrix of dots. In the aperture 8 settings, the dots appear to have a tail pointing outward from center. While this effect is partially attributable to radial blur, coma is also evident since the tails seem to expand from dot origin.

3.1.3. White background

Vignetting is an optical effect that occurs when the physical structure of the camera restricts light intensity from imaging correctly. Elements within the camera - aperture, lenses, etc - restrict the range of rays allowed through the system. The intensity of the image decreases radially outward following a cosine to the fourth law as a function of the angle of incidence to the sensor:

$$I_r = I_{center} \cos^4(\theta) \quad (\text{eq 3-1})$$

Where I_r is the light intensity at some radial distance r from the center, I_{center} is the intensity at the center and θ is the axial angle between I_r and I_{center} . Figure 3-8 shows this radial decrease mapped to an image.

Figure 3-8: Cause (left) and effect (right) of vignetting in an image.

This radial decrease in light can be larger than predicted by the cosine relationship due to the physical construction of the camera; the $\cos^4$ relationship represents the best case scenario. Vignetting can be avoided by stopping down the aperture and thus works in opposition to spherical aberrations.

A sheet of white paper served as a background for image collection. The resulting images by the NephCams at aperture settings of 1.6 (left), 4 (middle) and 8 (right) can be seen in figure 3-9. These images have not been normalized to show intensity effects. The image of a white background will show the presence or absence of vignetting; images should have a flat intensity. If vignetting is present, then the background image will appear curved.

Figure 3-9: NephCam images taken of a white sheet of paper at 1.6 (left), 4 (center) and 8 (right) aperture.

As the aperture is stopped down, the magnitude of the background drops off significantly as can be seen by the transition from red-yellow in the 1.6 aperture to purple-blue in the 8 aperture. This is to be expected since the amount of light reaching the CCD decreases with aperture size. The curvature of the background intensity from vignetting also decreases with decreasing aperture; at the 1.6 aperture size, the white sheet of paper appears to have some curvature to it.

3.1.4. Checkerboard

Image contrast is an important feature of high quality images. Maximum contrast is desirable; the difference in image intensity between light and dark should be maximized. Contrast works against total image intensity, higher contrast occurs when total intensity is lower. By optimizing contrast, greater resolving power is obtained. The modular transfer function (MTF) is a measure of the contrast across an image. It is calculated by normalizing the image intensity to the maximum intensity and then finding the difference between maximum and minimum:

$$MTF = \frac{Maximum - Minimum}{Maximum} \quad (\text{eq 3-2})$$

Ideally, the MTF is 1. In reality, significantly lower values are obtained; 0.2 represents a minimum MTF to extract usable information from an image. Sharper gradients in MTF's

are also preferred; transition between light and dark should occur as quickly as possible. In actual images, a tradeoff between maximum contrast and the contrast gradient usually occurs. In figure 3-10, a simulated image of a contrast line profile (alternating maximally dark and light bands) is shown. Three extremes of the resulting MTF are shown for figure 3-10 in figures 3-11, 3-12 and 3-13 as a reference for the NephCam images in figure 3-14.

Figure 3-10: Square wave image simulated using IgorPro. Minimum and maximum are 0 and 255, respectively.

Figure 3-11: Left, line profile with maximum contrast and sharp gradients. Right, MTF of this line profile.

Figure 3-12: Left, line profile with maximum contrast and weak gradients. Right, MTF of this line profile.

Figure 3-13: Left, line profile with weak contrast and sharp gradients. Right, MTF of this line profile.

In figure 3-11, ideal contrast is obtained. A distinct sharp edge between light and dark is visible. This is evident in the image shape (left) and MTF (right) by the sharp transition from light to dark (1 to 0). In figures 3-12 and 3-13, ideal contrast is not obtained. In figure 3-12, the transition from light to dark is smooth with a range of intermediate gray values. The plot of MTF (right) mirrors this non-ideality. In figure 3-13, the contrast gradient is very sharp, however total contrast between light and dark is decreased (0.5 to 1 instead of 0 to 1). Actual camera systems typically operate somewhere between the extremes in figures 3-12 and 3-13. Ideal contrast, figure 3-11, is rarely achieved.

Images of checkerboards provide a good diagnostic tool for image contrast and modular transfer functions. An image of the actual checkerboard used is shown in figure 3-14. The checkerboard images taken using the NephCams are shown in figure 3-15 for aperture settings of 1.6 (left), 4 (middle) and 8 (right).

In an ideal MTF, the transition between light and dark should be quick and hold the maximum or minimum values across the light or dark spot, respectively. If our checkerboard was perfect then these transitions would be seen as sharp transitions between the light and dark. However, these checkerboards were produced using a Xerox photocopier; the checkerboard pattern is not perfect and the transitions between light and dark are not as sharp as seen in figure 3-14 (that figure has been white balanced and contrast corrected for clarity). So, steeper gradient between light and dark represent a better MTF.

Figure 3-14: Image of checkerboard taken by digital Nikon D40 9 MPixel SLR camera backlit with ambient lighting. Target has been white balanced and corrected to give maximum contrast and highlight shape.

Figure 3-15: Intensity normalized checkerboard images with apertures of 1.6 (left), 4 (center) and 8 (right).

From the MTF images in figure 3-15, changes in contrast are centro-symmetric; the relative change between the maximum and minimum values decreases radially outward. The 8 aperture images show the greatest contrast at the middle of the image (differences between black and white are the sharpest and the strongest). However, the contrast of the 8 aperture image decreases significantly at the edges of the image. In fact, the MTF approaches an almost constant value at the edges implying that contrast here is essentially nil. In the 1.6 aperture image, the difference between light and dark is approximately constant across the image; close to 0.3. However, due to vignetting the absolute intensity of the image is decreasing radially outward. The aperture 4 setting falls somewhere between these 2 extremes, but the MTF still approaches a constant value at the edges.

These MTF's point to design constraints in NephCam image quality. The NephCams require the ability to tell light from dark - i.e. what is being measured as scattering and what is not? The smaller apertures allows for greater sensitivity to scattering in the middle of the image but little at the edges. The larger aperture does not give optimal sensitivity, actually it is just above the usable limit, but the sensitivity across the image is nearly constant. The implication is that if vignetting can be corrected at the larger aperture settings, then the 1.6 aperture can produce the best images. With the smaller aperture settings, the sensitivity may be greater but ultimately the angular scattering information near the edges of the images is lost, which is undesirable. It is harder to account for imperfections in the MTF if the MTF is not constant across the image, but imperfections in the absolute MTF (contrast) can be corrected if the MTF is constant.

3.1.5. Single line

To mimic the distribution of laser light measured by the NephCams, pieces of black masking tape were used on a white sheet of paper to create a single white line on an otherwise black background. The line was approximately 3 mm thick and was imaged using the same LED box setup as before. The collected images of the single line are shown in figure 3-16.

Figure 3-16: Normalized NephCam images of a single line with aperture settings of 1.6 (left), 4 (center) and 8 (right).

The white line shows the culmination of all of the imaging effects observed above. As the aperture is stopped down, image intensity is blurred more in the radial direction. The single line appears to have wings along the x-axis of the image at smaller apertures. The decrease in contrast near the edges of the image are also evident at smaller apertures; there is a loss in distinction between the white line and the background. Vignetting is also evident in the 1.6 aperture image; near the center of the image the background intensity is significantly higher than at the edges. However at this aperture setting the imaged line and background are clearly distinct across the entire image. As a result, the 1.6 aperture was chosen as the operational setting for the NephCam.

3.2. NephCam size based calibration experiments

The NephCam was initially calibrated using size-selected aerosols; polydisperse aerosols contain too much information and variation to initially characterize the NephCam response. By limiting the aerosols present to a narrow size bin, the effects of size on both collection efficiency (and thus calibration slope) and image shape could be elucidated. An optical response model of light scattering collected by the NephCam was constructed as a theoretical comparison to the measured data.

Using the physical parameters of the NephCams, ray tracing methods were employed to determine what the image shape collected by the NephCams *should* look like as a function of particle size. The intermediate goal was to be able to apply the NephCam response model to a distribution of aerosol particles to see if the measured and modeled image shapes correlated. The end goal is to be able to invert observed image shapes for size distribution information, however that goal is beyond the scope of this work.

The design of the NephCams and the basic parameters used in the model are illustrated in figure 3-17. The x- and y-axes are in the horizontal and vertical directions, respectively. All components of camera and aerosols are assumed to be centered and positioned relative to (0,0). A collection of aerosol particles (black, red and purple dots) are assumed to be in line with the laser beam (green line, $h\nu$) which propagates from left to right (backward to forward scattering, respectively); these aerosols have location (x_0, y_0) relative to (0,0). A 1" plano-convex light-harvesting lens is placed at its focal length (D_f) above (0,0). A CCTV lens for image collimation and magnification is placed above the back edge of the focusing lens at distance D_{CCTV} . The CCD is above the output face of the CCTV lens by distance D_{CCD} .

The naming convention used presently is: Point locations in the model are defined by lowercase (x_n, y_n) values. The uppercase values represent physical distances in the real setup like the focal length (D_f) and offset distance between the light-harvesting lens and CCTV (D_{CCTV}). The vector propagating away from a point (x_n, y_n) is (dx_n, dy_n) .

The angle of incidence of the vector $(x_n, y_n) + (dx_n, dy_n)$ to a surface are Greek letters with the subscript n (i.e. α_n). The angle of departure of the vector $(x_n, y_n) + (dx_n, dy_n)$ are Greek letters with the subscript n+1 (i.e. α_{n+1}). Greek letters are incremented as different parts of the camera system are traversed; α , β , ϵ correspond to the front edge of the light harvesting lens, the back edge of the light harvesting edge and the CCTV lens, respectively. The letters γ and δ were omitted to avoid confusion with y and d.

The model was built in x, y space only, whereas the actual NephCams operate in real space; x, y, z. All of the model calculations are a simulation of centerline image along the horizontal image when particles are at the maximum laser beam intensity. The

Figure 3-17: Physical design of NephCam and relevant parameters for defining the optical response model. Three discrete aerosol particles and the laser beam are represented by black, red and purple dots and a green line at the bottom of the figure. The CCD detector is the green bar at top and the main light-harvesting lens is shown in dark blue. The CCTV lens system is shown in gray and the lenses on either side as blue bars. Scattered radiation propagating through the camera is shown as black arrows. Normal vectors are shown as orange double-headed arrows.

diode laser used presently has a radially symmetric Gaussian intensity. Thus, the images generated by this model correspond to particles that pass directly through the center of the laser beam. On either side of the laser beam (horizontally) the intensity of the laser drops off as defined by the Gaussian profile. The mapping of a 3-D Gaussian surface to a 2-D image results in a Lorentzian image shape. The radial symmetry of the laser beam along the z-axis allows for the conservation of phase function and size information along this axis with intensity being the only changing parameter.

To trace rays through the system, the location of aerosol particles must first be defined. In x, y space:

$$\begin{bmatrix} x_{aerosol} \\ y_{aerosol} \end{bmatrix} = \begin{bmatrix} x_0 \\ y_0 \end{bmatrix} \quad (\text{eq 3-3})$$

where $x_{aerosol}$, $y_{aerosol}$ is the location of the aerosol particles. In keeping with the naming conventions used throughout the rest of the model, the location ($x_{aerosol}$, $y_{aerosol}$) will be referred to as (x_0, y_0). For simplicity, all real positions and distances (in the model's x, y space) will be given in the units of pixels for ease of mapping points to the ThorLabs DCU224M's CCD (1280 pixels along x, 1 pixel equals 4.65 μm) instead more familiar units of inches or mm.

The relative intensity and direction of light scattered by a particle is governed by the phase function, which is a function of both the refractive index and size parameter (χ). In x, y model space, the direction and intensity of scattered photons can be represented by:

$$\begin{bmatrix} x_{scatter} \\ y_{scatter} \end{bmatrix} = P \begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix} + \begin{bmatrix} x_0 \\ y_0 \end{bmatrix} \quad (\text{eq 3-4})$$

where θ is the angle between forward laser propagation and the scattered radiation and P is the power of the scatter. The points along the light-harvesting lens that are able to collect scattered light are constrained such that angle between the incident radiation (α_1) and lens normal ($\overline{n_{lens,front}}$) are less than 90° ; it is physically impossible to collect scattered light at obtuse angles using this design. The scattering angles (θ) that actually reach the CCD range between 65° and 115° depending upon the aerosol particle's x location within the laser beam.

The focal length and thus the location of the front edge of the light-harvesting lens can be calculated by first applying the lens maker's equation to the 1" focusing lens:

$$\frac{1}{D_f} = (n - 1) \left[\frac{1}{R_1} - \frac{1}{R_2} \right] \quad (\text{eq 3-5})$$

Where D_f is the focal length, n is the refractive index of the lens, and R_1 and R_2 are the radii of curvature of the front and back sides of the lens, respectively. The light-harvesting lens in the NephCams is a plano-convex lens; therefore $R_2 = \infty$. Locations on the front side of the lens (x_1, y_1) can then be calculated from:

$$\begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x \\ R_1 + D_f - \sqrt{R_1^2 - x^2} \end{bmatrix} \quad (\text{eq 3-6})$$

Where x is the x location of the points along the lens, R_1 is radius of curvature of the front side of the lens as calculated from eq 3-5, and D_f is the focal length. The location of the 1" lens is assumed to be located D_f pixels above (0,0). The scattering angle (θ) intersecting a point on the lens (x_1, y_1) is calculated from:

$$\begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = I \begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix} + \begin{bmatrix} x_0 \\ y_0 \end{bmatrix} \quad (\text{eq 3-7})$$

where (x_1, y_1) is dictated by equation 3-6 and (x_0, y_0) is the location of the aerosol particle and I is a scalar to make the points intersect. The normal vector to the light harvesting lens ($\bar{n}_{front,0}$):

$$\bar{n}_{front,0} = \begin{bmatrix} x_1 \\ -\sqrt{R_1^2 - x_1^2} \end{bmatrix} \quad (\text{eq 3-8})$$

The angle between the scattered radiation and lens normal (α_0) is calculated using the dot product:

$$\cos(\alpha_0) = \frac{\bar{I} \cdot \bar{n}_{front,0}}{\|\bar{I}\| \|\bar{n}_{front,0}\|} = \frac{\begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix} \cdot \begin{bmatrix} x_1 \\ -\sqrt{R_1^2 - x_1^2} \end{bmatrix}}{R_1} \quad (\text{eq 3-9})$$

The $\cos(\alpha_0)$ also serves as a weighting term for the collection efficiency of the 1" lens relative to the angle of incidence. For computational efficiency, the model is iterated across all lens points that could collect scattered radiation, rather than across the entire range of scattering angles θ ($0^\circ - 180^\circ$). This implies that radiation can only be collected by pixels between the tangential crossing of the lens in either the maximum or minimum direction. This tangential crossing occurs when the lens normal and scattered radiation are orthogonal ($\alpha_1 = 90^\circ$). Using this approach, the angle of scattered radiation is determined from the location of the aerosol particle and the current lens location being used. (Computationally and programmatically this method is easier than trying to trace each ray as a function of θ through the lens.)

Using Snell's law, the scattered radiation is refracted towards the lens normal (α_1) upon entering the lens:

$$n_0 \sin \alpha_0 = n_1 \sin \alpha_1 \quad (\text{eq 3-10})$$

where n_0 and n_1 are the refractive indices of air (1) and quartz (1.519473), respectively.

The vector that propagates through the light-harvesting lens ($d_{x,1}$, $d_{y,1}$) is calculated from the normal vector to the back side of the front of the light-harvesting lens ($\overline{n_{front,1}}$):

$$\overline{n_{front,1}} = \begin{bmatrix} -x_1 \\ \sqrt{r_1^2 - x_1^2} \end{bmatrix} \quad (\text{eq 3-11})$$

The vector (dx_1 , dy_1) is calculated from the dot product of α_1 :

$$\cos \alpha_1 = \frac{\overline{d_1} \cdot \overline{n_{front,1}}}{\|\overline{d_1}\| \|\overline{n_{front,1}}\|} = (\overline{dx_1} \cdot \overline{n_{front,1,x}}) + (\overline{dx_1} \cdot \overline{n_{front,1,y}}) \quad (\text{eq 3-12})$$

If the magnitudes of $\overline{d_1}$ and $\overline{n_{front,1}}$ are 1:

$$\begin{bmatrix} dx_1 \\ dy_1 \end{bmatrix} = \begin{bmatrix} \frac{2\cos(\alpha_1)n_{front,1,x} \pm \sqrt{[2\cos(\alpha_1)n_{front,1,x}]^2 - 4(\cos^2\{\alpha_1\} - n_{front,1,y}^2)}}{2} \\ \sqrt{1 - dx_1^2} \end{bmatrix} \quad (\text{eq 3-13})$$

There are 2 unique solutions to this equation, and they correspond to different vectors of scattered radiation propagating through the lens. While iterating through the model, the (-) solution is initially needed until a "cross-over" point is reached when the scattered radiation and normal vector on the inside of the lens become parallel. After this point the (+) solution is used.

From (x_1, y_1), the front of the lens location, propagation to the back of the lens (x_2, y_2) is calculated from the (dx_1, dy_1) vector:

$$\begin{bmatrix} x_2 \\ y_2 \end{bmatrix} = \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} + I \begin{bmatrix} dx_1 \\ dy_1 \end{bmatrix} \quad (\text{eq 3-14})$$

where I is an intensity scalar; (dx_1, dy_1) was normalized to derive eq 12.

To properly constrain the back of the lens, the total width of the lens is limited to 5462 pixels (1") and the back of the lens is 387 pixels (1.8 mm) behind the edge for the front of the lens. Thus, y_2 has a predefined value of:

$$y_2 = y_{\max, \text{front of lens}} + \text{back of lens thickness} \quad (\text{eq 3-15})$$

where $y_{\max, \text{front of lens}}$ is the maximum y_1 value obtained from equation 3-6. The angle of intersection (β_2) between the ray propagating through the lens and the back of the lens then needs to be calculated. Since the back of the lens is parallel to the laser beam, the normal vector for this surface is:

$$\overline{n_{\text{back},2}} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (\text{eq 3-16})$$

And

$$\cos(\beta_2) = \frac{\overline{d_1} \cdot \overline{n_{\text{back},2}}}{\|\overline{d_1}\| \|\overline{n_{\text{back},2}}\|} = \begin{bmatrix} dx_1 \\ dy_1 \end{bmatrix} \cdot \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (\text{eq 3-17})$$

Therefore:

$$\beta_2 = \cos^{-1}(dy_1) \quad (\text{eq 3-18})$$

Since the intersection angle of the scattered ray and the back of lens normal is known, the exit angle of the scattered radiation relative to lens normal (β_3) can be calculated from Snell's law:

$$n_1 \sin \beta_2 = n_0 \sin \beta_3 \quad (\text{eq 3-19})$$

where n_0 is the refractive index of air and n_1 is the refractive index of the lens. These have identical definitions as in equation 3-10, above. The ordering has been reversed to represent the ray exiting the lens into air. The propagation vector for the ray leaving the back of the focusing lens (dx_2, dy_2) is then:

$$\begin{bmatrix} dx_2 \\ dy_2 \end{bmatrix} = \begin{bmatrix} \sin^{-1}\{\cos(\beta_3)\} \\ \cos(\beta_3) \end{bmatrix} \quad (\text{eq 3-20})$$

Since the exit location and direction of the scattered radiation is known, the ray can now be traced to the entrance of the CCTV lens (x_3, y_3):

$$\begin{bmatrix} x_3 \\ y_3 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix} + I \begin{bmatrix} dx_2 \\ dy_2 \end{bmatrix} \quad (\text{eq 3-21})$$

where I is a scalar; (dx_2, dy_2) is normalized. The location of y_3 is constrained by the separation distance between the back of the 1" focusing lens and the CCTV lens

$$y_3 = y_2 + D_{CCTV} \quad (\text{eq 3-22})$$

Likewise, the intersection angle of the propagated ray and the CCTV lens is:

$$\varepsilon_2 = \cos^{-1}(dy_2) \quad (\text{eq 3-23})$$

The CCTV lens can be treated as an optical telescope; 2 lenses separated by a given distance and have known focal lengths at the entrance (f_o , objective) and exit (f_e , eyepiece) lenses:

$$\begin{bmatrix} x_4 \\ \sin(\varepsilon_4) \end{bmatrix} = \begin{bmatrix} -f_e/f_o & f_o + f_e \\ 0 & -f_o/f_e \end{bmatrix} \begin{bmatrix} x_3 \\ \sin(\varepsilon_2) \end{bmatrix} \quad (\text{eq 3-24})$$

where x_3 and ε_2 are the x location and entrance angle of the scattered ray approaching the CCTV lens, x_4 and ε_4 are the x location and exit angle of the ray leaving the CCTV lens.

The direction of light exiting the CCTV lens system is then:

$$\begin{bmatrix} dx_4 \\ dy_4 \end{bmatrix} = \begin{bmatrix} \sin(\varepsilon_4) \\ \cos(\varepsilon_4) \end{bmatrix} \quad (\text{eq 3-25})$$

If the CCTV lens system is treated as though it has unit thickness, the y -location of the CCD (y_{CCD}) is defined by the separation distance between the CCTV lens and the CCD:

$$y_{CCD} = y_3 + D_{CCD} \quad (\text{eq 3-26})$$

The intersection of the scattered radiation and the CCD can then be solved from:

$$\begin{bmatrix} x_{CCD} \\ y_{CCD} \end{bmatrix} = \begin{bmatrix} x_4 \\ y_4 \end{bmatrix} + I \begin{bmatrix} dx_4 \\ dy_4 \end{bmatrix} \quad (\text{eq 3-27})$$

The x-location of the CCD is constrained between pixels -640 and 639; the CCD has a defined size of 1280 pixels. For every aerosol pixel used, the model is iterated across all lens points and the rays propagating through the system are calculated. Any scattered ray that intersects the CCD is marked and the total intensity of the CCD at that pixel is incremented to include the additional scatter.

As shown in section 3.2.3 White Background, the intensity of light detected by the CCD has a $\cos^4$ weighting relative to the angle of intersection between the incoming ray and the camera. In figure 3-17, this corresponds to ε_5 . This value is multiplied by the intensity of the scattered ray (P in equation 3-4) as defined by the phase function.

The model is based on a discrete number of aerosol particles contained within the laser beam at any given instant in time; i.e. it is not possible to model fractions of a particle.

One thing to note about the model is that around the center of the image, the image shape shows discontinuity. This is a direct result of the model being numerically based; a discrete number of pixels was used to model the aerosols, lens systems and CCD. Near the center when the vector reaching the CCTV lens is translated to the CCD, the vector will skip for particles that are not directly centered on the front 1" focusing lens. This causes the intensity around this region to be over and under mapped since there is only a discrete number of points that can be used in the calculation. In reality, a

continuous axis is present and these skips are absent because the available range of angles and trajectories available is infinite. Increasing the number of pixels used in the model does reduce this effect, but causes the model to have a prohibitively long run-time.

Another thing to note about the NephCam images is that the image shapes are reversed on the CCD relative to the direction of laser propagation as a result of the lens system employed. To remain consistent within my presentation of images and image shapes, all images will be presented assuming the direction of laser propagation is from left to right and thus backward and forward scatter correspond to the left and right sides of the image, respectively.

3.2.1. 300 nm AS

Following the model outlined above, images for single particles at different locations within the laser beam were calculated. The phase function for a 300 nm AS particle is shown in figure 3-18. Figure 3-19 is the same phase function as figure 3-18, but it has been truncated to roughly represent the maximum range of scattering angles that can be collected by the 1" light-harvesting lens to serve as a point of reference for the ensuing discussion.

Figure 3-18: Phase function of a 300 nm AS particle as a function of scattering angle. Axes have been reversed to keep with the notion that forward scattering (0°) is to the right and backward scattering (180°) to the left.

Figure 3-19: Truncated phase function to represent the maximum range of scattered angles collected by the 1" light-harvesting lens.

The intersection angle (α_0) of the scattered radiation and the focusing lens as a function of scattering angle and particle position along the x-axis is shown in figure 3-20; x-axis locations correspond to -418 (black), 0 (red) and +418 (purple) pixels. The locations of these particles in the physical setup are shown with the same colors in figure 3-17. These locations represent a particle behind camera center, at camera center and a particle forward of camera center. As the scattering angle reaches the limits of the collection range the value of α_0 approaches 90° . Figure 3-21, shows the values of $\cos(\alpha_0)$ as a function of scattering angle (θ). This $\cos(\alpha_0)$ term represents the relative weighting that must be applied to the phase function for the collection efficiency of the 1" light-harvesting lens. When scattering angle is near 90° , collection efficiency is a maximum (1) and quickly decreases towards 0 as the limit of collected scattering is approached. The maximum collection efficiency shifts from angles greater than 90° to angles less than 90° as the particle location shifts forward in the camera's image.

Figure 3-20: Angle of intersection of light scattered by a particle with an x pixel location of 0 with the 1" focusing lens.

Figure 3-21: Cosine weight factor for scattered radiation by a particle at x pixel location of 0.

When the $\cos(\alpha_0)$ weighting is applied to the phase function in figure 3-19, the phase function's shape changes; minimum intensity now occurs at the image's edges. As particle location shifts from behind center to forward of center, the range of scattering angles collected also shifts towards the forward direction as shown in figures 3-22 and 3-23. Figure 3-22 is the amplitude as a function of scattering angle and figure 3-23 is the amplitude as a function of light harvesting lens pixel. The 2 curves show the same information, but the trends are slightly different as a result of lens curvature. In figure 3-23, it is important to note that depending upon whether the aerosol particle is behind or in front of image center the collected amplitude reaches 0 in the forward and backward directions, respectively, as a result of the $\cos(\alpha_0)$ weighting.

The phase function transmitted through the 1" light-harvesting lens is then translated upwards through the CCTV lens to the CCD. Since the CCD is smaller than both the light-harvesting lens and the CCTV lens, additional truncation of the phase function is observed as a result of the angle of departure (β_2) of the scattered ray from the focusing lens. The resulting truncated amplitude distribution as a function of scattering angle that reaches the CCD is shown in figure 3-24, for an aerosol particle behind center (black), center (red) and forward of center (purple). Translating these scattering angles to physical pixels on the CCD results in figure 3-25.

Figure 3-22: Intensity of scattered radiation being transmitted by the focusing lens as a function of scattering angle.

Figure 3-23: Intensity of scattered radiation being transmitted by the focusing lens as a function of point along the 1" light-harvesting lens.

Figure 3-24: Intensity of scattered light reaching the CCD as a function of scattering angle.

From figures 3-24 and 3-25, it is evident that different portions of the phase function are translated upwards to the CCD depending upon aerosol location. As aerosol particles shift forward in the laser beam, more backward scatter is collected by the CCD. However, when these scattering angles are translated to CCD pixel location in the model (figure 3-25), a portion of the scattered radiation appears to not reach the CCD. This is not true in the actual images but is a result of the using discrete points in the model instead of a continuous set of points. For aerosols behind image center, backscatter is not completely modeled. For aerosols forward of image center the opposite is true; forward scatter is not completely modeled. In figure 3-25, intensity values of 0 can be seen for the -418 and 418 pixels in the backward and forward directions, respectively. For aerosols located at image center, this effect is not present. The result of these edge effects on model output can be seen in figure 3-26 for modeled aerosol concentrations larger than one; the single particle case is assumed to be located at image center.

Figure 3-25: Intensity of scattered light reaching the CCD as a function of CCD pixel for aerosols located at x pixels of -418 (black), 0 (red) and 418 (purple); pixel locations relative to CCD shown in figure 1.

Figure 3-26: Normalized amplitudes of different model concentrations of 300 nm AS aerosol: 1 particle (black), 10 particles (red), 100 particles (green) and 1000 particles (blue).

Figure 3-27 below shows an actual average scattering image collected by the NephCam. In comparing figures 3-26 and 3-27, images shapes are not very similar. This discrepancy arises from two effects: the DMA sizing mechanism and NephCam MTF. The DMA sizes particles based upon electrical mobility; similar ratios of charge to size will have the same electrical mobility:

$$Z \propto \frac{q}{d_m^\gamma} \quad (\text{eq 3-28})$$

where Z is the electrical mobility, q is the charge, d_m is the equivalent mobility diameter of an equivalent spherical particle and γ is a shape factor that accounts for slip and drag

inside of the DMA. Presently, γ was assumed to be 1.6. This value was chosen because similar values have been used previously for coated soot particles; while AS is not expected to have the same morphology as coated soot, it is not expected to be a completely spherical particle either (Bueno, Havey et al. 2011). Calculated diameter values for multiply charged particles assuming base diameter of 300 nm can be seen in table 3-1. From these diameter values and the DMA's product literature, transmission ratios as a function of size and charge were calculated for each size bin. These values were then scaled to generate a discrete set of particles for modeling as seen in table 3-1 for 300 nm AS. Fractions of a particle were rounded to the nearest whole number since only a whole number of particles can be modeled. The result of considering these multiple size to charge effects can be seen in figure 3-28.

Figure 3-27: Actual average scattering image collected by the NephCam for 300 nm AS aerosol

Table 3-1: Multiple charge to size particles and fraction for a 300 nm AS aerosol

Diameter (nm)	Charge	Fraction	Concentration at:			
			1 particle	10 particles	100 particles	1000 particles
300	1	0.744	1	7	74	744
463	2	0.170	0	2	17	170
596	3	0.059	0	1	6	59
714	4	0.018	0	0	2	18
820	5	0.007	0	0	1	7
919	6	0.002	0	0	0	2

The inclusion of multiple charge-to-size effects has distinct effects on modeled image shape as seen in figures 3-28 and 3-29. In terms of total intensity, the inclusion of larger particles causes a marked increase in backward scatter and decrease in forward scatter for low particle concentrations (figure 3-28 A, 10 particles). As particle concentration increases, the inclusion of larger particles causes a dramatic increase in the total modeled intensity since larger particles are more efficient light scatterers. In shifting to the normalized intensity distributions versus pixel location, it can be seen that the inclusion of larger particles causes a shift towards the backward direction as particle concentration is increased as seen in figure 3-29; this effect was not obvious in figure 3-28.

Figure 3-28: Variation in model output with (red) and without (black) the inclusion of multiple charge to size effects for a 300 nm AS aerosol at total particle concentrations of 10 (A), 100 (B) and 1000 (C).

Figure 3-29: Normalized amplitudes of different concentrations of 300nm AS aerosol including the multiple charge to size effects in table 3-1. Total particle concentrations are 1 (black), 10 (red), 100 (green) and 1000 (blue).

The inclusion of multiple charge-to-size particles partially explains the discrepancy between measured and modeled image shapes figures 3-26 and 3-27. Another source of discrepancy is the MTF of the NephCam. In all model calculations, the MTF was assumed to be 1; i.e. maximum relative difference between light and dark. In reality, the MTF of the 1.6 aperture setting of the NephCams is closer to 0.3 (figure 3-15). To correct for the non-ideal contrast, the normalized NephCam images were re-scaled:

$$Amplitude_{corrected} = \frac{Amplitude_{normalized} - (\min(Amplitude_{normalized}) - 0.1)}{0.3} \quad (\text{eq 3-29})$$

where $Amplitude_{corrected}$ is the corrected amplitude, $Amplitude_{normalized}$ is the normalized amplitude at a given pixel, and $\min(Amplitude_{normalized})$ is the minimum value of the entire array. An additional offset of 0.1 was included since the minimum value of the array does not represent a dark pixel but rather something above dark (due to Rayleigh scattering and stray light). After applying these corrections, a new normalized x-axis average image was generated and can be seen as the magenta trace in figure 3-30. All of

the data shown in figure 3-29 has been re-plotted with the same color scheme for comparison along with the original image shape in copper.

Figure 3-30: Normalized amplitudes of different concentrations of 300 nm AS aerosol including the multiple charge to size effects in table 3-1. Total particle concentrations are 1 (black), 10 (red), 100 (green) and 1000 (blue). The copper and magenta traces represent the original x-axis average image from the NephCam and the image after MTF correction has been applied.

The application of contrast correction to the original NephCam x-axis average significantly increases the agreement between modeled image shapes with multiple charge-to-size effects and measured image shapes as seen in figure 3-30. Across the center of the image, the traces that include larger particle effects overlap well with the measured image; the actual image appears to span the range of image shapes between the 10 and 1000 particle model shapes. This implies that the actual distribution of multiple charge-to-size particles is different than that presented here. Further, the distribution of multiple charge-to-size particles is expected to shift depending upon the base size distribution. A better understanding of the actual particle sizes and distributions present in the camera is necessary for improving model predictions. The non-monotonic behavior of the actual image is most likely a result of particle distribution effects; the model assumes that all particles are evenly and linearly spaced across the image. In

reality, this spacing is probably not accurate and instead a random or statistical distribution of particles within the image beam should be used. In the backward scatter and forward scatter directions (approaching pixels 0 and 1240, respectively), the measured and modeled images do not agree as well, but this is probably due to improper characterization of edge effects in the model.

3.2.2. 100 nm AS

Similar trends are seen for other AS particle sizes; the 100 nm case is shown below. In figure 3-31, normalized image shapes for 100 nm AS - with multiplets - at concentrations of 10 (red), 100 (green) and 1000 (blue) are shown. The 1 particle case has been omitted because the normalized amplitude for a single particle at 100 nm is a flat line at 1.0; model output is only 3 decimal places and higher precision is required for these values. However, the actual model does operate using more significant digits. In table 3-2, the particle sizes included as multiplets and their modeled concentrations are shown. Again, image shape agreement between the actual image and the model improves after the MTF has been applied (Contrast, magenta). Good agreement between the actual image and the model is also obtained, but this arises from the fact that 100 nm particles have a phase function that is very symmetric in all directions. Agreement could be further improved by including a 306 nm particle in the model calculations; it was not included because the probability of obtaining a particle of 306 nm with a +6 charge is essentially 0 (larger particles are more accommodating to higher charges).

Figure 3-31: Normalized model amplitudes for a 100 nm AS aerosol with multiplets assuming 10 (red), 100 (green) and 1000 (blue) aerosol particles. Actual image shape is shown in copper and the corrected image shape after MTF correction has been applied.

Table 3-2: Multiple charge to size particles and fraction for a 100nm AS aerosol

Diameter (nm)	Charge	Fraction	Concentration at:		
			10 particles	100 particles	1000 particles
100	1	0.8469	8	85	847
154	2	0.1259	1	13	126
199	3	0.0227	0	2	23
238	4	0.0035	0	0	4
273	5	0.0006	0	0	1
306	6	0.0005	0	0	0

3.2.3. 700 nm AS

The modeled and measured image shapes for 700 nm AS particles are shown in figure 3-32 for 1 (black), 10 (red), 100 (green) and 1000 (blue) particles. The actual image obtained by the camera is shown in copper and the image after contrast correction in magenta. Only single size particles (no multiplets) were modeled for this size bin; the 1 μ m impactor on the SMPS prevents the 1.080 μ m +2 particle from getting through to the camera. Agreement between the modeled and measured image shapes is again improved after the contrast correction but is not as good as the smaller particle sizes. This is most likely a result of single particle effects. The measured extinction during the 700 nm experiments was approximately 45 Mm⁻¹ which translates to roughly 30 particles/cc in

the extinction measurement and only 1 particle being imaged at any given moment in time. For the smaller particle sizes, the number concentration of particles was significantly higher (greater than 1,000/cc). Thus, the linear spacing of particles within the laser beam may not be as appropriate for the larger size as the smaller size.

Figure 3-32: Normalized model amplitudes for a 700 nm AS aerosol assuming 10 (red), 100 (green) and 1000 (blue) aerosol particles. Actual image shape is shown in copper and the corrected image shape after MTF correction has been applied. Multiplets are not included in these calculations.

3.3. Calibration slopes as a function of particle size

The image shapes generated from the model were also used to simulate calibration curves for the NephCam as a function of size. In processing the actual NephCam images for scattering intensity, averages across the horizontal axis of the image are taken and then the resulting curve is fit to a Lorentzian; peak amplitude corresponds to scattering intensity. However, the model developed only uses a single axis; so the average intensity across a simulated image was used as a surrogate for peak amplitude. Also, the model operates by calculating the image shape as a function of an aerosol distribution present in the laser beam over an undetermined amount of time and all calculated intensities are based upon a relative intensity calculated using Mie Theory.

Thus these simulated images cannot be directly linked to any given exposure length, but the trends seen in the simulated images can be applied to the NephCam data.

Particle size affects both the image shapes (as shown above) and the calibration curves for the NephCam. In keeping with the trends noticed in the image shape calculations, the effect of multiple charge-to-size particles were included here. Figures 3-33 and 3-34 show modeled calibration curves for 100 nm and 500 nm AS aerosols, respectively. In figure 3-33 the calibration curve is noticeably non-linear as a result of larger particle effects in the calculated images and scattering values. This non-linearity is represented as a negative parabolic term in the calibration curve. As particle size is increased, these non-linear effects from multiple charge-to-size particles decreases; the modeled calibration curve for 500 nm AS in figure 3-34 appears linear. These trends can be seen for the NephCam AS data in figures 3-35 and 3-36 for 100 nm and 500 nm, respectively. One major difference between the modeled and actual 100 nm AS data is the magnitude of downward curvature. This arises because the model must assume a discrete number of aerosol "pixels" to model while the actual images represent a continuous measurement of particles in time.

The decrease in negative parabolic curvature with size arises because the relative change in total scattering by multiplets decreases with increasing particle size. In the case of 100 nm particles, the 154 nm, 199 nm, 238 nm 273 nm and 306 nm multiplets are 12, 52, 126, 253 and 468 times as efficient at scattering as the 100 nm particle. For a 500 nm particle, a 771 nm particle is only 2.5 times more efficient. So, while the 500 nm particles might show some negative parabolic curvature, it is going to be much less than for the 100 nm particle. For particles 700 nm and larger, multiplets are not present

because of a $1\mu\text{m}$ impactor on the DMA; a +2 charge particle with the same electrical mobility as a 700 nm particle is $1.080\mu\text{m}$ in diameter.

Figure 3-33: Plot of modeled scattering versus amplitude for 100 nm AS aerosol. The negative parabolic shape of the curve arises from the presence of multiple charge to size particles as shown in table 3-2.

Figure 3-34: Plot of modeled scattering versus amplitude for a 500 nm AS aerosol assuming multiple charge to size particles were present.

Figure 3-35: Plot of measured extinction vs. calculated Lorentzian amplitude for 100 nm AS aerosol using a 3rd order polynomial.

Figure 3-36: Plot of measured extinction vs. calculated Lorentzian amplitude for 300 nm AS aerosol.

The negative parabolic term in the calibration curves continuously decreases as particle size increases for both the modeled and actual NephCam calibrations as shown in figures 3-37 and 3-38. This term follows similar trends for both measured and modeled data except at the 150 nm data point. The modeled data is always increasing and goes to 0 at 400 nm. The measured data is increasing from 150 nm upwards but the 100 and 150 nm data sets show similar parabolic terms. At diameters 400 nm and larger, the negative parabolic terms show no statistical difference from 0 except at 600 nm. The cause of this effect is unknown but is probably tied to single particle effects at this size bin. Because the negative parabolic terms goes to 0 above 400 nm, linear calibrations were also calculated for the actual data as seen in figures 3-39 and 3-40.

Figure 3-37: Plot of modeled calibration 2nd order terms as a function of size for AS.

Figure 3-38: Plot of actual calibration 2nd order terms as a function of size for AS.

The calibration slopes (1st order term) decrease as particle size increases in both the modeled and measured data from 100 nm to 500 nm as seen in figures 3-39 and 3-40. Above 500 nm, the calibration slopes oscillate around a constant value. This decrease and then oscillation in calibration slope is a direct result of the truncation angles and collection efficiency of the NephCams. The NephCams are only capable of measuring an angular range between $\sim 65^\circ$ and 115° from forward and as particle size increases scattering shifts towards the forward direction. This means that as particle size increases, the NephCams collect less angular intensity. However, while the total scattered intensity increases above 500 nm, the relative collection efficiency oscillates around a common value as seen in figure 3-41. This is the same trend that is seen in the NephCam calibration slope.

Figure 3-39: Plot of modeled calibration 1st order term as a function of size for AS using linear (black dots) and polynomial fits (red squares).

Figure 3-40: Plot of actual calibration 1st order term as a function of size for AS using linear (black dots) and polynomial fits (red squares).

The modeled and measured NephCam calibration intercepts do not show any definitive trends. In the modeled data, the intercepts oscillate around 0 as seen in figure 3-42. This is probably a result of the set of particles and the ratio of different particle sizes chosen for the model. If different collections of particles had been modeled then the intercepts might go towards 0. In the measured calibration intercepts, figure 3-43, many of the polynomial fits show little statistical difference from 0. However, at smaller particle sizes the intercepts for the linear calibration fits are statistically different from 0.

Figure 3-41: Plot of NephCam scattering collection versus total scattering (collection efficiency) as a function of size for AS particles.

Figure 3-42: Plot of modeled calibration intercepts as a function of size for AS using linear (black dots) and polynomial fits (red squares).

Figure 3-43: Plot of actual calibration intercepts as a function of size for AS using linear (black dots) and polynomial fits (red squares).

After modeling and physically determining the NephCam calibration slope, the NephCams were used to determine the scattering coefficients of Nigrosin aerosol. These coefficients were then compared to measured extinction values from the HC-CRDT so

that an SSA value could be determined as a function of size. A plot measured and calculated Nigrosin SSA versus size can be seen in figure 3-44. At small particle sizes (< 300 nm), the NephCams and ring-down do not do a very good job of measuring the SSA. However, as size increases measurement of the SSA improves except at the 400 nm size bin. The reason for occurrence is unknown. Data disagreement at smaller particle sizes is thought to arise from the multiple charge to size problem and the fact that scattering increases more rapidly than absorption for small particles (absorption increases as D^3 while scattering as D^6). So, the presence of multiplets would have a larger effect on total scattering in the smaller particle limit versus larger sizes. Another possible source of discrepancy is that the NephCams were calibrated using AS aerosols which has a refractive index of $1.53 + 0i$. Nigrosin's refractive index is $1.7 + 0.31i$. This change in refractive index could be affecting the interpretation of NephCam measurements. This effect is still to be modeled.

Figure 3-44: Plot of calculated SSA for Nigrosin aerosols as a function of size. Extinction was measured by the HC-CRDT and scattering was determined using the size-selected calibration curves presented above.

3.4. NephCam Summary

The NephCam has been shown to be capable of being calibrated as a function of particle size. Further, the image shapes measured by the NephCam has been shown to be

related to the modeled image shape for AS aerosols as a function of size once contrast effects and the sizing mechanism of the DMA are considered (multiple size to charge effects). The SSA of an absorbing aerosol has been calculated using the HC-CRDT as an extinction measurement. The inversion of the NephCam measurement from any arbitrary image shape to determine average particle size and scattering is still a work in progress. Further modeling and measurements of aerosols with known properties need to be conducted. However, in going forward, there are some specific details that need to be addressed:

A sizing mechanism that completely removes the multiple charge to size effect needs to be used. Many of the modeling studies were forced to assume things about the size distributions that may or may not have been true in reality. Addressing whether these assumptions were actually justified is required.

The width of the aerosol sample within the NephCam body needs to be decreased. Currently, a 1/2" Cu tube is expanded to a 1" tube at the inlet of the NephCam. This allows for slight diffusional broadening of the aerosol sample within the body of the NephCam. Instead, the size of the flow should be stepped down so that the imaged width of aerosols is less than the width of the image in the NephCam. This would prevent multiply scattered rays that originated outside of the camera's imaging area from reaching the detector. The exit side of the NephCam can be left at the current size since this doesn't have any effect on the images.

Another detector(s) needs to be added to the NephCam. Specifically, a detector situated in the forward direction is necessary. This would allow the NephCam an additional piece of information when trying to extract information about particle size,

shape and total scattering intensity. Right now, because particle size is known, the truncation angle error can be corrected. In the event that particle size is not known this error cannot be corrected. The addition of another detector in the backwards direction would give even more information about the shape function of the aerosol under investigation. Particle sizing by DLS for nano-particles is typically done at 7° off of forward. Incorporating a similar of measurement may facilitate the extraction of size information of aerosols under investigation.

A beam splitter with a detector to measure laser intensity in real time is required. Currently, laser intensity is inferred from polynomial background gray fits. However, the laser stability may be less than what is currently inferred from the polynomial fits. Having a real time measurement of laser intensity in time will allow for better characterization of laser amplitude and the actual intensity of the scattering measurement.

The speed of data collection needs to be addressed. Currently, the triggering and subsequent data collection is limited by the semaphore control of the camera drivers. Realistically, faster images need to be taken to optimize the intensity and size information obtained. However, depending upon the exact magnitude of scattering towards the camera sensor by particles dictates the minimum exposure time allowable. When only large particles are present, the cameras can be operated in a free-run video mode for real time capturing of scattering coefficients. However, under most circumstances the total scattering by particles and light directed towards the CCD is less than minimum amount detectable by the CCD in video capture mode (15 fps). Optimization of the camera setup may allow for the NephCam to be run in a video collection mode at lower than maximum frame rates (~ 1 fps) for real time determination of scattering and image shape. To use

this type of video (instead of image collection) an individual computer is necessary for each camera. Hard drive and RAM installed on each computer is another issue (i.e. at 15 fps, video requires ~ 1 MB per second and the RAM to support a live video feed).

Image contrast needs to be reassessed. Under the current setup, a decision between maximum contrast and constant contrast across an image had to be made. The choice was to go with constant contrast across an image. However, in making this choice changes in image intensity had to be inferred (see equation 3-29) relative to some "dark" value and it was only marginally better than unusable (0.3 vs. 0.2, respectively). But, it was possible to make measured and modeled image shapes agree by inferring a contrast difference between the models (which assume perfect contrast) and the measured images.

4. Results & Discussion - Humidification experiments

4.1. Allan Variance

Allan Variance experiments are conducted to determine the optimal integration length for minimum noise in a measurement. To perform this Allan Variance, the HC-CRDT was allowed to sample clean air for 4 days (96 hours). An Allan Variance plot can be seen in figure 4-1 for the visible on the Humidified channel. Raw ring-down data as a function of data points is the red trace at the top. The computed Allan Variance is the black trace below that as a function of integration time. The lighter gray trace represents the theoretical variance if only white noise was present. The computed Allan variance initially follows the gray trace which decreases as $\sqrt{N}$. After approximately 200 data points (13 seconds) the theoretical and actual variance start to deviate and the variance starts increasing after 1600 data points (107 seconds) due to instrumental drift. Only one channel is shown since similar plots were generated for each channel and wavelength.

Allan variance is also reported as an Allan Deviation - variance equals standard deviation squared. This corresponds to the maximum precision in any measurement. Calculated Allan Deviations for each channel and wavelength of the HC-CRDT are shown in table 4-1 as a function of integration time. Values for the Ambient-B IR channel have been omitted since that channel is non-functional. As the integration length is increased, the deviation does decrease for the IR and UV channels. In the visible and the UV of the Humidified channel, the minimum deviation is obtained at 120 seconds and increases minimally in going from 120 to 240 seconds. As a result, 240 seconds was chosen as the optimal integration time as it did represent the minimum deviation for many of the channels.

Figure 4-1: Allan variance plot for the visible on the Humidified channel. Red data at the top of the figure is the actual ring-down data as a function of data points. Dark black trace at the bottom shows actual variance as a function of integration time in points on a logarithmic scale. Light gray trace is the ideal variance as a function of integration time if only white noise was present.

Table 4-1: Allan deviation results as a function of integration time for the HC-CRDT

Seconds	Pulses	Channel	IR ($\pm\text{Mm}^{-1}$)	Vis ($\pm\text{Mm}^{-1}$)	UV ($\pm\text{Mm}^{-1}$)
1	15	Ambient-A	5.73	0.57	4.98
		Ambient-B	--	1.11	21.52
		Dry	9.80	1.91	8.98
		Humidified	3.63	0.44	12.59
60	900	Ambient-A	0.75	0.27	1.12
		Ambient-B	--	0.36	2.87
		Dry	1.27	0.42	1.31
		Humidified	0.48	0.10	2.49
120	1800	Ambient-A	0.57	0.24	0.93
		Ambient-B	--	0.40	2.00
		Dry	0.90	0.38	0.98
		Humidified	0.36	0.09	2.03
240	3600	Ambient-A	0.51	0.26	0.96
		Ambient-B	--	0.51	1.50
		Dry	0.66	0.41	0.86
		Humidified	0.28	0.11	2.12

4.2. Characterizing direct sums fitting routine

The direct sums fitting routine has been previously shown to have good accuracy and precision when extracting ring-down coefficients at a ring-down time of $1.5\mu\text{sec}$ and a Gaussian noise level of 1% (Everest and Atkinson 2008). However, in fitting raw data obtained by the CRD, these values are highly dependent on the base ring-down time and the noise encountered. Figure 4-2 shows the precision of the direct sums fitting routine for 3600 fits (240 seconds) assuming 1% (black) and 10% (red) periodic random noise in a simulated ring-down signal at various extinction levels. As the base extinction increases, the precision decreases and is always worse than that calculated by the Allan variance. For extinction levels above 3000 Mm^{-1} this implies that measurement errors are directly linked to the fitting routine not converging on the correct value.

Figure 4-2: Precision of 3600 simulated ring-down fits using the direct sums algorithm as a function of the actual extinction assuming that periodic random noise at 1% and 10% levels.

4.3. Characterizing HC-CRDT transmission efficiency without Humidity controls

In switching from the size-selected experiments to the humidity controlled experiments, the aerosol delivery system was rearranged. For these experiments, aerosols were sampled directly through a URG-2000-30EQ cyclone into a mixing chamber and the DMA was operated in parallel to the HC-CRDT. (In the size selected

experiments, the DMA was in series with the 2nd mixing chamber and HC-CRDT providing particle size selection before measurement.) Here, well-characterized full size distributions were desired instead of a single particle size, hence the change in configuration.

In the visible, agreement with the Ambient-A channel was within 10% for the Dry and Humidified channels (without the dryer and humidifier) and within 20% for the Ambient-B channel, which is within instrument precision. In the IR agreement was not as good but this was not surprising because the extinction in the IR was very near the LOQ for all channels. Higher extinction values would have been desirable, but this causes the UV extinction coefficients to be prohibitively high for measurement. In the UV, good agreement ($< 1\%$) of the Ambient-B channel and the dry ($< 12\%$) and humidified ($< 16\%$) channels with the Ambient-A channel was obtained. Unlike the Visible channel, some of the UV values did not agree to within instrument precision, so minor correction factors were applied to this data.

4.4. Humidifier and dryer particle transmission

To compare the effects of humidity on particle optical properties, it was necessary to first correct for the incomplete transmission of particles through the humidifier and dryer. Particle transmission data for the 20 ppm AS and 20 ppm Nigrosin were similar, so only figures for the AS will be shown. Figures 4-3, 4-4, and 4-5 show the results of the particle transmission testing experiments in the absence of the humidifier or dryer, with only the dryer and with only the humidifier, respectively. The number of particles counted upstream of the dryer and humidifier by the CPC3007 is approximately constant across all experiments. The downstream particle concentration obtained from the

CPC3776 changes in each experiment but is always higher than the number counted by the CPC3007. This is not unexpected because of the lower minimum size detected by the CPC3776, and can still allow a transmission loss measurement if the "no dryer or humidifier" case is taken as the basis for comparison.

Figure 4-3: Time series data of 20 ppm AS particle transmission testing without humidifier or dryer present. Three cycles of measurement, interspersed with filtered air measurements, are shown.

Figure 4-4: Time series of 20 ppm AS particle transmission testing with dryer.

Figure 4-5: Time series data for 20 ppm AS particle transmission testing with humidifier.

The particle number concentration from the CPC3776 was highest when the humidifier and dryer were not present as seen in figure 4-3, followed by when the dryer was present (figure 4-4); and the humidifier showed the lowest particle transmission (figure 4-5). By taking the ratio of the particles counted by the CPC3007 to the CPC3776, ratios for particle transmission can be generated, as seen in table 4-2. When neither the humidifier nor dryer were present, the CPC 3007 counted an average of 66% of the particles counted by the 3776 when using 20 ppm AS. When the dryer and humidifier were present, these ratios rise to 71% and 85% due to downstream losses, implying a 9% loss of particles in the dryer and a 22% loss in the humidifier. Similar values were measured when using the 20 ppm Nigrosin solution. These particle count ratios are used to normalize transmission relative to the absence of both the dryer and humidifier as shown in table 4-3. The particle transmission through the dryer is an average of 91% and transmission through the humidifier is an average of 78%.

Combining particle transmission experiments through the Humidifier and dryer and the rest of the HC-CRDT, the correction factors applied to all future data can be seen in table 4-4 to make the Ambient-B, Humidified and Dry channels agree with the Ambient-A channel. These values represent scaling factors that were multiplied to obtained data instead of fractional transmission values like those shown in tables 4-2 and 4-3.

Table 4-2: Average and standard deviations of the ratio of particles counted by the CPC3007 to the CPC3776 using the humidifier, dryer or Cu tube

Species	Humidifier		Dryer		Neither	
	Average	SD	Average	SD	Average	SD
20 ppm Nigrosin	0.83	0.02	0.72	0.01	0.65	0.01
20 ppm AS	0.85	0.01	0.71	0.01	0.66	0.01

Table 4-3: Particle transmission through the humidifier and dryer systems by particle type

Species	Humidifier		Dryer	
	Average	SD	Average	SD
20 ppm Nigrosin	0.79	0.02	0.90	0.02
20 ppm AS	0.77	0.01	0.92	0.01
Average	0.78	0.02	0.91	0.01

Table 4-4: Correction factors to Ambient-A applied to other channels for non-size selected data

Channel	Ambient-B	Dryer	Wetter
IR	--	1.10	1.28
Vis	1.00	1.10	1.28
UV	1.00	1.24	1.52

4.5. Measures of particle growth by humidity

The optical properties of particles are a direct function of particle composition and size. Particle composition affects absorption and scattering through the refractive index. Scattering is also affected by particle size, where larger particles are more effective scatterers.

All particles exhibit growth via water uptake with increasing RH, but depending upon the type of growth (hygroscopic with hysteresis, hygroscopic or hydrophobic) the magnitude varies. Hygroscopic particles readily uptake water over all ambient RH. Particles that are hygroscopic and exhibit hysteresis can be present as either solid or liquid aerosols at a given RH depending on the RH history that the particle has been subjected to. Hydrophobic particles do not take up water readily until high RH values are reached, but slight variations in size as a function of RH are observed even at low RH due to adsorption.

There are different parameters that are alternatively used to describe droplet growth as a function of RH. The simplest, droplet growth factors (β) are the ratio of particle size at an elevated RH to dry particle size:

$$\beta = \frac{D}{D_0} \quad (\text{eq 4-1})$$

where D is the particle diameter at elevated RH and D_0 is the dry particle diameter. The measurement of β commonly uses a Tandem Differential Mobility Analyzer (TDMA) instrument. In these experiments, only the change in diameter of particles is of interest and experiments measuring the change in particle diameter as a function of water uptake, organic uptake, or simply SOA growth have been performed in a similar manner with this instrument (Gysel, Weingartner et al. 2001; Stanier, Pathak et al. 2007; Lewis, Arnott et al. 2009). From the experiments reported in this work, β can only be inferred since the HC-CRDT is an optical measurement. Instead, $f(\text{RH})$ and $\gamma(\text{RH})$ are the commonly applied measures of particle growth:

$$f(\text{RH}) = \frac{b_{\text{ext,high RH}}}{b_{\text{ext,dry}}} \quad (\text{eq 4-2})$$

where $b_{\text{ext}}(\text{dry})$ and $b_{\text{ext}}(\text{RH})$ are the extinction coefficients of an ensemble of aerosol particles at dry and ambient RH. In many cases the dry RH is taken to be any RH less than 40% (Baltensperger, Barrie et al. 2003). As will be shown below, this value is not low enough to consider some types of particles "dry" for the purposes of determining $f(\text{RH})$. For many efflorescent salts an RH less than 40% is acceptable. For some salts (e.g., NaNO_3) and hygroscopic aerosols not exhibiting efflorescence or hygroscopic aerosols it is not.

The values of $f(RH)$ have been modeled well by equation 4-3 for aerosols showing monotonic growth and hygroscopicity:

$$f(RH) = 1 + a \left(\frac{RH(\%)}{100} \right)^b \quad (\text{eq 4-3})$$

Where a and b are parameters obtained from a non-linear curve fitting procedure (Carrico, Kus et al. 2003; Pan, Yan et al. 2009). The form of $f(RH)$ for hydrated hygroscopic aerosols that exhibit efflorescence and deliquescence has been modeled by:

$$f(RH) = c \left(1 - \frac{RH(\%)}{100} \right)^{-g} \quad (\text{eq 4-4})$$

where c and g are also model fit parameters. This last $f(RH)$ function has been used repeatedly to describe the RH dependence of ambient aerosols, regardless of whether the aerosol demonstrates deliquescence behavior or not (Kotchenruther, Hobbs et al. 1999; Carrico, Kus et al. 2003). Depending upon the measurements available, $f(RH)$ can instead be expressed as $\gamma(RH)$:

$$\gamma_{ext}(RH) = \frac{-d \ln b_{ext}}{d \ln(100 - RH)} \quad (\text{eq 4-5})$$

$$\gamma_{ext}(RH) = \frac{\ln(b_{ext,high\ RH}) - \ln(b_{ext,low\ RH})}{\ln(100 - RH_{low}) - \ln(100 - RH_{high})} \quad (\text{eq 4-6})$$

where $b_{ext}(RH)$ and $b_{ext}(\text{dry})$ are the extinction coefficients at high and low RH, respectively, and RH_{high} and RH_{dry} are the measured relative humidities (%). Identical expressions can be composed for the scattering and absorption effects of RH, but the application to scattering is more common than absorption since the change in scattering with RH is larger and more systematic than that of absorption. The application of $\gamma(RH)$ is similar to that of the Ångström exponent in that it simulates an assumed power law dependence of extinction on RH (instead of wavelength).

The relative humidity growth factor $\gamma(\text{RH})$ in equations 4-5 and 4-6 is essentially the same as g in equation 4-4, since $\gamma(\text{RH})$ can be derived from g by taking the logarithmic derivative of equation 4-4. Both $f(\text{RH})$ and $\gamma(\text{RH})$ contain similar information, but the measurement context is slightly different. Proper measurement of $f(\text{RH})$ requires the ability to cycle RH and collect "humidograms", time dependent measurements of the aerosol optical properties that are synchronized to the RH dependence. Pair-wise $f(\text{RH})$ values can be calculated as long the optical properties are measured at 2 or more RH's but less information is provided. The measurement of humidograms allows for the elucidation of hysteretic behavior in aerosol growth because the RH is cycled between high and low extremes and efflorescence and deliquescence can be directly observed. The disadvantage is that obtaining humidograms is time-consuming; typically 30 minutes or more are required for a single loop, and the aerosol composition and concentration should optimally remain constant for this whole period.

Because it assumes a form for the growth of particles with RH, the measurement of $\gamma(\text{RH})$ only requires measurement of optical properties at 2 or more relative humidities. In this approach, parallel measurements of the various RH-dependent properties (e.g., extinction coefficients) are usually made, generally in real time. When the property is measured at 3 or more RH values (high, medium, dry), pair-wise values for $\gamma(\text{RH})$ from equation 4-6 will be similar for both pairs (medium to high RH and medium to low RH) when hysteresis is not present. In this case, a non-linear fit can be used to obtain $\gamma(\text{RH})$ from equation 4-5 using as many measurements as are available. If a hysteretic aerosol is present and the low RH is below the efflorescence RH, then $\gamma(\text{RH})$

will have different values for each $\gamma(\text{RH})$ pair present, indicating that the non-linear fit would not be applicable.

While $f(\text{RH})$ and $\gamma(\text{RH})$ represent the integral versus differential effect of RH on particle growth respectively, both conventions will be used in my presentation of data collected. The HC-CRDT is usually used to measure $\gamma(\text{RH})$ but is also able to obtain humidograms and thus $f(\text{RH})$; $f(\text{RH})$ will be the preferred form when linking measured data to model results. The $\gamma(\text{RH})$ will be preferred when only diagnostic information is desired.

4.6. Changes in refractive index due to water uptake

Global climate models use effective refractive indices to predict the radiative forcing of aerosols (Bond and Bergstrom 2006). In many cases, the base refractive index used in the calculation is inferred based upon a given particle type - scattering salts, black carbon, brown carbon, etc. These base refractive indices are typically an oversimplification to other types of aerosol actually present (mixed organics, coated organics, core-shell type particles, mixed salt and organics) and particles are typically assumed to be spherical for ease of calculation using Mie theory. The assumption of sphericity may be justified when averaging over a large enough ensemble of particles, but the effects of particle composition cannot be ignored. The change in refractive index with relative humidity is inferred from different refractive index mixing rules, including the volume mixing, Maxwell-Garnett, and partial molar refraction models described in the next sections. As a result, the radiative forcing predictions of GCM's by aerosols as a function of RH give variable results that may or may not even correspond to what is actually present and occurring in the atmosphere. Improvement in the understanding of

particle refractive indices (and therefore optical properties) as a function of RH is of importance for better simulations of aerosol radiative forcing in global climate models.

4.6.1. Water uptake and dilution effects on particle refractive index

Water uptake by particles with increasing humidity alters the inherent optical properties of the particle (approaching those of water) through changes in composition, morphology and structure. If dry particle size is known, then changes in particle size are attributable to the adsorption or absorption of water and the resulting particle composition can be calculated. The refractive index and optical properties of the hydrated particle can then be calculated by assuming the particle is spherical and homogeneous. Not accounting for refractive index changes with water uptake can result in an overestimation of the optical properties; as a result the inferred radiative forcing by the particle takes on significant error and may even be of the wrong sign/direction (Erlick, Abbatt et al. 2011).

4.6.1.1. Volume mixing

Refractive index mixing rules represent an approximation to the solution of Maxwell's equations for particles of mixed composition either as a result of formation mechanisms or water uptake. The simplest of these mixing rules, the volume mixing rule, states that the effective refractive index of a particle is simply a function of the volume fractions of the species present:

$$n_{eff} = \sum f_i n_i \quad (\text{eq 4-7})$$

where n_{eff} is the effective index of the particle and f_i and n_i are the volume fraction and bulk refractive index of species i . The real and imaginary terms of the effective refractive index are calculated separately. The volume mixing rule is an oversimplification of the actual refractive index of an inhomogeneous particle but is useful because of its

simplicity and ability to account for any number of aerosol components (Erlick, Abbatt et al. 2011).

4.6.1.2. Maxwell-Garnett

The Maxwell-Garnett (MG) mixing rule is typically applied to particles with absorbing inclusions in a non-absorbing bulk where the inclusions are small relative to the size of the particle. Here, the MG mixing rule will be applied to all particles of mixed composition regardless of whether the inclusions are absorbing. The MG mixing rule is based on changes in the dielectric constant of a particle with inclusions:

$$\epsilon_{eff} = \epsilon_{particle} + \frac{3f\epsilon_{particle}(\epsilon_{inclusion} - \epsilon_{particle})}{\epsilon_{inclusion} + 2\epsilon_{particle} - f(\epsilon_{inclusion} - \epsilon_{particle})} \quad (\text{eq 4-8})$$

where ϵ_{eff} is the effective dielectric constant, f is the volume fraction of the inclusions and $\epsilon_{inclusion}$ and $\epsilon_{particle}$ are the dielectric constants of the inclusions and the particle matrix, respectively. The dielectric constant (ϵ) is related to the refractive index (n) by:

$$n = \sqrt{\epsilon} \quad (\text{eq 4-9})$$

This mixing rule can be extended to any particle of mixed composition if only a single type of inclusion is present in an otherwise homogeneous particle (Chyýlek, Srivastava et al. 1988).

The MG mixing rule assumes that the inclusions are non-interacting, spherical and randomly distributed within the particle. Second-order effects of interactions by inclusions within a particle are ignored. The MG mixing rule can be expanded into different forms if the inclusions are not spherical but needles, oblate or prolate discs, or other defined shapes (Bohren and Huffman 1983; Sihvola 2008). However, for the salts and organics investigated in this work these other forms are not necessary because all

particle types investigated are water soluble. One of the major drawbacks to the MG mixing rule is that only a single type of inclusion can be considered when calculating the effective refractive index.

4.6.1.3. Partial molar refraction

In the partial molar refraction mixing rule, the effective refractive index of a particle is based upon the volume mixing of all species present and their molar refractions. The molar refraction (R) of a species is:

$$R = V \frac{(n^2 - 1)}{(n^2 + 2)} \quad (\text{eq 4-10})$$

Where n is the complex refractive index and V , the molar volume, is:

$$V = MW / \rho \quad (\text{eq 4-11})$$

where MW is the molecular weight of the species and ρ is the density. Once the molar refractions of the individual species are known, the effective molar refraction of a mixture (R_{eff}) is:

$$R_{\text{eff}} = \sum x_i R_i \quad (\text{eq 4-12})$$

Where x_i is the mole fraction of species i and R_i is the molar refraction of species i . The effective molar volume of a mixture (V_{eff}) is:

$$V_{\text{eff}} = \sum x_i MW_i / \rho_i \quad (\text{eq 4-13})$$

where x_i is the mole fraction of species i , MW_i is the molecular weight of species i and ρ_i is the density of species i . The effective refractive index of the particle can then be calculated by re-arranging equation 4-10, to solve for n :

$$n_{eff} = \left(\frac{1 + 2R_{eff}/V_{eff}}{1 - R_{eff}/V_{eff}} \right)^{1/2} \quad (\text{eq 4-14})$$

In (Stelson 1990), the partial molar refraction was only applied to real refractive indices. Since eq 4-14 can be derived from eq 7 by a simple algebraic rearrangement, it should then follow that this equation is also applicable to refractive indices with imaginary components.

The partial molar refraction mixing rule assumes that all components within the mixture are ideal; no 2nd order interactions between the species are present. The partial molar refraction mixing rule has the advantage that multiple components can be included as with the volume mixing rule.

4.6.2. RF inaccuracies from refractive index changes

The volume, partial molar refraction and MG mixing rules give similar results in the determination of the real part of the refractive index for a test aerosol, as seen in figure 4-6. However, these three mixing rules give significantly different values for the imaginary refractive index as seen in figure 4-7. The volume mixing rule gives the highest imaginary refractive index, while the MG rule has an imaginary refractive index that is an average of 10% lower and a partial molar refraction that is an average of 14% lower.

Figure 4-6: Plot of real effective refractive index of Nigrosin by volume fraction in water as calculated using the volume (solid, red), partial molar refraction (dash, green) and Maxwell-Garnett (dash-dot, blue) mixing rules.

Figure 4-7: Plot of imaginary effective refractive index of Nigrosin by volume fraction in water as calculated using the volume (solid, red), partial molar refraction (dash, green) and Maxwell-Garnett (dash-dot, blue) mixing rules.

The variation in refractive index from the application of the three mixing rules directly translates into the predicted optical properties of a particle. In figures 4-8 through 4-10 Mie theory predictions of the extinction, scattering, and absorption coefficients and SSA of a single 250 nm Nigrosin particle were calculated using the refractive indices shown in figures 4-6 and 4-7. In figure 4-8, the extinction coefficient using the volume mixing rule is the highest while using partial molar refraction and the MG mixing rules gives almost identical results. In the plots of scattering and absorption, figures 4-9 and 4-10, slightly different trends emerge. The calculated scattering values are almost identical for all mixing rules with partial molar refraction marginally higher.

Predicted absorption coefficients decrease from volume mixing to MG to partial molar refraction. The absorption differences are the primary driver of the extinction differences. In the plot of SSA, figure 4-11, the absorption trends are mirrored in SSA; SSA increases from volume mixing, to MG to partial molar refraction. The variations in the imaginary refractive index are the primary driver of all of these differences. But, ultimately these small differences cause significant variations in the radiative forcing calculation of an aerosol with this refractive index and size.

Figure 4-8: Plot of extinction versus volume fraction Nigrosin (versus water) for a single 250 nm particle using the volume (red), partial molar refraction (green) and Maxwell-Garnett (blue) mixing rules.

Figure 4-9: Plot of scattering versus volume fraction Nigrosin (versus water) for a single 250 nm particle using the volume (red), partial molar refraction (green) and Maxwell-Garnett (blue) mixing rules.

Figure 4-10: Plot of absorption versus volume fraction Nigrosin (versus water) for a single 250 nm particle using the volume (red), partial molar refraction (green) and Maxwell-Garnett (blue) mixing rules.

Figure 4-11: Plot of SSA versus volume fraction Nigrosin (versus water) for a single 250 nm particle using the volume (red), partial molar refraction (green) and Maxwell-Garnett (blue) mixing rules.

4.7. Modeling water uptake with RH

All particles exhibit growth at high RH. However, the magnitude of that growth is a function of particle composition and size. Using the Kelvin equation (eq 4-15) surface water uptake and consequent aerosol growth as a function of RH can be modeled.

$$\left(\frac{RH}{100a_w}\right) = \exp\left[\frac{\gamma(MW)}{D\rho RT}\right] \quad (\text{eq 4-15})$$

where a_w , γ , D , ρ and T are the activity of water, particle surface tension, particle diameter, particle density and temperature in Kelvin. Using the refractive index mixing

rules outlined above, the optical properties as a result of this growth can also be calculated.

4.7.1. Inputs

4.7.1.1. Refractive Index

Table 4-5 shows the bulk refractive indices, molecular weights and ERH/DRH for the species measured by the HC-CRDT and modeled here. The MW of Nigrosin was taken as 202g/mole (from the Sigma Aldrich, Inc. product literature). Depending upon supplier and source of Nigrosin, the MW has also been quoted as 616.49 g/mole. The density of bulk Nigrosin was assumed to be 1 g/mL since a reference value could not be found. The other model parameters of Nigrosin listed below were assumed to be the same as NaNO₃ since both exhibited similar growth characteristics and a literature value was not available.

Table 4-5: Refractive indices, molecular weights, solid density and ERH/DRH for modeled species from (Tang 1996)

Species	n	k	MW (g/mole)	Density (g/mL)	ERH (%)	DRH (%)
NaNO ₃	1.587	0	84.9947	2.261	0.05 - 30	74.5
NaCl	1.55	0	58.44	2.165	46 - 48	75.3
NH ₄ NO ₃	1.554	0	80.052	1.725	25 - 32	62
AS	1.53	0	132.14	1.76	37 - 40	80
Nigrosin	1.701	0.31	202	1	--	--

4.7.1.2. Density

For salt particles (sodium chloride, sodium nitrate, ammonium nitrate and ammonium sulfate aerosols), density has been parameterized as a polynomial function of weight percent salt in the particle (Tang and Munkelwitz 1994):

$$\rho = 0.9971 + \sum A_i x^i \quad (\text{eq 4-16})$$

where A_i is a fit parameter and x is the weight percent of the salt in the particle. In this model, the density at 100% salt was taken as the actual salt density from table 4-5 instead of the value calculated using eq 4-16. Values for these parameters of the species used in this work can be seen in table 4-6.

Table 4-6: Fit parameters for eq 4-16 for modeled species density

Species	Weight Percent Range	A_1	A_2	A_3	A_4
NaNO_3^a	0 - 98	6.512×10^{-3}	3.03×10^{-5}	1.44×10^{-7}	0
NaCl^b	--	7.41×10^{-3}	3.741×10^{-5}	2.252×10^{-6}	-2.06×10^{-8}
NH_4NO_3^b	--	4.05×10^{-3}	9.0×10^{-6}	1.024×10^{-8}	0
AS ^a	0 - 78	5.92×10^{-3}	-5.036×10^{-6}	1.024×10^{-8}	0
Nigrosin	--	6.512×10^{-3}	3.03×10^{-5}	1.44×10^{-7}	0

a (Tang and Munkelwitz 1994)

b (Tang 1996)

4.7.1.3. Activity

For salt particles, water activity has been parameterized as a polynomial function of weight percent salt in the particle (Tang and Munkelwitz 1994):

$$a_w = 1.0 + \sum C_i x^i \quad (\text{eq 4-17})$$

Where C_i is a fit parameter and x is the weight percent of the salt in the particle. Values for these parameters can be seen in table 4-7.

Table 4-7: Activity fit parameters for eq 4-17 for modeled species

Species	C_1	C_2	C_3	C_4
NaNO_3^a	-5.52×10^{-3}	1.286×10^{-4}	-3.496×10^{-6}	1.843×10^{-8}
NaCl^b	-6.366×10^{-3}	8.624×10^{-5}	-1.158×10^{-5}	1.518×10^{-7}
NH_4NO_3^b	-3.65×10^{-3}	-9.155×10^{-6}	-2.826×10^{-7}	0
AS ^a	-2.715×10^{-3}	3.113×10^{-5}	-2.336×10^{-6}	1.412×10^{-8}
Nigrosin	-5.52×10^{-3}	1.286×10^{-4}	-3.496×10^{-6}	1.843×10^{-8}

a (Tang and Munkelwitz 1994)

b (Tang 1996)

4.7.1.4. Surface tension

Surface tension is also a parameter in the Kelvin equation. For salt particles, parameters to calculate the surface tension of a solution droplet of mixed composition have been previously determined (Dutcher, Wexler et al. 2010). The surface tension ($\sigma(T)$) of a particle composed of salt and water is:

$$\ln(\sigma(T)) = y_w * \ln[\sigma_w(T)] + y_s * \ln[\sigma_s(T)] \quad (\text{eq 4-18})$$

Where $\sigma_w(T)$ and $\sigma_s(T)$ are the surface tension contributions from pure water and a molten salt and y_w and y_s are the mole fractions of water and salt, respectively. The surface tension contribution from water $\sigma_w(T)$ can be calculated from:

$$\sigma_w(T) = 235.8 \left(\frac{647.15-T}{647.15} \right)^{1.256} \left[1 - 0.625 \left(\frac{647.15-T}{647.15} \right) \right] \quad (\text{eq 4-19})$$

Where T is the temperature in Kelvin and $\sigma_w(T)$ is in mN m^{-1} (or mJ m^{-2}). The surface tension contribution of the molten salt $\sigma_s(T)$ can be calculated from:

$$\sigma_s(T) = c_1 + c_2 T \quad (\text{eq 4-20})$$

Where c_1 and c_2 are fit parameters and T is the temperature in Kelvin. Values for c_1 and c_2 can be seen in table 4-8.

Table 4-8: Molten salt parameters for the calculation of surface tension, adapted from (Dutcher, Wexler et al. 2010)

Species	c_1 (mN m^{-1})	c_2 ($\text{mN m}^{-1}\text{K}^{-1}$)
NaNO_3	155.5	-0.0613
NaCl	191.16	-0.07188
NH_4NO_3	148.4	-0.105
AS	228.5	-0.146
Nigrosin	155.5	-0.0613

The terms $\sigma_w(T)$ and $\sigma_s(T)$ can be expanded to account for concentration effects at high water and salt concentrations. At high water concentrations, salt ions can be thought

of as being solvated by water forming hydration shells. For water, the $\sigma_w(T)$ term can be expanded:

$$\sigma_w(T) = \sigma_w(T) + y_s(a_{ws} + b_{ws}T) \quad (\text{eq 4-21})$$

Where a_{ws} and b_{ws} are parameters fitted to the data. The same expansion can be done for salt:

$$\sigma_s(T) = \sigma_s(T) + y_w(a_{sw} + b_{sw}T) \quad (\text{eq 4-22})$$

Where a_{sw} and b_{sw} are parameters fitted to the data. In the limit of high salt concentration, the water droplets can be thought of as being solvated by salt ions; i.e. the salt has a regular structure (Dutcher, Wexler et al. 2010). The order of subscripts in this system is important: the left subscript indicates the high concentration species and right subscript is the low concentration species. Values for a_{ws} , b_{ws} , a_{sw} and b_{sw} can be found in table 4-9 (taken from (Dutcher, Wexler et al. 2010)).

Table 4-9: High concentration limit solution and salt parameters for the calculation of surface tension

Species	a_{ws} (mN m ⁻¹)	b_{ws} (mN m ⁻¹ K ⁻¹)	a_{sw} (mN m ⁻¹)	b_{sw} (mN m ⁻¹ K ⁻¹)
NaNO ₃	19.359	0	0	0
NaCl	232.54	-0.245	-142.2	0
NH ₄ NO ₃	-24.245	0.14	0	0
AS	0	0.366	0	-0.289
Nigrosin	19.359	0	0	0

Rewriting equation 4-17 to include equations 4-21 and 4-22 allows calculation of the surface tension of the modeled particles:

$$\ln(\sigma(T)) = y_w * \ln[\sigma_w(T) + y_s F_{ws}(T)] + y_s * \ln[\sigma_s(T) + y_w F_{sw}(T)] \quad (\text{eq 4-23})$$

4.7.1.5. Size distribution data

In this work, the aerosol size distributions were determined by 2 methods: mean diameters and geometric standard deviations were taken directly from the SMPS (produced by the TSI Aerosol Instrument Manager software) and the same parameters were calculated by fitting the raw size distributions (particle number concentration vs. DMA diameter setpoint) using a log-normal curve. Further explanation is provided in section 5.9.1. These base particle sizes were necessary to infer particle growth from that on the Dry and Ambient channels to that on the Humidified channel as measurement of particle size distributions at the RH of the Humidified channel were not possible using the setup employed. From this growth, the optical properties of the Humidified channel relative to the Dry and Ambient channels could be calculated.

4.7.1.6. RH

RH values for the SMPS were inferred from the measurements by the Ambient-A RH/T sensor. This sensor was on a separate flow line in parallel to the SMPS, but the time separation between the 2 measurements was minimal. The SMPS recirculates excess flow as sheath flow so the actual value of the RH measured by the Ambient-A channel could be slightly lower or higher than that in the SMPS depending upon whether the ambient RH was decreasing or increasing, respectively.

4.7.2. Assumptions

There are four primary assumptions used in this model to calculate particle growth as a function of relative humidity and to predict the resulting aerosol optical properties: 1) particle growth as a function of relative humidity is controlled by the Kelvin equation and the Köhler effect is negligible due to small particle size, 2) temperature was constant at 293 K, 3) all measured particles are spherical and the optical

properties can be calculated using Mie theory and 4) all particles are completely homogenous with respect to water; no core-shell morphologies are expected. These assumptions are examined in greater detail in the next four paragraphs.

The assumption that particle growth is controlled by the Kelvin equation ultimately serves as the basis for the calculation of particle diameter as a function of RH. The measured geometric mean diameters for dry particles were typically in the range of 50 to 60 nm, except for NaNO_3 which had a significantly smaller geometric mean diameter near 25 nm. For particles in this size regime, the Kelvin equation serves as the limiting case for particle growth. To assume that particles were able to freely grow in this size range (as would be predicted without the Kelvin equation) results in significant over predictions of growth and thus the optical properties. The RH of the humidified channel was typically around 80 to 85% RH. For the types of particles measured here, the Köhler effect is negligible since the humidified channel is not supersaturated with water vapor ($\text{RH} < 100\%$).

For the model calculations, the temperature was taken to be a constant value of 293K. In reality, the temperature of the lab varied between 290K and 295K, and small temperature fluctuations were noticed during all experiments. In an absolute sense, the temperature fluctuations were small ($< 5 \text{ K}$), so it is not expected to affect modeling results significantly.

Mie theory was used to calculate the optical properties of all particles for all RH. Aerosol optical properties (extinction/scattering) were calculated using a LabView adapted version of the C code written by Bohren and Huffman (1983); and modified by

Martin Fierz (Fierz 2005). Absorption was calculated from the difference between extinction and scattering.

The assumption that Mie theory was applicable to all measured particles implies that all of the particles were spherical at all RH's. Sodium chloride tends to effloresce into a cubic shape as dictated by its crystal lattice, but for simplicity it was modeled as a spherical homogeneous particle. This assumption also implies that the particles are either completely mixed or a core-shell morphology of 2 homogeneous components. Mie theory calculations can be performed on either morphology. However, the core-shell morphology is not expected since all modeled particles are water soluble.

4.7.3. Model overview

Using the Kelvin equation (eq 4-15) and equations 4-16 through 4-23, the equilibrium RH for a droplet with a defined mole fraction salt and water can be calculated. This implies that the water activity and resulting equilibrium size can also be predicted for a given RH. A plot of mole fraction water versus particle size and RH is shown in figure 4-12, for AS aerosol. The 2 nm particle (solid black) has an ERH of approximately 35%. This is where the mole fraction of the salt goes to 1. At any RH below 35%, this particle would theoretically exist as a pure crystalline solid. However, as particle size increases from 2 nm to 5 nm, the ERH drops significantly to around 20%. As the particle continues to grow, ERH further decreases and approaches a limit around 10%. Although these calculations imply that an AS particle should effloresce around 10 - 15%, actual ERH is 37 - 40% (Tang 1996). This discrepancy is caused by the fact that the difference in size between hydrated AS and crystalline AS near the ERH is small

compared to other types of salts (i.e. NaCl). As a result, a smooth but very gradual increase in size is observed above 10% RH until the ERH is crossed.

Figure 4-12: Plot of % RH versus mole fraction AS for various particle diameters at 293K.

Using all of the parameters outlined above, particle growth as a function of RH can be calculated as follows. A base size distribution at 0% RH is inferred from the SMPS data and log-normal fits. At 0% RH, any particle type can be assumed to be in its dry state (effloresced for most salts). The size distribution is initially assumed to have a log-normal size distribution and is simulated as 1000 points evenly distributed between 1 nm and 1000 nm in $\log_{10}$ space. (Uniform increments in log space is the preferable way to map the size distribution since this mirrors the way that the SMPS measures size distributions.) Minimum size was limited to 1 nm because smaller particles do not significantly affect the optical coefficients, even after being subjected to significant growth. Maximum particle size was limited to 1000 nm to represent the size cut point of the SMPS impactor and URG cyclone on the sampling line. From this base size distribution, initial extinction and scattering coefficients are calculated using the Mie code.

After initial extinction and scattering coefficients at 0% RH are calculated, the RH is increased to a target RH and particle growth as a function of water uptake is calculated. Particle diameters are incremented upward by 0.001 nm and volume fraction water and salt (used generically here to represent solutes, not always referring to NaCl) are calculated assuming that all changes in particle size are a result of water uptake. The resulting mole fractions of salt and water are then calculated using the density and molecular weights of salt and water. The resulting RH is calculated from the Kelvin equation using the parameters outlined in section 5.7. The new particle diameter is continuously incremented until the RH calculated by the Kelvin equation equals the target RH. This process of mapping an initial diameter to a final diameter at a given RH can be seen graphically in figure 4-13, for an AS aerosol. The solid black line represents the base particle size. As RH is increased, the magnitude of particle growth from a base size also increases, but non-linearly.

Figure 4-13: Map of particle growth as a function of RH for AS aerosol.

After particle growth as a function of RH is calculated for each initial dry size, the resulting size distribution is mapped. The shift in size distribution can be seen in figure 4-14, for a AS aerosol with a geometric mean of 52 nm and a geometric standard deviation of 1.5.

Figure 4-14: Size distributions at various RH's for an AS aerosol with an initial mean diameter of 52 nm and a geometric standard deviation of 1.5. The solid black line represents the initial (RH = 0%) size distribution.

For particles below the ERH, a solution to the Kelvin equation may not exist. This can be seen in figure 4-14, for 10% RH (red small dash). For all particle diameters, the initial and final (10% RH) particle sizes are overlapping. When particles are below the ERH, model iteration is ceased when the final diameter is more than 2.5 times the initial diameter and a solution has not been found. Here, the particle is assumed to still be in its dry state resulting in no change in particle diameter as a function of RH.

Once the new size (and composition) for a particle has been calculated from the Kelvin equation, the resulting refractive index is calculated using the volume mixing, MG and partial molar refraction mixing rules. The extinction and scattering coefficients for the size distribution are then calculated from the Mie code. Calculation of $f(RH)$ was

done assuming the dry RH was 10%, the average RH of the Dry channel of the HC-CRDT.

4.8. AS Results

A 100 ppm AS solution was aerosolized for measurement by the HC-CRDT. RH and temperature data for each channel are shown versus time in fractional day of year (DOY) in figures 4-15 and 4-16, respectively. On all plots, the Ambient-A, Ambient-B, Dry and Humidified channels are represented as black circles, red squares, green triangles and blue stars, respectively. Shading on the Dry and Humidified channels represents different locations (upstream/downstream from the instrument) of RH/T sensors on the same channel.

The RH of the dilution air for the 100 ppm AS aerosol was started high and slowly decreased over time, as the ambient RH measured on the Ambient-A, Ambient-B and at the valve on the Dry channel show(Fig. 4-13). The RH of the Humidified channel was constant at $71.7 \pm 0.6\%$ RH immediately after the humidifier and $80.7 \pm 0.5\%$ RH at the cavity exit. The Dry channel RH was also constant at $4.2 \pm 0.2\%$ RH immediately after the dryer and $7.7 \pm 0.3\%$ at cavity exit. The Vaisala HMP50 RH/T sensors used in this study have stated accuracies of $\pm 3\%$ RH and $\pm 0.6^\circ\text{C}$. The RH stability of these sensors is quoted as $\pm 2\%$ over 2 years. Thus, these measurement differences are within the limits of measurement accuracy for these sensors. For comparison to modeled results, the RH and temperature of the aerosol stream at the cavity exit was taken since this is closest to the CRD measurement within the instrument.

Figure 4-15: Plot of 4 minute averaged 100 ppm AS RH data versus fractional day of year (DOY) measured by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels. Different color shades represent multiple RH measurements on the same channel.

Figure 4-16: Plot of 4 minute averaged 100 ppm AS temperature data versus time in fractional day of year (DOY) measured by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels. Different color shades represent multiple RH measurements on the same channel. The Dry channel's upstream temperature is omitted due to sensor malfunction.

Extinction coefficients of the 100 ppm AS aerosol measured at the visible wavelength by all channels of the HC-CRDT are shown in figure 4-17. All data points represent 4 minute averages. As the RH of the dilution air is decreased, the measured extinction coefficients on all channels decrease; an small increase in the RH was noticed before the RH started decreasing in the middle of the data set. Measured extinction values on the ambient channels tracked with this trend.

Figure 4-17: Plot of 4 minute averaged 100 ppm AS extinction data versus time in fractional day of year (DOY) measured in the visible (532 nm) by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

For the purpose of modeling water uptake by AS particles, a mean diameter and geometric standard deviation had to be determined from the size distribution data. The SMPS calculates these terms as part of the AIM software package. However, significant noise was noticed at the high particle sizes (> 500 nm) as a result of the sheath and aerosol flow rates that were used, 2.2 to 1.5 Lpm, respectively. These settings mean that our measured size distributions could have geometric standard deviations up to 1.52 (low side) and 2.10 (high side) times greater than calculated because of the ratio of sheath to aerosol flow (Knutson and Whitby 1975). Essentially, the geometric width of any size bin could be larger or smaller than reported by the SMPS due to the electrical mobility bandgap present at these flow settings. The raw size distributions measured by the SMPS were fit to a log-normal curve for a second determination of the geometric mean and standard deviation for comparison. The geometric mean diameters and standard deviations from the SMPS measured data (black circles) and log-normal fits (red squares) can be seen in figure 4-18 and 4-19, respectively.

A clear transition due to efflorescence can be seen in the geometric data at an RH near 30%. The measured and log-normal fit geometric mean diameters for the effloresced particles were determined to be 53.66 ± 0.43 nm and 51.86 ± 0.52 nm, respectively. The measured and log-normal fit geometric standard deviations for the effloresced particles were 1.64 ± 0.01 nm and 1.60 ± 0.01 nm, respectively. For modeling, 52 nm was chosen as the mean diameter and the geometric standard deviations were 1.7 ± 0.2 . This range was chosen because it partially includes the contribution from sheath to aerosol flow rates and also represents the widest standard deviation range seen by any of the experiments (see NaNO_3 , section 4.7 below).

Figure 4-18: Geometric mean diameter versus Ambient-A RH for a 100 ppm AS aerosol. Geometric mean diameters were measured by the SMPS (black circles) and calculated using a log-normal fit of the data (red squares).

Figure 4-19: Geometric standard deviation versus Ambient-A RH for a 100 ppm AS aerosol. Geometric standard deviations were measured directly by the SMPS (black circles) and calculated using a log-normal fit of the data (red squares).

Using a geometric mean of 52nm and geometric standard deviations of 1.5 and 1.9, AS growth as a function of RH was calculated using the model. The results of these calculations can be seen in figure 4-20. The calculated geometric mean is the solid black line while geometric standard deviations of 1.5 and 1.9 are the dark gray dash and light gray dash-dot, respectively. The very light gray shading represents the width of the size distributions. The SMPS geometric mean, and that mean + or - 1 geometric standard deviation are shown as red squares, green triangles and blue stars, respectively. From this plot, good agreement between the measured and modeled size distributions can be seen; the means are overlapping and the measured geometric SD falls between the upper and lower limits.

Figure 4-20: Plot of size distributions measured by the SMPS versus modeled size distributions using the Kelvin model for AS aerosol. SMPS geometric mean shown as red squares, mean + 1 geometric SD as green triangles and mean - 1 SD as blue stars. For model calculations, geometric mean was 52 nm at 0% RH. Dark grey dashes and light gray dash-dot traces represent size distribution widths using a geometric standard deviation of 1.5 and 1.9, respectively.

Using the modeled particle size data, the $f(RH)$ of the AS particles in visible were calculated as seen in figure 4-21. The $f(RH)$ for the 1.5 and 1.9 geometric standard deviations are shown as the dark gray dash and light gray dash-dot; $f(RH)$ values for

modeled data was calculated assuming a dry RH of 10%. The $f(RH)$ for the Ambient-A relative to the Dry and the Humidified relative to the dry are shown as the black circles and blue stars, respectively. Good agreement between the Ambient-A and Humidified data relative to the modeled data can be seen as both data sets fall on or between the standard deviation bounds of 1.5 and 1.9.

Figure 4-21: Plot of $f(RH)$ in the visible for the AS size distributions modeled in figure 4-20 using partial molar refraction. Geometric mean diameter was taken to be 52 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the dry channel, respectively.

Calculated $\gamma(RH)$ values for the visible are shown in figure 4-22. A natural log-linear fit of all 3 data points was done between the Ambient-A, Humidified and Dry channels in addition to calculation of discrete values using equation 4-6 between the Humidified and Ambient-A channels (red squares), Humidified and Dry channels (blue stars) and Ambient-A and Dry channels (green triangles). The gray box through the middle of the data is the range of modeled $\gamma(RH)$ calculated from figure 4-21. The $\gamma(RH)$ value between the fit and both data sets using the humidified channel show good agreement with each other and the model. This results From AS having a smooth growth

curve with RH; AS does effloresce and deliquesce, however the magnitude of growth increase (c in equation 4-4) is small. For salts showing stronger efflorescence and deliquescence, such as sodium chloride, a difference between these 3 values is indicative of this efflorescence/deliquescence occurring. The Ambient-A to Dry $\gamma(\text{RH})$ shows a large amount of scatter and does not agree well with the other values. This is a result of small differences between the measured extinctions and RH values. For this reason, the $\gamma(\text{RH})$ values are the most reliable when the RH of the ambient channel is situated between the Humidified and Dry channels.

Figure 4-22: Calculated $\gamma(\text{RH})$ in the visible using a natural log linear fit (black circles) for the Humidified relative to Ambient-A channel (red squares), Humidified relative to dry channel (blue stars), Ambient-A relative to dry channel (green triangles). The range of modeled $\gamma(\text{RH})$ values are shown as the gray box.

The 4 minute averaged AS data for the UV can be seen in figure 4-23. As with the visible data set, changes in extinction track well with changes in the RH.

Comparisons of the measured $f(\text{RH})$ values to the modeled ones can be seen in figure 4-24; the refractive index of AS in the UV was taken to be 1.55 from a polynomial fit of the data in (Toon, Pollack et al. 1976). The $f(\text{RH})$ for the Ambient-A channel agrees well with the model. However, the $f(\text{RH})$ on the Humidified channel does not agree as well and stems directly from the raw ring-downs. Base extinction on the Humidified channel

was approximately 4100 Mm^{-1} so the accuracy of the measured values is questionable. In reality, the measured aerosol extinction should have been near 1000 Mm^{-1} however separating out this much extinction from noise at the already short ring-down times is near impossible.

Figure 4-23: Plot of 4 minute averaged 100 ppm AS data measured in the UV (355 nm) by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

Figure 4-24: Plot of $f(\text{RH})$ in the UV for the AS size distributions modeled in figure 4-20 using partial molar refraction. Geometric mean diameter was taken to be 52 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(\text{RH})$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(\text{RH})$ values calculated relative to the dry channel, respectively.

The 4 minute averaged AS data for the IR can be seen in figure 4-25. Again, extinction tracks well with RH. Comparisons of the measured $f(\text{RH})$ values to the modeled ones can be seen in figure 4-26; the refractive index of AS in the IR was taken

to be 1.51 from a polynomial fit of the data in (Toon, Pollack et al. 1976). All measured and model values agree well.

Figure 4-25: Plot of 4 minute averaged 100 ppm AS data measured in the IR (1064 nm) by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

Figure 4-26: Plot of $f(RH)$ in the IR for the AS size distributions modeled in figure 4-22 using partial molar refraction. Geometric mean diameter was taken to be 52 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the dry channel, respectively.

4.9. NaNO_3 Results

Sodium nitrate is an interesting particle because of its behavior upon hydration and dehydration. Crystalline NaNO_3 does effloresce and deliquesce like most other ionic salts; aerosols produced directly from the crystalline solid will show this trend. However, if NaNO_3 is aerosolized from a liquid solution, the efflorescence and deliquescence

effects are sometimes not seen; instead NaNO_3 behaves more like a purely hygroscopic aerosol presumably because it forms an amorphous solid (Gysel, Weingartner et al. 2001; Hoffman, Laskin et al. 2004). This lack of efflorescence can be seen in the normalized size distributions versus Ambient-A RH shown in figure 4-27. Some of size distributions that were collected are not shown for clarity. In this figure it is evident that as RH decreases, the size distribution smoothly shifts to smaller particle sizes. If prompt efflorescence/deliquescence were being observed, then a sharp transition would have been evident.

Figure 4-27: Normalized size distributions of NaNO_3 as a function of RH. (Some of the size distributions collected have been removed for clarity.)

A 100 ppm NaNO_3 solution was aerosolized for measurement by the HC-CRDT. RH and temperature data for each channel are shown in figures 4-28 and 4-29, respectively. On all plots, the Ambient-A, Ambient-B, Dry and Humidified channels are represented as black circles, red squares, green triangles and blue stars, respectively. Shading on the Dry and Humidified channels represents different locations (upstream/downstream from the instrument) of RH/T sensors on the same channel.

Figure 4-28: Plot of 4 minute averaged 100 ppm NaNO₃ RH data measured by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels. Different color shades represent multiple RH measurements on the same channel.

Figure 4-29: Plot of 4 minute averaged 100 ppm NaNO₃ temperature data measured by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels. Different color shades represent multiple RH measurements on the same channel. The Dry channel's upstream temperature is omitted due to sensor malfunction.

The RH of the dilution air for the 100 ppm NaNO₃ aerosol was started high and slowly decreased over time, as the ambient RH measured on the Ambient-A, Ambient-B and at the valve on the Dry channel show(Fig. 4-13). The RH of the Humidified channel was constant at $72.5 \pm 0.5\%$ RH immediately after the humidifier and $82.1 \pm 0.2\%$ RH at the cavity exit. The Dry channel RH was also constant at $3.8 \pm 0.2\%$ RH immediately after the dryer and $7.8 \pm 0.3\%$ at cavity exit. Again, differences are within the accuracy limit of the sensors.

Extinction coefficients of the 100 ppm NaNO_3 aerosol measured at the visible wavelength by all channels of the HC-CRDT are shown in figure 4-30. All data points represent 4 minute averages. As the RH of the dilution air is decreased, the measured extinction coefficients on all channels decrease. On the ambient channels, this is expected since NaNO_3 is a hygroscopic aerosol. The decrease in extinction in the Dry and Humidified channel is most likely due to incomplete loss and uptake of water from kinetic limitations, respectively, by the NaNO_3 particle in the dryer and humidifier. (Particle may have not completely equilibrated at the measured RH.)

Figure 4-30: Plot of 4 minute averaged 100 ppm NaNO_3 extinction data measured in the visible (532 nm) by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

4.9.1. Uncertainty in geometric mean diameter and standard deviation

As with the NaNO_3 particles, a mean diameter and geometric standard deviation for AS had to be determined from the size distribution data. The raw size distributions measured by the SMPS were fit to a log-normal curve for a second determination of the geometric mean and standard deviation for comparison. The geometric mean diameters and standard deviations from the SMPS measured data (black circles) and log-normal fits (red squares) can be seen in figure 4-31 and 4-32, respectively.

Figure 4-31: Geometric mean diameter versus Ambient-A RH for a 100 ppm NaNO₃ aerosol. Geometric mean diameters were measured by the SMPS (black circles) and calculated using a log-normal fit of the data (red squares). Error values on slope and intercept are 2 σ .

Figure 4-32: Geometric standard deviation versus Ambient-A RH for a 100 ppm NaNO₃ aerosol. Geometric standard deviations were measured directly by the SMPS (black circles) and calculated using a log-normal fit of the data (red squares).

The geometric mean diameter (figure 4-31) shows an increase with the Ambient-A RH. Comparing the SMPS data to the log-normal fits, similar values are returned. The slopes of the SMPS data and log-normal fits were 0.60 ± 0.03 nm/RH% and 0.79 ± 0.04 nm/RH%, respectively and the intercepts were 26.22 ± 0.70 nm and 24.68 ± 1.04 nm. Errors represent 2 σ . While the slopes are significantly different from each other, the intercept values near 25 nm do not show any significant difference. For the geometric standard deviations (figure 32), the values fluctuate between a maximum of 1.90 and a minimum of 1.60 with a weak RH dependence. Average values for the SMPS data and

log-normal fits are 1.69 ± 0.07 and 1.74 ± 0.14 , respectively. Errors are 2σ . Again, a significant difference between the 2 values does not exist.

The combined data from the SMPS and log-normal fits of that data were used to establish geometric mean diameters and standard deviations for the model because it allows for a better idea of the effects of uncertainty in the values. From both of these methods, the modeled geometric mean diameter and standard deviation were taken to be $25 \text{ nm} \pm 2 \text{ nm}$ and 1.7 ± 0.2 , respectively. A plot of modeled particle growth versus actual particle growth as a function of RH is shown in figure 4-33. Solid black line in the middle of the figure is the modeled geometric mean diameter. Dark gray dashes and light gray dash-dots represent calculations using geometric standard deviations of 1.5 and 1.9, respectively. The very light gray shaded region represents the width of the size distribution using each geometric standard deviation. The geometric mean measured by the SMPS as a function of RH measured on the Ambient-A channel is shown as the red squares. That mean + or - 1 geometric standard deviation is shown as the green triangles and blue stars, respectively.

The $f(\text{RH})$ values calculated from the modeled data using partial molar refractions relative to 10% RH and measured data relative to the Dry channel is shown in figure 4-34. Again, the dark gray dash and light gray dash-dot represent values calculated using a geometric mean of 25 nm and a geometric standard deviation of 1.5 and 1.9, respectively. The very light gray shaded region between the 2 lines represents the range of calculated $f(\text{RH})$ values using different geometric standard deviations. The black circles and blue stars represent the $f(\text{RH})$ on the Ambient-A and humidified channels, respectively. Only

the average geometric mean diameter of 25 nm is shown as small shifts in mean diameter do not significantly affect model results.

Figure 4-33: Plot of size distributions measured by the SMPS versus modeled size distributions using the Kelvin model for NaNO_3 aerosol. SMPS geometric mean shown as red squares, mean + 1 geometric SD as green triangles and mean - 1 SD as blue stars. For model calculations, geometric mean was 25 nm at 0% RH. Dark grey dashes and light gray dash-dot traces represent size distribution widths using a geometric standard deviation of 1.5 and 1.9, respectively.

Figure 4-34: Plot of $f(RH)$ in the visible for the size distributions modeled in figure 4-22 using partial molar refraction. Geometric mean diameter was taken to be 25 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the dry channel, respectively.

From figure 4-33, it is evident that the size distributions measured by the SMPS and those calculated using the model do not agree well; the model significantly under-predicts changes in particle diameter as a function of RH. However, from the measured

and calculated $f(RH)$ values in figure 4-34, it appears that the calculations are modeling the optical properties of the system reasonably accurately using the parameter set given. The disagreement may stem from a kinetically limited loss and gain of water by amorphous NaNO_3 ; NaNO_3 particles have been previously shown to adopt a metastable amorphous state upon drying to very low RH and under vacuum conditions (Hoffman, Laskin et al. 2004). Kinetically limited deliquescence and efflorescence in similar semi-solid amorphous substances on time scales less than minutes to hours has been linked to high viscosity and low diffusivity of water into or out of the particle (Mikhailov, Vlasenko et al. 2009).

The aerosols measured by the SMPS were sampled immediately after being drawn into the second mixing chamber (through an impactor). The RH of these aerosols was measured in the Ambient-A channel at approximately the same time, but on a separate flow line. The extinction coefficient measurements in all channels of the HC-CRDT occurred significantly after the size distributions were measured by the SMPS (approximately 20 sec). Particles must travel through roughly 3m of flow lines after the second mixing chamber before reaching the CRD (the valving system, RH control system and NephCams are all upstream of the ring-down measurement). The particle sizes measured by the SMPS may represent an over-estimate of the particles measured in the CRD if the aerosol has not fully equilibrated at the desired RH. Further, the extra equilibration time allowed by the CRD measurement may not even be long enough to get NaNO_3 into its dry state.

This kinetically limited loss and uptake of water by NaNO_3 can also be seen in the raw ring-down data shown in figure 4-30. As the RH is decreased in time (figure 4-28)

the extinction measured by all of the channels decreases. In the Dry channel, the RH after the ring-down measurement remained constant at around 8% RH. As the RH of the incoming aerosol was decreased, the extent of equilibration of the Dry channel was effectively increased because of a decrease in the humidity gradient (ΔRH) between the ambient and Dry channels. As a result, the extinction coefficients measured in the Dry channel decreased. The reverse is true on the Humidified channel which maintained a constant RH near 82% after the ring-down measurement. As the RH of the incoming aerosol decreased, the extinction coefficient measurements in the Humidified channel also decreased due to an effective decrease in equilibration time for growth. The result is a wider range of calculated $f(RH)$ values than would be expected when the RH was stable in time. This effect can also skew the geometric standard deviation of the particles being measured. Larger particles will be less affected by the kinetically limited uptake of water due to the Kelvin effect, and as a result, the width of the size distributions can be larger than those modeled here.

This kinetic effect is not expected to be as pronounced for the other aerosols. The geometric mean diameters of all other particle types are approximately twice as large as NaNO_3 ; 60 nm versus 25 nm, so the NaNO_3 particles have to lose approximately 8 times as much water after generation in the same amount of time. Further, other salts exhibit prompt efflorescence; a rapid transition from an aqueous solution to a solid salt particle with some amount of water adsorbed to the surface. The surface water then quickly dissipates. With the NaNO_3 particles, the particle is a solution that is becoming more and more concentrated with decreasing RH as it transitions to an amorphous solid (Hoffman, Laskin et al. 2004). The lack of a clear phase transition implies that loss of water is

kinetically limited by how quickly it can be removed from the concentrated solution rather than how quickly pure water can evaporate from a highly curved solid surface.

A final point about the size distributions that should be recognized. The SMPS recirculates excess flow as sheath air and there is a finite RH equilibration time for this process. When the incoming aerosol RH is changing, the RH measured by the HC-CRDT on the ambient channel is not necessarily the same as the RH inside of the DMA. For experiments where the RH was decreased from an initially high value, the RH inside of the DMA could be higher than that recorded in the HC-CRDT. As a result, particles may be presumed to be larger at the measured RH than they actually are. The reverse is also true when doing experiments where the RH is increased from an initially low value. Effects where the RH inside of the SMPS is different than that in the rest of the system because of the sheath flow have been documented (Hämeri, Laaksonen et al. 2001; Biskos, Malinowski et al. 2006; Biskos, Paulsen et al. 2006; Biskos, Russell et al. 2006). Because of the slow growth/shrinkage of NaNO_3 as function of RH, this effect is expected to be minimal for the current aerosol but may be an issue for other particle types.

Measured 4 minute averages of the NaNO_3 aerosol in the UV and IR can be seen in figures 4-35 and 4-37, respectively. The modeled and measured $f(\text{RH})$ values for the UV and IR can be seen in figures 4-36 and 4-38, respectively. The refractive index of NaNO_3 in the UV and IR was assumed to be 1.61 and 1.57, respectively. A literature value for these 2 wavelengths was not available so the trend that refractive index changed by 0.02 between wavelengths (as is the case for AS and NaCl) was applied. In the UV, good agreement between the Ambient-A channel and $f(\text{RH})$ exists, but the Humidified

channel does not agree as well. This disagreement stems from the clean air extinction being approximately 3600 Mm^{-1} . Good agreement between the modeled and measured values exists in the IR for the Ambient-A and Humidified channels. A few points in the Humidified data do not agree as well as the rest of the data set. These points occurred at the end of the data series when the Ambient humidity had reached a minimum. This disagreement stems from the kinetically limited uptake of water by the particles.

Figure 4-35: Plot of 4 minute averaged 100 ppm NaNO_3 data measured in the UV by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

Figure 4-36: Plot of $f(\text{RH})$ in the UV for the size distributions modeled in 4-33 using partial molar refraction. Geometric mean diameter was taken to be 25 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(\text{RH})$ values.

Figure 4-37: Plot of 4 minute averaged 100 ppm NaNO₃ data measured in the IR by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

Figure 4-38: Plot of $f(RH)$ in the IR for the size distributions modeled in figure 4-33 using partial molar refraction. Geometric mean diameter was taken to be 25 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values.

4.10. NaCl Results

A 20 ppm NaCl aerosol was measured using the HC-CRDT and modeled using the Kelvin model described above. Unlike the NaNO₃ aerosol, NaCl is a strongly hygroscopic aerosol that exhibits distinct and significant efflorescence and deliquescence. The RH and temperature temporal profiles for a NaCl aerosol experiment is shown in figures 4-39 and 4-40.

The central portion of this data set has been removed because water droplets formed in the dilution flow lines during the increase in RH in time. When the dilution air flow is initially passed through a water bubbler humidifier, water droplets can form in the dilution flow line until an equilibrium RH is reached. These droplets are also transported into the aging chamber and other flow lines, invalidating all measurements. When experiments were run where the RH profile was decreasing in time, the RH of the system was allowed to equilibrate before data collection was begun. The process of lowering the RH only requires passing the dilution air through a diffusion dryer, so this problem of water in the lines is not encountered, as could be seen with the other data sets.

Figure 4-39: Plot of 4 minute averaged 20 ppm NaCl RH data measured by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels. Different color shades represent multiple RH measurement on the same channel.

As the RH of the incoming aerosol was increased in time, the extinction measured in the ambient-A visible channel also increased. Unlike the NaNO_3 aerosol, both the Dry and Humidified channel remained relatively constant in time. This is due to the fact that NaCl forms a crystalline solid upon losing water; i.e., demonstrates a prompt deliquescence/efflorescence transition and that kinetic limitations for the transition are not a factor in this case (Mirabel 2000).

Figure 4-40: Plot of 4 minute averaged 20 ppm NaCl temperature data measured by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels. Different color shades represent multiple RH measurements on the same channel. The Dry channel's valve temperature is omitted due to sensor malfunction.

Figure 4-41: Plot of 4 minute averaged 20 ppm NaCl extinction data measured in the visible by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

The RH in the ambient channel can clearly be seen to have increased in time (figure 4-41). In figures 4-42, geometric mean diameters measured by the SMPS and values calculated by a log-normal fit of the raw data (black circles and red squares, respectively) are seen to have changed in response to the change in RH. At low RH, the measured and fit average mean diameters are 43.11 ± 1.80 nm for the SMPS measured and 46.80 ± 1.22 nm from the fits, respectively. As the ambient RH was increased these values shifted to 55.18 ± 1.84 nm and 60.02 ± 1.91 nm. Toward the end of the experiment, the geometric mean diameters appear to be decreasing a bit, which may be

linked to differences in RH between the Ambient-A RH sensor and the actual RH inside of the DMA. For modeling of the NaCl aerosol, the dry aerosol was taken to be 44 nm in diameter.

Figure 4-42: Geometric mean diameter versus Ambient-A RH for a 20 ppm NaCl aerosol. Geometric mean diameters were measured by the SMPS (black circles) and calculated using a log-normal fit of the data (red squares).

Figure 4-43: Geometric standard deviation versus Ambient-A RH for a 20 ppm NaCl aerosol. Geometric standard deviations were measured directly by the SMPS (black circles) and calculated using a log-normal fit of the data (red squares).

The geometric standard deviations shown in figure 4-43 are relatively constant with increasing RH. The average geometric standard deviations for the measured and fit data were 1.64 ± 0.02 and 1.57 ± 0.02 , respectively. In keeping with the range of size distributions observed in the NaNO_3 data, the modeled geometric standard deviations were 1.70 ± 0.20 because of nonidealities in the SMPS measurement.

Modeled growth results for the efflorescence transition of NaCl versus data from the SMPS as a function of relative humidity are shown in figure 44. At low RH ($< 30\%$) the salt is in its crystalline form. No growth from the initial size of 44 nm is observed. A steep jump between 30% and 40% RH can be seen; this is indicative of the efflorescence transition of NaCl. Model steps were set to 10% RH, so where the exact transition occurs was not calculated, hence the gradual rise in diameter between 30% and 40% RH instead of a steep jump. This ERH value is slightly lower than values reported previously in the literature of 46 - 48%, but is most likely a result of the parameter set used. The ERH of the NaCl aerosol measured in this work was also less than the literature value as seen in figure 4-42 where hydrated aerosol were still observed at 46%.

Unlike the NaNO_3 aerosol, a distinct transition due to hydration was observed indicating that the model is capable of picking up this effect. The measured and modeled diameters do not agree as well at higher RH, the measured values are consistently less than the modeled ones. The log-normal fit data was not shown for clarity, however better agreement is observed. As with the drop in extinction coefficient near the end of the time period in figure 4-41, this is thought to be a direct result of the RH in the DMA being less than that actually measured by the Ambient-A channel. Shifting of the measured data to lower RH by approximately 10% would give significantly better agreement.

One other potential source of size disagreement is non-sphericity effects on the sizing mechanism of the DMA. The DMA sizes particles based upon mobility as a function of charge within an electric field and particles are assumed to have a spherical morphology. If non-spherical morphologies are introduced, as is the case for NaCl, then particle size measured by the DMA is an equivalent mobility diameter. As a result of slip

and drag induced by non-spherical shapes, the DMA over-measures particle diameters. So, the base particle size for the NaCl particles could actually be closer to 40 nm than the 44 nm used in modeling. For the hydrated particles at higher ambient-RH, spherical morphology can be assumed since the particles are in a droplet form, so these values would be accurate.

Figure 4-44: Plot of size distributions measured by the SMPS versus modeled size distributions using the Kelvin model for NaCl aerosol. SMPS geometric mean shown as red squares, mean + 1 geometric SD as green triangles and mean - 1 SD as blue stars. For model calculations, geometric mean was 44 nm at 0% RH. Dark grey dashes and light gray dash-dot traces represent size distribution widths using a geometric standard deviation of 1.5 and 1.9, respectively.

The modeled growth of NaCl was then used to calculate the $f(RH)$ as can be seen in figure 4-45. Black dots and blue stars represent the Ambient-A and Humidified channels relative to the Dry channel. The dark gray dash and light gray dash dot traces represent modeled $f(RH)$ using the size distribution data in figure 4-44. From this plot, it is evident that the model is doing a good job of predicting the $f(RH)$ of an NaCl aerosol using the range of values used. NaCl displays significantly more growth than AS and $NaNO_3$ as a function of RH and the $f(RH)$ shows the same trend.

Figure 4-45: Plot of $f(RH)$ in the visible for the size distributions modeled in figure 4-44 using partial molar refraction. Geometric mean diameter was taken to be 44 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the Dry channel, respectively.

The $f(RH)$ model calculations versus actual $f(RH)$ data in the IR and UV are shown in figures 4-46 and 4-48, respectively. Figures 4-47 and 4-49 are the 4 minute averaged extinction data for the IR and UV channels collected by the HC-CRDT, respectively.

The $f(RH)$ data in the IR shows good general agreement with model calculations although there is slight disagreement for some of the data points. This disagreement is most likely a result of the small absolute magnitude of the IR signals, many of the dry IR measurements were at or near the LOQ for the HC-CRDT on that channel. As a result, small fluctuations in measured values on the dry channel can cause significant fluctuation in the calculated $f(RH)$ data.

Figure 4-46: Plot of $f(RH)$ in the IR for the size distributions modeled in figure 4-44 using partial molar refraction. Geometric mean diameter was taken to be 44 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the Dry channel, respectively.

Figure 4-47: Plot of 4 minute averaged 20 ppm NaCl data measured in the IR by the Ambient-A (black circles), Dry (green triangles) and Humidified (blue stars) channels.

The $f(RH)$ in the UV shows good agreement with model predictions, although some of the measured $f(RH)$ values are low relative to predictions especially the last 4 data points in figure 4-48. The clean air extinction during the NaCl data set started around 3500 Mm^{-1} but ended around 3750 Mm^{-1} as a result of the water droplets in the flow lines. This increase in the clean air extinction is most likely impacting the accuracy of the measurement on the Humidified channel.

Figure 4-48: Plot of $f(RH)$ in the UV for the size distributions modeled in figure 4-44 using partial molar refraction. Geometric mean diameter was taken to be 44 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the Dry channel, respectively.

Figure 4-49: Plot of 4 minute averaged 20 ppm NaCl data measured in the UV by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

4.10.1. NaCl $\gamma(RH)$

The NaCl aerosol provides a unique insight into the behavior of $\gamma(RH)$ because of the significant size loss upon efflorescing. Modeled values of $\gamma(RH)$ in the IR, visible and UV for an NaCl aerosol with a geometric mean of 44 nm and a geometric standard deviation of 1.5 can be seen in table 4-10. High RH was taken to be 82%. NaCl effloresces around 40%, so both the 10% and 30% RH particles are in their effloresced state; the extinction values for each are identical. The 30% RH has a higher $\gamma(RH)$

because the ΔRH between the high RH and the RH under investigation is less. The $\gamma(RH)$ for the 50% RH case is the lowest because NaCl shows significant loss of size upon efflorescing (c in equation 4-4 is large). However, this $\gamma(RH)$ represents the true value of $\gamma(RH)$ since it is truly showing the curvature of $f(RH)$ since at both RH's the particles are in their hydrated state. The $\gamma(RH)$ value for the 10% and 30% cases is superficially large because of this water loss effect.

Table 4-10: Calculated $\gamma(RH)$ from modeled NaCl data with a geometric mean of 44 nm and geometric standard deviation of 1.5 relative to a high RH of 82%.

Channel	10% RH	30% RH	50% RH
IR	1.99	2.35	1.19
Vis	1.92	2.27	1.17
UV	1.88	2.23	1.15

These trends are mirrored in table 4-11 for $\gamma(RH)$ values in the visible determined from the measured NaCl data. Only visible data was included for simplicity. This data has been split between low and high representing the first and second half of the data set where the RH was approximately 10% and 50%, respectively. The $\gamma(RH)$ calculated between the Ambient-A and Dry channels is the smallest value because the NaCl particles should be in their effloresced state and extinction on each cavity should be identical. However, due to the small absolute magnitude of the signal (approximately 10 Mm^{-1}), small fluctuations in the measured value caused significant variation in γ . Also, when the RH on the Ambient-A channel was low, all of the other γ values were superficially high because of water loss. The $\gamma(RH)$ value between the Humidified and Ambient-A channels when RH was high (and Ambient-A particles were hydrated), represents the actual $\gamma(RH)$ value for the particles; only here is $\gamma(RH)$ actually a measure

of the curvature of $f(RH)$. Because of this discrepancy between γ values, when calculated discretely, between the Ambient-A, Humidified and Dry channels, it is possible to determine whether efflorescent particles are present. Calculating a 3-point fit of the data misses this effect entirely. In the event that all the values are the same, then efflorescence is not present.

Table 4-11: Calculated $\gamma(RH)$ in the visible from the measured NaCl data

RH	3-pt fit	Humidified -> Ambient-A	Humidified -> Dry	Ambient-A -> Dry
Low	1.84	1.85	1.83	1.34
High	1.70	1.47	1.73	2.21

4.11. Nigrosin results

The $f(RH)$ for a black carbon surrogate particle, Nigrosin, was also measured using the HC-CRDT. Unlike black carbon, Nigrosin is water soluble and is not expected to form a core-shell type morphology when exposed to elevated RH levels. Also, like most organics, Nigrosin is relatively hydrophobic and does not experience significant growth until high RH. A plot of the RH and temperature on all channels can be seen in figures 4-50 and 4-51. In this set of data, the RH was decreased in time so problems with water in the dilution lines (as with NaCl) were avoided.

Figure 4-50: Plot of 4 minute averaged 20 ppm Nigrosin RH data measured by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels. Different color shades represent multiple RH measurement on the same channel.

Figure 4-51: Plot of 4 minute averaged 20 ppm Nigrosin temperature data measured by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels. Different color shades represent multiple RH measurements on the same channel. The Dry channel's valve temperature is omitted due to sensor malfunction.

The geometric mean diameters and standard deviations measured by the SMPS and calculated by a log-normal fit of the data are shown in figures 4-52 and 4-53, respectively. The Nigrosin particles do demonstrate continuous growth as a function of RH, however this growth is much weaker than for the salt particles. The intercepts on the geometric mean diameters for Nigrosin are significantly different 53.92 ± 1.10 nm and 58.89 ± 1.04 nm for the values obtained directly from the SMPS and log-normal fits of the data. These differences are attributable to differences in the geometric standard deviations between the measured and fit calculations; 1.66 ± 0.02 versus 1.57 ± 0.03 , respectively. For model calculations, the average geometric mean diameter between both methods was used: 56.5 nm. As with other aerosols, the modeled geometric standard deviation was 1.7 ± 0.2 .

Figure 4-52: Geometric mean diameter versus Ambient-A RH for 20 ppm Nigrosin aerosol. Geometric mean diameters were measured by the SMPS (black circles) and calculated using a log-normal fit of the data (red squares). Error values on slope and intercept are 2σ .

Figure 4-53: Geometric standard deviation versus Ambient-A RH for a 20 ppm Nigrosin aerosol. Geometric standard deviations were measured directly by the SMPS (black circles) and calculated using a log-normal fit of the data (red squares).

A parameter set for modeling the uptake of water by Nigrosin was not available in the literature. The molecular mass of Nigrosin was assumed to be 202 g/mole as provided from the Sigma-Aldrich product literature. Density of pure solid Nigrosin was taken to be 1 g/mL. Density, activity and salt-to-water interaction parameters were set equal to that of NaNO_3 . Nigrosin is a water soluble organic, is not expected to effloresce or deliquesce, shows weak growth with increasing RH and could form an amorphous solid upon significant drying; it is also possible that Nigrosin forms a gel or glass like

particle upon drying similar to other types of organics (Mikhailov, Vlasenko et al. 2009).

As a result, NaNO_3 was deemed to be the most appropriate values of those available.

The Kelvin model was run to calculate the growth of Nigrosin as a function of RH and the resulting optical parameters. There is extremely good mapping between the measured geometric mean diameters from the SMPS and modeled results as shown in figure 4-54.

Figure 4-54: Plot of size distributions measured by the SMPS versus modeled size distributions using the Kelvin model for Nigrosin aerosol. SMPS geometric mean shown as red squares, mean + 1 geometric SD as green triangles and mean - 1 SD as blue stars. For model calculations, geometric mean was 44 nm at 0% RH. Dark grey dashes and light gray dash-dot traces represent size distribution widths using a geometric standard deviation of 1.5 and 1.9, respectively.

The raw visible extinction data in time is shown in figures 4-55. As the RH on the ambient channel decreases, so too does the extinction measured by that channel.

Unlike the salt particles, the relative amount of this decrease is less due to the hygroscopicity of Nigrosin.

Figure 4-55: Plot of 4 minute averaged 20 ppm Nigrosin extinction data measured in the visible (532 nm) by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

Calculated $f(RH)$ values using the Kelvin model and from the raw data are shown in figure 4-56. The relative magnitude of change in extinction with RH is dampened relative to all of the other particle types, including $NaNO_3$. The model does a good job of mapping $f(RH)$ at lower RH, but is undercalculating $f(RH)$ at higher RH. It is also interesting to note that the orientation of the 1.5 and 1.9 geometric standard deviations are reversed relative to all of the other particle types. For all of the salts, $f(RH)$ increased with decreasing geometric standard deviation, while it is increasing with increasing geometric standard deviation here. This is most likely due to the absorbing character of Nigrosin. As Nigrosin takes up water, the refractive index shifts towards that of water. Absorption by the particle decreases and approaches a minimum limit as water uptake occurs, however scattering by the particles increase due to increasing particle size. It seems from this plot that the relative magnitude of the 2 processes (absorption decreasing and scattering increasing) are approximately equal as seen by the small $f(RH)$ values measured.

Figure 4-56: Plot of $f(RH)$ in the visible for the size distributions modeled in figure 4-54 using partial molar refraction. Geometric mean diameter was taken to be 44 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the Dry channel, respectively.

4.11.1. Calculation of Nigrosin refractive index at other wavelengths

Another caveat to modeling the change in optical properties of Nigrosin is that values for the refractive index in the IR and UV have not been previously quantified, so a value must be inferred. At 532 nm, the refractive index of Nigrosin has been reported as $1.70 (\pm 0.04) + 0.31i (\pm 0.05i)$ (Lack, Lovejoy et al. 2006). To derive an effective refractive index for Nigrosin in the UV and IR, some mathematical manipulation was necessary.

The imaginary term of the refractive index has been linked to the absorption by the bulk (A_{Bulk}) (Bohren and Huffman 1983):

$$A_{Bulk} = \frac{4\pi k}{\lambda} \quad (\text{eq 4-22})$$

where k is the imaginary part of the refractive index and λ is the wavelength. The absorption of Nigrosin in the bulk was not performed, however an absorption spectrum of a 20 ppm Nigrosin solution was collected as shown in figure 4-57.

Figure 4-57: Plot of absorbance versus wavelength for a 20 ppm Nigrosin solution measured using a Beckman DU-530 between 300 nm and 1100 nm. ($\lambda_{\text{step}} = 5.0$ nm)

Many black carbon-like aerosols show a λ^{-1} dependence on absorption. However, the absorption character of Nigrosin does not completely follow this trend as can be seen in figure 4-57. As wavelength decreases, absorption increases until 580 nm, where it turns over and starts decreasing. This decrease persists until 420 nm when the spectrum turns over again and starts increasing. Below 420 nm, the spectrum is monotonically increasing.

Since the absorption spectrum was collected on a 20 ppm Nigrosin solution prepared in de-ionized water any absorption by the solution was attributed to Nigrosin. By taking the ratio of Nigrosin absorbance at multiple wavelengths an effective imaginary term in the refractive index was calculated for wavelengths other than 532 nm:

$$k_2 = k_{532} \left(\frac{\lambda_2}{532 \text{ nm}} \right) \left(\frac{A_{\text{Bulk},2}}{A_{\text{Bulk},532}} \right) \quad (\text{eq 4-23})$$

where all variables are defined as in eq 4-22. For aerosol particles, the refractive index constants can be related to absorption cross-section (σ_{abs}), the number of particles (N) and the wavelength of light (λ) by (Moosmüller, Chakrabarty et al. 2009):

$$N\lambda\sigma_{\text{abs}} = 6\pi Im \left\{ \frac{m^2 - 1}{m^2 + 2} \right\} \quad (\text{eq 4-24})$$

where m is the complex refractive index and Im stands for the imaginary portion of the term in brackets. Here, $N^*\sigma_{\text{abs}}$ was taken to be proportional to A_{Bulk} . It then follows from eq 4-24 that

$$\frac{(532\text{nm})A_{\text{Bulk},532}}{\lambda_2 A_2} = \frac{\text{Im}\left\{\frac{m_{532}^2 - 1}{m_{532}^2 + 2}\right\}}{\text{Im}\left\{\frac{m_2^2 - 1}{m_2^2 + 2}\right\}} \quad (\text{eq 4-24})$$

where all terms are defined similarly to eq 4-24 and the subscripts denote wavelength.

Using equation 4-23 followed by equation 4-24, values for the real and imaginary terms of the refractive index of Nigrosin in the IR and UV were determined to be $1.64 + 0.07i$ and $1.69 + 0.17i$, respectively; see table 4-12.

Table 4-12: Absorbance and imaginary refractive index versus wavelength for Nigrosin solution at the 3 wavelengths used in the HC-CRDT

Wavelength (nm)	A	n	k
1064	0.051	1.64	0.07
532	0.427	1.7	0.31
355	0.355	1.69	0.17

Plots of the measured UV extinction and $f(\text{RH})$ in the UV for the Nigrosin aerosol are shown in figures 4-58 and 4-59, respectively. Unlike in the visible, the UV does not show significant differentiation between the Humidified, Dry and Ambient channels. This is most likely due to the decrease in strength when shifting to the UV from the visible. This trend is mirrored in $f(\text{RH})$; all values are near 1. The modeling of $f(\text{RH})$ is over calculating the value, but the general trend of very little increase in extinction with RH is maintained. It is also possible that extinction in the UV by the humidified channel is being under-measured as the clean air extinction was approximately 3750 Mm^{-1} .

Figure 4-58: Plot of 4 minute averaged 20 ppm Nigrosin data measured in the UV by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

Figure 4-59: Plot of $f(RH)$ in the UV for the size distributions modeled in figure 4-54 using partial molar refraction. Geometric mean diameter was taken to be 44 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the Dry channel, respectively.

Plots of the measured IR extinction and $f(RH)$ in the IR for the Nigrosin aerosol are shown in figures 4-60 and 4-61. Like with the UV, very little differentiation between the Humidified, Dry and Ambient channels exists. This is most likely due to absorption strength going towards 0 in the IR. Further, since growth of Nigrosin as a function of RH is very weak, all $f(RH)$; all values are near 1. The modeling of $f(RH)$ is close to the measured values. The absolute magnitudes of all measured values in the IR are close to the LOQ for the HC-CRDT this is probably the most prominent source of error.

Figure 4-60: Plot of 4 minute averaged 20 ppm Nigrosin data measured in the IR by the Ambient-A (black circles), Ambient-B (red squares), Dry (green triangles) and Humidified (blue stars) channels.

Figure 4-61: Plot of $f(RH)$ in the IR for the size distributions modeled in figure 4-54 using partial molar refraction. Geometric mean diameter was taken to be 44 nm. Dashed dark gray line and dash-dot light gray line represent geometric standard deviations of 1.5 and 1.9 respectively. Lighter shading in between these 2 traces show the range of $f(RH)$ values calculated between these 2 limits. Solid black dot and blue stars are the Ambient-A and Humidified channel visible $f(RH)$ values calculated relative to the Dry channel, respectively.

5. Conclusions & Future Directions

The NephCam imaging system was optimized by imaging targets for astigmatism, calibration dot matrices for distortion and coma, a white background for vignetting, checkerboards for contrast and a white line on a black background to simulate the actual diode laser's image shape. The 1.6 aperture on the camera was chosen because it allowed for the most intensity, lack of astigmatism and coma as evidenced by the white background and targets, respectively. But, relative to the larger aperture settings, the 1.6 aperture must be corrected for the effects of vignetting; image intensity drops off as $\cos^4$ from center. The 1.6 aperture also has less total contrast across an image - 0.3 for the 1.6 aperture versus 1 for the 8 aperture - but the 1.6 aperture was preferable because the contrast was constant across an image as seen by the modular transfer functions. While it is possible to correct for the effects of vignetting, it is not possible to correct for changes in contrast.

A model was developed to link theoretical image shape to those actually captured by the NephCam. The model was based entirely upon ray tracing methods and all physical parameters of the camera system were considered. When considering only a single size of particle, model and image shapes do not agree very well. However, the inclusion of multiple charge-to-size effects present from the DMA's sizing mechanism improved agreement significantly. Finally, the inclusion of contrast effects from the 1.6 aperture - contrast is only 30% - resulted in further improvement in agreement between modeled and actual image shapes.

The NephCam was calibrated as a function of particle size for AS aerosols. The HC-CRDT was operated in tandem to generate scattering coefficients; absorption for AS

is negligible so extinction and scattering are equivalent. Because of the multiple charge-to-size effects from the DMA, smaller particle diameters required a 2nd order polynomial calibration curve instead of a linear one. In this size regime, the measured scattering coefficients increases faster than measured peak amplitudes. However, as base particle size increased above 400 nm the magnitude of the non-linear effects decreased to 0. In this size regime, the relative increase in scattering versus peak amplitude goes towards 1 as a result of camera collection angles and collection efficiency. Also, size-selected particles with base diameters 700 nm or larger do not exhibit multiple charge-to-size effects because of the 1 μ m impactor on the DMA; these particles are removed by impaction. The SSA of size selected Nigrosin particles was calculated and good agreement was observed at larger particle sizes. At smaller particle sizes the multiple charge-to-size effect caused the SSA to be over measured.

Relative humidity dependent extinction coefficients of various water soluble particles were measured: AS, NaNO₃, NaCl and Nigrosin. The effect of water uptake on the measured extinction coefficients was modeled using the Kelvin equation and 3 refractive index mixing rules: volume, Maxwell-Garnett and partial molar refraction. Good agreement between modeled results and actual data were observed for all of the salt particles except in the UV of the humidified channel. This disagreement stems from the measured extinction on this channel being too high to accurately measure values. Less agreement between the Nigrosin measured and modeled data was obtained as a result of inferring Nigrosin's water uptake behavior; it was assumed to behave identically to NaNO₃. Also, the absorbing character of Nigrosin could be affecting these values since effective refractive indices were inferred from the mixing rules. While all 3 mixing rules

worked well for the non-absorbing salts they may not be as appropriate for absorbing species. In the future, this disagreement should be revisited with the inclusion of a scattering measurement; a single NephCam would not have given enough information, so only extinction was measured.

In moving forward with the NephCams a better algorithm for extracting the underlying particle size from image shape must be extracted. Shape effects in the images arise from higher order Bessel terms being present when light interacts with a particle. A similar situation is true with atomic orbitals; as atoms increase in size, the number of available orbitals increases and the shape of the orbitals change depending upon type (i.e. S, P, D, F). My thoughts toward extracting size information *a priori* from the image shape is that the NephCam will have to be trained to extract the convolution of Bessel functions from a set of particles; Principle Component Analysis is the most likely scheme. The speed of data collection by the cameras must be increased so that the extraction of this type of information is possible. The large number of particles being measured with a 10 sec exposure time makes this extraction physically impossible. Extending NephCam usage to all 4 channels of the HC-CRDT will help with this problem to some extent as changes in scattering as a function of RH should help in the derivation of size and refractive index of particles on the dry channel.

In moving forward with the HC-CRDT, more data needs to be collected. Some small problems, like vibration sensitivity and clean air baselines, need to be addressed. But, the instrument is ready to collect humidification data on many different particles types; specifically carbonaceous and ambient aerosols. Currently, a wood-burner is being developed in our lab to examine the optical properties of different types of smoldering

wood combustion as a function of RH. The measurement of ambient aerosols using the HC-CRDT will allow for the elucidation of particle growth and transformation mechanisms which is currently a point of intense research among the aerosol community. Instrument inter-comparisons are also of interest to validate the HC-CRDT.

6. References

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