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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Absorbing aerosols at high relative humidity: closure between hygroscopic growth and optical properties" *by* J. M. Flores et al.

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We are grateful for the time and effort you have invested reviewing our work. Below are the responses to your comments.

The use of the term 'closure' in the title is not accurate.

We have changed the title of the paper to: "Absorbing aerosols at high relative humidity: linking hygroscopic growth to optical properties"

Describe the laboratory measurements in abstract.

The abstract has been modified to read the following: "One of the major uncertainties in the understanding of Earth's climate system is the interaction between solar radiation and aerosols in the atmosphere. Aerosols exposed to high humidity areas will change their chemical, physical, and optical properties due to their increased water content. To model hydrated aerosols, atmospheric chemistry and climate models often use the volume weighted mixing rule to predict the complex refractive index (RI) of aerosols when they interact with high relative humidity, and, in general, assume homogeneous mixing. This study explores the validity of these assumptions. A humidified cavity ring down aerosol spectrometer (CRD-AS) and a tandem hygroscopic DMA (differential mobility analyzer) were used to measure the extinction coefficient and hygroscopic growth factors of humidified aerosols, respectively. The measurements were performed at 80% and 90% RH at wavelengths of 532 nm and 355 nm using size-selected aerosols with different degrees of absorption; from purely scattering to highly absorbing particles. The ratio of the humidified to the dry extinction coefficients (fRHext(%RH,Dry)) is measured and compared to theoretical calculations based on Mie theory. Using the measured hygroscopic growth factors and assuming homogeneous mixing, the expected RIs using the volume weighted mixing rule are compared to the RIs derived from the extinction measurements. We found a weak linear dependence or no dependence of fRH(%RH,Dry) with size for hydrated absorbing aerosols in contrast to the non-monotonically decreasing behavior with size for purely scattering aerosols. No discernible difference could be made between the two wavelengths used. Less than 7% differences were found between the real parts of the complex refractive indices derived and those calculated using the volume weighted mixing rule, and the imaginary parts had up to a 20% difference. However, for substances with growth factor less than 1.15 the volume weighted mixing rule assumption needs to be taken with caution as the imaginary part of the complex RI can be underestimated."

It is not clear to me how the authors got the RI from measurements of size-selected extinction alone.

We have added the following paragraph to the methodology section: "For homogeneous spheres, the extinction coefficient (αext) is described by: α_ext=Nσ_ext=1/4 πNDˆ2 Q_ext (2) where σext is the extinction cross section, N is the particle concentration, D the particle diameter, and Qext the extinction efficiency (which is the ratio of the optical extinction cross section to the geometric area of the particle). The extinction efficiency at a given wavelength and RI is only a function of the particle size. The particle size is normally expressed as a dimensionless size parameter (x) which is the ratio of the particle circumference to the wavelength (λ) of the incident light (x = πD/λ). The RI of aerosols can then be retrieved by using Mie theory and finding the theoretical Qext curve that best fits the measured Qext values for the different aerosol size parameters measured."

There is no discussion of uncertainty in extinction or size measurements and how they propagate through to refractive index.

We have added the following discussion: The retrieval algorithm described in Abo-Rizq et al. (2007) was used to retrieve the complex refractive indices. The algorithm simultaneously varies n and k and scans through all physically possible values of the complex RI within a chosen resolution until it minimizes χ2: χˆ2 (n,k)=$\sum$_($i = 1)\hat{}N((Q_(extmeasured) - Q_(extcalculated)(n,k))_\hat{}2)/(\varepsilon$_iˆ2) (3) where N is the number of diameters measured, and ε is the estimated error in the measurement. To estimate the retrieval uncertainties in n and k (Δn and Δk), it is assumed that the standard deviations of the measurements are normally distributed, and that the values of χ2 follow a χ2-distribution for the two degrees of freedom, n and k. The algorithm returns the values of n and k that satisfy $\chi02 \leq \chi2 \leq \chi02$ + 2.298 where the value 2.298 denotes the 1σ deviation from the minimum χ2 (χ02). Miles et al. (2010) showed that the accuracy in the retrieval of the real part of the RI has a minimum error of -0.5% and +0.3%, to account for this error we've added a further 1% error to the retrieval uncertainties.

A discussion of how multiple-charge particles effect the SMPS measurements is needed.

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Following the comments from the reviewers we have now added a correction for multiply charged particles. We have also added the following section to the methodology section:

Multiple charge corrections

When choosing a mobility diameter from the DMA, singly and multiply charged particles are transmitted through the sample flow. The multiply charged particles affect the optical measurements, leading to overestimation of the optical extinction cross section. In order to reduce biases arising from multiply charged particles we used a solution concentration of 500 mg L-1 for sizes between 200 nm to 300 nm, and a 1000 mg L-1 solution for 350 nm to 550 nm diameter aerosol. These solution concentrations yielded between 2.7–7% and up to 1% of doubly and triply charged particles, respectively. These percentages were used to correct for the contribution to the total extinction at each sampled diameter using literature values of the complex refractive indices, when available (e.g. ammonium sulfate), and to correct the size distributions measured by the SMPS. When RI literature values were not available, only the size distributions were corrected. The median diameter from the corrected SMPS size distribution was taken as the measured diameter.

Data showing the wavelength dependence of the measurements is not presented. Extinction for particles with the composition used should be very different at different wavelengths and should provide another means for determining RI, yet this was not discussed.

We are not sure to what data the reviewer refers to. For the laboratory experiments we show in Figure 3 the optical growth at two wavelengths: 532 nm and at 355 nm as a function of size. In Table 1 we show all of the retrieved RIs for both wavelengths used. If the reviewer refers to the modeling calculations, these calculations have been removed from the manuscript.

Fig 3,4,6 captions do not match figure

The mistake was noticed by the editor and a corrected version was implemented on the 26th of January, 2012. We apologize for the mistake.

Exponential curve should be drawn in Figure 2 and 3 to demonstrate claim.

The discussion of exponential behavior has been removed and the following has been added:

“The ammonium sulfate measurements show, generally, that fRHext(80%RH,Dry) and fRHext(90%RH,Dry) decreases with size non-monotonically. Garland et al. (2007) parameterized AS at 80% RH with an exponential function, however the theoretical calculations and measurements of fRHext at both RHs show that the relationship is not fundamentally exponential as it shows the existence of the Mie resonance structure.”

Figure 5 not discussed in text.

Figure 5 is discussed in the following paragraph:

“For the IHSS Pahokee peat and nigrosine aerosols, there is an overestimation of the retrieved imaginary part with respect to the calculated one with the volume weighted mixing rule at both wavelengths and RHs. Both substances have a small GF (GF(80%)=1.09 and GF(90%)=1.17 for Pahokee peat, and GF(80%)=1.12 and GF(90%)=1.24 for nigrosine), which raises the question of their internal structures after humidification. It is not clear whether there is a complete dissolution or whether a small shell of water forms around the particles forming a core-shell structure. To explore whether there could be an optical distinction for Pahokee peat and nigrosine, the extinction efficiency as a function of size parameter was calculated separately for each case. For the homogenously mixed case, Qext-homogeneous was calculated with the RI obtained from the volume weighted mixing rule. For the core-shell structure, Qext-core-shell was calculated using the diameter measured after humidification as the total diameter, and the dry diameter selected by the first DMA as the core diameter. The RI of the core was taken from the dry measurements, and the RI of water was used for the

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RI of the shell. The codes by Liu et al. (2007a) and Bohren and Hoffmann (1983) were used to calculate Qext-core-shell and Qext-homogeneous, respectively. Lastly, the ratio of Qext-core-shell to Qext-homogeneous was calculated and plotted as a function of size parameter for both wavelengths in Figure 5. From Figure 5 at 80% RH, where the Pahokee peat and nigrosine particles only grew 9% and 12%, respectively, there is less than a 5% difference between the values obtained with a core-shell structure and those obtained by assuming homogenous mixture for size parameters less than 2.5. For 90% RH, the differences between the core-shell structure and a homogeneously mixed particle are more noticeable, with up to a 7% difference for the Pahokee peat. A clear distinction between the two mixing assumptions can be observed at size parameters greater than 3 with lower Qext values for a core-shell structure than for a homogeneously mixed case. Therefore, the nigrosine measurements shown in Figure 4b, show that the difference between the measurements (open circles) and the homogeneous mixing assumption (solid line) is greater at larger size parameters than the core-shell calculation (red solid symbols); which suggest a core-shell structure. However, the measured Qext still differs from the core-shell and homogeneous model at the intermediate sizes for nigrosine and it also does not seem to explain adequately the results for Pahokee peat at 80% RH and 532 nm (Figure 4a). Therefore we cannot conclusively say whether the core shell model explains fully the result. There is the possibility that partial dissolution of nigrosine or Pahokee peat dissolved into the surrounding water, causing the “coating” to be slightly absorbing. At the same time, the size of the “core” will have shrunk making our original assumptions of size and complex RI incorrect. Unfortunately, with the precision of the experiments performed in this study it is not possible to examine this hypothesis. However, we do observe from Figure 4 and 5 that if an aerosol with a GF < 1.15 is assumed to be homogenously mixed, when in reality its internal structure resembles a core-shell, it will result in an underestimation of the imaginary part of the complex refractive index when the RI is calculated with the volume weighted mixing rule.”

Pg 1020, spell out ammonium sulfate. The abstract has been restructured

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Pg 1026, “use d”. Fixed

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