Sensitivity of Aerosol Refractive Index Retrievals Using Optical Spectroscopy

Kyle J. Zarzana,1,2 Christopher D. Cappa,3 and Margaret A. Tolbert1,2

1Cooperative Institute for Research in Environmental Sciences, University of Colorado—Boulder, Colorado, USA
2Department of Chemistry and Biochemistry, University of Colorado—Boulder, Colorado, USA
3Department of Civil and Environmental Engineering, University of California, Davis, California, USA

Accurate refractive index values are required to determine the effects of aerosol particles on direct radiative forcing. Theoretical retrievals using extinction data alone or extinction plus absorption data have been simulated to determine the sensitivity of each retrieval. A range of aerosol types with a range of different refractive indices were considered. The simulations showed that the extinction-only retrieval was not able to accurately or precisely retrieve refractive index values, even for purely scattering compounds, but the addition of a simulated absorption measurement greatly improved the retrieval.

1. INTRODUCTION

The complex refractive index describes how light interacts with a substance. The refractive index is wavelength-dependent and is given by \( m = n + ki \), where to first order the real part \( n \) describes the scattering, and the imaginary part \( k \) describes the absorption. For atmospheric aerosol particles, the refractive index, in conjunction with the particle shape and size, can be used to determine the amount of light that is scattered and absorbed by the particle. Accurate values for aerosol refractive indices are required to determine the effects of particles on climate, but at present these numbers are poorly constrained, particularly for organic aerosol, and the direct effect of aerosol particles on climate remains one of the largest sources of uncertainty in total radiative forcing (IPCC 2013).

Cavity ring-down (CRD) and cavity enhanced extinction spectroscopy (CEES) have been used by numerous groups to determine the refractive index of aerosol particles (Pettersson et al. 2004; Dinar et al. 2008; Hasenkopf et al. 2010; Nakayama et al. 2010b; Cappa et al. 2011; Redmond and Thompson 2011; Washenfelder et al. 2013; Toole et al. 2013). CRD and CEES measure extinction, the sum of scattering and absorption, so for measurements made at a single size, a purely scattering substance cannot be distinguished from a substance that also absorbs light. The scattering and absorption by a particle behave differently as a function of particle size, so in principle extinction measurements at numerous sizes allow for the retrieval of the complex refractive index, assuming a size-independent refractive index. In addition to measuring only extinction, measurements of the scattering or the absorption can be made separately using either nephelometry or photoacoustic spectroscopy (PAS), respectively. A combination of CRD and PAS has been used by several groups to determine the refractive indices of organic aerosol (Lack et al. 2006; Lambe et al. 2013; Nakayama et al. 2013).

Despite the large number of experiments performed using CRD or CRD+PAS, there have been few studies systematically assessing these techniques’ ability to accurately and precisely retrieve refractive indices. Miles et al. (2011) and Mason et al. (2012) examined several sources of error, including incorrect particle counting and doubly charged particles, while Toole et al. (2013) reported a method for removing systematic errors in particle sizing and counting. However, these studies only examined nonabsorbing compounds, and, except for Toole et al. (2013), fixed \( k \) at 0. Instrument setups have been validated using polystyrene latex spheres (PSLs) or ammonium sulfate (AS), but since neither system is absorbing (and in the case of PSLs is monodisperse), these may not be appropriate test systems. Several groups have used nigrosin, a black dye, as a model for absorbing aerosol, but there is a wide range of retrieved values in the literature. Dinar et al. (2008) report a value of \( m = 1.65 + 0.24i \), while Hasenkopf et al. (2010) report a value of \( m = 1.72 + 0.34i \). Additionally, it is unclear how precise these retrievals are. Dinar et al. (2008) report an
uncertainty of only ±3% in the retrieved $k$ value for nigrosin, but Washenfelder et al. (2013) report uncertainties ranging from ±25 to ±50% for the same compound, albeit at shorter wavelengths. Issues with both the precision and accuracy of refractive index values will affect the values of radiative forcing that are calculated with those numbers, and a better understanding of the limitations of refractive index retrieval methods is needed.

The present work is a computational study that attempts to establish theoretical limits on the accuracy and precision of retrieving refractive indices using either solely CRD data (extinction) or CRD data combined with PAS data (extinction plus absorption). Several systems are examined to determine the sensitivity over a range of atmospherically relevant refractive index values.

2. METHODS

While this study is purely computational, we first describe typical experimental methods used in previous studies before describing the computations performed here. To determine the refractive index, the extinction (and possibly absorption) are measured at several different diameters (Lack et al. 2006; Dinar et al. 2008; Hasenkopf et al. 2010; Cappa et al. 2011; Washenfelder et al. 2013). Particles are sized using a differential mobility analyzer (DMA) and counted using a condensation particle counter (CPC). Alternatively, extinction and absorption are measured for the entire particle distribution, which is then measured using a scanning mobility particle sizer (SMPS) (Lambe et al. 2013; Nakayama et al. 2013). The measured optical values are then compared to optical values calculated for a range of different refractive indices to find the refractive index that produces calculated values that best match the measurements.

To test whether data from CRD alone or from CRD+PAS can be used to accurately retrieve refractive index values, synthetic datasets (hereafter “measured” data) were constructed using the refractive indices of several model compounds. Noise was added to the datasets to simulate the effects of experimental uncertainties. The refractive index that best fits the noisy data was then retrieved. In the following two subsections we first discuss sources and magnitudes of possible errors and then provide further details on the calculations.

2.1. Sources and Magnitudes of Error

In this study we have only considered the effects of random experimental errors. Experimental error exists in determining the particle diameter, measuring the optical values, measuring the total number of particles present, and measuring the fraction of singly and doubly charged particles present. We have assumed that the DMA is correctly calibrated, and that all particle sizes are correct. However, even a small DMA sizing error could produce significant changes in the extinction. If the DMA is set to pass 200 nm particles but instead passes 205 nm particles, this represents a sizing error of only 2.5%, but for a range of refractive indices this sizing error increases the extinction cross-section by 10%. Errors in the DMA must be corrected (Miles et al. 2011; Toole et al. 2013), and any sizing issues will increase the uncertainty in the retrieval. Our uncertainties therefore are lower limits.

For CRD measurements with sampling times on the order of minutes, the uncertainty in the extinction coefficient is typically near ±5% (Langridge et al. 2011; Lambe et al. 2013). Additionally, Washenfelder et al. (2013) report similar levels of error for a CEES system, and this is the value used for the present study. Similarly small uncertainties for absorption measurements for PAS instruments have been reported (Lack et al. 2012), though higher levels are possible (Lambe et al. 2013). The extinction and absorption coefficients can be converted into cross-sections by dividing the extinction and absorption coefficients by the number concentration, $N_T$, which is measured by the CPC. The precision of the CPC is determined by Poisson statistics, and a sufficiently long averaging time can reduce the uncertainty, as characterized by a standard deviation, to low (±1%) levels (Washenfelder et al. 2013). The accuracy of the CPC is given by the manufacturer, and is typically given as ±10%, but Toole et al. (2013) report a method to reduce this to ±2 or 3% (Figure 3 of that paper), and a ±3% uncertainty in the concentration will only increase the uncertainty in the cross-section to ±5.8%.

Particles are sized based on their electrical mobility, assuming that they have only one charge (singlets). However, a certain fraction will have two charges (doublets), and a large doubly charged particle can pass through the DMA along with smaller singly charged particles. Since the doublets have a larger extinction (and absorption) than the singlets, their contribution to the measured signal must be evaluated. For example, for singly charged 200 nm particles the doublet size is 315 nm. If these particles have a refractive index of $m = 1.65 + 0.05i$ at a wavelength of 532 nm, and the singlet fraction is 0.95, only 70% of the extinction and 79% of the absorption will be due to singlets. Changing the singlet fraction to 0.97 increases their contribution to the extinction and absorption to 80% and 86%, respectively. If a retrieval is attempted with a singlet fraction of 0.97 instead of the true value, then it is likely that an incorrect refractive index will be retrieved.

For experiments where the optical signal is measured at several discrete sizes, to the best of our knowledge the only method employed for accounting for doublets, short of removing them entirely as done by Radney et al. (2014), is to determine the fraction of doublets at each size and then include their contribution to the extinction and absorption in the retrieval (Pettersson et al. 2004; Lack et al. 2006; Freedman...
et al. 2009; Hasenkopf et al. 2010; Cappa et al. 2011; Redmond and Thompson 2011; Mason et al. 2012; Zarzana et al. 2012; Washenfelder et al. 2013), which requires the assumption that the refractive index is size independent. Assuming there are no triplets, the fraction of singlets at a given size is

\[ f_1 = \frac{N_1}{N_T} = \frac{N_1}{N_1 + N_2}, \]

where \(N_1\) is the concentration of singlets, \(N_2\) is the concentration of doublets, and \(N_T\) is the total particle concentration.

While the uncertainty in \(N_T\) can be reduced to low levels, achieving the same reductions in the uncertainty in the charge fraction may not be as simple. Pettersson et al. (2004) used an optical particle counter (OPC) to estimate the uncertainty in the doublet number concentration at \(\pm 20\%\), and for a larger doublet fraction (\(>0.05\)) this level of uncertainty will have a significant (\(>10\%\)) effect on the measured cross-sections. The refractive index of the particles is needed to convert the signal from the OPC into a distribution, but since the refractive index will not be known, the uncertainty may be greater.

Washenfelder et al. (2013) measured the size distribution with an SMPS, and then used that distribution to assess the charge fraction when the DMA was set to a given diameter. An SMPS typically scans over a large diameter range during a short (several minute) time, limiting the precision of the concentration measurement and subsequent charge fraction determination. This method requires the assumption that the size distribution has not changed between when the SMPS scan was performed and when the measurement at a single size was made. Additionally, the equations used to calculate the fraction of particles with a given charge have biases from the true values (Wiedensohler 1988), and while small (a few percent), they should be included when assessing the charge fraction uncertainty.

Radney et al. (2013) used a second DMA coupled to a CPC behind the first DMA to directly measure the concentration of particles with a given charge. The uncertainties in the concentrations were on the order of 2–3\%, which translate into charge fraction uncertainties of roughly 5\% for both the singly and doubly charged fractions. For this work we have considered charge fraction uncertainties of 0\%, 2\%, and 5\%, although these numbers could be much larger depending on the experimental parameters.

### 2.2. Calculations

Two different sets of systems were examined: a group of non or mildly absorbing compounds, and a group of strongly absorbing compounds. The first group was composed of ammonium sulfate (AS), a purely scattering compound; brown carbon (BrC), a mildly absorbing compound; and a haze analog from Saturn’s moon of Titan, a mildly absorbing compound with \(n\) and \(k\) values less than those for BrC. Three strongly absorbing systems were examined: nigrosin, a black dye that has been used by several groups as a model absorbing system (Lack et al. 2006; Dinar et al. 2008; Hasenkopf et al. 2010); the value for black carbon (BC) used by Hess et al. (1998) (Hess BC); and the value for BC recommended by Bond and Bergstrom (2006) (Bond BC). Literature values for the refractive indices at a wavelength of 532 nm are listed in Table 1.

Black carbon (BC) in the atmosphere commonly has a complex morphology that will affect the optical properties (Bond and Bergstrom 2006; Radney et al. 2014), but for the purposes of this study all particles are assumed to be spherical. The two BC values are for a wavelength of 550 nm, but we assume that the refractive index at 532 nm is the same.

All calculations were done in Igor Pro 6.3 (Wavemetrics, Lake Oswego, OR, USA). Synthetic datasets were constructed for each system. The simulated datasets consisted of a diameter and the singly charged particle fraction, which were used in conjunction with the refractive index to calculate the effective absorption and extinction cross-sections (see below), simulating what would be measured during an actual refractive index retrieval.

Each dataset consisted of using 2, 4, 6, 8, or 12 diameters, which spans the range of the number of diameters used in previous studies. Bluvshtein et al. (2012) proposed a two diameter retrieval method, where one diameter was drawn from a range where the extinction is sensitive to \(n\), and the second

| System name               | \(n\) | \(k\)          | Reference                  |
|---------------------------|------|----------------|----------------------------|
| Ammonium sulfate (AS)     | 1.53 | \(1 \times 10^{-7}\) | Toon et al. (1976)         |
| Brown carbon (BrC)        | 1.65 | 0.05           | Similar to Dinar et al. (2008) |
| Titan                     | 1.35 | 0.03           | Hasenkopf et al. (2010)    |
| Nigrosin                  | 1.65 | 0.24           | Dinar et al. (2008)        |
| Black carbon (Hess BC)    | 1.74 | 0.44           | Hess et al. (1998)         |
| Black carbon (Bond BC)    | 1.95 | 0.79           | Bond and Bergstrom (2006)  |
diameter was drawn from a range where the extinction is sensitive to $k$, which for a wavelength of 532 nm corresponds to diameters of 169–254 nm ($k$ sensitivity) and 339–406 nm ($n$ sensitivity), respectively. For our two diameter retrieval, diameters at the center of those ranges (211 and 372 nm) were used. For our four diameter retrieval, diameters at the edges of these ranges (169, 254, 339, and 406 nm) were used. For the six and eight diameter sets, evenly spaced diameters between 170 nm and 520 nm were chosen. Two different 12 diameter sets were used: a wide set with evenly spaced diameters between 150 nm and 700 nm (12w), and a narrow set with evenly spaced diameters between 150 nm and 425 nm (12n).

Within a given diameter set, each diameter had a fraction of singly charged particles assigned to it. To minimize the contribution of doubly charged particles, Miles et al. (2011) recommended using sizes to the right of the peak in the number distribution, so the fraction of singly charged particles increased as diameter increased. Two different ranges of doubly charged particles were considered: a narrow range, similar to that seen by Freedman et al. (2009), where the doublet fraction never exceeded 0.1; and a wider range, similar to what was observed by Washenfelder et al. (2013), where the maximum doublet fraction was 0.2.

For each particle size, both the extinction and absorption cross-sections are the sum of the cross-sections for the singly and doubly charged particles, weighted by the fraction of singly and doubly charged particles. The effective cross-section is given by Equation (2):

$$\sigma_{\text{eff}} = f_1 \sigma_1(n, k, \lambda, D_{p,1}) + f_2 \sigma_2(n, k, \lambda, D_{p,2}),$$

where $f_1$ and $f_2$ are the fractions of singly and doubly charged particles, and $\sigma_1$ and $\sigma_2$ are the cross-sections for the singly and doubly charged particles, which depend on the refractive index, wavelength $\lambda$, and particle diameter, $D_p$. The doublet fraction, $f_2$, is $f_2 = 1 - f_1$. Equation (2) was used with the correct values for the refractive index and charging fractions to determine the true values for the extinction and absorption cross-sections.

At each diameter, there was a charge fraction, an extinction cross-section, and possibly an absorption cross-section. To simulate experimental noise, the measured values were independently perturbed by using a uniform random number generator to decide if the measurement was too high, too low, or correct. The points that were chosen to be too high were increased by the preselected error for that measurement; e.g., if the extinction at 200 nm was selected to be too high, then the extinction cross-section measurement at that size was increased by 5%. The points that were chosen to be too low were decreased in a similar manner. Noise was added to the absorption cross sections and the fractions of singly charged particles at each diameter in the same way, and then the fraction of doubly charged particles was calculated. This procedure was performed for each of the data points at each diameter used in the retrieval. In principle, if the fraction of doublets at a given size increased, the optical signals should also increase. However, since independent instruments are used to determine these quantities, it is possible in the simulation for the optical values at a given diameter to be too low and the doublet fraction to be too high.

Extinction and absorption cross-sections were calculated for a range for refractive index values. For AS, BrC, and Titan, the $n$ range was $\pm 10\%$ of the true value, with steps of 0.005. The $k$ range was from 0 to 0.1, with steps of 0.001 for the two absorbing compounds and 0.0005 for the nonabsorber. For the three strongly absorbing systems, the $n$ and $k$ ranges were $\pm 0.2$ of the true values, with steps of 0.01.

For each RI value in the range, the effective extinction, $\sigma_{\text{ext}, \text{calc}}$, and absorption, $\sigma_{\text{abs}, \text{calc}}$, cross-sections were calculated at each diameter using Equation (2) with the measured charging fractions and compared to the measured cross-section at that size. For retrievals using CRD data alone, a merit function similar to that used by Washenfelder et al. (2013) was used and is given by

$$\text{MF}_{\text{CRD}} = \frac{1}{N} \sum_{i=1}^{N} \frac{(\sigma_{\text{ext}, \text{meas}} - \sigma_{\text{ext}, \text{calc}})^2}{\sigma_{\text{ext}, \text{meas}}^2},$$

where $N$ is the number of diameters. The merit function was calculated for each possible refractive index, and the value that minimized the merit function was taken as the correct refractive index.

Since absorption has a slight dependence on $n$, one cannot first fit the absorption data to determine $k$ and then use that value to fit the extinction data, and so a weighted sum method (Deb 2001) was used to simultaneously fit the CRD and PAS data. The refractive index that minimized the resulting merit function

$$\text{MF}_{\text{CRD+PAS}} = \frac{1}{N} \sum_{i=1}^{N} \frac{(\sigma_{\text{ext}, \text{meas}} - \sigma_{\text{ext}, \text{calc}})^2}{\sigma_{\text{ext}, \text{meas}}^2} + \frac{1}{N} \sum_{i=1}^{N} \frac{(\sigma_{\text{abs}, \text{meas}} - \sigma_{\text{abs}, \text{calc}})^2}{\sigma_{\text{abs}, \text{meas}}^2},$$

was taken to be the best fit.

While similar, Equations (3) and (4) are not equations for $\chi^2$. Since uncertainty exists not only in the measured quantity but also in the calculated quantity (due to the uncertainty in the charge fractions and potentially the diameter), the standard $\chi^2$ equation cannot be used (Taylor 1997; Bevington and Robinson 2003), and a more extensive treatment is required (Marshall and Blencoe 2005; Cantrell 2008; Chavent 2010). Additionally, the distribution for such a treatment most likely will not follow a $\chi^2$ distribution (Macdonald and Thompson 1992). For simplicity, the measured cross-section at each
diameter was used as the weight for that size; that is, the difference between the measured and calculated cross-sections at a given diameter was divided by the measured cross-section. Changing the weight did not affect the final results (Figures S1 and S2 in the online supplementary information [SI]).

The fitting procedure was repeated numerous times but with a different set of random errors in the extinction, charge fraction, and absorption (if necessary). For the two and four diameter sets, between 100 and 1000 runs were performed. For the sets with six or more diameters, the number of runs was scaled to reduce runtime, and approximately $10^4$ runs each were performed for those diameter sets. For select sets the number of runs was increased by a factor of 10, and the results were the same as the other sets.

3. RESULTS

3.1. Non and Weak Absorbers

Shown in Figure 1a are all of the $n$ and $k$ values retrieved using just CRD data for BrC ($m = 1.65 + 0.05i$) for the narrow doublet range and the wide twelve diameter range. Each point represents the value retrieved from a run with a different set of random errors in the extinction and doubly charged fraction. The errors in the extinction and doubly charged fraction were both 5%. A wide range of $n$ and $k$ are retrieved, including $k$ values that are over 50% greater or smaller than the true value of 0.05.

Box and whisker plots for the retrieved RI values for BrC, AS, and Titan using all the diameter sets are shown in Figures 1b–d, respectively. The whiskers are the 5th and 95th percentiles, and the boxes are the 25th and 75th percentiles. The marker denotes the average value from all the runs with that diameter set.

For all three systems, the spread (the range between the 25th and 75th percentiles) in both $n$ and $k$ is quite large when using only two diameters, and for ammonium sulfate the average $k$ value is 0.01, which is incorrect for a nonabsorbing compound. As the number of diameters increases, the spread in the $n$ and $k$ values decreases, but even at 12 diameters (for both diameter ranges) the spread in $k$ is roughly ±10%. For ammonium sulfate, the $k$ range is from 0 to 0.004, but for a 150 nm particle a $k$ of 0.004 gives a single scatter albedo (the ratio of scattering to extinction, SSA) of 0.94, which for a nonabsorbing aerosol again is not correct. Decreasing the

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FIG. 1. Refractive index values retrieved using just CRD data. (a) Scatter plot of retrieved values using CRD data for brown carbon. The gray circle denotes the true value. (b–d) Box and whisker plots for refractive index values retrieved using the different diameter sets for brown carbon, ammonium sulfate, and Titan. The dashed lines denote the true values.
charge fraction uncertainty to 2% (not shown) had a minimal effect on the spread. For the wider doublet range, the same trends were observed, though the spread in values was larger.

The plots shown are for a large number of runs, and while retrievals that give $k$ values significantly off of the true value are less likely, they are still possible. If only one retrieval is performed due to sample or time limitations, care needs to be taken when using that number. Using more diameters will decrease the likelihood of retrieving an erroneous value, but this may not be possible, and the refractive index could have a large uncertainty.

Due to computation limitations, it was not possible to simulate a retrieval using the entire size distribution. Increasing the number of diameters improved the retrieval, but the diameters used were spaced at minimum 50 nm apart, while the diameters measured by the SMPS can be closer, particularly at smaller sizes. It is possible to retrieve the refractive index from extinction measurements because absorption and scattering behave differently as a function of size, and if the extinction is measured for closely spaced diameters, the improvement in the retrieval may not be as great as one would expect. Additionally, the simulations run here started with perfect data with only random errors, and real data will likely result in much greater spreads in refractive index values (Zarzana et al. 2012; Washenfelder et al. 2013), especially since the errors are likely to be size-dependent.

Two methods for reducing the uncertainty relative to the CRD-only retrieval were considered: removing the doubly charged particles and adding a second optical measurement. Removing the doublets resulted in a large decrease in the range of retrieved values for the two diameter retrieval, but for the other diameter sets, there was not much reduction in the spread (Figure S3). For the 12 diameter ammonium sulfate retrieval, the 25th to 75th percentiles for $k$ range from 0 to 0.002, which for a particle 150 nm in diameter gives a single scatter albedo of 0.97, which is still incorrect.

While doublets could be eliminated using an impactor (Toole et al. 2013) or by selecting particle sizes far from the peak of the distribution so that doublets have minimal contribution (Freedman et al. 2009; Hasenkopf et al. 2010; Zarzana et al. 2012), such options may not be practical, particularly when one does not have control over the particle distribution. The use of a mass selection instrument behind the DMA could be used to remove doubly charged particles (Nakayama et al. 2010a; Radney et al. 2013, 2014). This requires knowledge of the particle density, which could be determined by scanning

![Effect of adding an absorption measurement.](image_url) FIG. 2. Effect of adding an absorption measurement. (a) Scatter plot of retrieved values using both CRD and PAS data for brown carbon. The gray circle marks the true value. (b–d) Box and whisker plots for refractive index values retrieved using the different diameter sets for brown carbon, ammonium sulfate, and Titan. The dashed lines denote the true values.
the mass analyzer voltage, but this may not be practical. However, for a retrieval using just CRD data, the use of one of these techniques is needed to increase the accuracy in the retrieved results.

The effect of adding a second optical measurement was explored by performing a retrieval using data from both a CRD and a PAS (Figure 2). The errors in the extinction, absorption, and doubly charged particles were all 5%. With the addition of the PAS, the spread in the k values decreased dramatically. For the two absorbing systems the spread is only 2%, and for AS the average k is zero for all cases except the two diameter case, where it is 0.0005 (SSA = 0.992). Increasing the error in the absorption to 10% (not shown) and 20% (Figure S4) increased the spread in k, but even for the two diameter retrieval the spread was similar to or better than the spread from the best CRD retrievals. Virtually the same results were obtained when the wider doublet range was used (not shown). Thus, the addition of an absorption measurement, even one with significant (>10%) uncertainty, dramatically improves the retrieval.

The low n values retrieved for AS were investigated by rerunning the four diameter retrieval using different diameters. Using four diameters from 150 to 300 nm produced n values very close to the literature value of 1.53 (4b in Figure 2c). The two low retrievals used many diameters between 300 and 450 nm, a region where the extinction cross-sections converge for many different k values (Figure 6d). Thus, the use of diameters in that range can give inaccurate results. This range depends on n, so performing the retrieval over as broad a size range as possible is beneficial.

As has been pointed out previously (Toole et al. 2013), it is easy to obtain fits to extinction data that appear correct but give incorrect refractive indices. An example of this is given using the BrC retrievals. Shown in Figure 3a are the measured extinction cross-sections (markers) for one eight diameter retrieval. The contribution of the doubly charged particles was subtracted from the measured values to allow for comparison to the calculated values. Using only the extinction (CRD) data, a refractive index of \( m = 1.645 \pm 0.049 i \) was retrieved. The calculated extinction cross-sections for this refractive index (dashed line) match the data quite well, even though the retrieved k is 20% lower than the true value of 0.05. Additionally, extinction cross-sections were calculated for the range of refractive indices retrieved using eight diameters (similar to the range in Figure 1a). The shading shows spread in extinction cross-sections, and even though refractive indices with n and k values far from the true values were retrieved, the spread in extinction cross-sections is quite narrow. This illustrates how easy it is to find n and k pairs that match extinction data well, and, conversely, that there is not a unique n and k pair that provides an unequivocal best fit.

While the CRD-only refractive index produces calculated extinction cross-sections that agree well with the measured extinction cross-sections, the absorption cross-sections calculated using that refractive index do not agree well with the measured absorption cross-sections. The measured (markers) and calculated absorption cross-sections using the CRD-only refractive index (dashed line) are shown in Figure 3b. There is poor agreement between the measured and calculated values, which is unsurprising given that the retrieved k value is 20% lower than the true value. The lighter shading shows the spread in absorption cross-sections calculated using all refractive indices retrieved using only CRD data (Figure 1a). In contrast to the spread in extinction cross-sections, the spread in absorption cross-sections is quite large.

Also shown in Figure 3 are calculated extinction and absorption cross-sections for the refractive index retrieved using the same extinction and charge fraction data, but also with absorption data. For the CRD+PAS retrieval, a refractive index of \( m = 1.645 + 0.049 i \) was retrieved, which is very close to the true value. In addition to matching the extinction data, the absorption cross-sections calculated with this refractive index match the absorption data very well. The darker shading shows the spread in extinction and absorption cross-sections calculated with all retrieved CRD+PAS refractive indices (Figure 2a). While the spread in extinction cross-sections is nearly identical to the spread for the CRD-only

![FIG. 3. Measured extinction (a) and absorption (b) cross-sections (points), and calculated cross-sections (lines) derived from refractive indices retrieved using either CRD or CRD+PAS data. The shading shows the range of cross sections for all retrieved refractive indices. The range of retrieved values is similar to the spread in Figures 1a and 2a.](image-url)
case, in contrast the spread in absorption cross-sections is restricted to a narrow band that matches the data. Fitting only extinction data is quite easy and can produce values far from the true one, but the constraint imposed by having to simultaneously fit extinction and absorption greatly improves the fit and reduces the range of possible values.

3.2. Strong Absorbers

The same simulations were performed for the three strongly absorbing compounds. The results for the CRD runs with 5% errors in the extinction and charge fraction are shown in Figure 4, and the results with no doublet error are shown in the SI (Figure S5). The results from the CRD+PAS run with 5% errors in all three quantities are shown in Figure 5.

For the CRD-only run, there is significant spread in the $k$ values. This spread decreases as more diameters are used, though not as much for the Bond BC value, and either removing doubly charged particles or adding a PAS measurement improves the fit. As before, the spread in the retrieved values was reduced more by adding a PAS than by removing doublets, but for the strong absorbers the effect was not as prominent as for the mild/nonabsorbing compounds. For those systems, when a PAS was added, the spread in $k$ was reduced to ±2%, even with only four diameters. For nigrosin and the Hess BC, similar reductions were observed, but for the Bond BC the spread was reduced to only ±8%, and this was only achieved with 12 diameters.

3.3. Discussion

A possible reason for the larger spread in refractive index values for the strong absorbers is shown in Figure 6. For four systems, Bond BC, nigrosin, BrC, and AS, the extinction and absorption cross-sections were calculated for the true refractive index value. The $k$ values were then changed by ±10% and ±20%, and the percent difference between the perturbed cross-section and the true cross-section was calculated for diameters from 150 nm to 750 nm. Since the $k$ for AS is zero, no absorption cross sections were calculated, and $k$ values of 0.005, 0.01, 0.02, and 0.03 were used to calculate the new extinction cross-sections.
The value used in Mie theory is the size parameter, defined as

\[ x = \frac{\pi D_p}{\lambda}, \]  

where \( D_p \) is the particle diameter and \( \lambda \) is the wavelength of incident light. The size parameter allows for comparisons at other wavelengths, and is plotted on the top axis for the corresponding diameter on the bottom axis, assuming a wavelength of 532 nm.

For Bond BC particles (Figure 6a) larger than 225 nm, the percent differences in extinction and absorption cross-sections are less than 5%, even for \( k \) values \( \pm 20\% \) off of the true value. This effect exists for Hess BC (not shown) and nigrosin (Figure 6b), though it starts at diameters of 250 nm and 300 nm, respectively. The uncertainty in the optical measurements is usually \( \pm 5\% \) at best. If the difference between the cross-sections is less than 5%, then for a given \( n \) value there are a range of \( k \) values that adequately fit the data.

A similar effect is seen for AS (Figure 6d), where for diameters greater than 250 nm, the percent difference in cross-sections for a \( k \) of 0 and a \( k \) of 0.01 is less than 5%, making a robust retrieval of a \( k \) of zero difficult.

In contrast, for BrC (Figure 6c), while the extinction cross-sections quickly converge for different values of \( k \), the difference between the absorption cross-sections is at least 5% (and often greater) over the whole size range. Adding a PAS to directly measure the absorption puts significant constraints on the range of possible \( k \) values and makes the retrieval of the correct one much more likely. Additionally, for AS, while it is possible to retrieve a nonzero \( k \) for a nonabsorber using just CRD data, the addition of the absorption measurement will make the retrieval of a nonzero \( k \) unlikely.

The greatest differences were observed for small particles, and in principle a CRD retrieval using these sizes would produce better results. However, the cross-sections at these sizes are prohibitively small, and large concentrations (>1000 particles/cm³) are required just to be at the instrument detection limit, let alone to make a reliable measurement.

When \( n \) was varied (Figure S6), there again was little change in either the absorption or extinction cross-sections for the two BC values. Since the optical properties of BC depend more on size and morphology than on refractive index (Bond and Bergstrom 2006), the minimal changes in cross-sections for a small \( k \) and a large \( k \) make the retrieval of the correct one much more difficult.
for the spherical particles used here is not surprising. In contrast, the extinction cross-sections for AS showed greater than 10% differences until roughly 600 nm. The differences for both the absorption and extinction cross-sections for BrC oscillated between 0 and greater than 10% depending on the size. If extinction measurements were made using diameters where the difference was maximized, it is likely that $n$ could be retrieved with some accuracy. However, the ideal diameters will depend on the refractive index, which is not known ahead of time.

The traces in Figure 6 are for a wavelength of 532 nm. At that wavelength, the percent differences in extinction cross-section for smaller particles exhibit differences that are greater than typical instrument precisions (5%), but this is not the case at shorter wavelengths. For example, at a wavelength of 532 nm the size parameter for 200 nm particles is 1.18. For AS, the percent difference in extinction cross-section for all $k$ values but 0.005 is greater than 5% (though a $k$ of 0.005 for AS is incorrect). The refractive index of AS is nearly the same at 405 nm as at 532 nm (Toon et al. 1976), however, the size parameter for 200 nm particles is now 1.55, which means that the difference between cross-sections for a $k$ of 0 and a $k$ of

![FIG. 6. Effect of changing the imaginary part of the refractive index by ±10 and ±20% on the extinction (solid lines) and absorption (dashed lines) cross-section.](image)

![FIG. 7. Percent difference in radiative forcing due to different refractive index values for ammonium sulfate (a, b, c) and brown carbon (d, e, f). The true value is shown by the marker.](image)
0.01 is less than 5%, making it difficult to distinguish between those two $k$ values.

The effects of uncertainty in the refractive index are shown in Figure 7. Forcing values were calculated using the same equations and base-level assumptions as in Dinar et al. (2008) for spherical AS and BrC particles with diameters of 100, 150, and 200 nm at a wavelength of 532 nm. Forcing values were then found for particles with the same diameter but with refractive indices that differed from the correct values. The percent difference between the forcing using the correct refractive index and the alternate refractive index was then calculated. A negative difference (darker shading) indicates the alternate refractive index leads to more cooling than the base refractive index, while a positive difference (lighter shading) means that the particles cause less cooling.

For 150 nm particles, a seemingly small uncertainty of ±0.01 in the $k$ value translates into an uncertainty in the forcing of roughly ±20%. The forcing uncertainty is smaller at 200 nm and larger sizes, but the smaller sizes are more climate relevant (Heald et al. 2014), and since particles of many sizes are present in the atmosphere, the total forcing uncertainty for all particle sizes will be large. The large uncertainty in refractive indices retrieved using only CRD measurements will translate into much larger uncertainties in the calculated forcing values, limiting the value of those numbers. The constraints placed on $k$ by the addition of absorption data in the retrieval not only reduces the spread in $k$ values but also greatly reduces the uncertainty in radiative forcing calculated using those numbers.

4. CONCLUSION

Accurate aerosol refractive indices are needed to quantify the effect of particles on direct radiative forcing. While in the past refractive indices have been determined using just extinction data, the results in this work show that the range of values retrieved using this method is potentially too large to be useful. Additionally, it is difficult to retrieve the correct $k$ value for nonabsorbing compounds. While there are experimental methods that can help reduce the uncertainty when using only extinction, the uncertainty will remain large, particularly for the $k$ value, and these techniques may not be practical in many instances. However, the addition of an absorption measurement significantly improves the retrieval of the refractive index, and while there is still uncertainty associated with the retrieval, it is far less than when extinction measurements alone are used.

ACKNOWLEDGMENTS

The authors thank E. M. Waxman and J. L. Jimenez (University of Colorado Boulder) for useful discussion, and E. R. Lewis (Brookhaven National Laboratory) for the Mie codes.

FUNDING

Kyle J. Zarzana was supported by NASA grants NNX09AE12G and NNX11AD82G. Christopher D. Cappa was supported by NSF grant ATM-0837913.

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher’s website.

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