Retrieval of Aerosol Optical Properties from Infrared Extinction Spectra

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Abstract:

A new method for the retrieval of particle refractive index from infrared aerosol extinction spectra is presented. The method uses a classical damped harmonic oscillator (CDHO) model of molecular absorption in conjunction with Mie scattering to model extinction spectra, which are then fitted to measurements using a numerical optimal estimation algorithm. The main advantage of this method over the more traditional Kramers-Kronig approach is that it allows the full complex refractive index spectra, along with the parameters of the particle size distribution, to be retrieved from a single extinction spectrum.

As well as a description of the algorithm, results from its application to laboratory spectra of super cooled ternary solution aerosol (imitation PSC particles) measured at the Rutherford Appleton Laboratory's Molecular Spectroscopy Facility are be presented.

Introduction:

Remote sensing of the atmosphere using mid-infrared radiometers and spectrometers – from satellite, aircraft and ground based platforms – is one of the primary tools in determining atmospheric composition. Knowledge of atmospheric aerosol’s refractive index is of key importance in determining the accuracy of both retrieved aerosol parameters and other parameters from such measurements.

The primary aerosols found in the stratosphere are composed of sulphuric acid solution or, in the case of polar stratospheric clouds, ternary solutions of H2SO4, HNO3 and water. Laboratory measurements of the optical properties these solutions, mostly from absorption and reflection spectroscopy by thin films, have shown their refractive index to be strongly dependent not only on composition, but also temperature. Although current laboratory data have undoubtedly improved the accuracy of refractive indices used in the analysis of mid-infrared atmospheric measurements, there remain significant differences between the individual data sets and McPheat *et al.* (2002) showed that there are discrepancies between extinction spectra resulting from thin films and those from aerosol (see Wagner *et al.* (2003) for an overview of laboratory sulphate/ternary solution refractive index measurements).

Although some measurements of aerosol based refractive indices are available, they cover a narrow range of compositions and temperatures, due largely to the greater complexity of aerosol experiments in comparison to thin film measurements, particularly when the refractive index is a desired output. When applied to aerosol extinction spectra, the traditional Kramers-Kronig method for determining the refractive index requires two spectra for each composition/temperature combination (Clapp *et al.* 1995). It is therefore necessary to measure spectra for two separate particle size distributions, without altering either particle composition or ambient temperature. In the case of volatile liquid aerosol, this presents significant experimental difficulties. In addition, Wagner *et al.* (2003) suggest that, if the initial guess at the spectral refractive indices are not sufficiently accurate, Kramers-Kronig will produce incorrect results.

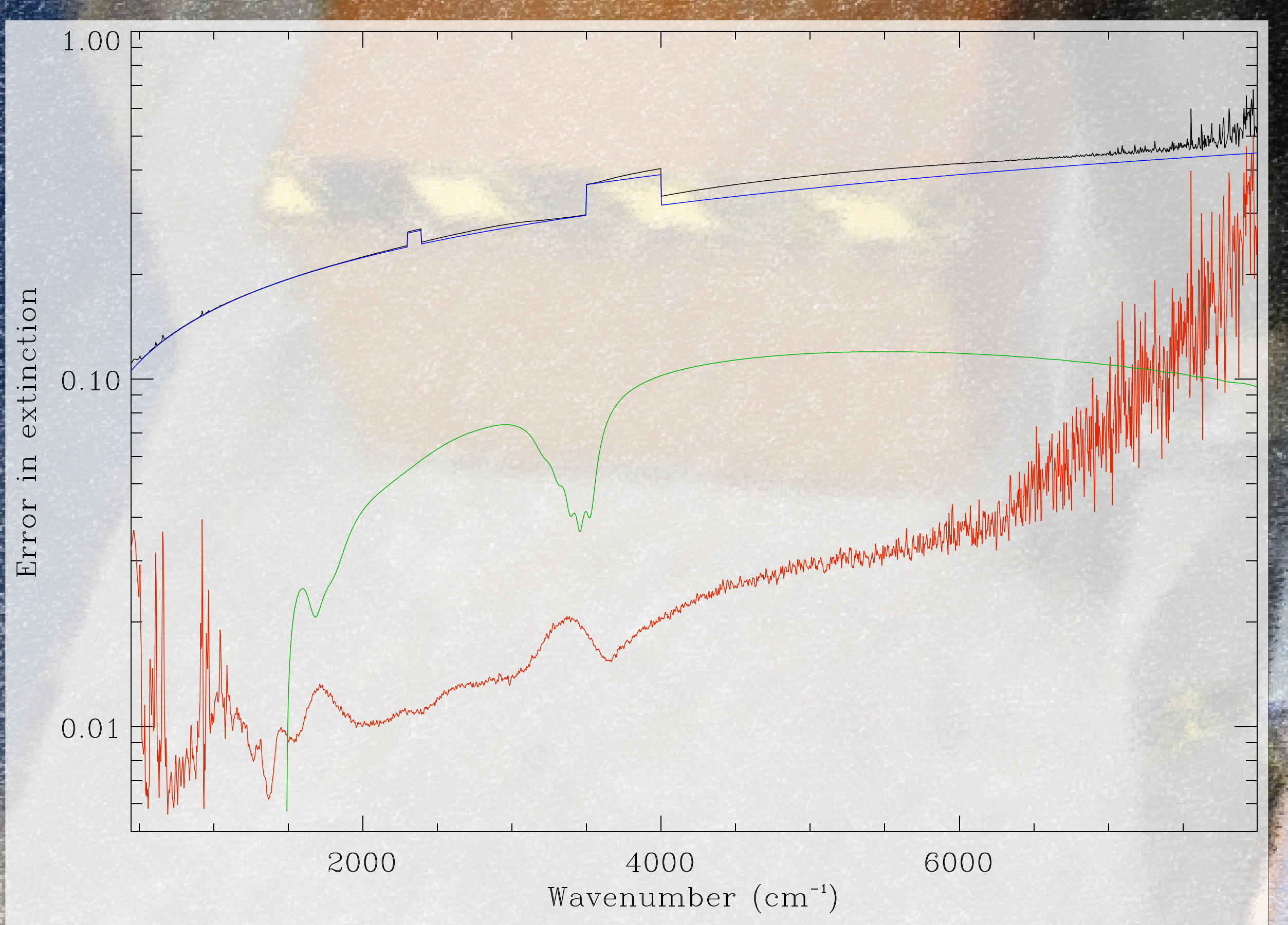

Figure 1: Comparison of error sources present in the retrieval. The black line shows the total uncertainty, the blue line represents the forward model error, the green line is the uncertainty due to the forward model by the inclusion of the m^2 error and the red line is the measurement noise.

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Background Image: The large aerosol cell at the RAL MSF.

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Analysis technique:

The heart of the analysis scheme is the CDHO band/Mie scattering forward model. The CDHO model is made up of a series of *j* harmonic oscillator bands, defined by their central wavenumber (υ_j), width (γ_j) and strength (S_j). These bands are related to the complex dielectric constant ($\epsilon'(\nu) + i\epsilon''(\nu)$)of the material in question by the equations (Bertie *et al.* 1994):

$$\epsilon'(\nu) = \epsilon_\infty + \sum_j \frac{S_j(\nu_j^2 - \nu^2)}{(\nu_j^2 - \nu^2)^2 + \gamma_j^2\nu^2} \qquad (1)$$

$$\epsilon''(\nu) = \sum_j \frac{S_j\gamma_j\nu}{(\nu_j^2 - \nu^2)^2 + \gamma_j^2\nu^2} \qquad (2)$$

These are in turn related to the complex refractive index ($m = n + ik$) using the Lorentz-Lorenz relation:

$$n(\nu) = \sqrt{\frac{\left[\sqrt{\epsilon'(\nu)^2 + \epsilon''(\nu)^2} + \epsilon'(\nu)\right]}{2}} \qquad (3)$$

$$k(\nu) = \sqrt{\frac{\left[\sqrt{\epsilon'(\nu)^2 + \epsilon''(\nu)^2} - \epsilon'(\nu)\right]}{2}} \qquad (4)$$

Eqns. (1) to (4) are used to calculate spectral refractive indices from a set of band parameters. The value $\epsilon_\infty = m^2$ is the value the dielectric constant takes at zero wavelength, and is included as a fixed parameter based on relevant published values of refractive index at visible wavelengths. These refractive indices are then used to produce an aerosol extinction spectrum using a Mie scattering model and an assumed particle size distribution. In the case of liquid aerosol the lognormal distribution is the most common, and the extinction is given by:

$$\beta^{ext}(\nu) = \frac{N_0}{\ln S}\sqrt{\frac{\pi}{2}} \int_0^\infty rQ^{ext}(\nu, m, r) \exp\left[-\frac{(\ln r - \ln r_m)^2}{2\ln^2 S}\right] dr \qquad (5)$$

Where N_0 is the number density of particles, r_m is the median particle radius, the standard deviation of ln *r* is ln *S* and $Q^{ext}(\upsilon, m, r)$ is the extinction efficiency of a particle of radius *r*, as given by Mie theory.

This forward model is used to produce and optimal estimate fit to measured aerosol extinction spectra using the Levenburg-Marquardt technique. An important feature of the analysis scheme is that all relevant derivatives are analytically calculated, using derivatives of Eqns. (1) to (5) and expressions for the derivatives of Q^{ext} (Grainger *et al.* 2004). The use of analytical derivatives , rather than using numerical techniques, greatly decreases the time required to calculate the jacobians, while also increasing their accuracy.

Error analysis:

The analysis produces not only estimates of the refractive indices, but also the parameters of the size distribution and error estimates on all retrieved quantities. Error analysis takes into account:

- Measurement errors
- Uncertainty in *a priori* information
- Forward model error, due to it’s approximate nature, as well as uncertainty as to the optimum set of band parameters to use and the true nature of the particle size distribution.
- Forward model parameter error (uncertainty in the *m* value).

Most previous refractive index data bases do not contain error estimates, which means they become and unquantified error source in any work making use of them. The optimal estimation method used to fit the model spectra in this technique includes a full error characterisation. Figure 1 shows the relative sizes of the three error contributions taken into account in the analysis. It is clear that the dominant error source is the forward model. The forward model error results from:

- The approximate nature of the CDHO model (in that it does not truly describe the physical processes producing the absorption). This is particularly true in the case of asymmetric absorption features (such as the OH stretch region between 3500 - 4000 cm^{-1}) cannot be reproduced with a symmetric oscillator model.
- Poor *a priori* knowledge of the band structure which best describes the absorption. There have been relatively few studies of sulphuric or nitric acid which have provided locations and strengths of absorption bands.
- Poor *a priori* knowledge of the particle size distribution.

Example results:

Figure 2 shows an infrared absorption spectrum of sulphuric and nitric acid ternary solution aerosol, measured at the Rutherford Appleton Laboratory Molecular Spectroscopy Facility (RAL MSF), along with the fitted spectrum produced by the CDHO/Mie model and the normalised residuals. The spectrum was taken using the RAL MSF large aerosol cell (McPheat *et al.* 2001) in conjunction with a Bruker IFS 66v/S infrared Fourier transform spectrometer operating at 4 cm^{-1} resolution. The retrieval scheme has clearly produced a fit well within the measurement/forward model errors (indeed, the fit is within measurement error for the majority of the spectral range). The largest discrepancy is clearly around the 3500 - 4000 cm^{-1} OH feature.

The refractive index spectra which result from this fit are displayed in Figure 3. The error estimates on the refractive index are below 10% in the real part (*n*) for all wavenumbers above 500 cm^{-1}, and below 1% above ~4000 cm^{-1}. Uncertainties in the imaginary part (*k*) are relatively larger, due to the small absolute values involved, and are approximately 10% below ~3000 cm^{-1}, rising to ~100% at higher frequencies.

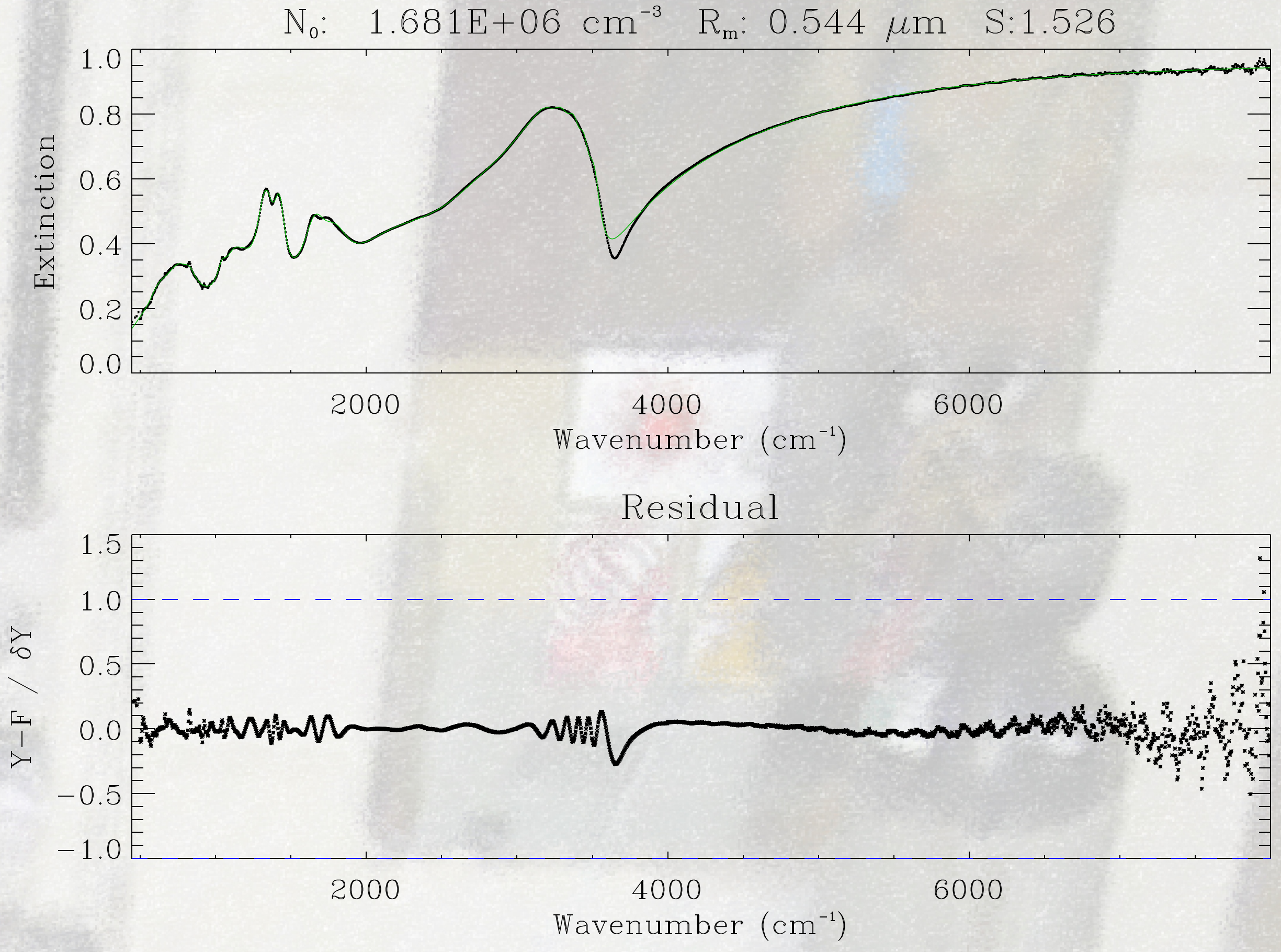

Figure 2: Ternary solution aerosol (at 195 K) extinction spectra (top panel, black points) along with the CDHO model fit (green line). The lower panel shows the residuals, normalised to the total error, and the retrieved size distribution parameters are given at the top.

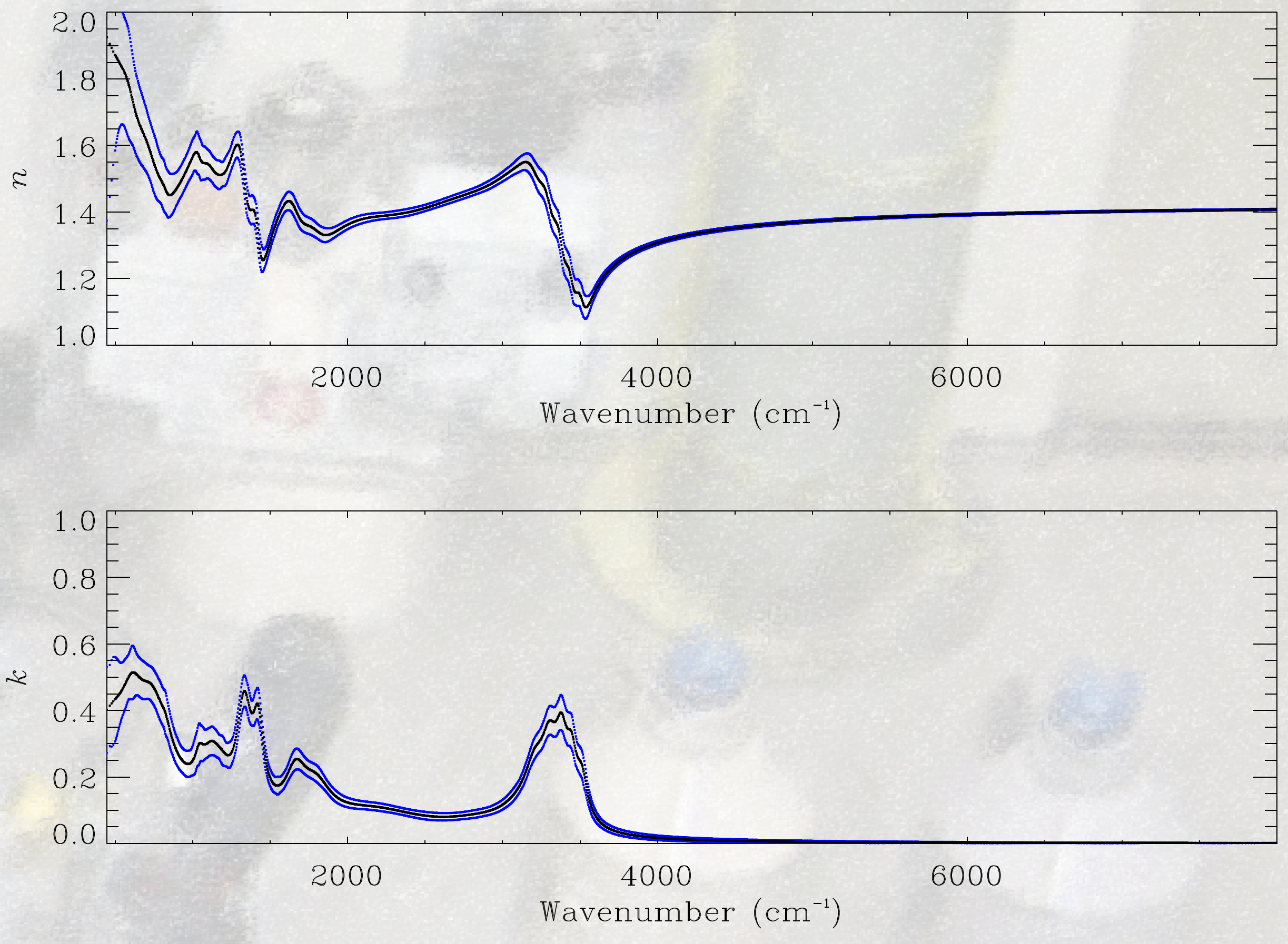

Figure 3: Refractive indices retrieved from the extinction spectra shown in Figure 2 and the associated 1 σ error estimates.

Discussion and conclusions:

The CDHO/Mie forward model, in conjunction with and optimal estimation retrieval method, has been found to provide a way of retrieving aerosol particle refractive indices, as well as the parameters of the particle size distribution, from a single aerosol extinction spectrum. As well as state estimates, the method provides full error characterisation. At present the error analysis indicates that the retrieval accuracy is limited by forward model error, which is at least in part due to poor *a priori* knowledge of the particle size distribution and appropriate absorption bands to be included in the CDHO model. It is planned to include independent measurements of the size distribution in future measurements to address the former of these limitations. It is also hoped that future measurements will include a measured estimate of the *m* parameter, in order to better define the refractive index a higher frequencies.

This analysis technique represents an important step towards accurately characterising the optical properties of atmospheric aerosols. The technique has potential applications in the analysis of a wide range of aerosol types and measurements, both laboratory and atmospheric.

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