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Predicting infrared spectra of atmospheric dust samples of mixed composition particles

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Abstract

A Mie-Bruggeman model is used to predict the shape and orientation-averaged infrared extinction and absorption spectra of a Saharan dust sample of mixed composition and size. The common minerals of atmospheric dust samples, clays in this case, have strong infrared transitions which match the particle size and probing wavelengths giving rise to interesting lineshape distortions. These distortions may need to be considered for quantitative analysis of infrared spectra measurements of atmospheric dust samples.

Keywords: Predict infrared extinction; Absorption spectra; Atmospheric dust mixtures; Lineshape distortions with particle size; Mie-Bruggeman model

1. Introduction

The advent infrared (IR) Lidar on a global scale (Vezin et al., 1997, Geiser et al., 2006), the importance of dust in weather prediction (Kok 2010, Mulcahy et al., 2014), and the effects of particulate matter on human health (Dockery et al., 1993, Dominici, et al., 2003) motivate the development of IR spectral models that can deal with the complexities of atmospheric dust samples (Mogili et al., 2008, Klueser et al., 2016). The Coe Group has previously developed a method to record scatter-free IR spectra of individual dust particles

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of ~4 μm size by trapping the particles in the holes of a metal plasmonic mesh (Cilwa et al., 2011, Malone et al., 2012, Luthra et al., 2015). We have also measured many single particle spectra of pure materials known to be in dust samples (Lioi et al., 2013). Permittivities versus wavelength were extracted for these components and a Mie-Bruggeman model was developed that predicts the extinction or absorption spectra of any desired mixture of the calibrating components. It can predict as a function of composition and particle size, but averages over shape and orientation effects (Meland et al., 2012) which are also important. The Mie-Bruggeman model identifies primary issues associated with extracting quantitative information from IR spectra of atmospheric dust mixture samples and serves as a starting point of comparison for those interested in shape and orientation effects (Meland et al., 2012). The calibration components currently include calcite, dolomite, gypsum, illite, kaolinite, montmorillonite, quartz, yeast, polyethylene, humic acid/salt, and hydrated alumina, but new components can always be added to improve the model provided that a set of single particle spectra can be recorded of the additional component. The use of the Mie-Bruggeman model is illustrated in this work by modelling a Saharan dust (Mallone et al., 2011, Laskina et al., 2012, Lenes et al., 2012, Ryder et al., 2013) sample with a mineral composition from the literature (Alexander 2015) and a particle size distribution that was measured upon transport across the Atlantic Ocean (Maring et al., 2000). Some organics were added to the mixture to illustrate this feature of the model. Common minerals of atmospheric dust samples have strong IR transitions which match the particle size and probing wavelengths giving rise to strong lineshape distortions (Ravi et al., 2013). The quantitative analysis of IR spectral measurements of atmospheric dust samples may need to consider these distortions in order to choose the best wavelengths for future studies.

2. Mie-Bruggeman Model

The Mie-Bruggeman model has been previously described (Lioi, Cilwa et al. 2013), so only a brief description is given here as illustrated in Figure 1. Given the permittivities (ε_i) and volume fractions (f_i) of each component as indexed with i, an effective permittivity is predicted for the mixture (ε_{eff}) which is used to predict a Mie spectrum (Bohren & Huffman 2007) of the mixture assuming some particle diameter, i.e. this is a shape and orientation averaged prediction for a sample. The prediction is compared to a dust sample spectrum of interest and the volume fractions and particle diameter are changed in a gridded nonlinear least squares fashion to improve the agreement. Previously, this (Luthra et al., 2015) method has given good results for the average single particle IR spectra of dust samples from our laboratory air, a home air filter, and the 9/11/2001 World Trade Center event. The volume fractions of the components are good if all of the important components in the sample are part of the calibration, likewise there will be systematic errors if important components are not in the calibration list. To illustrate use of the model, it is applied to some data from the literature on Saharan dust as it crosses the ocean.

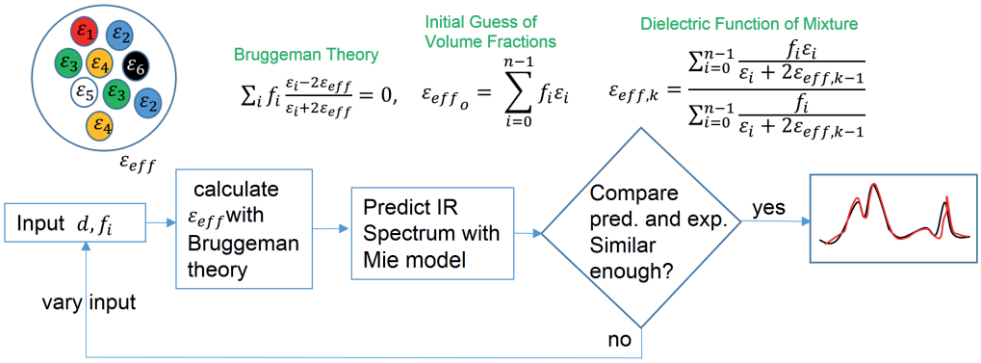

Fig. 1. The Mie-Bruggeman model for predicting the IR spectra of particles with mixed components such as atmospheric dust. A mixed composition particle is illustrated at the top left consisting of components with known permittivities (ε_i). The model numerically predicts (top right equations) the effective permittivity (ε_{eff}) of the mixture, then predicts the IR spectrum of the mixture from a Mie theory approach. Volume fractions are varied iteratively to fit the sample being modelled

3. Saharan dust over the Atlantic Ocean

Saharan dust studies abound (Schulz, Prospero et al. 2012). Mineral compositions of field samples from the south central Saharan Desert by empirical mineralogy have been reported (Alexander 2015) as 9% dolomite, 31% illite, 16% kaolinite, 34% montmorillonite, 1% amorphous silica, and 9% feldspar. Organics were added at the (Cilwa, McCormack et al. 2011) ~10% level in the form of yeast and polyethylene to give volume fractions of 0% calcite, 8.2% dolomite, 0% gypsum, 28.2% illite, 14.6% kaolinite, 30.9% montmorillonite, 9.1% quartz (we changed feldspar to quartz since feldspar is not yet in our calibration), 4.6% yeast, 4.6% polyethylene, 0% humic acid/salt, and 0% hydrated alumina for our illustration of Mie-Bruggeman spectral modeling. After obtaining a permittivity for the mixture, IR spectra were calculated with a Mie program in MATLAB based on seminal work (Bohren and Huffman 2007) at sizes from 0.5 to 15 µm diameters with incremental steps of 0.5 µm. The IR absorption spectra of these Mie mixed-composition particles are shown in Figure 2. The spectral intensities in cross section units were normalized by the particle volume. If there were no particle effects, i.e. in a Beer's Law limit, all of these spectra would be the same. Many common minerals, like the clays in Saharan dust, have strong vibrational transitions at ~1000 cm-1 which is similar to the particle size and probing wavelength, so one can expect strong lineshape distortions (Ravi et al., 2013). To better see the lineshape distortions with particle diameter, the results in Figure 2 have been rotated and zoomed in Figure 3 to better observe the particle size lineshape distortions. The largest particles at 15 µm diameter give a broad and flattened profile at ~1000 cm-1 which is the particle analog of the thickness saturation of films, while particles of ~5 µm diameter give the most intensity due to well know Mie resonance effects. Clearly the strongest vibrational peak in the IR absorption spectrum can change dramatically with size.

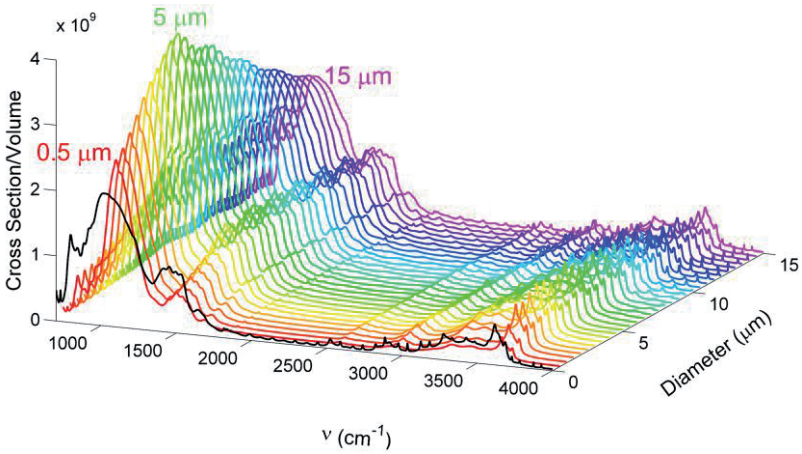

Fig. 2. Effect of particle diameter on the IR absorption spectra of particles of mixed composition characteristic of Saharan dust dominated by clays. The black trace is the weighted average over the size. The intensities are relative

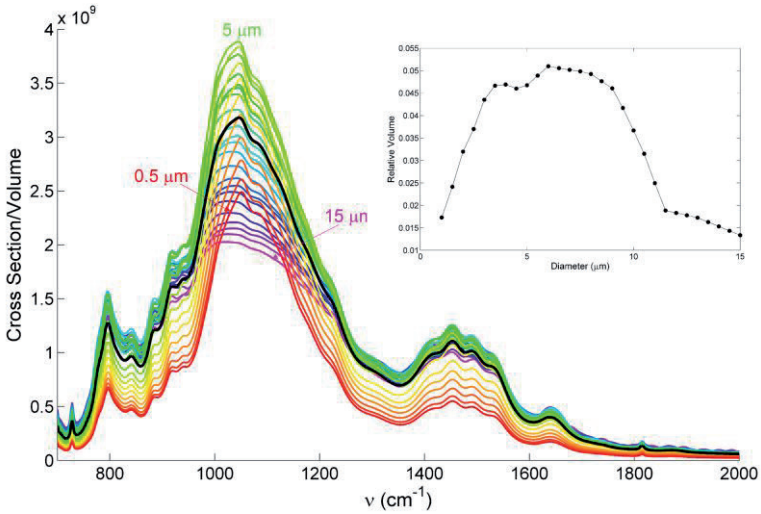

Fig. 3. Rotated and zoomed view of the effect of particle diameter on the IR absorbance spectrum of a characteristic Saharan dust mixture from Figure 2 in order to better observe the lineshape distortions due to particle diameter. The black trace is the weighted average of these spectra based on the weights of the inset distribution as measured at the Canary Islands (Maring, Savoie et al. 2000)

In order to investigate the effect of a particle size distribution on the IR spectrum, the published volume distribution versus particle size of Saharan dust as measured at Izana, Tenerife, Canary Islands by Maring et al. (2000) was digitized and interpolated at each of the particle diameters from 0.5 to 15 µm diameters with incremental steps of 0.5 µm to provide weights. This distribution was not log normal due to loss of larger particles upon transport across the ocean, had multiple maxima, and was most intense in the 3-10 µm size regime (see Figure 3, p. 4 therein). The normalized weighted sum over the Maring et al. (2000) particle size distribution is presented as a black trace in Figure 3. If the size

distribution changes with transport across the ocean, as shown by similar measurements in Puerto Rico, then the IR spectrum changes, even if the chemical composition is unchanged.

Most atmospheric dust work involves the measurement of extinction spectra which are dominated by scattering effects. Figure 4 compares the weighted average absorption and extinction spectra for the Saharan dust mixture and size distribution under consideration. The two spectra are on the same relative scale. There are many dispersive contributions in the extinction spectrum which will change dramatically with changes in the particle size distribution.

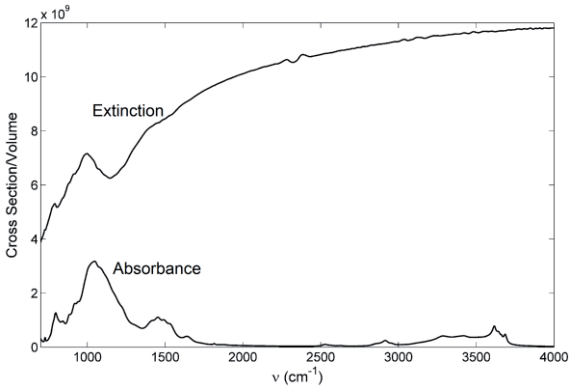

Fig. 4. The weighted average over the size distribution of the extinction and absorption spectra of the Saharan dust mixture under consideration

4. Conclusion

Due to the presence of very strong vibrational transitions in the common minerals of atmospheric dust, the most intense IR signals that might be observed by infrared Lidar are likely to be strongly affected by chemical composition, hence the utility of the Mie-Bruggeman model for mixed composition particles. Users can vary the composition and, in the context of a particular size distribution, predict the spectral response.

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