Infrared Backscattering by Irregularly Shaped Particles: A Statistical Approach

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ABSTRACT

Shape can strongly affect scattering by particles at wavelengths near bulk absorption bands. An example is scattering by many components of the atmospheric aerosol at wavelengths in the transmission window centered around 10 μm. An exact solution to the problem of scattering by an irregular particle, even if it were available, would yield more detail than necessary. An alternative approach is to formulate the irregular particle scattering problem in terms of the kinds of averages inherent in the optical properties of an ensemble of particles. Such a statistical method has been applied to an ensemble of small irregular particles by averaging over a range of electromagnetic microstates, in this instance randomly oriented anisotropic oscillators (i.e., Rayleigh ellipsoids). Infrared backscattering spectra calculated by this method agree better with laboratory-measured spectra for ammonium sulfate particles than those calculated using Mie theory.

1. Introduction

The application of Mie theory to atmospheric aerosols implies that they scatter and absorb radiation as if they were spheres. In many instances this is not an unreasonable assumption, but in some it is. There is abundant experimental evidence that Mie theory can be inadequate in predicting optical properties of nonspherical particles, particularly extinction by small irregular particles near bulk infrared absorption bands (see, e.g., Genzel and Martin, 1972, 1973; Huffman and Bohren, 1980) and scattering by large irregular particles (see, e.g., Holland and Gagne, 1970; Zerull and Giese, 1974; Perry *et al.*, 1978).

Several mechanisms have been identified as being responsible for the differences in optical properties between irregularly shaped particles and equivalent spheres. In this paper we have concentrated our efforts on a mechanism that finds its greatest expression in very small dielectric particles in which resonant lattice oscillations occur at infrared frequencies.

Resonant lattice oscillations, which typically occur in frequency regions near bulk infrared absorption bands where the real part of the complex dielectric function is negative, produce cross-section resonances that are often highly shape dependent. This is a specific example of a more general result: the response of any physical system capable of resonant oscillation depends on boundary conditions; in this instance, the particle's shape.

Many materials that are components of the atmospheric aerosol (e.g., ammonium sulfate, quartz and other silicates) have bulk absorption bands in the infrared transmission window centered around 10 μm (see Fig. 1). In these infrared regions, small irregularly shaped particles can have cross sections that are up to an order of magnitude different from those predicted for equivalent spheres. Such discrepancies between Mie theory and measurements can profoundly affect the analysis of atmospheric remote sensing data obtained by instruments such as a tunable CO_2 laser.

Exact solutions to the problem of scattering by particles more complex than spheroids are cumbersome. As a particle departs from regularity, more and more parameters are required to characterize its shape. Very rapidly, the problem of obtaining an exact solution becomes intractable. Even if an exact solution to scattering by a single irregular particle were available, the immense detail yielded by such a solution would be of little value for many applications: the details of individual-particle scattering are lost in measured optical properties of polydispersions. With this in mind, perhaps the best approach to the solution of scattering by an ensemble of irregularly shaped particles is to formulate the problem in terms of the kinds of averages inherent in the optical properties of such an ensemble.

In this paper a statistical approach is taken in which the observable properties of an ensemble of irregular particles are obtained by suitably averaging over a range of electromagnetic microstates. This has been done previously by Aronson and Emslie (1975), and independently by Huffman and Bohren (1980), for absorption spectra of irregular particles that are small compared with the wavelength. These authors

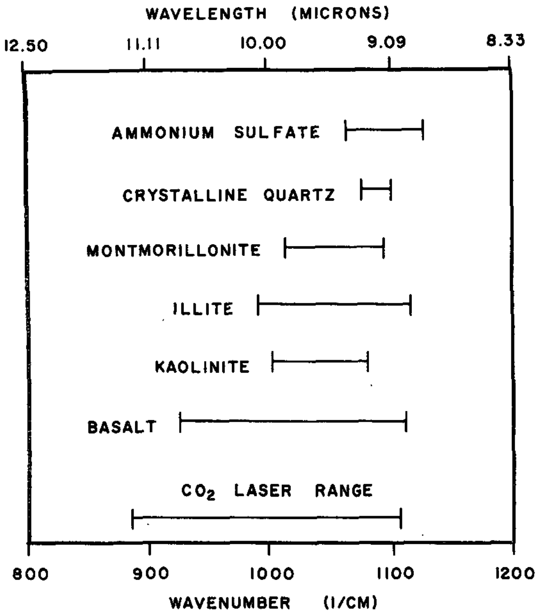

FIG. 1. Absorption bands for several atmospheric aerosol materials. The bars delineate the frequency range over which the imaginary part of the complex refractive index falls to half its maximum value. The range of CO_2 laser frequencies is shown for comparison.

enumerated microstates in terms of elementary ellipsoidal oscillators with random orientation. Averages were then taken over the entire range of ellipsoidal shapes. The results of this approach for absorption spectra have been encouraging.

In the following sections we extend the statistical method to the average angle-dependent scattering cross section for an ensemble of small irregularly shaped particles. In particular, we derive an expression for the average backscattering cross section of such an ensemble. Calculations using this expression are then compared with measurements and with Mie theory, and some applications to atmospheric remote sensing are discussed.

2. Shape effects in the Rayleigh approximation

Simple expressions for scattering and absorption by dielectric particles of regular shape may be obtained from electrostatics theory (Rayleigh theory), provided they satisfy the conditions $x \ll 1$ and $|m|x \ll 1$, where m is the complex relative refractive index at wavelength λ, and the size parameter $x = 2\pi a/\lambda$, where a is a characteristic length of the particle. Such simple expressions can provide insight into how shape affects the optical properties of small particles.

The field scattered by a sufficiently small sphere of radius a is the same as that radiated by an oscillating electric dipole with moment

$$\mathbf{p} = \alpha E_0 e^{-i\omega t}\hat{e}_i,$$

where the polarizability α is given by

$$\alpha = 4\pi a^3 \frac{\epsilon - 1}{\epsilon + 2}. \tag{1}$$

The unit vector $\hat{e}_i$ is in the direction of the incident electric field E_0, and $\epsilon = \epsilon' + i\epsilon''$ is the complex dielectric function of the material at the frequency ω. The dielectric function of the surrounding medium is unity.

By a suitable integration of the scattered field we can obtain cross sections for absorption and scattering:

$$\left.\begin{aligned} C_{\text{abs}} &= k\,\text{Im}\{\alpha\} \\ C_{\text{sca}} &= \frac{k^4}{6\pi}|\alpha|^2 \end{aligned}\right\},$$

where the wavenumber $k = 2\pi/\lambda$ (Bohren and Huffman, 1983, p. 140). From the form of the polarizability (1), it follows that cross-section resonance occurs when

$$\epsilon' = -2, \quad \epsilon'' = 0. \tag{2}$$

The *angle-dependent* cross sections will also be resonant when (2) is satisfied.

For a small sphere, the induced dipole moment is parallel to the applied field. However, for a small ellipsoid arbitrarily oriented with respect to the applied field, the induced dipole moment is, in general, not parallel to the applied field: the polarizability is a cartesian tensor. If we take x, y, z to be a coordinate system fixed relative to the ellipsoid, and x', y', z' to be a system fixed relative to the incident field, then the components of the induced dipole moment in the primed coordinate system for an arbitrarily oriented ellipsoid may be expressed by (Bohren and Huffman, 1983, Ch. 5)

$$\begin{bmatrix} p_{x'} \\ p_{y'} \\ p_{z'} \end{bmatrix} = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix} \begin{bmatrix} E_{0x'} \\ E_{0y'} \\ E_{0z'} \end{bmatrix}, \tag{3}$$

where

$$\alpha_{ik} = \alpha_{ki} = \sum_{j=1}^{3} \alpha_j a_{jk} a_{ji}.$$

Here a_{jk} are direction cosines (e.g., $a_{12} = \hat{e}_x \cdot \hat{e}_{y'}$), and each α_j, where

$$\alpha_j = 4\pi abc \frac{\epsilon - 1}{3 + 3L_j(\epsilon - 1)}, \quad j = 1, 2, 3,$$

corresponds to the polarizability when the applied field is along one of the three semiaxes of lengths a, b and c. The L_j are geometric factors dependent on the ratio of semiaxes of the ellipsoid; they satisfy the condition $L_1 + L_2 + L_3 = 1$ (van de Hulst, 1957, p. 71). For a sphere, $L_1 = L_2 = L_3$.

Let us now consider a *collection* of randomly oriented, identical ellipsoids of volume v. The average absorption and scattering cross sections for such a collection may be written in the form (Bohren and Huffman, 1983, Ch. 12)

$$\left.\begin{aligned} \langle C_{\text{abs}} \rangle &= \frac{kv}{3} \operatorname{Im}\left[\sum_{j=1}^{3} \frac{1}{\beta + L_j}\right] \\ \langle C_{\text{sca}} \rangle &= \frac{k^4 v}{18\pi} \sum_{j=1}^{3} \left|\frac{1}{\beta + L_j}\right|^2 \end{aligned}\right\}, \tag{4}$$

where $\beta = \beta' + i\beta'' = (\epsilon - 1)^{-1}$.

Cross-section resonance conditions clearly follow from (4):

$$\epsilon' = \frac{L_j - 1}{L_j}, \quad \epsilon'' = 0. \tag{5}$$

Three such resonance conditions, each of which depends on L_j, are possible for the collection of randomly oriented, identical ellipsoids.

The conditions for scattering resonance, (2) and (5), are never exactly satisfied for real materials. For the materials shown in Fig. 1, however, and many others, (2) and (5) may be *nearly* satisfied in infrared frequency regions, called surface mode regions, where ϵ' is negative (see Bohren and Huffman, 1983, Ch. 12 for a discussion of surface modes in small particles). Surface mode regions in nonmetals are the result of lattice vibration modes in crystals; they occur almost exclusively in the infrared on the high-frequency side of bulk absorption bands. The resonance that occurs when (2) or (5) is nearly satisfied is called the first-order surface mode.

A comparison between the resonance conditions (2) and (5) reveals a simple example of the effect of shape on cross sections. In a surface mode region, an ensemble of randomly oriented identical ellipsoids will have an average cross-section spectrum that contains resonance features considerably different from those of an ensemble of spheres. Further, if the ensemble is composed of particles of *irregular* shape, the average cross section would likely differ considerably from both; spectral features would be determined by the average of all the individual particle's resonances, each occurring at frequencies dependent on its irregular shape.

Measured cross-section spectra of small irregularly shaped particles in a surface mode region have been found to differ substantially from those calculated using Mie theory (see, e.g., Genzel and Martin, 1972; Bohren and Huffman, 1983, Ch. 12). The measured spectral features are generally shifted and broadened relative to those calculated for spheres, resulting in large discrepancies over a wide range of frequencies.

3. Angle-dependent cross sections for a continuous distribution of ellipsoids

Expanding on an idea first proposed by D. P. Gilra, Huffman and Bohren (1980) derived an expression for the absorption cross section by averaging over all possible ellipsoidal shapes, a continuous distribution of ellipsoids (CDE). This was done in the hope that first-order surface modes in such a distribution are similar to those in an ensemble of irregularly shaped particles. The encouraging agreement between measurements and CDE theory for absorption cross sections suggests that this approach may be successfully applied to angle-dependent scattering, particularly the backscattering direction, in order to account for shape effects near bulk infrared absorption bands.

At any scattering angle the relation between incident and scattered fields may be written in matrix form:

$$\begin{bmatrix} E_{\parallel s} \\ E_{\perp s} \end{bmatrix} = \frac{e^{ik(r-z)}}{-ikr} \begin{bmatrix} S_2 & S_3 \\ S_4 & S_1 \end{bmatrix} \begin{bmatrix} E_{\parallel i} \\ E_{\perp i} \end{bmatrix}, \tag{6}$$

where the elements S_k (k = 1, 2, 3, 4) of the amplitude scattering matrix depend on the scattering angle θ and the azimuthal angle ϕ, the coordinate z is defined by the direction of propagation of the incident light, r is the distance from the particle, $E_{\perp i}$ and $E_{\parallel i}$ refer to the incident field components that are perpendicular and parallel to the scattering plane, and $E_{\perp s}$ and $E_{\parallel s}$ are the scattered field components.

Consider now the form of the amplitude scattering matrix for a *single* arbitrarily oriented ellipsoid. We can solve for the S_j by relating (6) to the expression for the electric field radiated by an oscillating dipole (Stratton, 1941, p. 453) where the components of the induced dipole moment are given by (3) (Bohren and Huffman, 1983, p. 154).

With expressions for the amplitude scattering matrix elements we can determine the relation between the incident and scattered light where the characteristics of the light are specified by the Stokes parameters I, Q, U and V. The general relation between incident and scattered Stokes parameters is (see, e.g., Bohren and Huffman, 1983, Ch. 3)

$$\begin{bmatrix} I_s \\ Q_s \\ U_s \\ V_s \end{bmatrix} = \frac{1}{k^2 r^2} \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \begin{bmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{bmatrix}, \tag{7}$$

where the elements S_{ij} of the scattering matrix are of second degree in S_k. By taking averages of the S_{ij} over all possible orientations, we can determine the form of (7) for a *collection* of identical randomly oriented ellipsoids (Bohren and Huffman, 1983, Ch. 5):

$$\begin{bmatrix} I_s \\ Q_s \\ U_s \\ V_s \end{bmatrix} = \frac{1}{k^2r^2} \times \begin{bmatrix} \langle S_{11}\rangle & \langle S_{12}\rangle & 0 & 0 \\ \langle S_{12}\rangle & \langle S_{22}\rangle & 0 & 0 \\ 0 & 0 & \langle S_{33}\rangle & 0 \\ 0 & 0 & 0 & \langle S_{44}\rangle \end{bmatrix} \begin{bmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{bmatrix}$$

$$\left.\begin{aligned} \langle S_{11}\rangle &= \frac{3k^2\langle C_{\rm sca}\rangle}{8\pi}\frac{1}{2}\left(\frac{6-M}{5}+\frac{2+3M}{5}\cos^2\theta\right) \\ \langle S_{12}\rangle &= \frac{3k^2\langle C_{\rm sca}\rangle}{8\pi}\frac{1}{2}(\cos^2\theta-1)\frac{2+3M}{5} \\ \langle S_{22}\rangle &= \frac{3k^2\langle C_{\rm sca}\rangle}{8\pi}\frac{1}{2}(\cos^2\theta+1)\frac{2+3M}{5} \\ \langle S_{33}\rangle &= \frac{3k^2\langle C_{\rm sca}\rangle}{8\pi}\frac{2+3M}{5}\cos\theta \\ \langle S_{44}\rangle &= \frac{3k^2\langle C_{\rm sca}\rangle}{8\pi}M\cos\theta \end{aligned}\right\}, \qquad (8)$$

where the average scattering cross section $\langle C_{\rm sca}\rangle$ is given by (4), and

$$M = \frac{\mathrm{Re}\{\alpha_1^*\alpha_2 + \alpha_1^*\alpha_3 + \alpha_2^*\alpha_3\}}{|\alpha_1|^2 + |\alpha_2|^2 + |\alpha_3|^2}.$$

The scattering matrix (8) is for the *average* particle in such a collection. As required, it reduces to that for a single sphere when $\alpha_1 = \alpha_2 = \alpha_3$.

The relation (8) contains all of the information needed to calculate average angle-dependent scattering cross sections for a collection of small, identical, randomly oriented ellipsoids. We may now proceed to determine an expression for the average backscattering cross section $\langle\sigma_b\rangle$ from (8) and then integrate over a continuous distribution of ellipsoidal shapes.

From the form of (8) and symmetry arguments it is obvious that the scattered radiance in the backward direction ($\theta = 180°$) is independent of the polarization of the incident light. We therefore take it to be unpolarized: $Q_i = U_i = V_i = 0$. We may now define the average total cross section by

$$\langle C_{\rm sca}\rangle = \int_{4\pi} \frac{\langle S_{11}\rangle}{k^2} d\Omega.$$

Thus, $\langle S_{11}\rangle/k^2$ is the differential scattering cross section $d\langle C_{\rm sca}\rangle/d\Omega$, so the value of $\langle S_{11}\rangle/k^2$ at 180° may be interpreted as $\langle\sigma_b\rangle$. It follows from (4) and (8) that

$$\langle\sigma_b\rangle = \frac{k^4(|\alpha_1|^2 + |\alpha_2|^2 + |\alpha_3|^2)}{60\pi^2} + \frac{k^4\,\mathrm{Re}\{\alpha_1^*\alpha_2 + \alpha_1^*\alpha_3 + \alpha_2^*\alpha_3\}}{240\pi^2}. \qquad (9)$$

This is the average backscattering cross section for a collection of randomly oriented identical ellipsoids. Here $\langle\sigma_b\rangle$ contains two distinct terms: the first is just proportional to $\langle C_{\rm sca}\rangle$ while the second involves cross-terms of the polarizability.

The polarizability terms in (9) contain the geometric factors L_j, and so following Huffman and Bohren (1980) we can model the average backscattering cross section for a collection of small irregular particles by integrating (9) over all possible values of L_1 and L_2 weighted by a shape probability function $P(L_1, L_2)$:

$$\begin{aligned}\langle\langle\sigma_b\rangle\rangle &= \int_0^1\int_0^{1-L_1}\langle\sigma_b\rangle P(L_1, L_2)dL_1dL_2 \\ &= \frac{k^4v^2}{60\pi^2}(A_1 + A_2 + A_3) + \frac{k^4v^2}{240\pi^2} \times \mathrm{Re}\{I_1 + I_2 + I_3\}, \qquad (10)\end{aligned}$$

where

$$A_1 = \int_0^1\int_0^{1-L_1}\frac{P(L_1, L_2)}{|\beta + L_1|^2}dL_2dL_1,$$

$$A_2 = \int_0^1\int_0^{1-L_1}\frac{P(L_1, L_2)}{|\beta + L_2|^2}dL_2dL_1,$$

$$A_3 = \int_0^1\int_0^{1-L_1}\frac{P(L_1, L_2)}{|\beta + 1 - L_1 - L_2|^2}dL_2dL_1,$$

$$I_1 = \int_0^1\int_0^{1-L_1}P(L_1, L_2)\frac{1}{(\beta^* + L_1)(\beta + L_2)}dL_2dL_1,$$

$$I_2 = \int_0^1\int_0^{1-L_1}P(L_1, L_2) \times \frac{1}{(\beta^* + L_1)(\beta + 1 - L_1 - L_2)}dL_2dL_1,$$

$$I_3 = \int_0^1\int_0^{1-L_1}P(L_1, L_2) \times \frac{1}{(\beta^* + L_2)(\beta + 1 - L_1 - L_2)}dL_2dL_1,$$

One could tailor the shape probability function to reflect some order that might exist in the irregular particle collection being modeled, but in the absence of such information it is best to take $P(L_1, L_2) = 2$, a distribution for which all ellipsoidal shapes are equally probable (Huffman and Bohren, 1980). The integrals A_1, A_2 and A_3 may be evaluated to give

$$A_1 = A_2 = A_3 = \frac{2 + 2\beta'}{\beta''}\tan^{-1}\left[\frac{\beta''}{|\beta|^2 + \beta'}\right] - \ln\left[1 + \frac{2\beta' + 1}{|\beta|^2}\right]. \qquad (11)$$

The integrals I_1, I_2 and I_3 may be reduced to

$$I_1 = I_2 = I_3 = \int_0^1 \frac{\log[(\beta + 1 - L_1)/\beta]}{\beta^* + L_1} dL_1, \quad (12)$$

where $\log z$ is the principal value of the logarithm of the complex number z. The definite integral in (12) has no explicit antiderivative and so must be evaluated by a numerical technique, in this instance an adaptive quadrature method that can account for the often wildly varying nature of the integrand (see, e.g., Young and Gregory, 1972).

Thus, we can express $\langle\langle\sigma_b\rangle\rangle$ as

$$\langle\langle\sigma_b\rangle\rangle = \frac{k^4v^2}{20\pi^2}\left\{\frac{2+2\beta'}{\beta''}\tan^{-1}\left[\frac{\beta''}{|\beta|^2+\beta'}\right] - \ln\left[1+\frac{2\beta'+1}{|\beta|^2}\right]\right\} + \frac{k^4v^2}{40\pi^2} \times \int_0^1 \mathrm{Re}\left\{\frac{\log[(\beta+1-L_1)/\beta]}{\beta^*+L_1}\right\} dL_1. \quad (13)$$

Here $\langle\langle\sigma_b\rangle\rangle$ may be used to model the average backscattering cross section of a polydispersion of irregular particles provided that the optical properties of the same polydispersion of equivalent spheres are well approximated by Rayleigh theory.

4. Comparison of theory with measurements and sphere calculations

A test of the validity of $\langle\langle\sigma_b\rangle\rangle$ must be provided by comparisons with measurements of backscattering by irregular particles near infrared absorption bands. Unfortunately, measurements of small particle backscattering spectra in the infrared are rare indeed, particularly for well-defined particle size distributions. However, Mudd *et al.* (1982) have made measurements of the volume backscattering coefficient β_π for small irregular ammonium sulfate particles at several wavelengths near a bulk absorption band at 1085 cm^{-1}.

Before making a comparison between the measured backscattering spectrum and that calculated in the CDE approximation, we must convince ourselves of the applicability of the small particle assumption to the size distribution created by Mudd and his coworkers. Figure 2 shows the results of a test of this assumption. Using the size distribution parameters of Mudd *et al.* and the optical constants for ammonium sulfate measured by Toon *et al.* (1976), calculations of β_π were made for volume-equivalent spheres using both the Rayleigh approximation and Mie theory. The percentage difference between the two calculations is a measure of the correctness of calculating cross sections by electrostatics theory. Figure 2 shows that in the frequency range covering both Mudd's measurements and the surface mode region (940–1150 cm^{-1}), the approximate and exact calculations differ by at most a factor of 0.45, and over most of this frequency range by a factor of less than 0.1.

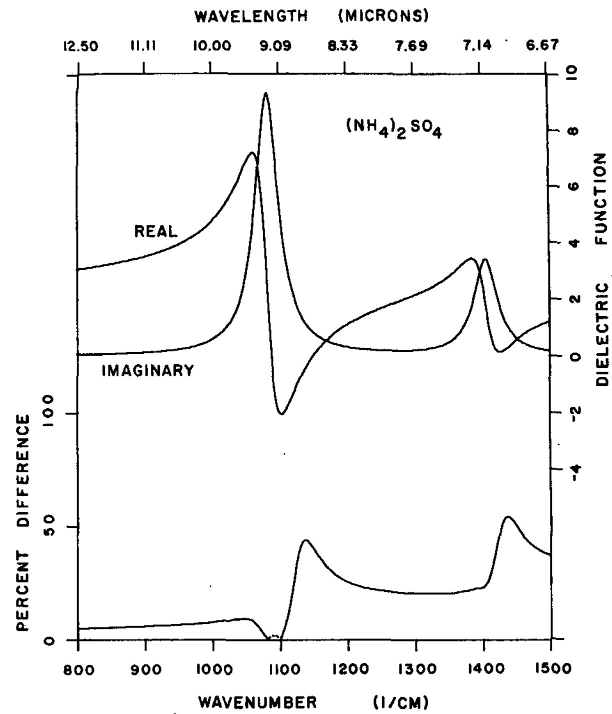

FIG. 2. Infrared calculations of the percentage difference between the volume backscattering coefficient for ammonium sulfate spheres calculated by Mie theory and Rayleigh theory (bottom). The complex dielectric function for ammonium sulfate from Toon *et al.* (1976) reveals the surface mode region (top).

The differences that do exist between the exact and approximate theories occur for two reasons. First, in the frequency region where ϵ' is negative, higher-order surface modes are beginning to become excited in the largest spheres in the distribution; the Rayleigh approximation accounts only for first-order surface modes. Second, the Rayleigh approximation is less valid for shorter wavelengths.

Figure 2 shows that a comparison between the measurements of Mudd *et al.* and calculations using the CDE expression are valid for this size distribution, despite the fact that some individual particles at the large end of the distribution do not satisfy the Rayleigh criterion.

A comparison of normalized volume backscattering coefficient spectra measured by Mudd *et al.* with calculations using (13) is made in Fig. 3. Calculations using Mie theory are also presented for comparison. The CDE calculations give a much improved representation of the measured irregular particle backscattering spectra over the Mie calculations. Note that β_π in Fig. 3 is plotted logarithmically. The backscattering resonance peak calculated by (13) is shifted and broadened relative to the peak for spheres due to the distribution of shapes in the CDE expression. As

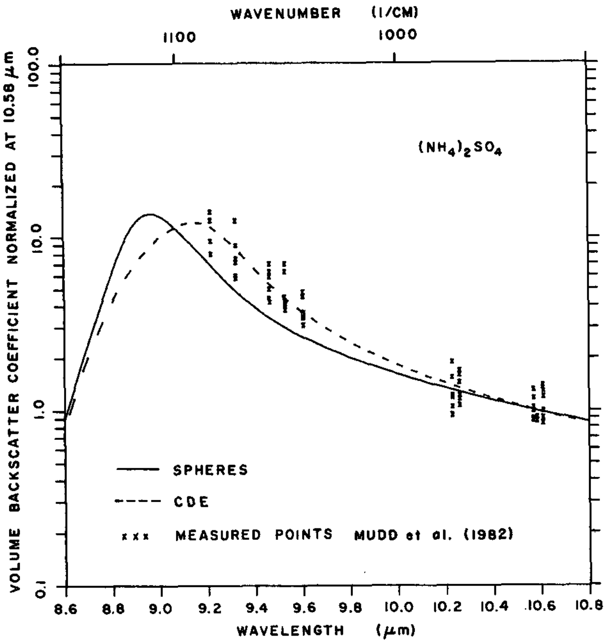

FIG. 3. Measured infrared values of the normalized volume backscattering coefficient for irregular ammonium sulfate particles (Mudd *et al.*, 1982) compared with calculations done in the CDE approximation and by Mie theory.

shown in the figure, the distribution of shapes does a good job of modeling the distribution of surface mode resonances in the collection of irregular particles.

It should be mentioned that in Fig. 3 the values of β_π have been arbitrarily normalized to their 10.59 μm value. This is consistent with the presentation of data by Mudd *et al.* H. T. Mudd (personal communication, 1982) reports that the absolute values of their measurements of β_π at 10.59 μm were less than Mie calculations by a factor of about 5; our calculation of the absolute value by CDE theory exceeds the Mie calculation by a factor of 1.5 at this wavelength. The low absolute values measured by Mudd *et al.* are inconsistent with all theories of which we are aware. Whether this is due to a general inability of theory to predict absolute values of backscattering cross sections, or to the inherent difficulties in making absolute value measurements, is open to question at this time. We are inclined to believe that the latter is more probable.

It is important to note that it is the *averaging* of surface mode resonances of the ellipsoids in the CDE approximation that leads to its agreement with the spectrum of surface mode resonances in a collection of irregular particles. There does not exist a correspondence between any *individual* irregular particle's surface mode resonances and those of any particular ellipsoid; averaging over a broad distribution of both irregular particles and ellipsoids is the process that produces agreement between theory and measurement.

5. The CDE approximation and atmospheric remote sensing

For a size distribution of sufficiently small irregular particles, the CDE approximation appears to be preferable to Mie theory as the tool of prediction and interpretation of backscattering measurements done at IR frequencies near surface mode regions. This is an important result for several forms of remote sensing done at frequencies around 10 μm because many atmospheric aerosol materials have surface mode regions associated with their bulk absorption bands in this frequency region (see Fig. 1).

Calculations of β_π as a function of frequency have been performed using Mie and CDE theory for several lognormal size distributions containing representative mixtures of materials commonly found in the atmosphere: ammonium sulfate, quartz and other silicates. Figure 4 shows a comparison between backscattering predicted by Mie theory and the CDE expression for a lognormal distribution of ammonium sulfate particles mixed with quartz particles. Crystalline quartz has a strong surface mode region in the 1080–1210 cm^{-1} frequency range; ammonium sulfate has a less strong surface mode region between 1090 and 1150 cm^{-1}. The optical constants of crystalline

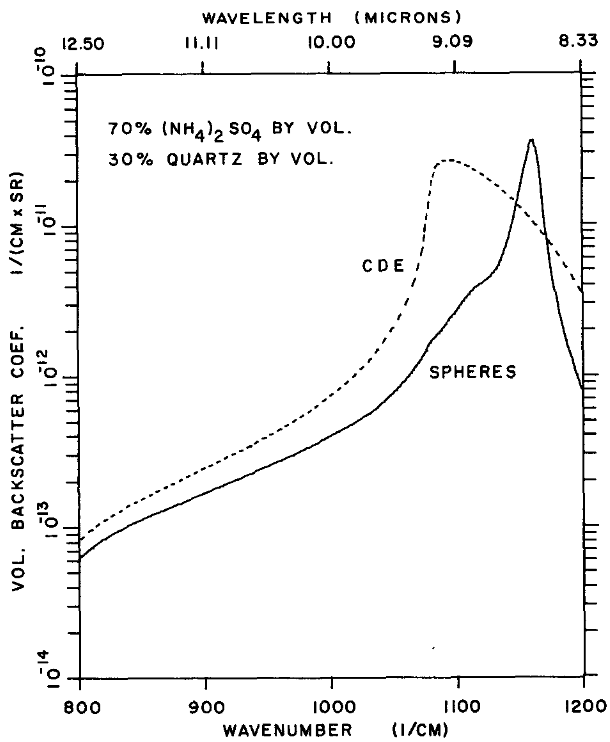

FIG. 4. Infrared calculations of the volume backscattering coefficient for a lognormal size distribution containing 30% quartz and 70% ammonium sulfate by volume. Sphere calculations are compared with calculations done in the CDE approximation. The geometric mean radius on a volume basis for the distribution is 0.2 μm. The geometric standard deviation is 1.86.

quartz and ammonium sulfate used in the calculations are taken from Spitzer and Kleinman (1961), and Toon *et al.* (1976), respectively. The CDE calculations differ by up to an order of magnitude from the calculations for spheres. Based on the results of the previous section, we believe that measured spectra for such a particle distribution would agree better with the CDE calculations than with the Mie calculations.

The results of a similar calculation are shown in Fig. 5, where the lognormal distribution consists of a mixture of ammonium sulfate and montmorillonite particles. Note that β_π is plotted linearly in this figure. The optical constants for montmorillonite taken from Toon *et al.* (1977) show a surface mode region, similar in strength to that of ammonium sulfate, between 1045 and 1100 cm^{-1}. Although the difference between the Mie and CDE calculations for this mixture is less than for the distribution containing quartz, it is still appreciable over a wide range of frequencies. Perhaps more important, the spectral features in the 1050–1130 cm^{-1} region predicted by Mie theory are absent from the results of the CDE calculations: the backscattering cross section resonance peaks of montmorillonite at 1080 cm^{-1} and of ammonium sulfate at 1110 cm^{-1} are shifted and broadened by the CDE calculations. The result is that only one spectral peak remains, whereas Mie theory predicts two distinct peaks. Results such as this should be considered if one contemplates using a differential backscattering spectroscopy technique to infer particle composition, as has been proposed by Colburn and Pollack (1975) and Wright *et al.* (1977).

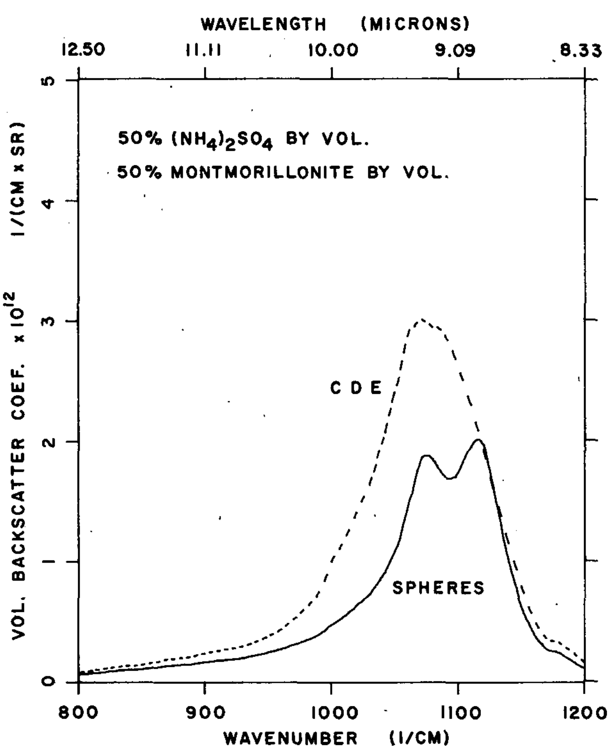

FIG. 5. As in Fig. 4 except the lognormal size distribution contains 50% ammonium sulfate and 50% montmorillonite by volume.

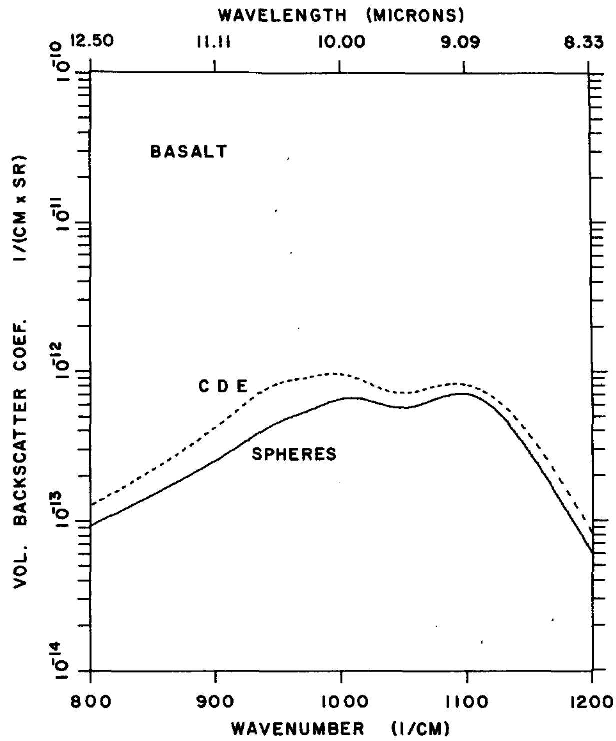

FIG. 6. As in Fig. 4 except the lognormal size distribution contains only basalt.

Not all aerosol species have surface mode resonances as strong as quartz and montmorillonite. By way of illustration we present in Fig. 6 calculations for a lognormal distribution of basalt particles. Basalt, while not generally regarded as a component of the atmospheric aerosol, has nonetheless been used in optical models of the tropospheric aerosol (Toon and Pollack, 1976). Measured optical constants of basalt by Pollack *et al.* (1973) show no true surface mode region, although ϵ' approaches zero near 1110 cm^{-1}. For this particle distribution, the CDE expression and Mie theory are in somewhat better agreement, differing by, at most, a factor of about 2; the cross-section resonances are weaker, and thus shape effects are less important.

The results of these calculations may be looked upon as illustrating the significance of irregular particle shape on the volume backscattering coefficient for these aerosol materials. Although the size distributions used for these calculations contain significantly fewer large particles than are found in the atmosphere, we believe that measurements of β_π for atmospheric size distributions would in many instances differ from Mie calculations in a similar manner to the differences between Mie and CDE calculations shown in Figs. 4–6.

6. Concluding remarks

The scattering matrix elements given in (8) are general in that they may be used to calculate average angle-dependent scattering cross sections for any scattering angle, not just the backward direction. However, for scattering angles other than 180°, the polarization of the incident light would determine the form of the resulting average cross section.

Although we have concentrated our discussion on shape effects in surface mode regions, it should be noted that these effects are not confined exclusively to such regions. Bohren and Huffman (1983) showed that where the dielectric function is well behaved (e.g., insulators at visible wavelengths, basalt between 1100 and 1200 cm^{-1}), absorption cross sections for small discs and needles are slightly greater than for spheres. Similar weak shape effects are likely for angle-dependent scattering by small irregularly shaped particles. As shown in Fig. 6, the CDE expression models these weak shape effects. Between 1100 and 1200 cm^{-1}, the ratio of β_π calculated from (13) to that calculated from Mie theory is about 1.5:1.

The CDE expression is a modest first step in solving the general problem of scattering by irregular particles of arbitrary size. No claims are made that it can be generally used in place of Mie theory in the analysis of scattering by atmospheric aerosols. Mie theory is applicable to scattering by atmospheric hazes and other solution droplets such as stratospheric sulfuric acid, and it continues to be a good first approximation to scattering by larger irregularly shaped particles. However, the CDE expression may be applied in conjunction with Mie theory in aerosol scattering problems. Measurements of tropospheric aerosol size distributions show a bimodal structure with the smaller mode dominated by sulfates of ammonia (see, e.g., Patterson *et al.*, 1980). In many instances, the CDE approximation may be used to calculate IR backscattering by this smaller particle fraction, thus accounting for shape effects in at least some of the particles.

However, particles in the larger size fraction of atmospheric aerosol size distributions are not sufficiently small that the CDE expression (13) may be used. This is not to say that the optical properties of these larger size distributions exhibit no shape effects; indeed they do. Theory predicts that not only first-order, but also higher-order surface modes are excited at frequencies appropriate to a larger particle's shape (see, e.g., Fuchs and Kliewer, 1968, for a discussion of higher-order modes in spheres). Thus, an appropriate next step is to suitably extend the CDE method to account for the effects of shape on higher-order modes, and in so doing, increase its generality.

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