Spectral Reflectance and Emittance of Particulate Materials. 2: Application and Results

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Experimental data on the spectral emittance of particulate minerals, obtained using a Michelson interferometer operating between 300 cm\(^{-1}\) and 1400 cm\(^{-1}\) are compared with the results of a new theory of the spectral reflectance (emittance) of such materials. The comparisons show that the theory predicts the infrared spectra of minerals quite well both for single substances and mixtures, over the wide particle size range between 0.3 \(\mu\) and 330 \(\mu\). The good agreement suggests that the theory can be used in the application of remote infrared spectroscopy to such problems as the compositional analysis of the surface of a planet.

Introduction

For many years it has been recognized that infrared spectroscopy provides unique information on the composition of minerals. This results from the rich vibrational spectra that may be obtained in the infrared region. While most workers have concentrated their efforts on laboratory transmission spectra, such potentially important remote sensing techniques as emission and reflection were in fact investigated by Coblentz\(^1\) almost three quarters of a century ago. The advent of the space program reawakened an interest in this topic, and a number of groups proposed remote infrared spectroscopy as a valuable tool for evaluating planetary surface mineralogy from orbiting or flyby spacecraft. The instrumental capability for obtaining excellent remote data has continued to improve, as demonstrated by recent results from the Mariner Mars\(^2\) and Nimbus\(^3\) orbiting spacecraft.

While the reflectance spectra of polished mineral samples provide many strong features suitable for relatively simple interpretation, the spectra of roughened or particulate samples change in important ways with the degree of roughness or the particle size and packing density. For some time, it was believed by many investigators that the spectra of finely divided minerals approximate blackbody spectra and thus contain very little or no information as to composition. We showed\(^4\) both experimentally and theoretically that this was not true but that the problem was simply one of the signal-to-noise ratio. Others\(^5,6\) examined the effects of particle size on spectral shape and found that different spectral features had widely differing behaviors as a function of particle size. In some cases\(^7\) peaks could even turn into troughs. As the greatest difficulties inherent in the prospects for remote mineral analysis by infrared spectroscopy were clearly those of interpretation, we began the development of a new theory of the reflectance or emittance of particulate solids several years ago.\(^8\) The current status of the theory is detailed in the preceding paper\(^9\) (hereafter referred to as Part 1).

An earlier version of the theory produced relatively good agreement with experimental data\(^10\) in the coarse-particle regime. The agreement in all particle size ranges has continued to improve through a process of successive refinement of the assumptions as discrepancies appeared in the comparison of theoretical predictions with experimental measurements.

Apparatus

Our measurements have been made on a 7-35 \(\mu\) (1400-300 cm\(^{-1}\)) Michelson interferometer spectrometer system, which uses a germanium-coated CsI beam splitter and a Barnes TGS pyroelectric detector. The samples are heated from below and mounted on a lazy Susan turntable so that alternate measurements can be made without breaking the vacuum or inert gas atmosphere. Vacuum measurements can be made to investigate the effects of high thermal gradients on the spectra.

The powders are generally supported in a sample tray 0.6 cm deep with a total volume of 3.04 cm\(^3\). This tray is instrumented for temperature measurements by embedding a thermistor in the base and stringing two sets of 0.05-cm differential copper-constantan thermocouples 0.2 cm and 0.5 cm above the base (Fig. 1). The gradient between the upper two stations is extrapolated to the nominal surface in

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order to provide a first estimate of the surface temperature. Thermistors located on the interferometer detector case, on the black shield that surrounds the sample chamber, and on the experimental blackbodies provide the other temperatures required for data reduction.

The experimental blackbodies are constructed of aluminum and have concentric 30° V-grooves cut into the surface. They are coated with Parsons black paint (Eppley Laboratory) because previous results using Nextel black paint (Minnesota Mining and Manufacturing Co.) indicated the presence of spectral features near 1090 cm⁻¹ and 460 cm⁻¹, owing to the presence of small glass beads in the Nextel paint. The Parsons black standard was run against a Carbolac-1 black powder sample (9-ma carbon particles) as well as Nextel-coated standard, and the data indicate a spectrally flat emittance for the Parsons standard from 1400 cm⁻¹ to about 500 cm⁻¹. The emittance of the Parsons standard then appears to fall monotonically reaching apparent values of about 0.97 near 350

data

\textbf{Data Reduction}

The data reduction procedure involves Fourier transformation of the interferograms of the sample and the two experimental blackbodies which are run at temperatures close to that of the sample and differ by about 5°C. High signal-to-noise data are obtained with a sample surface temperature about 15°C above the near-ambient interferometer and shield temperatures in about 20 min with a spectral resolution of about 3 cm⁻¹.

The spectral emittance \( \epsilon_s(\nu) \) of the sample is the spectral radiance \( N_s(\nu) \) of the sample divided by the spectral radiance \( B_s(\nu) \) of a blackbody at the same temperature as the sample. We calculate \( B_s(\nu) \) from the Planck function using the inferred surface temperature of the sample. We determine \( N_s(\nu) \) from the measured output spectrum \( E_s(\nu) \) of the sample by means of the instrument transfer function and a correction for radiation from the shield that is reflected from the sample.

The transfer function relates radiance \( N(\nu) \) to spectral output voltage \( E(\nu) \) obtained by Fourier transformation of the interferogram. We assume that the formula is linear and of the form

\[
N = N_o + (E/R) \tag{1}
\]

where \( N_o \), the input radiance that produces zero output signal, is equal to the radiance of the instrument in the direction toward the sample. To determine \( N_o \) and \( R \) we replace the sample successively by two blackbodies at temperatures \( T_1 \) and \( T_2 \). Then, from Eq. (1)

\[
\epsilon_1 B_1 = N_o + (E_1/R), \tag{2}
\]

\[
\epsilon_2 B_2 = N_o + (E_2/R), \tag{3}
\]

where \( \epsilon_1 \) and \( \epsilon_2 \) are the emittances of the blackbodies, which would allow for small departures from perfect blackbody behavior. From Eqs. (2) and (3) we obtain for \( R(\nu) \) and \( N_o(\nu) \):

\[
R(\nu) = \left\{ \frac{E_1 - E_2}{\epsilon_1 B_1 - \epsilon_2 B_2} \right\} \tag{4}
\]

and

\[
N_o(\nu) = \frac{1}{2} \epsilon_1 B_1 + \epsilon_2 B_2(1/R)(E_1 - E_2) \tag{5}
\]

With the sample in place we determine the net radiance \( N_s \) of the sample from the measured spectral output \( E_s \) by means of Eq. (1)

\[
N_s = N_o + (E_s/R) \tag{6}
\]

and where \( R \) and \( N_o \) are known from Eqs. (4) and (5). On combining Eqs. (4)–(6) we can express \( N_s \) directly in terms of the measured quantities \( E_1 \), \( E_2 \), and \( E_s \):

\[
N_s = \frac{1}{2} \epsilon_1 B_1 + \epsilon_2 B_2 + \frac{1}{2} \left( \epsilon_1 B_1 - \epsilon_2 B_2 \right) \frac{(2E_1 - E_2)(E_1 - E_2)}{(E_1 - E_2)} \tag{7}
\]

Finally, the emittance \( \epsilon_s \) of the sample is computed from the formula

\[
\epsilon_s = \left| \frac{N_s - B_s[1 - (\Omega/\pi)] - B_s(\Omega/\pi)]}{B_s - B_s[1 - (\Omega/\pi)] - B_s(\Omega/\pi)]} \right| \tag{8}
\]

which is based on simple radiative transfer considerations. Here \( B_c \) is the radiance of the cavity or shield (assumed to be a blackbody) at temperature \( T_s \) surrounding the sample, \( B_s \) is the radiance of the interferometer aperture (also assumed to be a blackbody at temperature \( T_1 \)), \( B_s \) is the Planck function for the temperature \( T_s \) of the sample, and \( \Omega \) is the solid angle subtended at the sample by the interferometer aperture. The cavity walls are coated with 3M Nextel black paint, which, together with multiple reflections, should make it an almost perfect blackbody. In the data reduction up to the present we have assumed that the blackbodies are indeed black, so that \( \epsilon_1 = \epsilon_2 = 1 \).
As the surface of the powder cannot be microscopically smooth (we draw a spatula edge across the powder surface to prevent gross roughness), and as the depth of origin of the radiation is a function of the optical constants at the various frequencies, we cannot expect the definition of the surface to be very exact. Further, the position of the stretched thermocouple wires has some error and the possibility of a poor equilibrium between the radiation field and the shiny thermocouples is quite likely.

For all of these reasons we chose to estimate our surface temperature by a radiative expedient based on what is generally known as the principal Christiansen frequency.\textsuperscript{11,12} When the refractive index $n$ of a substance approaches unity and the absorption index $k$ is quite small ($\leq 10^{-2}$), the amount of surface reflection is negligible and the refractive scattering is minimal. Thus the emittance is maximum and close to unity. This combination of the optical constants occurs at slightly higher frequencies than the first principal reststrahlen band. It cannot in principle occur for a mixture of materials as the location of the Christiansen frequency will be different for each species. Even two orientations of birefringent minerals have slightly different Christiansen frequencies. We take the value for the average of the two orientations of corundum to be 1020 cm$^{-1}$ and for quartz to be 1360 cm$^{-1}$ from data of Barker\textsuperscript{13} and Spitzer and Kleinman.\textsuperscript{14} We assume that the only significant temperature error in our data reduction scheme is that of the surface temperature. We then use the extrapolated surface temperature as a first estimate of the true surface temperature and calculate an emittance spectrum. The computer program is constructed so that this temperature may be varied and the procedure is to make the required changes in this temperature so as to provide a unit emittance at the principal Christiansen frequency.

We have found that the extrapolated surface temperature and the temperature derived by the Christiansen frequency technique differ by a few tenths of a degree in cases of relatively low temperature gradients (about 5$^\circ$/cm to 10$^\circ$/cm as measured by our upper differential thermocouple) that occur in atmospheric pressure runs. Under conditions of high temperature gradients (vacuum) the procedure is quite inaccurate, and we plan to discuss this in a future communication. All the data are plotted as reflectance ($R = 1 - \epsilon$) for convenience in comparison with the theory. The validity of this procedure, which is simply an application of Kirchhoff's law for \textit{infinitely} thick media, has been previously shown.\textsuperscript{11}

\textbf{Comparison of Theory and Experiment}

As discussed in Part 1\textsuperscript{3}, our theory consists of two subtheories. The first, which is based on geometrical optics supplemented by certain wave optics con-

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig2}
\caption{Comparison of theoretical and experimental reflectance of corundum powders.}
\end{figure}
120-μ sample was obtained from the Norton Company, the 0.3-μ sample from Adolf Meller Co., and the other samples are LWA powders obtained from the Microabrasives Corporation of Westfield, Massachusetts. The particle sizes shown on the figure for the LWA powders are Microabrasives designations except for the 3.5-μ sample. This is Microabrasives LWA 3, but our particle size counts indicated a value of about 3.8 μ. The shape of the spectrum between 630 cm\(^{-1}\) and 900 cm\(^{-1}\) and the particle size effect in regions of the spectrum where the particles are opaque was correctly predicted only after we included the wave optics additions to the basic geometrical optics model to account for the effects of particle edges\(^{10}\) and surface asperities. The edge effect which dominates at the lower particle sizes (ds) of the coarse-particle theory produces the 1/d dependence of the reflectance spectra in this region of high absorption by the particles. The fact that the 630-900 cm\(^{-1}\) feature persists to relatively large particle sizes (120 μ) was explicable only after scanning electron micrographs (Fig. 3) revealed the presence of small steplike surface asperities for this material. If the number of these asperities is proportional to the surface area of the particles, they will produce no d-dependent effect (see Fig. 4). The surface density of these asperities is an adjustable parameter in the theory. The scale factor for the 1/d effect of the particle edges has been chosen, as discussed in Part 1\(^{9}\), by means of reasonable but somewhat arbitrary physical assumptions. We have used the same factor for all jagged particles. The general level observed in the reststrahlen regions for large particles in all of our work is higher than predicted by the theory. We believe this to be the result of deficiencies in our continuum-type radiative transfer model as the particles in such regions are highly opaque and therefore give rise to a large change in the radiative fluxes in a single layer of particles, which violates the assumptions of a continuum model. Correction of the theory by means of a discrete layer model is required, as pointed out also in Part 1.

As reduction of particle size generally results in increasing porosity (decreased packing density) and the fine-particle theory shows a decided porosity-dependent effect owing to the dilution of the optical constants by high void fractions, we have carried out several experiments with the 0.3-μ powder as a function of packing density. The results showed that as packing density is increased, the principal effect is to increase the spectral contrast in the two features at 450 cm\(^{-1}\) and 580 cm\(^{-1}\). The data shown in Fig. 2 for the 0.3-μ sample were obtained by compressing it gently, thus increasing the volume fraction of material to 0.19 from 0.09, which is its state as prepared by our usual techniques. The spurious feature observed near 930 cm\(^{-1}\) in the theoretical spectra for the 3.5-μ and 10-μ cases would be considerably reduced if a particle size distribution had been used. It is to be noted that the peak in the experimental spectrum in this general region shifts

siderations, is applicable in the coarse-particle region which extends down to particle sizes roughly comparable with the free space radiation wavelength. The second, a fine-particle theory, is based on the Lorentz-Lorenz theory of dielectrics and Rayleigh scattering by particles immersed in the medium whose optical properties are set by the Lorentz-Lorenz field. In order to bridge the two theories for those particle sizes falling in the ill-defined region between the regions of clear applicability of either theory, we have at present resorted to a simple empirical bridging formula that gradually merges the results of the two subtheories.

Figure 2 shows a comparison of the experimental and theoretical results for corundum powders. The

Fig. 3. (a) Scanning electron micrograph of steplike asperities, 30-μ corundum, ×740. (b) Scanning electron micrograph of steplike asperities and additional fines. 120-μ corundum, ×370.
to higher frequencies as the average particle size is reduced. This may very well be the effect of a contribution by the feature in question. The feature is caused by the onset of a refractive contribution to the scattering as the particles become more transparent for frequencies approaching the Christiansen frequency at 1020 cm\(^{-1}\). This contribution falls off rapidly as the frequency approaches still closer to the Christiansen point. A similar explanation applies to the theoretically predicted convex shape of the spectra at frequencies above 1020 cm\(^{-1}\) contrasted with the concave shape shown by the experimental data.

Figure 4 shows the theoretical corundum spectra as calculated for the 120-\(\mu\) and 30-\(\mu\) particle sizes by options in our program that either, (i) treat the particles as smooth spheres, (ii) include both the effects of edges and surface asperities, (iii) include edges, but no asperities, and (iv) include asperities but no edges. As can be seen, both edges and asperities are necessary to account for the particle size dependence in the reststrahlen regions and the shape of the 630-900 cm\(^{-1}\) feature in the 120-\(\mu\) particle size sample. The amount of surface asperities used for these plots is \(NV = 3 \times 10^{-7}\) cm (see Part 1). This value, which corresponds to the average thickness of the asperity layer, indicates that a substantial change in reflectance is caused by a relatively small amount of these asperities. The effect is caused by the high efficiency of absorption by ellipsoidal particles having \(n \ll 1\) and \(k \sim 1\) such as occur in reststrahlen bands. The amount of asperities appears compatible with photomicrographs of the particles. In a similar fashion the scale factor for the \(d\) dependence described in Part 1 by the value \(b = \lambda/4\pi\) is somewhat arbitrary and might be slightly adjusted for a better fit to the data. At the present time \(b = 0.09\) is used for all of our theoretical computations. However, as these factors are unlikely to be known precisely for arbitrary unknown samples, we have not yet optimized the fit.

The phenomenon of additional absorption by the needlelike dipoles that represent the edges and the more general spheroidal dipoles that represent surface asperities was an important innovation in our coarse-particle theory. We therefore attempted to prove the reality of these effects by carrying out several critical experiments. The first of these was a comparison of a single crystal emittance spectrum of randomly oriented sapphire with the emittance spectrum obtained after substantial surface abrasion with 15-\(\mu\) diamond paste. The results are shown in Fig. 5, and a stereo pair of scanning electron micrographs of a replica of the surface are shown in Fig. 6. Figure 5 shows that the anomalous shape of the powder spectrum in the 630-900 cm\(^{-1}\) region can be produced in a single crystal spectrum by providing surface asperities.
The second critical experiment was carried out by running two samples of corundum beads (Fig. 7). These beads were produced for us by D. Spooner and R. Bechtold of the Lockheed Electronics Geophysics section. The mechanism of bead production is to feed small particles of corundum into a hydrogen–oxygen flame where partial melting occurs. After air cooling, small amounts of a number of other Al₂O₃ phases were observed by x-ray diffraction, but annealing at 1400°C for more than 4 h removed the other phases, resulting in pure α-Al₂O₃.

Figure 8 shows scanning electron micrographs of the sapphire beads. Surface asperities similar to those shown for most samples of crushed corundum (Fig. 3) still occur on these beads. Some nonspheroidized material still exists, principally in the smaller sized sample, but the particles have been largely de-edged. The changed level of the spectra in the 575–900 cm⁻¹ region and the noticeably smaller particle size effect when contrasted with the data for comparable-sized particles in Fig. 2 both confirm the assumed mechanism of edge absorption. We believe that the
Fig. 7. Experimental spectra of corundum beads.

Fig. 8. Scanning electron micrographs of corundum beads.
residual edges in the 35-μm beads are largely responsible for the fact that the spectrum of this sample is still somewhat below the spectrum of the 130-μm beads in the 575-900 cm⁻¹ region. We note that the level of the spectrum of the 35-μm beads lies between the level of the 60-μm and 120-μm corundum powders. A dendritic growth can be seen in the scanning electron micrographs of the bead surfaces. This material is apparently responsible for the shape variation in the 630-900 cm⁻¹ region. Such a result is in accord with a number of theoretical experiments we have conducted by varying the shapes of the asperities (Part 1).

The empirical bridging formula used in the region between 0.3 μ and 12 μ where both theories are being extended beyond their range of applicability appears to provide better results than either theory alone. This can be seen in Fig. 9, where the results of both individual theories and the bridged theory are compared with experimental results for 3.5-μ corundum powder. The relatively greater strength of the feature near 535 cm⁻¹ with smaller particle size can be seen in the experimental data for the 3.5-μ and 10-μ particles (Fig. 2). This is apparently a residue of the strong fine-particle feature shown by the theory (Fig. 9) to peak near 570 cm⁻¹, and it was used in an attempt to ascertain a reasonable bridging relationship. This relationship can probably be improved upon, but its optimization is somewhat dependent on the optimization of the other adjustable factors as well as the replacement of the monodisperse assumption with a more realistic particle size distribution function. The real particles, of course, have a size distribution, but the theoretical results shown in this paper are all for monodisperse particles.

Figure 10 shows the theoretical and experimental results for quartz powders. Once again the theoretical spectra for the coarser particles do not attain values as high as those observed in the experimental data in the reststrahlen regions. For the theoretical runs we assumed no surface asperities, since the 1100-1200 cm⁻¹ feature in quartz, which is similar to the previously discussed 630-900 cm⁻¹ feature in corundum, is only observed at the smallest particle sizes. However, clinging fine particles are commonly observed to be present in samples of larger particle size. In our theory they would act in much the same way as surface asperities. The data shown for the sample marked 0-20 μ provide a good example of the effect of such fines. The average particle size for this sample is near 10 μ, but the effect of the large number (but small volume fraction 0.007) of particles less than 2.85 μ is such as to give a more pronounced feature in the 1100-1200 cm⁻¹ region than
Fig. 10. Comparison of theoretical and experimental reflectance of quartz powders.

Fig. 11. Scanning electron micrographs (×85) of 170-μ quartz particles.
is observed for the 4.5-μ sample. In fact, the latter sample was obtained only after a discrepancy was observed between the experimental particle size and that necessary to produce the feature, using the same value of \( b \), the scale factor for the 1/d edge effect as was used for corundum. That discrepancy led us to reexamine the particle distribution in the 0–20-μ sample and the wide distribution found suggested that a narrower size range for this important experiment was in order. The 4.5-μ sample was then obtained from Duke Standards of Palo Alto, California. They indicate a 1–4.5-μ range for the sample. Our particle counts give 4.6 μ for the volume-averaged size of this material, and it has an obviously narrower particle size distribution than the 0–20-μ sample. The 0–20-μ sample can be reasonably well fitted by the theory, if we use an asperity factor of \( NV = 1.5 \times 10^{-5} \) cm to represent the clinging fine particles. This fit tends to confirm our idea that a small volume of clinging fines represents the same kind of extra absorption as do surface asperities. This effect was first observed in some of our early work, when some large quartz particle samples were run as received and after a wet-sieving procedure was used to remove the small volume fraction, but large numbers of clinging fine particles. Figure 11 shows photomicrographs of the samples of quartz powders of large particle size (170 μ) as received and after removal of the fines. Figure 12 shows the resultant spectra. The very large effect shown in Fig. 12 was produced by a quite small volume fraction of the fines. As with the surface asperities, the effect appears most significant in regions of high absorption.

As with corundum we note a spurious theoretical feature (Fig. 10) slightly to the high frequency side of the principal reststrahlen band for samples of intermediate particle size (4.5 μ and 10 μ). This feature does not occur in the experimental data which as before is actually for a particle size distribution. We again note an apparent shift of the reststrahlen feature toward higher frequencies as the particle size is reduced and believe that the theoretical feature contributes to the shift. It is significant that the feature in question is also produced theoretically in Mie theory calculations for the intermediate particle sizes, but with smaller amplitude. Further study of this problem is in progress.

Figure 13 shows experimental and theoretical results for garnet powders obtained from Barton Mines of North Creek, New York. The particle sizes used to calculate the theoretical spectra for these samples were obtained by microscopic techniques. They are slightly larger than the analyses given by Barton Mines. No surface asperities were invoked in computing the theoretical spectra because microscopic examination showed no need for such a factor. The optical constants used as input parameters for the garnet data were obtained by fitting the spectrum of a large polished sample with a set of classical oscillator parameters, using the Lorentz line shape, by well-known techniques. The minor discrepancy observed near 500 cm\(^{-1}\) is thought to be caused by a slightly deficient set of dispersion parameters, since an insufficient number of points were taken in the spectrum of the single crystal to resolve the small feature by least-squares analysis.

The experimental and theoretical spectra of two mixtures of quartz and corundum powders are shown in Fig. 14. Each mixture actually represents a mixture of four components since quartz and corundum are both uniaxial crystals so that two sets of optical constants are required to represent each of them. In these cases the experimental data were processed using the measured sample temperatures instead of applying the usual Christiansen technique since this technique cannot be justified for the case of mixtures. It is clear from the theoretical results shown in this figure that there is no frequency where the reflectance is very close to zero such as would occur at the principal Christiansen frequency for a pure sample. The experimental results can be seen to confirm this theoretical conclusion. It is worth noting that the reflectance is close to zero for both
quartz and corundum individually even though they can be regarded as birefringent mixtures. The reason is that the optical constants for the ordinary and extraordinary rays differ very little. We observe that the departure from zero reflectance is substantially greater for the finer particles. Thus arbitrarily setting the lowest point in the spectrum of a mixture at zero reflectance or unit emittance would make a substantially greater error for the finer particle data than for the coarser particle data. It is also quite significant that for the finer particle sample the lowest point in the spectrum occurs near 1160 cm\(^{-1}\). This corresponds to the Christiansen frequency of neither component. Thus an identification technique based on the principal Christiansen frequency would fail for this mixture.

For both mixtures the shapes of the theoretical spectra quite adequately represent the experimental data. While the general level of the theoretical spectrum of the mixture of finer size powders is also in good agreement with the experimental spectrum, the same cannot be said for the spectrum of the mixture of coarse powders. Once again, we believe this discrepancy is due to our use of a continuum model rather than a discrete layer model.

It is worth noting, however, that for remote sensing applications where the problem is the inverse one of determining mineral compositions from spectral data, the general spectral level is much less important than the detailed structure of the spectral features.

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Fig. 14. Comparison of the theoretical and experimental reflectance of mixtures of quartz and corundum.

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