Infrared Optical Constants of Ammonium Sulfate, Sahara Dust, Volcanic Pumice, and Flyash

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Spectra of the real and imaginary parts of the refractive index \( m = n' - i n'' \) from 2.5 \( \mu \text{m} \) to 40 \( \mu \text{m} \) of ammonium sulfate, Sahara dust (as collected at Barbados), volcanic dust (pumice), and dust from a coal-fired power plant are presented. With a peak absorption index \( n'' = 1.0 \) at 10 \( \mu \text{m} \) Sahara dust turns out to be the strongest absorber in the atmospheric window. The dispersion of \( n' \) is also very pronounced near 9 \( \mu \text{m} \) and 20 \( \mu \text{m} \). Volcanic and coal-fire dust also absorb in the window region stronger than most of our earlier-investigated more normal aerosol fractions. The data for ammonium sulfate are compared with Remsberg's measurements on an aqueous solution.

Introduction

Recently, we presented measurements of the ir absorption index \( (n'') \) and refraction index \( (n') \) of some dry, natural aerosol substances from 2.5 \( \mu \text{m} \) to 40 \( \mu \text{m} \). These were primarily water-soluble residues of rain and snow water from arctic to tropical locations, but also soot and dust as recovered from the water, and sea salt. We now present the optical constants of ammonium sulfate, Sahara dust, volcanic dust, and dust of a coal-fired power plant.

\((\text{NH}_4)_2\text{SO}_4\)—or at least its ions—is known to be a main constituent of the water-soluble part of ground-level aerosol, impurities in precipitation, and stratospheric aerosol. It also is the principal inorganic species that showed up in our aerosol spectra, causing the strong absorption and the sharp dispersion of the refractive index near 9 \( \mu \text{m} \). Clearly, the optical constants of watery ammonium sulfate solutions as investigated by Remsberg are also important in high humidity aerosol conditions.

The Sahara dust samples are those collected close to the sea surface at Barbados. The meteorological conditions of this transport at a few kilometers’ altitude in African air masses across the Atlantic may well be related to the unique radiative properties of this dust, which turns out to be the best particulate absorber in the 10-\( \mu \text{m} \) atmospheric window, even compared to soot.

Knowledge of the ir optical constants of volcanic dust is important for assessing its radiative properties in the stratosphere, where its residence time is in the order of one year. It may thus, in periods of strong volcanic activity, be related to global variations of climate.

It will be interesting to compare optical properties of dust (flyash) from a coal-fired power plant with those reported earlier for dust recovered from precipitation samples.

In any atmospheric radiative balance considerations not only the ir aerosol properties, but also shortwave scattering and absorption, i.e., the effect on solar radiation, enter in. To this end we also measured by a simple method the absorption of our samples in the shortwave range.

Measurements and Results

As discussed previously, ir spectra of the mass absorption coefficient \( k \) or of the imaginary part of the refractive index, \( n'' = k\lambda/4\pi \), were obtained by recording transmittance by the KBr disk technique. The real part of the refractive index \( n' \) was calculated from the near-normal reflectance of disks of the pure aerosol substances, taking (mostly small) corrections by \( n'' \) into consideration. The methods are essentially those used by Czerny and Wilmot, replacing cleaved crystals by pellets for the absorption measurements. The density was calculated from weight and volume of disks of pure substances.

Ammonium Sulfate

The absorption index [Fig. 1(a)] shows sharp bands at 3.1 \( \mu \text{m} \), 7 \( \mu \text{m} \), 16 \( \mu \text{m} \), and especially 9 \( \mu \text{m} \), and the refraction index strong dispersion in the same \( \lambda \) regions. Pellets of proper concentration were used to derive band and background absorbance. Spectra of medium absorbance are qualitatively identical to mull spectra presented by Miller and Wilkins. As found earlier, the lower pellet concentrations gave higher absorbance. The uncertainties are about 30%. However, background absorbance
near 4 \mu m and 13 \mu m could still be too high due to scattering in the visually rather milky high concentration pellets. The \( n' \) values shown in Fig. 1(b) were derived from the reflectance of disks of pressed powder of ammonium sulfate (density measured 1.765 as compared with the literature value of 1.769), but reflectance of two faces of a crystal were identical apart from small differences where reflectance is very low. In these cases, \( n' \) is manually best deduced and checked for consistency by using the inversion of Fresnel’s equation,

\[
n' = \frac{(1 + R)/(1 - R)}{2R}, \quad n'' = \frac{(1 + R)/(1 - R)}{2},
\]

In Fig. 1(a) we included the data for water\(^8\) and Remsberg’s\(^8\) results for an aqueous solution of \((NH_4)_2SO_4\). Some disagreement exists in the exact position of the 7-\mu m and 9-\mu m absorption bands, which may be due primarily to the different matrices. The 9-\mu m absorption maximum in Miller and Wilkins’s\(^7\) mull spectrum of ammonium sulfate and that in Remsberg’s\(^5\) solution are slightly displaced against ours; at 7 \mu m, Remsberg’s maximum is displaced. Practically only the course of \( n' \) determines the high reflectance of pure ammonium sulfate. Although \( n' \) of the solution peaks at 9.5 \mu m, the high absorbance at the shortwave side shifts the peak of its reflectance also to 9 \mu m. From reflectance measurements at a concentrated solution we obtained for the 9-\mu m band nearly the same \( n' \) values as Remsberg.

We also measured transmittance of a relatively coarse powder of \((NH_4)_2SO_4\) (radius \( \approx 15 \mu m \)) that had been deposited on a polyethylene film. As shown in Fig. 2, transmittance was higher in \( \lambda \) regions where \( n' \) is low. This is in agreement with a simple model (Ref. 2, Fig. 4). However, conditions are different if particles are much smaller, i.e., when absorption becomes more important, as may be seen later in the case of the extinction of ammonium sulfate aerosol.

Fig. 1. Real (a) and imaginary (b) part of the refractive index of solid ammonium sulfate (--), 35% aqueous solution (---, Ref. 3), and water (---). Dashes indicate the absorption index obtained for different pellet concentrations (a, 0.05 mg cm\(^{-2}\); b, 0.50 mg cm\(^{-2}\); c, 5.0 mg cm\(^{-2}\)). Arrows indicate the band positions according to Miller and Wilkins.\(^7\) The dashed branches in (b) refer to observed reflectance (right-hand ordinate) before correction for \( n'' \).

Fig. 2. Transmittance of a coarse powder of ammonium sulfate. Interference pattern and the few absorption bands of the supporting polyethylene film were omitted. The cause of the 3.4-\mu m absorption is not clear.
Sahara Dust

The samples had been collected on nylon mesh at Barbados. Mineralogical analyses of similar samples indicates mainly clay, illite, and kaolinite along with traces of quartz. Whether reddish (from admixture of iron oxide) or gray, our samples exhibited very similar infrared absorption and reflectance spectra. The absorption index (Fig. 3, top) calculated with a measured bulk density of $\rho = 2.50$ g cm$^{-3}$ rises, after a weak maximum at 2.9 $\mu$m, to $n'' = 1.0$ at 10 $\mu$m and assumes this value again at 20 $\mu$m. Pellets containing 0.7 mg cm$^{-2}$ and 2.3 mg cm$^{-2}$ dust gave within 20% the same absorption values. The course of the refraction index $n'$ with wavelength is very similar to that of our aerosol water-solubles, just that the position of the strong dispersion near 9 $\mu$m is shifted to about 9.7 $\mu$m. At 0.5 $\mu$m, we measured with an Abbé refractometer $n' = 1.50$. The absorption index is 0.0045 at 0.5 $\mu$m and 0.009 at 0.7 $\mu$m according to transmittance measurements of KBr pellets with a wide-angle detector.

Fig. 3. Optical constants $n'$ and $n''$ of Sahara dust as compared with those of aerosol water-solubles, and $n''$ of volcanic dust and flyash. The dotted part of the $n'$ curve of Sahara dust refers to observed reflectance $[n' = (1 + R)/(1 - R)]$ before correction for $n''$. 

Fig. 4. Wavelength dependence of extinction and scattering coefficients for Sahara dust and dust from precipitation. At 9 $\mu$m, the effect of different values of $n''$ is shown for dust from rainwater. Values of 0.45 $\mu$m for $n' = 1.50, n'' = 0.01$ are $\sigma_E = 9.44 \times 10^{-8}$ m$^{-1}, \sigma_SC = 8.74 \times 10^{-8}$ m$^{-1}$. 

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Volcanic and Coal-Fire Dust

The two investigated volcanic samples were from an earlier-described collection. The Izu-2 dust (0.05-mm to 0.5-mm shards) was sampled during ashfall and is dark gray ash with feldspar. The Hawaii sample (Kilauea Iki) was slightly weathered vesicular glass similar to perlite. The flyash of ocre color was from the last electrostatic cleaning chamber of a power plant fired with powdered coal. Under the electron microscope, the particles are spheres with a most frequent radius of 0.3 μm. Water added to the powder assumed a pH of 8, and evaporation left a white residue (gypsum?) of 8% of the original mass.

The KBr transmission spectra of all these samples were very similar and hardly different from those of greenish lightweight pumice (Utah 50.1) investigated by the Spectroscopic Studies Branch, Terrestrial Science Laboratory of AFCRL. The course of n" (Fig. 3) resembles that of rainwater dust (Fig. 1, Ref. 2) and Sahara dust with an intermedian peak value of the absorption index near 10 μm. In the visual range (0.5 μm), we obtained n" = 0.007 for the two volcanic samples. Pellets of the pure, finely ground substance showed, contrary to previously investigated dust samples (including Sahara dust) visually no trace of gloss, and reflectance was also insufficient in the ir. Below 8 μm, it was only 0.5%. The peak reflectance values for volcanic dust were 8% at 11 μm and 14% at 40 μm. Thus, n' could not be determined but is certainly similar to that of other dust samples. This lack of reflection may be related to the hardness of the grains causing voids in the pellets. The water uptake was 7-10%. The density of the pressed pellets of volcanic dust was found to be 0.6 mg cm⁻³ (Utah 50.1) and 1.92 g cm⁻³ (pumice), and of the coal dust 2.45 g cm⁻³, corrected for the voids. Absorption indices of the flyash in the shortwave range were n" = 0.0048 at 0.5 μm and 0.010 at 0.9 μm as determined with KBr pellets containing 0.6 mg cm⁻² and 2.5 mg cm⁻² flyash; they are therefore very close to those of Sahara dust.

Extinction and Scattering of Dust Aerosols

In Fig. 4 we present the extinction and scattering coefficients for an aerosol of Sahara dust and dust from rain water samples (optical constants of sample γ") in Fig. 1, Ref. 2. The size distributions were dN(r) = 5.71 × 10⁻⁴ r⁻⁴.⁵ dr[cm⁻³ μm⁻¹] with the limiting radii r = 0.06 μm and 10 μm and a total particle number of 3.09 cm⁻³. Scattering of Sahara dust falls generally off with λ⁻¹.⁵, as would be expected for nonabsorbing aerosol of such size distribution, but rain dust scattering is much lower from 2.5 μm to 5 μm due to the lower n' values. It is also the strong influence of n' that causes the extrema of scattering in the 9-μm region.

The extinction coefficient (scattering and absorption), governed by the absorption index, is generally much more λ-independent. However, the extinction near 10 μm is above the main level by a factor of 2 in the case of rain dust and by a factor of 3 for Sahara dust. The single scattering albedo, i.e., the ratio αₛₑ/αₛₑ, is relatively high up to 5 μm, but in the order of 0.1 at larger wavelengths.

Extinction and scattering has also been computed for dry water-soluble aerosol substance and sea salt. It is noteworthy that the 8-μm minimum also shows up in these data (though very weak only in sea-salt aerosol and not at all in water aerosol). However, peak extinction and scattering are located at 9 μm. Thus, measurements in the water vapor window of the ratio of extinction at 9 μm and 10.6 μm (or of the scattering coefficient at 9 μm and 9.6 μm) should give a sensitive discrimination regarding the aerosol composition, i.e., between water solubles and dust.

Conclusions

The study shows that less common atmospheric aerosol substances generally have optical constants in the 10-μm window similar to those of continental anthropogeneous aerosols. The cause of the relatively strong dependence of n" on pellet concentration found for ammonium sulfate needs further study, as well as the discrepancies in band position. However, presentation of the data of this salt is not meant to be applicable to tropospheric aerosol, and it is still questionable whether the data could be used for optically modeling stratospheric aerosol. In that case, the temperature dependence of the dispersion would have to be investigated, too. Of the other samples, Sahara dust exhibits the strongest 9-μm absorption, and the absorption spectrum is more distinguished than that of volcanic dust and flyash, which both are glassy melts, probably without crystalline structure. Dust from rainwater has generally the same absorption spectrum as volcanic dust and flyash, though absorption is lower but more sharply peaked near 10 μm. In the visual range, the absorption index of Sahara dust, volcanic dust, and flyash is quite low, while that of rainwater dust was found to be two to three times higher. Reflection and refractive index of volcanic dust and flyash could probably be obtained from pieces of molten and polished dust. The strong 10-μm extinction peak by a Sahara-dust aerosol, which, however, is still only one-tenth of the extinction at 0.45 μm for the size distribution considered, is much better centered at the atmospheric water vapor window than that of the less strongly absorbing rainwater dust and aerosol water solubles, thus its effect on window transmission and on total long wave radiation should be most easily observable.

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References

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