Radiation Absorption by Droplets of Sulfuric Acid Water Solutions and by Ammonium Sulfate Particles

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ABSTRACT

The absorption spectra of 49%, 73% and 98% sulfuric acid water solutions for wavelengths of 0.3–6.5 μ and those of ammonium sulfate for 0.3–25 μ are either measured for the purposes of this study or quoted from the literature. Sulfuric acid water solutions have an absorption in the range 1.6–6.5 μ. Absorption by 49% and 73% solutions is particularly strong. It is much stronger than absorption by liquid water over most of the range. Ammonium sulfate has no absorption of any significance from 0.3 to 2.85 μ but has four absorption bands in the range 2.85–25 μ, the largest absorption occurring at about 9.25 μ in the terrestrial radiation "window."

The conclusions are as follows: 1) sulfuric acid water solution droplets will absorb solar radiation in the near IR, about 2 μ; 2) ammonium sulfate particles will not absorb solar radiation; and 3) both will, of course, scatter solar radiation.

The above results are relevant to the absorption of solar radiation by droplets or by solid particles in the lower stratosphere as well as to a similar absorption in the lower atmosphere of industrially polluted areas.

1. Introduction

It appears that Waldram (1945) was the first to conclude that aerosols found in the lower atmosphere of areas affected by industrial and urban pollution are responsible for a comparatively substantial absorption, as distinct from scattering, of light. Somewhat similar inferences were drawn subsequently by Roach (1961) and by Robinson (1962, 1966).

Absorption by "volcanic particles" was suggested by Newell (1970, 1971) to have produced the major temperature rise observed in the lower tropical stratosphere over wide areas following the violent eruption of Mt. Agung, Bali, in March 1963. Some scientists proposed (SMIC, 1971, p. 282; Sparrow, 1965, 1971) that the above warming may have had purely dynamical reasons. A more recent study by McInturf et al. (1971) concludes, tentatively, that of the 5°C or so temperature rise reported by Newell, something like 2°C may be a consequence of the eruption, except over Australia where the rise appears to have been greater. Further, while solar radiation data presented for the South Pole by Viebrock and Flowers (1968, Table 4) show a striking increase in the diffuse component (even many months after March 1963), the same data also leave room for the interpretation that, compared with the past, there was some extra absorption.

The controversy regarding the causes of the aforementioned stratospheric temperature rise is not yet resolved. Nevertheless, the absorption spectra presented below for substances which were found to have constituted the Agung particles make it plausible that there was some absorption by the stratospheric particles and that, therefore, the observed stratospheric warming following the Agung event was, at least in part, due to absorption of solar radiation by the particles. Since particles of a similar chemical nature are also found in the lower atmosphere of industrially polluted areas, the absorption spectra presented below are of some relevance to the latter regions as well.

2. The chemical nature of the particles

It seems that in the group of man-made particles, solid or liquid, sulfates occupy a prominent position (SMIC, 1971, p. 189). These sulfate particles are thought to form from gaseous SO₂. As SO₂ is globally distributed (SMIC, 1971, p. 192), it is reasonable to assume that some of this gas enters the stratosphere and takes part in reactions which turn it into sulfates. Moreover, it is almost certain that major volcanic outbreaks inject large amounts of sulfur-containing substances into the stratosphere. As far as surface observations go, eyewitness reports (Booth et al., 1963, pp. 444, 448) of the Mt. Agung eruption state that sulfurous fumes were present at Bali, and Mossop (1964, p. 827) quotes a private communication confirming the high sulfur content of solid products ejected by the volcano.

As to the more precise nature of the stratospheric particles, until about 1966 the prevalent view was that
the sulfates in question were primarily ammonium sulfate \((\text{NH}_4)_2\text{SO}_4\), see, e.g., Junge and Manson (1961), Mossop (1963, 1964, 1965), and Friend (1966). Some of these authors find ammonium persulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) as a minor constituent. However, more recent investigations by Rosen (1971), and to some extent those of Bigg et al. (1970) as well as those of Cadle et al. (1970), indicate that the particles are, principally, droplets of concentrated water solutions of sulfuric acid. Actually, already in 1961, Junge and Manson state that the stratospheric aerosol layer is primarily ammonium sulfate or sulfuric acid.

Turning now to the air layer near the earth surface, it appears (Junge, 1963, Section 2.3) that in industrial area sulfates, again, are of some importance. Ammonium sulfates make up many of the sulfate particles, but concentrated sulfuric acid droplets have also been reported (Corn, 1968, pp. 76–77) to be of appreciable incidence.

3. Spectral distribution of absorption

Information on this point appears to be extremely scanty. In Roach’s paper (1961, p. 363) cited earlier the author states that the absorption attributed to aerosols does not, in general, depart greatly from greenness except in a few cases of large absorption in the lower layers when it seems to be concentrated in the near IR. An essentially similar statement is made by Robinson (1966, p. 268). Roach finds that, on occasions, the absorption of concern is capable of producing instantaneous heating rates of 5C day\(^{-1}\) and rates in excess of 10C day\(^{-1}\) can occur in heavily polluted areas.

4. Absorption spectra

Since concentrated sulfuric acid or/ammonium sulfate seem to constitute an important part of the mass of particles in the lower stratosphere, in general, and even in the lower atmosphere of polluted areas, it is natural that one should give priority to an examination of the absorption characteristics of these substances with regard to electromagnetic radiation. Despite the fact that in this study our chief interest centers on the absorption of solar shortwave radiation \((0.3 \mu \leq \lambda \leq 2\) or \(3 \mu\), say), we will consider the wavelength range 2 or \(3 \mu \leq \lambda \leq 25 \mu\) as well because of its significance in terrestrial radiation.

Some of the required absorption spectra are published in the literature. A few of these investigations, especially those relating to water solutions of sulfuric acid, were made in the 1930’s. The published data do not cover the whole wavelength range of interest in meteorology. Moreover, we have felt that a re-examination of some of the published spectra would be desirable using more modern measuring techniques than were available then.

All the measurements carried out for us by colleagues (see Acknowledgments) and summarized below were taken at a temperature of 298K. This applies also, at least approximately, to results quoted from the literature, though one set of data (by Schutte and Heyns 1970) was obtained at a low temperature. Because the latter set is of some relevance to stratospheric conditions, it will be referred to again in Section 5.

The following instrumentation was used in the data measured for us:

- \(0.3 \mu \leq \lambda \leq 0.7 \mu\): UNICAM SP.800 Ultraviolet Spectrophotometer
- \(0.7 \mu \leq \lambda \leq 2.6 \mu\): Cary 14 Recording Spectrophotometer
- \(2.5 \mu \leq \lambda \leq 25 \mu\): Perkin-Elmer 337 Grating Infrared Spectrophotometer

a. Sulfuric acid water solutions

The solutions examined were either 48%, 72% and 96% or 49%, 73% and 98% \(\text{H}_2\text{SO}_4\).

1) \(0.3 \mu \leq \lambda \leq 0.7 \mu\)

Cells, fused silica; light source, deuterium lamp in the UV and tungsten lamp in the visible; light-path length, 1 cm.

No absorption of any importance was observed although the path length was made as long as 1 cm. An earlier study by Wagger and Chambers (1960) on 48% and 96% \(\text{H}_2\text{SO}_4\) water solutions, which covers the wavelength interval 0.225 to 0.4 \(\mu\), confirms the very weak absorption between 0.3 and 0.4 \(\mu\), in approximate agreement with our results.

2) \(0.7 \mu \leq \lambda \leq 2.6 \mu\)

The only investigations listed in some of the reference books, e.g. Gmelins Handbuch\(^2\) (1960, p. 643) and in an index published by the British Ministry of Aviation (1960), relate to work made in the 1930’s. These studies (van Arkel and Fritzius, 1931; Plyler and Barr, 1934) show a comparatively strong absorption from about 1.5 \(\mu\) toward the longer wavelengths. In view of the potential importance of such an absorption in a wavelength range where there still is about 10% of the energy in solar radiation (see Section 5), we have requested a re-examination of the absorption spectra by up-to-date instrumentation. This was done with a Cary 14 Spectrophotometer equipped with quartz cells, the light source being a tungsten lamp. The light path length was made small, viz. 0.1 mm, on account of the strong absorption. For comparison, the absorption spectrum of liquid water was taken by the same instrument.

Fig. 1 shows the results for \(1.5 \mu \leq \lambda \leq 2.6 \mu\) in terms of absorbance and transmittance. As usual, absorbance is defined as \(\log_{10}(I_0/I)\), where \(I_0 = I_0(\lambda)\) is the intensity of radiation of wavelength \(\lambda\) impinging on the cell and
$I = I(\lambda)$ is the intensity emerging from it. The transmittance is expressed as a percentage. The data are presented beginning with $\lambda = 1.5 \mu$ in view of the fact that below $1.5 \mu$ the absorption is very small. It is seen that beyond $1.6 \mu$ absorption by the sulfuric acid water solutions tends to increase with wavelength. However, our least concentrated solution has a peak near the peak of the major absorption band of liquid water at about $1.93 \mu$. As one might expect, the effect of the solvent is less pronounced in the case of the 73% $\text{H}_2\text{SO}_4$ solution and still less in the case of the 98% $\text{H}_2\text{SO}_4$ solution. Further, it is noted that (i) the 73% solution absorbs about as strongly as the 49% solution; and (ii) all the three solutions absorb more powerfully than liquid water excepting the region $1.88-1.95 \mu$ and excepting the 98% solution close to 2.5 $\mu$. The absorption by the two more dilute solutions is particularly strong in comparison with that of liquid water over most of our subrange.

The absorption presented in Fig. 1 is weaker than the absorption reported by Pyler and Barr (1934) although the feature of a more or less monotonic increase of absorption with wavelength is shared both by our data and those of Pyler and Barr. On the other hand, there is no indication at all of an absorption between 0.7 and 0.9 $\mu$ reported by Ganz (1936).

3) $2.5 \mu \leq \lambda \leq 25 \mu$

We were not able to measure beyond 2.6 $\mu$. However, Pyler and Barr, using a fluorite prism, measured as far as 6.5 $\mu$ and report a strong absorption between 5.2 and 6.5 $\mu$ for a 96% solution (see their Fig. 5 which presents data only for the 96% solution).

b. Ammonium sulfate

In the range of 0.3 to 0.7 $\mu$, the ammonium sulfate was actually a water solution (0.2 gm ml$^{-1}$). For $\lambda \geq 0.7 \mu$, it was a humid sample of ammonium sulfate in a KBr pellet.

1) $0.3 \mu \leq \lambda \leq 0.7 \mu$

Cell, quartz; light source, deuterium lamp in the UV, tungsten lamp in the visible; light path length, 1 cm.

*Gemlins Handbuch* (1955, p. 265) only mentions for solid ammonium sulfate absorption for IR$>3 \mu$ which presumably means that there is no absorption of importance below 3 $\mu$. The water solution examined for us indicates, indeed, no absorption in the present subrange.

2) $0.7 \mu \leq \lambda \leq 2.6 \mu$

Cell, KBr pellet; light source, tungsten lamp; light path length, ~1 mm. No absorption of any significance is indicated. Miller and Wilkins (1952, spectrum No. 85) publish absorption data for $2 \mu \leq \lambda \leq 18 \mu$, the short-wavelength end of their range coinciding with the long-wavelength end of ours. Their data too indicate very little absorption up to about 2.85 $\mu$.

3) $2.5 \mu \leq \lambda \leq 25 \mu$

Schutte and Heyns (1970, Fig. 2) have published absorption spectra for (dry) ammonium sulfate at 298K (and 17K) for the range 2.85 to 20 $\mu$. The data show four major peaks. The greatest absorption occurs at about 9.2 $\mu$ in the terrestrial window and is due to the $\text{SO}_4^{2-}$ ion. The band is comparatively wide. The other absorption peaks occur between 3 and 4 $\mu$, at about 7, and at about 16 $\mu$. The first is in a wavelength region where the atmosphere is semi-transparent, but there is little energy in the terrestrial radiation and still less in the solar radiation. The remaining two bands are situated at wavelengths where the gaseous atmosphere is opaque or nearly so.

Mossop (1964) reports that the sulfate particles [ammonium sulfate and persulfate, according to Junge and Manson (1961) and quoted by Mossop] are not completely dry when collected in the stratosphere. Since ammonium sulfate is a highly hygroscopic substance, ammonium sulfate particles found in the lower atmosphere are also likely to be humid. For these reasons, it is of interest to refer here to a spectrum of humid ammonium sulfate measured for us. The "cell"
was a KBr pellet, ~0.5 mm thick, of humid ammonium sulfate. The spectrophotometer used was a Perkin-Elmer 337 Grating IR Spectrophotometer, the light source being an incandescent ceramic tubing.

A comparison between Fig. 2 of the paper by Schutte and Heyns and the spectrum of humid ammonium sulfate reveals the following features: (i) the location of the peaks of the maxima of the four bands is unchanged; (ii) absorption at about 8 μ for λ > 18 μ is somewhat greater in the case of the humid sample; and (iii) the band at about 9.2 μ of the humid sample is wider toward the longer wavelengths: it covers a good part of the atmospheric window.

5. Discussion

It is clear from Section 4 that ammonium sulfate has practically no absorption in the wavelength range of solar radiation reaching the lower stratosphere and below. On the other hand, Schutte and Heyns’s measurements on dry ammonium sulfate and our parallel data for humid ammonium sulfate show that this substance has important IR absorption bands of significance in terrestrial radiation. Relatively strong and wide is the band about 9.2 μ in the atmospheric window and the problem arises if this absorption by ammonium sulfate is of importance to longwave radiation processes in the atmosphere. The problem of the role of ammonium sulfate particles in longwave radiation processes will be mentioned below, together with the role played by sulfurous acid droplets after a discussion of the absorption of solar radiation by these droplets.

The point of importance emerging from Section 4 is the absorption of solar radiation between about 1.6 and 2.6 μ by droplets of water solutions of sulfurous acid. The significance of that capability is emphasized by the results of Rosen (1971), and, to some extent, by those of Bigg et al. (1970) and Cadle et al. (1970), quoted in Section 2, indicating that the stratospheric particles are droplets of concentrated water solutions of sulfurous acid. Earlier, Mossop (1964, pp. 826-827) made the very interesting observation that the “dust” particles in the stratosphere gradually become coated with soluble material. According to him, “... after the incursion of dust from Mt. Agung, the quantity of coating material seems to have increased.” He expresses the conjecture that the most likely composition of that material is sulfurous acid.

If Mossop’s conjecture is correct, then two other conjectures arise:

1) The gradual rise of temperature in the lower stratosphere following the Mt. Agung eruption could be due, at least in part, to the gradual process of coating of the particles by sulfurous acid.

2) The greater temperature rise observed over Australia could be due to the greater transport of SO₃ and H₂S from the Australian continent to the stratosphere as compared with the transport from oceanic areas, thus making more sulfur-containing gases available for the formation of sulfurous acid.

Turning to the evidence concerning the spectral distribution of absorption of solar radiation by the particles, the observations quoted in Section 3 of Roach (1961, p. 363) and Robinson (1966, p. 268) to the effect that the inferred absorption by the particles is concentrated in the near IR, would be consistent with the assumption that the absorbing particles are sulfurous acid droplets. However, other aerosol particles may have a strong absorption. This matter requires, therefore, further consideration. The latter is all the more desirable as the really strong absorption by, say, the 73% H₂SO₄ water solution, occurs (see Fig. 1) at λ ≈ 2 μ where the available solar energy is but a few percent.

Assuming reasonable values of water vapor, ozone and dust content (prior to 1940!) and optical air masses from 1 to 5, Moon (1940) finds that nearly 10% of the solar radiation reaching the ground resides beyond 1.5 μ. More recent figures due to Elder and Strong and to Gebbie, quoted by Brooks (1955, p. 21), give nearly the same percentage. Thus, even after allowance is made for IR absorption by atmospheric gases, a not inconsiderable fraction of solar radiation remains available for absorption by particles whose effect is not included in the measurements or calculations mentioned above.

Since according to Fig. 1 for 1.6 μ ≲ λ ≲ 2.6 μ the absorption by water solutions of sulfurous acid increases nearly monotonically, and since in the same wavelength range the intensity of solar radiation decreases monotonically with wavelength, we may expect the maximum absorption to occur somewhere about the middle of the range. That is, we expect the maximum of absorption to occur about 2 μ.

Many of the absorption features change, sometimes becoming more pronounced, with a decrease in temperature [see, for example, the transmission measurements by Schutte and Heyns (1970) on solid ammonium sulfate at temperatures of 298K and 17K]. It is likely that absorption of solar IR by sulfurous acid droplets at the comparatively low stratospheric temperatures is somewhat different from that operating at the temperatures of the lower atmosphere.

6. Some outstanding problems

The fact that ammonium sulfate possesses absorption bands in the terrestrial IR has led us earlier to raise the problem of the role of ammonium sulfate particles in longwave radiation processes. This matter brings forth the parallel problem for sulfurous acid droplets.

In order to be able to apply the Mie theory for absorption and scattering by (spherical) particles in the IR, we have to know, among other things, the complex refractive index m for the particles, as a func-
tion of wavelength. Let us write that index in the form \( m = n - ik \), where \( n \) is known for both sulfuric acid and ammonium sulfate in the visible. However, no published values appear to be available for terrestrial IR wavelengths. The index \( n \) will vary with wavelength in a range where the absorption varies and thus we can expect, either on the basis of the absorption spectrum for dry ammonium sulfate by Schute and Heyns (1970) or on the basis of the measurements conducted for us on humid ammonium sulfate that the pertinent \( n \) will not be a constant in the IR. It is very likely that sulfuric acid also has ionic bands of absorption in the wavelength range of concern to us and if so \( n \) will vary with wavelength.

A computation of the Mie absorption efficiency factor for \( n = 1.43 \), for a set of values of \( k \) and for a series of Mie size parameter values, has just been completed (Neumann and Graber, to be published soon). This should facilitate the examination of the role of sulfuric acid droplets in longwave radiation processes once the appropriate values of \( k \) become available. The calculation can easily be extended to other \( n \) values pertinent to sulfuric acid solutions in the IR.

Another problem is the manner of dissipation of the energy of solar radiation absorbed by sulfuric acid droplets. That energy can be dissipated by (longwave) radiation and by the transfer of sensible (and latent?) heat to the air. Any radiative losses from the droplets at wavelengths of about 10 \( \mu \) cannot heat the air since the atmosphere is transparent (except for the absorption band of \( O_3 \) at 9.6 \( \mu \)) at about 10 \( \mu \). In order that the ambient air be heated by the solar energy absorbed by the droplets, it is necessary that the energy in question, or, at least for a not too small fraction of it, be transferred to the air as sensible heat.

7. Conclusions

1) Ammonium sulfate particles absorb practically no solar radiation.

2) Concentrated water solutions of sulfuric acid have an absorption in the solar IR from 1.6 \( \mu \) on toward longer wavelengths. 73% and 49% \( H_2SO_4 \) water solutions absorb much stronger than a 98% solution, though the difference between the 73% and 49% solutions is small. These solutions absorb much more strongly than liquid water over most of the range \( \lambda > 1.6 \mu \). An exception is a narrow range about 1.93 \( \mu \) where liquid water absorbs stronger. It is expected that absorption at the low temperatures of the stratosphere is somewhat different from that in the lower atmosphere, and that the absorption maximum should occur at about 2 \( \mu \).

3) Although sulfates make an important contribution by mass to the aerosol in the lower atmosphere of industrial areas and, more generally, in the lower stratosphere, absorption measurements should be made for other atmospheric contaminants even though their mass contribution is small.

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Note added in proof. At the time when the present paper was in the proof stage, Dr. Glenn B. Hoidale, Atmospheric Sciences Laboratory, U.S. Army Electronics Command, White Sands Missile Range, drew the author's attention to an unpublished Ph.D. thesis by Eugene E. A. Chernack "The Optical Constants \((n, k)\) of Ammonium Sulfate in the Infrared." That thesis work was done at the Department of Meteorology and Oceanography, New York University; the dissertation paper bears the date November 1969. In the thesis Chernack measures the optical constants of ammonium sulfate in the spectral intervals of 1.20 to 2.70 \( \mu \) and 3.48 to 10.77 \( \mu \).

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