NOTES AND CORRESPONDENCE

Dependence of Light Scattering Coefficients of Aerosols on the Relative Humidity: Its Relation to the Water-soluble and Insoluble Compositions

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Optical properties of aerosols change with the relative humidity, which affects on visibility, transfer of solar and terrestrial radiation through the atmosphere. It is difficult to take account of this humidity effect properly, since the way in which optical properties change with the relative humidity varies considerably reflecting the difference in chemical compositions and/or size distributions of natural aerosols. Hänel (1976) proposed several models to describe the humidity dependence of the optical properties, and Nilsson (1979) proposed more complicated models based on the data on chemical compositions and size distributions of atmospheric aerosols. These works aim at simulating the humidity dependence of the optical properties of atmospheric aerosols as closely as possible, but the relations between the humidity dependence and the aerosol chemical compositions are not clearly shown.

The way in which optical properties of aerosols change with the relative humidity depends on the content of water-soluble materials present in the aerosol, and perhaps also on the mixing conditions of soluble materials with insoluble ones. In this paper, the humidity dependences of light scattering coefficients in the visible region are calculated for aerosols having different content of water-soluble materials, based on different kinds of aerosol

models in which soluble and insoluble materials are mixed internally or externally with each other. A comparison is made between our calculations and nephelometer measurements for natural aerosols reported by other authors.

2. Aerosol models

There are many kinds of water-soluble materials contained in atmospheric aerosols; they can be classified into two groups according to their hygroscopic natures. One is liquid at any humidity and by absorbing water vapor it grows smoothly with increasing ambient humidity. The other is solid when the relative humidity is low. As the humidity reaches a certain value, the solid particle suddenly becomes a solution droplet by taking up water and above this humidity it grows smoothly. In the present study, we deal with sulfuric acid and ammonium sulfate as representative of the former and the latter groups, respectively. These materials are regarded as the main components of the tropospheric background aerosol (Junge, 1963; Charlson *et al.*, 1974). The complex refractive indices of sulfuric acid and ammonium sulfate in the dry state are $m=1.43-0.0i$ and $m=1.52-0.0i$, respectively, and the refractive index values of their aqueous solutions (which approach the value of water as the concentration decreases) are used.

Atmospheric aerosols also contain many kinds of water-insoluble materials. However, the hygroscopicity does not depend on these

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materials and in the present study we treat the insoluble component as having the complex refractive index $m=1.55-0.05i$. It should be noted that the humidity dependence of light scattering coefficients of highly absorbing particles (*e.g.* soot) may be different from that of weak- or non-absorbing particles. In atmospheric aerosols, however, the percentage of such highly absorbing particles will be not large, and we expect that the optical properties of atmospheric aerosols can be treated with the average refractive index value chosen here.

The following three kinds are considered for the aerosol models:

Internal: Aerosol particles are so-called mixed particles in which insoluble core is surrounded by water-soluble material. The ratio of the volume of soluble material to that of insoluble material is set constant over the range of particle sizes.

External I: Soluble and insoluble materials are suspended as different particles. The size distribution of insoluble particles is the same as that of the insoluble cores in the above Internal model. The size distribution of soluble ones is that of particles made by separating the soluble coating of each mixed particle in the Internal model.

External II: Soluble and insoluble materials are suspended as different particles. The size distributions of these two components are the same except for their number concentrations, and the size distribution of total particles—*i.e.*, the sum of the two component distributions—is exactly the same as that of the Internal model.

Particles are assumed to be spherical with the size distribution having the following power law form:

$$\frac{dN}{d \log r} = \begin{cases} C_1 & , \quad r_1 \leq r \leq r_2 \\ C_2 r^{-\nu^*} & , \quad r_2 \leq r \leq r_3 \\ 0 & , \quad \text{otherwise} \end{cases} \quad (1)$$

where N is the cumulative number of particles per unit volume of air, r is the radius of the particles (μm), C_1 and C_2 ($C_1=r_2^{-\nu^*} \times C_2$) are constants dependent on the number con-

centration of aerosol particles and are chosen to yield a total particle volume of $30 \mu\text{m}^3/\text{cm}^3$. The exponent ν^* is varied from 2.5 to 3.5. The distribution function (1) is applied at 0% relative humidity. In the case of the Internal model, the distribution function (1) refers to the outer radius of coated particles with the limiting radii chosen as $r_1=0.01$, $r_2=0.08$, and $r_3=7.0 \mu\text{m}$. These values of the limiting radii are also used for homogeneous particles in the External II model. In the case of the External I model, on the other hand, r_1 , r_2 , and r_3 take values smaller than 0.01, 0.08, and 7.0, respectively, depending on the ratio of the content of water-soluble to insoluble materials.

Next, we introduce a parameter to denote the content of water-soluble materials in the aerosol. The parameter ϵ is defined by

$$\epsilon = \frac{\text{volume occupied by soluble material in a particle}}{\text{total volume of a mixed particle}} \quad (2a)$$

for the Internal model, and by

$$\epsilon = \frac{\text{sum of the volumes of soluble particles}}{\text{sum of the volumes of soluble and insoluble particles}} \quad (2b)$$

for the External models. The above definitions (2a) and (2b) hold for 0% relative humidity.

Particle size distributions at different humidities were calculated on the assumption that particles grow in equilibrium with increasing ambient humidity. The ordinary Mie theory was applied to the calculation of the optical properties for the External models; for the Internal model the calculations were made using the theory of light scattering from a coated sphere (Mita, 1982).

3. Results

Light scattering calculations were performed mainly for a wavelength of $0.55 \mu\text{m}$, and partly for other wavelengths of 0.45 and $0.70 \mu\text{m}$. While absolute values of the extinction or scattering coefficients depend strongly on the wavelength, their relative change with humidity has little wavelength dependence. In the following only the results for $0.55 \mu\text{m}$ are presented.

3.1 Difference between the Internal and External models

Table 1 gives values of the scattering coefficient at some selected humidities for three kinds of aerosol models each containing 60% soluble material (H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$). It is seen that differences between the three models are small, indicating that the humidity dependence of the scattering coefficients is not much affected by the mixing conditions of soluble materials with insoluble ones. The values in this table are for a size distribution with $\nu^*=3.0$; however, similar tendency would be stated also in the case of other size distributions with $\nu^*=2.5$ and $\nu^*=3.5$.

3.2 Dependence on the size distribution

Fig. 1 shows scattering coefficients (relative to the value at 30% relative humidity) as a function of the relative humidity for aerosols having different exponents of the power law size distribution. It is seen that the steeper size distribution exhibits the larger increase with relative humidity. However, the differences between the three curves are not large.

3.3 Comparison with nephelometer measurements for atmospheric aerosols

Fig. 2 shows scattering coefficients (relative to the value at 30% relative humidity) as a function of the relative humidity for aerosols

Table 1 Light scattering coefficients at 30% relative humidity (β_{30}) and the ratio of the light scattering coefficients at other humidities (β_{RH}) to β_{30} for different kinds of aerosol models each containing 60% water-soluble material (H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$). Values are for the wavelength of $0.55\ \mu\text{m}$. Aerosol size distribution is the power law with $\nu^*=3.0$.

Aerosol model	H_2SO_4 , $\varepsilon=0.6$			$(\text{NH}_4)_2\text{SO}_4$, $\varepsilon=0.6$		
	$\beta_{30}\ (\text{km}^{-1})$	β_{70}/β_{30}	β_{90}/β_{30}	$\beta_{30}\ (\text{km}^{-1})$	β_{85}/β_{30}	β_{95}/β_{30}
Internal	0.141	1.56	2.77	0.086	2.35	3.66
External I	0.148	1.55	2.72	0.092	2.30	3.56
External II	0.146	1.54	2.68	0.091	2.28	3.51

Fig. 1 Light scattering coefficient (relative to the value at 30% relative humidity) at the wavelength of $0.55\ \mu\text{m}$ vs. relative humidity for aerosols with different size distributions each containing 60% H_2SO_4 (a) and $(\text{NH}_4)_2\text{SO}_4$ (b) as water-soluble material, based on the Internal model.

Fig. 2 Light scattering coefficient (relative to the value at 30% relative humidity) at the wavelength of $0.55\ \mu\text{m}$ vs. relative humidity for aerosols containing different amount of H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ as water-soluble material, based on the Internal model with the size distribution $\nu^*=3.0$. The parameter ϵ denotes the volume fraction of the soluble material in aerosols. Two examples of the nephelometer measurements for atmospheric aerosols reported by Charlson *et al.* (1974, Fig. 3 (A), (C)) are shown by (+) and (O).

containing different amount of soluble materials. As seen above, the differences between the Internal and External models or differences between the size distributions are small; therefore only the results for the Internal model with $\nu^*=3.0$ are presented.

Direct measurements of the scattering coefficients as a function of the relative humidity have scarcely been reported for atmospheric aerosols. In Fig. 2 two examples of such data from Charlson *et al.* (1974) obtained with integrating nephelometer are shown. It is seen that these two cases show the behavior between $\epsilon=0.3$ and $\epsilon=0.6$. Of course it is difficult to conclude immediately from this that the soluble content of these two cases of aerosols is 30 to 60%, since soluble materials other than those treated in this study may exist in atmospheric aerosols and since their size distributions may differ greatly from the power law. Nevertheless, the result here implies the possibility of measuring the soluble

content of atmospheric aerosols by these optical methods.

4. Summary

Based on aerosol models in which water-soluble and insoluble materials are internally or externally mixed with each other, the change of aerosol scattering coefficients in the visible region with the relative humidity was investigated using the theory of light scattering. Consequently it was found that the humidity dependence of aerosol scattering coefficients is not much affected by the mixing conditions between soluble and insoluble materials, nor is it much affected by the aerosol size distributions, at least for moderately absorbing aerosols with power law size distributions. Other light scattering quantities such as phase functions, though not studied in this paper, may be more sensitive to these internal configurations of aerosols (Prishivalko, 1977).

Next, the curves of the light scattering

coefficient vs. relative humidity were presented for aerosols with different content of soluble materials (H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$), and a comparison was made with nephelometer measurements for atmospheric aerosols reported by other authors. It may be possible to infer the water-soluble content of atmospheric aerosols by these optical methods.

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エアロゾルの光散乱係数の湿度への依存性

—特に水溶性および不溶性成分との関係について—

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