AGU MANUSCRIPTS
Submitted to *International Journal of Geomagnetism and Aeronomy*, 2002

Impact of the scattered solar radiation on interpretation of the results of ozone measurements

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Short title: IMPACT OF THE SCATTERED SOLAR RADIATION

Abstract. Analyzing diurnal series of ozone measurements it is shown that the radiant energy absorbed by the ozone layer in the Huggins band differs significantly from the theoretical value calculated by the Lambert's law. To register the passed solar radiation the spectrometer-ozonometer to measure radiation at nine wavelengths in the ultraviolet range was used. The relative intensity of the direct solar radiation passing through the atmosphere was measured at each wavelength. The applicability limits of the Lambert's law for the calculation of atmospheric ozone content by the multi-wavelength method were studied. It was found that the deviations from this law which allow to use the standard method only under solar zenith angles below 80° were due to the light scattering processes. A model which makes it possible to take into account the light scattering processes which become important under oblique beam propagation was proposed. The model was compared with the calculations on the basis of the multi-wave method. The reflection coefficients for several wavelengths were calculated using the four-flux model [*Isimaru,* 1978].

1. Introduction

It is well known that the stratospheric ozone determines the income of the biologically active ultraviolet solar radiation to the Earth's surface. It is a key element in the branched chain of photochemical reactions determining balance of many atmospheric gas constituents [*Hesstvedt*, 1969; *Hunt,* 1966]. Having strong absorption bands in the ultraviolet (UV), infrared (IR), and visible ranges of the solar radiation ozone determines the stratosphere temperature regime. The main ozone mass is located in the middle atmosphere at altitudes of 20–40 km. Precisely the middle atmosphere is a connecting link between the troposphere and various manifestation of space activity. Studies of the ozone behavior in the atmosphere presents a considerable interest, in particular from the point of view of the contribution of the energy absorbed by ozone to the atmospheric energy balance. Interacting with various forms of radiant energy the ozone layer may also serve as a model object in the analysis of the radiation propagation through a scattering medium. In particular, on the basis of ozonometer data one can study the correctness of application of the Lambert's law which most of the ozone content calculation methods from ground-based spectrophotometric measurements are based on [*Dobson,* 1957; *Kuznetsov*, 1975]. This law considers rectilinear propagation of radiation in the scope of the radiant approximation and may be used with high reliability for small solar zenith angles when the main air mass is below the ozone layer and the light is mainly scattered in the lower layers.

Rosenberg [1966] showed that the conclusions based on the Lambert's law become incorrect when the atmosphere is illuminated by a diffuse (rather than direct) light flux having approximately uniform angle distribution of the intensity. That is, the scattering processes make impossible application of the existing ozonometric methods just in the twilight. However measurements of the ozone content are of interest in this very period. It is known [*Pearce Fred*, 1997; *Randhawa*, 1970] that the variations of the radiation energetic composition which impact the ozone content in the atmosphere occur at sunrise and sunset. It will be shown below that the results of ozonometer measurements in twilight are impacted on the first turn by the diffuse component.

2. Details of the Experiment

The spectrophotometer-ozonometer constructed on the basis of a double quartz monochromator has been used to register the rectilinear solar radiation intensity in the ultraviolet spectral range [*Bekturganov et al.,* 1982]. Cloudless days were chosen for the measurements and the registration was carried out during the entire illuminated period of the day with a 5-min interval. To determine the total atmospheric ozone content the co-called multi-wave method was used. This method is based on the Lambert's law which may be written in the form

$$I(\lambda) = I_0(\lambda)\exp(-\alpha\mu(\theta)x - \beta m(\theta) - \delta m'(\theta)) \tag{1}$$

where $I(\lambda)$ is the solar radiation intensity on the Earth's surface; $I_0(\lambda)$ is the intensity of the radiation falling on the upper atmosphere boundary; $\alpha(\lambda)$ is the absorption coefficient of the ultraviolet radiation by ozone molecules; $\beta(\lambda)$ and $\delta(\lambda)$ are the scattering coefficients of the radiation by the air and aerosol; $\mu(\theta)$, $m(\theta)$, and $m'(\theta)$ are the ozone, atmospheric, and aerosol masses, respectively, providing calculation of the oblique ray behavior in the atmosphere, and x is the total ozone content. According to *Kuznetsov* [1975] the multi-wave method is based on the linear equation system obtained from relation (1). The intensity logarithms at nine wavelengths of the absorption spectrum in the Huggins bands were compared. This comparison made it possible to reveal the contribution of the absorption by the ozone molecule lines. Concrete numerical values of the Rayleigh's scattering coefficient calculated for each wavelength [*Vigrougx,* 1967] were used. The aerosol term $\delta m'$ the contribution of which was studied by *Kuznetsov* [1975] was described as $\Delta\lambda_i z m$ according to the assumption on the linear spectral dependence of the aerosol attenuation in a narrow wavelength range. Though a narrow spectral interval is considered the function $\alpha(\lambda)$ varies rather sharply and that makes it possible to evaluate the ozone content in the atmosphere applying the least square method to the system of equations

$$L_{i0} = L_i + \Delta\alpha_i \mu x + \Delta\beta_i m + \Delta\delta_i m' \quad i = 1, \ldots, 8 \tag{2}$$

where $L_i = \ln(I_{0i}/I_{00})$ are the reduced intensities on the Earth's surface, I_{00} is the intensity at a wavelength of 330.6 nm which is chosen as a reference one; and L_{i0} are similar intensities outside the atmosphere determined by the Buger-Langly method which had been used by many authors [*Fraser,* 1975; *Shaw,* 1979].

3. Results

Standard deviations $\langle \Delta L_{\text{calc}} - \Delta L_{\text{exp}} \rangle^2$ were calculated using series of the 5-minute data of the spectrophotometric measurements obtained during two days (Figure 1). The values of ΔL_{calc} were calculated on the basis of the Lambert's law using x, μ, and m parameters determined by the standard multi-wave method. Figure 1 shows that approaching $\theta = 75°$ the calculated intensities begin to differ significantly from the experimental ones.

The light scattering under large solar zenith angles may be a main process which can cause the visible deviations from the Lambert's law. It is essential that expression (1) takes into account only the forward light scattering. However the beam pattern of the Rayleigh scattering is symmetric, that is, if the scattering processes play an important role then the backward scattering of the light should be taken into account. Therefore one can suppose that the step-like increase in the errors is due to the backward scattering, that is, to the processes of multiple reflections of the light in the atmosphere.

4. Theoretical Method

Currently there exist several methods to describe propagation of scattered radiation in various media. They are: the theory of radiative transfer [*Chandrosekhar*, 1950], the *Kubelka and Munk* [1931] theory, and so on. The approach developed by *Suleymenov and Kuranov* [1997] which makes it possible to describe multiple reflections in arbitrary laminated media (this method is equally applicable to analyze both coherent and incoherent radiation) is the best to fit the goals of this paper.

Suleymenov and Kuranov [1997] showed that each isoplanar layer of the medium may be considered as an effective four-pole (Figure 2). In particular the atmosphere may be split into layers and for each of them the following relation will be fulfilled

$$\begin{pmatrix} u^- \\ v^- \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} u^+ \\ v^+ \end{pmatrix} \tag{3}$$

where the radiation fluxes $(u^+,\ v^+)$ arriving at the chosen layer from the right and from the left are entrance fluxes and the radiation fluxes $(u^-,\ v^-)$ leaving this layer from both sides are exit fluxes. The diagonal and nondiagonal matrix elements are the transmission coefficients under radiation propagation forward and backwards and reflection coefficients, respectively. It was also shown that a combination of two successive four-poles is described by the matrix

$$\mathbf{A} \times \mathbf{B} = \frac{1}{1 - a_{12}b_{12}} \begin{pmatrix} a_{11}b_{11} & Ba_{12} + b_{12} \\ Ab_{21} + a_{21} & a_{22}b_{22} \end{pmatrix} \tag{4}$$

This matrix expresses the composite four-pole parameters via parameters of the initial elements a and b.

This operation is as uncommutative as a usual matrix multiplication

$$\mathbf{A} \times \mathbf{B} \neq \mathbf{B} \times \mathbf{A} \tag{5}$$

However if one of these matrices is diagonal then the relation of commutativity is fulfilled.

Using the approximation of light propagation in the above considered system consisting of effective mirrors, the role of the light scattering processes in the ozonometric measurements may be qualitatively interpreted. In this case the atmospheric layers above and below the ozone layer serve as effective partially transmitting mirrors. In respect to the ultraviolet radiation the atmosphere is an analog of a three-mirror interference system in which multiple reflections may occur. The succession of the mirrors corresponds to the layer above the ozone maximum, the ozone layer itself, and the atmosphere above it. Since the ozone layer thickness is negligible as compared with the thickness of the layers laying above and below, only absorption of the solar ultraviolet radiation occurs and scattering processes in the layer itself may be neglected. In this case the matrix describing the ozone layer is diagonal. The matrices of the other layers are also diagonal if the scattering is neglected. This means that if the light scattering processes in the layer above the ozone maximum are manifested only slightly, then its exact vertical position in the atmosphere plays no role. In this case the **A** and **B** matrices may have any order. This situation corresponds to the applicability conditions of the multi-wave method [*Zyryanova et al.,* 1998]. This condition are broken if the scattering processes above the ozone layer become significant (under large solar zenith angles). In this case one should apply operation (2) to the nondiagonal (and uncommuting) matrices and also establish their particular form. To do that the reflection coefficients of the atmospheric layers above and below the ozone layer due to the Rayleigh scattering should be found.

5. Reflection Coefficient

To calculate the reflection coefficient of an individual layer one can use the four-flux model described by *Isimaru* [1978]. This model considers transformation into each other of four different fluxes: the collimated and diffuse downward fluxes, and collimated and diffuse upward fluxes. Figure 3 illustrates the interaction of these fluxes. The left-hand part of Figure 3 shows schematically that the radiation containing simultaneously both diffuse and collimate components falls on the atmospheric layer from the outside (line A). The figured grey and usual black arrows show conventionally the direction of the collimate and diffuse components, respectively. In the similar way the radiation containing both these components may come also from the Earth's surface (line B). The light is scattered within the layer, the collimate component being partially transferred into the diffuse one which can propagate in both directions. The right-hand part of Figure 3 illustrates in detail the interactions within the layer. Here a thin layer is indicated and the transformation of the downward and upward collimate fluxes into diffuse ones is shown. Figure 3 shows that some part of the radiation in both fluxes is scattered backwards (black dashed arrows).

The model described is convenient to use when within the medium there are no pronounced boundaries and absorption processes. In this case the behavior of the diffuse component is governed by the system of two differential equations

$$\frac{d}{dh}\begin{pmatrix} J^{+} \\ -J^{-} \end{pmatrix} = \begin{pmatrix} -\beta/2 & \beta/2 \\ \beta/2 & -\beta/2 \end{pmatrix}\begin{pmatrix} J^{+} \\ J^{-} \end{pmatrix} + \frac{\beta}{2}\begin{pmatrix} J_0 \\ J_0 \end{pmatrix} \tag{6}$$

where β is the Rayleigh scattering coefficient (multiplier 1/2 assumes that the scattered radiation provides the same contribution to oppositely directed fluxes), J^{+} and J^{-} are the intensities of the downward and upward light fluxes, respectively, and J^{0} is the intensity of the downward collimate flux. In equation (2), the collimate component transformed to the diffuse one because of light scattering plays the role of a "source." Summing and subtracting (6) we obtain equations for the integral light intensity $J = (J^{+} + J^{-})$ and direct diffuse light flux $(J^{+} - J^{-})$

$$\frac{d}{dh}\begin{pmatrix} J^{+} & -J^{-} \\ J^{+} & +J^{-} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ -\beta & 0 \end{pmatrix}\begin{pmatrix} J^{+} & -J^{-} \\ J^{+} & +J^{-} \end{pmatrix} + \beta\begin{pmatrix} J_0 \\ 0 \end{pmatrix} \tag{7}$$

which is reduced to the only diffuse equation with a source in the right-hand side

$$\frac{d^2J}{dh^2} = -\beta^2 J_0 \tag{8}$$

Here the vertical distribution of the collimate component is governed by the usual Lambert's law

$$J_0 = J_{00}\exp(-\beta h) \tag{9}$$

Taking into account (5) the general solution of equation (4) has the form

$$J = -J_{00}\exp(-\beta h) + C_1 + C_2 h \tag{10}$$

The main feature of the problem in question is that the boundary conditions are set up on the values of the upward and downward fluxes but not on the values of the integral intensity which fits equation (4). In other words, the value of the downward flux at the upper boundary of J_0^+ (we choose this point as the origin of the frame of reference with the h axis directed downward) may be considered as a given value. In a similar manner the condition of the complete absorption by the Earth's surface (point h_m) is expressed by $J^-|_{h_m} = 0$. The values of the upward and downward fluxes may be expressed via the distribution of the integral intensity and its derivative according to (3) and (4)

$$J^+ = \frac{J\beta - J'}{2\beta} \tag{11}$$

$$J^- = \frac{J\beta + J'}{2\beta} \tag{12}$$

Using relations (7) and (8) and taking into account the boundary conditions one can obtain the expression for the upward component:

$$J^- = (J_{00} + J_0^+)\frac{\beta(h_m - h)}{\beta h_m + 2} \tag{13}$$

One can see that the values of the downward fluxes (both diffuse and collimate components) enter in a similar way the expression obtained. Therefore one can determine the reflection coefficient which according to (9) will be

$$r = \frac{\beta(h_m - h)}{\beta h_m + 2} \tag{14}$$

For the case of oblique incidence the same equation may be expressed in terms of the scattering coefficient referred to the entire thickness of the layer considered $\beta_0 = \beta h_m$

$$r = \frac{\beta_0}{\beta_0 + 2\cos\theta} \tag{15}$$

Figure 4 shows an example of the calculated dependence of the reflection coefficient on the solar zenith angle in the range typical for middle latitudes. One can see that from noon to twilight this value increases by several times and that indicates once again to an increasing role of scattering processes in twilight.

6. Interpretation of the Experimental Results

For the beginning we note that if the light scattering processes are essential only in the atmospheric layers below the ozone layer then they almost do not impact the results obtained by the multi-wave method [*Zyryanova et al.,* 1998]. This is because the measurements are conducted in a narrow enough spectral range. On the contrary, the multi-wave method becomes inapplicable if scattering processes are essential in the atmosphere including the atmospheric layers above the ozone layer. We compare the calculation results obtained with the help of the multi-wave method and on the basis of the theoretical considerations described above. The operation (4) may be done assuming that the total air content above the ozone layer is about 5% of the its total mass and using the reflection coefficient (15) to determine the elements of matrix (3). This leads to the following expression for the transmission factor of the three-layer atmosphere

$$T = \frac{\exp(-\alpha x/\cos\theta)}{1 + \beta/\cos\theta + 0.05(1 - \exp(1 - \exp(-2\alpha x/\cos))(\beta^2/\cos^2\theta)} \tag{16}$$

On the basis of equation (16) the standard deviation $\langle L_{\mathrm{new}} - L_{\mathrm{lamb}}\rangle^2$ was calculated as a function of the solar zenith angle (Figure 5, curve 1). Here $L_{\mathrm{new}} = \log(I/I_0) = \log(T)$ and L_{lamb} was calculated using the multi-wave method. Real atmospheric parameters were used for the days shown in Figure 1. Figure 5 shows graphs based on the data in Figure 1 but presented in a more convenient scale for comparison (curve 2). One can see that the calculations performed for the model three-mirror system also indicate to the existence of the critical zenith angles at which the standard deviation increases abruptly. That means that precisely the atmospheric scattering processes above the ozone layer are responsible for their existence.

7. Conclusion

It is shown that at large solar zenith angles the standard deviations given by the known multi-wave method increase abruptly. The analysis of the causes of these errors carried out with the help of the optical methods of the laminated medium theory makes it possible to establish that under certain conditions the terrestrial atmosphere presents an analog of a three-mirror interference system and the atmospheric layers serve as partially transmitting mirrors for the ultraviolet radiation in the Huggins band.

The essential role played by the radiation diffuse component at large solar zenith angles is established. Using the four-flux model specific equations for calculations of the reflection coefficients of the atmospheric layers determined by processes of the backwards light scattering are obtained. A mathematical description of the radiation propagation through a layer structure is proposed, the description taking into account mutual transformation of diffuse and collimate light components.

Thus the results obtained in the paper spread outside the framework of the ozonometry. For instance, they can be used to study the energetic balance of the ozone layer during the dawn-dusk hours. Actually, since the reflection from the effective mirrors above and below the ozone layer in the twilight becomes significant, the radiation may be quite "captured" between them. Hence there follows a possibility of occurrence of significant disturbances of the ozone layer in the twilight.

The results obtained make it also possible to suggest that studies of light reflection processes from atmospheric layers may appear important for the analysis of interactions between atmospheric components and radiation in other spectral ranges.

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(Received 29 November 1999)

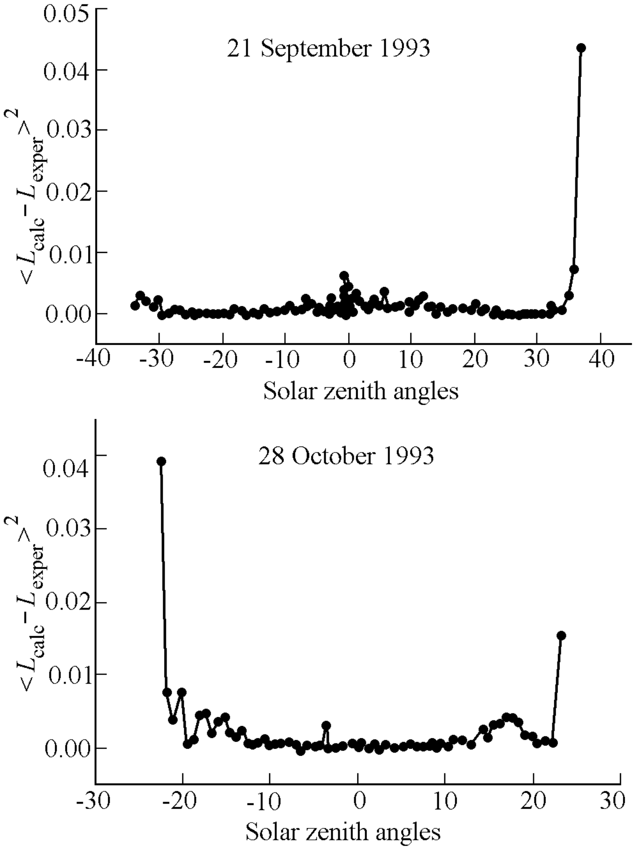

Figure 1. Dependence of the standard deviations of ozonometric measurements on the solar zenith angle.

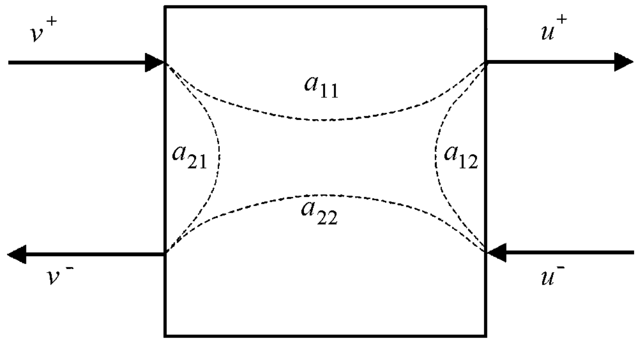

Figure 2. The light flux transformation by an effective four-pole.

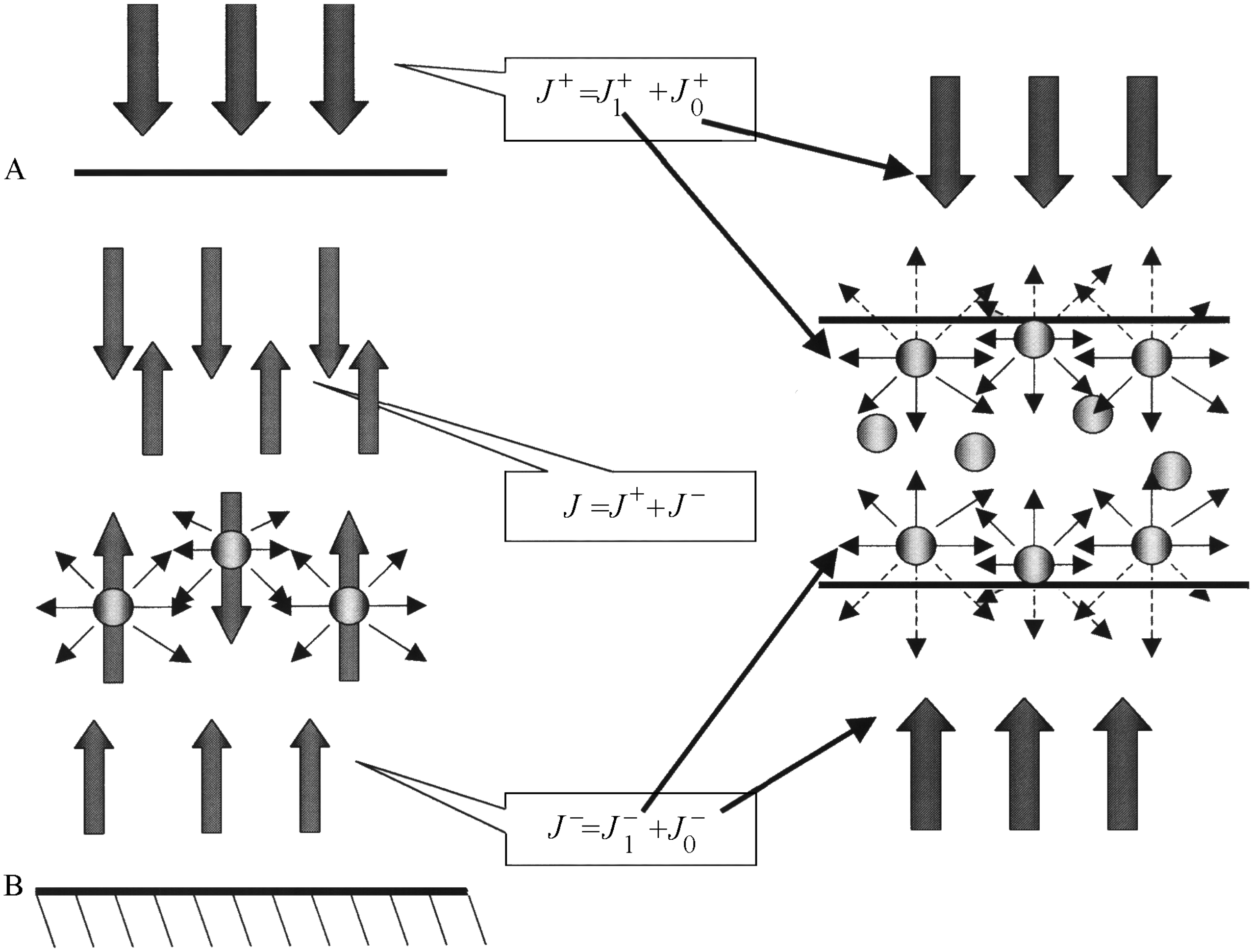

Figure 3. The Isimaru four-flux model.

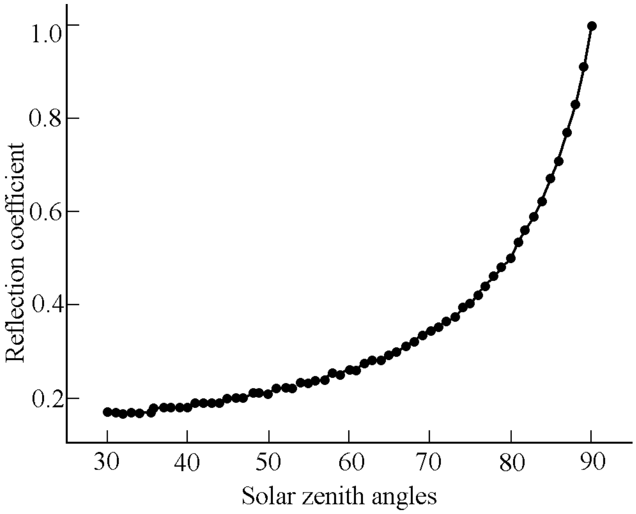

Figure 4. Dependence of the reflection coefficient on the solar zenith angle.

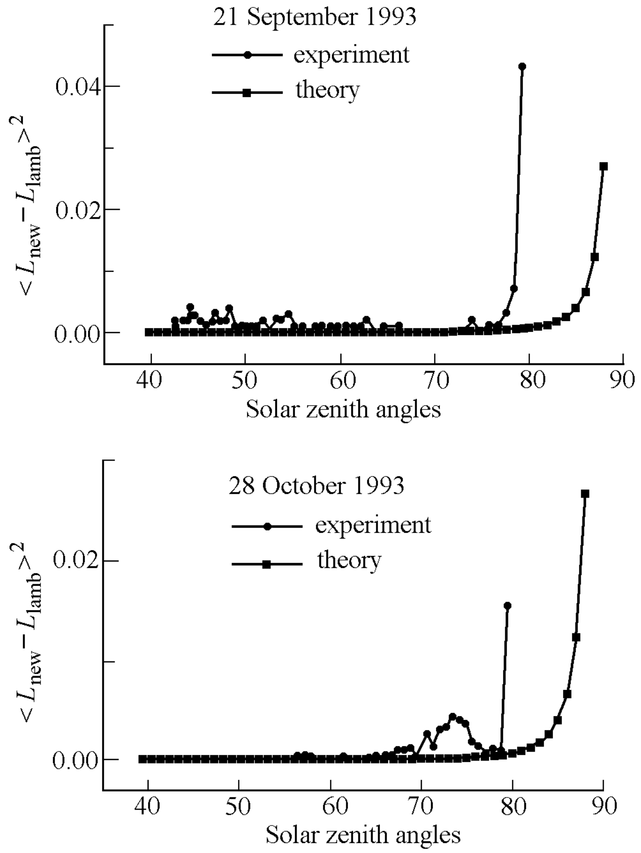

Figure 5. Comparison of the experimental and theoretical results.