Atmospheric transmission in ozone absorption bands for SP-6 spectrophotometer UV channels

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Received May 22, 2006

Calculation errors for the transmission function in a 300–350 nm spectral range are estimated involving the present-day information on ozone absorption cross sections. The effect of temperature vertical profile variations on the transmission function variability is studied. Peculiarities of the transmission function parameterization for SP-6 spectrophotometer UV channels are discussed.

Introduction

Ozone is one of the most important atmospheric components[1] absorbing the UV radiation, dangerous for living organisms; it also screens the proper Earth long-wave radiation, favoring in such a way the greenhouse effect. Therefore, regular monitoring of the gas–aerosol content of atmosphere, including ozone, is an urgent problem.[2] However, only recently a start have been made on implementation of a net of routine measurements of the aerosol optical thickness and total concentration of a series greenhouse gases (H_2O, O_3), based on SP-6 – SP-8 solar spectrophotometers (Ref. 3).

At present, the solar SP-6 photometer allows a determination of the above parameters, excluding the total ozone concentration (TOC). Solar spectrophotometry of atmosphere (the transparency method) is one of the efficient and sufficiently simple methods for measuring TOC. The first Russian instrument operating with a direct solar radiation was the Gushchin ozonometer.[4] The present-day realizations of ozonometers are presented by Dobson[4] and Brewer[6] photometers.

The results, presented in Ref. 7, on the TOC retrieval with the use of the UV-MFRSR radiometer show a good agreement with results obtained with the above devices (the difference is less than 4%). The TOC retrieving method is rather simple.[4,7] The error in TOC retrieving is closely connected with the error in calculation of the atmospheric transmittance, which, in turn, depends on the used spectroscopic information and parameterization errors. At present, there is a great amount of experimental data on the ozone cross sections obtained under different conditions (temperature, resolution, spectral range).[8,10–12]

The goal of this work is the parameterization of the transmission function for solving the problem of TOC retrieving from measurements of the direct solar radiation with the SP-6 spectrophotometer. To do this, we have estimated the errors in calculation of the atmospheric transmission function for the device's UV channels caused by ambiguities in the ozone cross sections and neglected variations in temperature profiles; we also have studied the form of the parametric dependence of the transmission function on the ozone absorbing mass.

Ozone absorption cross sections for calculation of transmission functions

Data on ozone absorption cross sections for atmospheric investigations within 300–350 nm can be found in Refs. 10–13 and in the HITRAN database (Ref. 8). Table 1 presents some characteristics of the cross sections.

Table 1. General characteristics of ozone absorption cross sections

Resolution, nm	Temperature, K	Wavelength range, nm	Reference
0.025	200, 220, 240, 260, 280, 300	245–343	8
0.01	218, 228, 243, 273, 298	195–345	10, 11
0.5	226, 263, 298	185–350	12
0.2–1.9	181, 214, 243, 291	244–340	13
1	206, 225, 271, 298	253–370	14

In the critical review[15] it is recommended to use experimental data on absorption cross sections for 300–350 nm range from Ref. 10 or Ref. 8. It should be noted that the absorption cross sections, given in the HITRAN database, were obtained through recalculation of experimental data[16] with the use of cubic splines. These data were obtained at a high resolution, cover most important atmospheric temperatures, and have the least systematic errors among all available data.

The comparison of data from Refs. 8 and 10 has shown that differences in the absorption cross sections within the interval of our interest do not exceed 2% at a temperature of 300 K; the differences in the spectral transmission of atmosphere at summer conditions and varying optical masses (m) were within 1% and visually these two calculations were indistinguishable.

0235-6880/06/08 654-04 $02.00

What about the data obtained with a lower resolution,[12] the calculation of transmissions with their use resulted in more smooth spectral dependence as compared to calculations with data from Ref. 8 and the difference reached 10%. Therefore, the calculations on the base of HITRAN data are more preferable, because they well describe the spectral dependence for ozone absorption cross sections and have a lower resolution as compared to data from Ref. 10, consequently, providing a good gain in time.

Method of calculation and parameterization of transmission functions for UV channels of the SP-6 solar photometer

The description of solar photometers in detail is given in Refs. 3 and 17. The SP-6 photometer in the UV range has four channels centered at 308, 324, 340, 371 nm wavelengths. The photometer instrumental functions were calculated based on experimentally measured spectral dependences of transmission of the corresponding interference filters and on the receiver sensitivity.

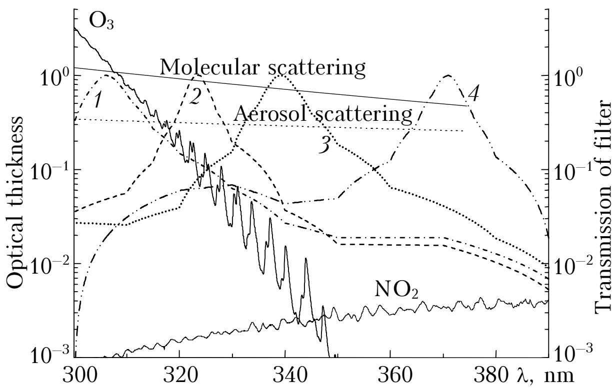

Fig. 1. Spectral dependences of optical thicknesses due to aerosol and molecular scattering, as well as O_3 and NO_2 absorption for vertical atmospheric paths of 0–100 km. Spectral transmission of filters with centers: 308 (*1*), 324 (*2*), 340 (*3*), and 371 nm (*4*).

The ozone and NO_2 absorption cross sections are taken from the HITRAN-2004 database; the aerosol optical thickness is constructed by data from AERONET for Tomsk city for 2003 year. Figure 1 shows that the aerosol and molecular scatterings have a distinct spectral dependence, being in such a way hampering factors in retrieving TOC. However, available analytical models, describing the molecular scattering behavior, allow one to take it into account in advance. The NO_2 effect at 308 and 324 nm wavelengths is insignificant and can be neglected in solving the inverse problem.

The spectrophotometer-measured solar radiation having passed through atmosphere can be calculated by the formula

$$S = CT_a(\lambda)T_R(\lambda)T_{gas}(\lambda),$$

where C is the calibration constant; T_a, T_R are spectral transmissions due to aerosol and molecular scattering, respectively; T_{gas} is the spectral transmission due to molecular absorption.

The transmission function at zenith angles less than 70° is

$$T_{gas}(\lambda) = \int_{\lambda-\Delta\lambda}^{\lambda+\Delta\lambda} F(\lambda')I_0(\lambda')\times$$
$$\times\exp\left(-\frac{1}{\cos\theta}\int_0^H \alpha(\lambda',h)\mathrm{d}h\right)\mathrm{d}\lambda \Bigg/ \int_{\lambda-\Delta\lambda}^{\lambda+\Delta\lambda} F(\lambda,\lambda')I_0(\lambda')\mathrm{d}\lambda,$$

where H is the atmospheric top boundary; $\alpha(\lambda', h)$ is the volume absorption coefficient at the height h and wavelength λ'; θ is the zenith angle of the Sun tilt; $F(\lambda, \lambda')$ is the spectrophotometer instrumental function at λ'; λ determines the position of maximal transmission of the instrumental function; $I_0(\lambda)$ is the solar radiation flux incident on the atmosphere top. The volume absorption coefficient is connected with the absorption cross section σ through the relation $\alpha = \sigma n_{O_3}$, where

$$n_{O_3} = n_0(P_{O_3}T_0/P_0T')$$

is the number of ozone molecules in 1 cm^3 volume at the air temperature T' and the ozone partial pressure P_{O_3}; n_0 is the Loschmidt number at $P_0 = 1$ atm and $T_0 = 273.15$ K.

To retrieve TOC from solar radiation measurements, the dependence of transmission on the absorbing gas mass must be known. As a rule, to obtain this dependence, the expression $T_{gas}(\lambda) = \exp(-\beta(mW)^n)$ from models of bands is used, where β and n are the model parameters determined from the fitting to the calculated absorption function; W is the TOC; $m = 1/\cos\theta$. When the distance between spectral lines is comparable with their half-width, typically $n = 1$. However, the modeling for the photometer instrumental function centered at 308 nm gave an unexpected result: the n value varied between 0.7 and 0.3 (Fig. 2).

The dependence of T on the ozone absorbing mass was also calculated with the use of the triangle instrumental function of 2 nm width at a half-width (the UV-MFRSR resolution). In this case n turned to be 1, as theoretically predicted.

To explain such behavior of n, we have addressed to the model of an isolated line with the Lorentz contour (Fig. 3*b*).

If the transmission is calculated for the rectangular instrumental function, then, depending on the optical thickness magnitude in the line center (τ), either weak line approximation $T = \exp(-\beta mW)$ at $\tau < 1$ or strong line approximation $T = \exp(-\beta\sqrt{mW})$ at $\tau \gg 1$ hold, i.e., the strong absorption approximation ($n = 0.5$) is fulfilled provided that the saturation is observed in the line

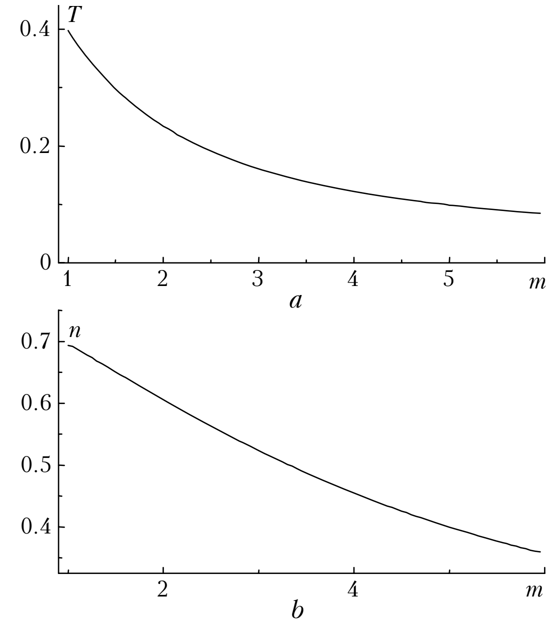

Fig. 2. Dependence of T on m (a) and n on m (b).

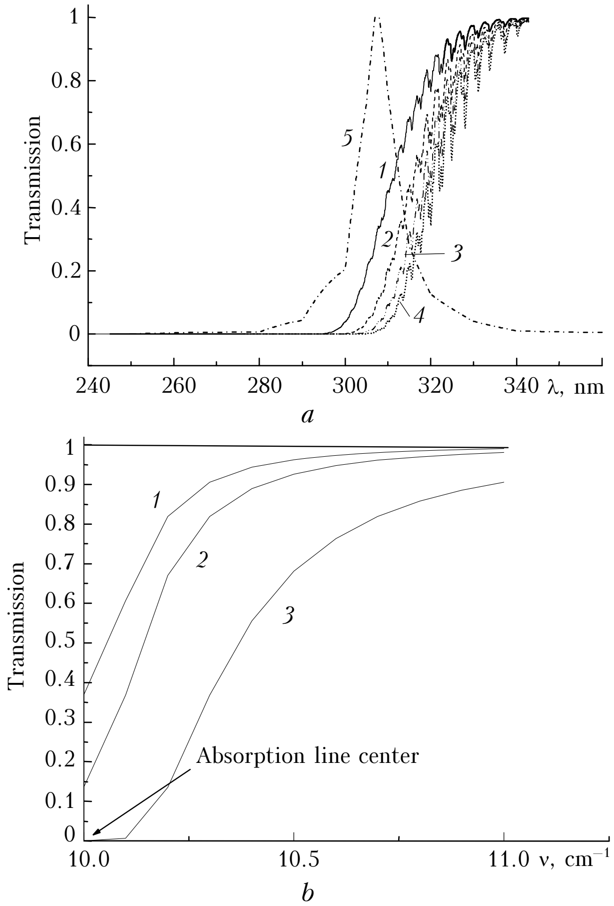

Fig. 3. Spectral transparence of atmosphere at different air masses m: *1–4* are for m = 1, 2, 3, 4; *5* for the spectral transmission of the device filter for the line centered at 308 nm (a); spectral transmission of an isolated line at different τ values: (*1* for τ = 0.5; *2* for 1; *3* for 3) (b).

center ($\tau \gg 1$). If to consider the ozone absorption band as some effective line, centered at 300 nm, then, as the air mass grows, a saturation takes place in the vicinity of line center of the SP-6 photometer instrumental function. The spectrum range to the left from 300 nm can be neglected, because the spectral transmission is close to 0 for all m values and any contribution in the transmission function is absent. All the above-said explains the inequality of n to 1.

Temperature variation effect on the transmittance variability

Transmission in bands of atmospheric gases depends not only on the absorbing mass, but also on vertical profiles of the air pressure and temperature. If the used spectral channel of the device noticeably depends on these parameters, then the retrieving problem becomes open to question, because the process of solar radiation measurement, as a rule, is not accompanied by measurements of temperature profiles. Therefore, the influence of variations in meteorological parameters on the transmittance in the channels used for TOC retrieval has been studied by us. To do this, the temperature profile was shifted by the standard deviation magnitude taken from Ref. 18. So, six temperature profiles were obtained: for each height the air temperature changed by $\pm\sigma_t$, $\pm 2\sigma_t$, $\pm 3\sigma_t$ (σ_t is the standard deviation of the temperature). Table 2 presents the obtained values for heights between 0.12 and 60 km.

Table 2. Standard deviation of the temperature for heights between 0.12 and 60 km

H, km	Temperature, K	Standard deviation, K
0.12	293.7	7
10	235.3	5.8
20	219.2	5.5
30	233.7	4.5
40	257.5	9
50	275.7	8.4
60	257.1	7

Modeling results have shown that in the 308 nm channel at a temperature profile changes by $\pm\sigma_t$, $\pm 2\sigma_t$, and $\pm 3\sigma_t$ the deviations in transmission do not exceed 0.7%, 1.3%, and 3%, respectively. Similar values for the 324 nm channel are 0.6, 1.7 and 2.8%, respectively, i.e. temperature variations insignificantly affect the transmittance in the ozone sensing channels.

Conclusion

At present, the calculation of atmospheric transmission in the bands of ozone absorption in the UV spectral range 300–350 nm can be very accurate when using absorption cross sections.[8,10] It is shown that temperature variations do not affect noticeably the atmospheric transmittance variability for 308 and 324 nm channels of the SP-6 spectrophotometer. It was found that for the 308 nm channel the optical thickness depends on the ozone absorbing mass nonlinearly.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Grant No. 04-07-90123).

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