Development of the molecular absorption models in application to problems of radiative transfer in the Earth's atmosphere

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The methods for modeling selective gas absorption to solve problems of radiative transfer in the atmosphere are reviewed with due regard of the recent advances in this field. Particular attention is given to presentation of the atmospheric transmission functions as a series of exponential functions. This presentation does provide not only high accuracy of calculations, but it is also efficient in considering multiple scattering.

Introduction

The study of climate and its changes is one of the most important problems in modern science. Radiative processes play a key part in this problem. These processes, in turn, are directly or indirectly connected with such factors as variations of the solar constant, transformation of the underlying surface properties, changes in the gas and aerosol composition of the atmosphere, etc.[1] Thus, some researchers,[2] believe that the 1% decrease in the solar constant that took place in the past provoked the Ice Ages on the Earth. Now the global climate change is associated with the greenhouse gases such as CO_2, CH_4, and N_2O, and freons, the doubled content of which also leads to about 1% change in the outgoing flux of thermal radiation. These data give the general idea on the accuracy needed when solving the radiative transfer equation in the problems on climate modeling.

Besides, because of the specific character of the problems on global circulation of the atmosphere, high degree of parameterization is required of the radiative transfer equation and, in particular, of the molecular absorption. Solution of the problem of radiation propagation in the Earth's atmosphere is often complicated by the necessity of taking into account the multiple scattering effects. High selectivity of the molecular absorption, in contrast to aerosol and molecular scattering, in the visible and infrared regions strongly complicates this problem. Thus, for example, the characteristic scale of the molecular absorption coefficient variability is comparable with a spectral line halfwidth and lies from 10^{-1} to 10^{-4} cm^{-1}. For a comparison, the characteristic scale of variations in the solar spectrum is about several wavenumbers (Ref. 3). The variability scale of optical properties of water, ice, and aerosols is even larger.[4,5] In this connection, efforts of many researchers have been focused on the development of highly efficient models for calculating the characteristics of molecular absorption, which provide for high degree of parameterization without any loss in accuracy. The complexity of this problems is in that two mutually exclusive requirements are to be met: minimal error and high speed of calculation.[6]

This paper presents a brief review of the history of the development of models that enable one to take into account the characteristics of molecular absorption in the problems of radiative transfer in the Earth's atmosphere as well as characterize the progress achieved in this field. Particular attention is given to recent advances associated with the presentation of the transmission functions in the form of series of exponential functions.

1. Thermal radiation of the cloudless atmosphere of the Earth

In the case of a nonscattering plane-parallel atmosphere which is in the local thermodynamic equilibrium, the radiative transfer equation can be written in the following form[7]:

$$\mu \frac{dI(\nu, \tau, \mu)}{d\tau} = I(\nu, \tau, \mu) - B(\nu, \tau),$$

$$\tau = \int_z^\infty k(\nu, z')\, dz',$$

where $k(\nu, z')$ is the coefficient of molecular absorption at the frequency ν and altitude z'; τ is the optical thickness, which plays the role of a spatial coordinate for the plane-parallel atmosphere; $\mu = 1/\cos\theta$, θ is the zenith angle of the path; $I(\nu, \tau, \mu)$ is the radiation intensity at the frequency ν; $B(\nu, \tau)$ is the Planck function. Taking into account that there are no sources of downwelling radiation ($I^{\downarrow}(\nu, 0) = 0$) at the upper boundary of the atmosphere ($\tau = 0$) and that the surface radiation at the lower boundary of the atmosphere ($\tau = \tau_0$) is equal to $I^{\uparrow}(\nu, \tau_0, \mu)$, the equations for upwelling and downwelling radiation can be readily obtained:

$$I^{\uparrow}(\nu, \tau, \mu) = I^{\uparrow}(\nu, \tau_0, \mu) \exp\{-(\tau_0 - \tau)/\mu\} + \int_\tau^{\tau_0} B[\nu, T(\tau')] \exp\{-(\tau' - \tau)/\mu\} \frac{d\tau'}{\mu},$$

$$I^{\downarrow}(\nu, \tau, \mu) = -\int_0^{\tau} B[\nu, T(\tau')] \times \exp\{-(\tau' - \tau)/\mu\} \frac{d\tau'}{\mu}, \quad \mu < 0.$$

In this paper we describe the methods of taking molecular absorption into account in the problems of radiative transfer. Therefore, below we present equations

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only for upwelling radiation, since the functional dependence of the downwelling radiation on the characteristics of molecular absorption is similar. The upwelling flux of monochromatic radiation can be calculated by the equation

$$F^{\uparrow}(\nu, \tau, \mu) = \int_{\Omega^+} \mu\, I^{\uparrow}(\nu, \tau, \mu)\, d\Omega = \\ = \int_0^{2\pi} d\varphi \int_0^1 d\mu\, \mu\, I^{\uparrow}(\nu, \tau, \mu). \quad (1)$$

The integral is taken over the lower hemisphere (Ω^-) for the downwelling flux and over the upper hemisphere (Ω^+) for the upwelling flux.

If the Earth's surface is considered as a black body, then

$$I^{\uparrow}(\nu, \tau_0, \mu) = B(\nu, T_0),$$

where T_0 is the surface temperature.

Using the integral exponential functions, we can obtain the following equation for the spectral flux:

$$F^{\uparrow}(\nu, \tau) = 2\pi\, B[\nu, T(\tau_0)]\, E_3(\tau_0 - \tau) + \\ + 2\pi \int_{\tau}^{\tau_0} B[\nu, T(\tau')]\, E_2(\tau' - \tau)\, d\tau'. \quad (2)$$

To estimate the net upwelling flux, Eq. (2) should be integrated over frequency. This is rather a complicated problem even with the use of modern computers, because the number of spectral lines stored in the current spectroscopic databases such as HITRAN–96 (Ref. 8) and GEISA–97 (Ref. 9) is about 10^6. To reduce the computations, the transmission function in the spectral interval $\Delta\nu$ with the center at ν is introduced. Since the optical thickness τ is frequency-dependent, either altitude z or pressure p should be used as an argument of the transmission function:

$$T_\nu(z_1, z_2, \mu) = \frac{1}{\Delta\nu} \int_{\Delta\nu} \exp\left\{-\frac{1}{\mu}\tau(z_1, z_2, \nu)\right\} d\nu. \quad (3)$$

The width of the interval $\Delta\nu$ is chosen narrow enough for the Planck function to be considered constant within it, while being sufficiently wide to include quite a large number of absorption lines.

By analogy with the transmission function, the diffuse transmission function is introduced in the following form:

$$T_\nu^f(z_1, z_2) = \frac{1}{\Delta\nu} \int_{\Delta\nu} E_3[\tau(z_1, z_2, \nu)]\, d\nu. \quad (4)$$

The diffuse approximation

$$2E_3(\tau) = \exp\left\{-\frac{1}{\mu_0}\tau\right\},$$

where $1/\mu_0 = 1.66$, is often used. In most practical applications this approximation is fulfilled sufficiently accurate.

Figure 1 illustrates the quality of this approximation. The validity of the diffuse approximation was thoroughly studied in Ref. 10, and it was shown that the highest errors are characteristic of only the lower troposphere for the downwelling flux, and their magnitude does not exceed 1 W/m^2.

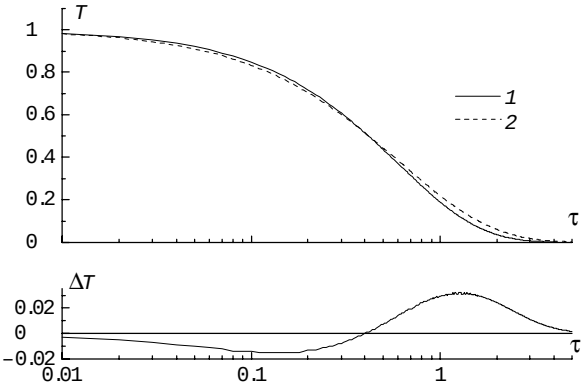


Fig. 1. Diffuse approximation for the transmission functions: $T^f(\tau)$ (curve *1*) and $T(\tau, \mu_0)$ (curve *2*); $\Delta T = T^f(\tau) - T(\tau, \mu_0)$.

Using diffuse approximation, one can obtain the following equations for the integral fluxes[7,11]:

$$F^{\uparrow}(z) = \pi \int_0^{\infty} B[\nu, T(\tau_0)]\, T_\nu(z_0, z, \mu_0)\, d\nu + \\ + \pi \int_{z_0}^{z} dz' \int_0^{\infty} d\nu\, B[\nu, T(z')] \frac{dT_\nu(z', z, \mu_0)}{dz'},$$

$$F^{\downarrow}(z) = -\pi \int_{z}^{z_\infty} dz' \int_0^{\infty} d\nu\, B[\nu, T(z')] \frac{dT_\nu(z, z', \mu_0)}{dz'}.$$

It should be noted that the use of the models that are based on the representation of the transmission functions as a series of exponential functions does not require the diffuse approximation to be used. This follows from the equation

$$T_\nu^f(z_1, z_2) = \int_1^{\infty} \mu d\mu \frac{1}{\Delta\nu} \int_{\Delta\nu} \exp\left\{-\frac{1}{\mu}\tau(\nu, z_1, z_2)\right\} d\nu = \\ = \int_1^{\infty} \mu d\mu \sum_{i=1}^{N} C_i \exp\left\{-\frac{1}{\mu}\tau_i(z_1, z_2)\right\} = \\ = \sum_{i=1}^{N} C_i\, E_3[\tau_i(z_1, z_2)]. \quad (5)$$

The above equations indicate that the main characteristic of the thermal radiation is the transmission function of the atmospheric layer along a given zenith direction (4). Given the transmission function of the gas mixture, it is easy to calculate the intensity and fluxes of thermal radiation. The transmission function should also be known to calculate the short-wave radiation in the spectral regions occupied by the absorption bands of the atmospheric gases.

Depending on the problem of atmospheric optics to be solved, the transmission functions should be known with a high or low spectral resolution. Thus, to interpret the data of the new-generation spaceborne devices used for atmospheric sounding, the radiative characteristics should be known with a high spectral resolution ($\Delta\nu \approx 0.002 - 0.1$ cm^{-1}) corresponding to the resolution of spectral devices installed on board a satellite. For calculation of the outgoing radiation with high spectral resolution, the direct

method (sometimes called a benchmark in the literature) is used.

For solution of radiative and climate problems it is not needed to know the fine structure of absorption spectra, since only integral radiative characteristics are of interest. Therefore, the spectral resolution needed for solution of these problems is usually determined by the absorption line width and can be about 100 cm^{-1}.

Now three groups of methods are extensively used for calculation of the transmission functions with the medium and low spectral resolution. These are the empirical methods, methods based on the absorption band models, and the method of direct line-by-line calculation. The methods from first two groups were developed in the pre-laser epoch. They are parametric: parameters in these methods are determined by fitting to laboratory data or data obtained by direct line-by-line calculations. These methods are used for calculation of extinction of a broad-band radiation in the atmosphere. The empirical methods formed a basis for the corresponding computational techniques, known as the SOI (State Optical Institute) technique,[12–14] SIAO (State Institute of Applied Optics) technique,[15–17] LOWTRAN,[18–20] and the MGO (Main Geophysical Observatory) technique.[21] Based on the model representation of the absorption bands, the combined technique for calculation of the transmission functions was developed.[22] The general for the developed techniques restriction in calculating the transmission function is the fixed spectral resolution.

With the development of modern computers, the line-by-line (LBL) method has become more common in use. This method is exact in its idea; it takes into account the contribution coming to absorption from each line. This methods has no limitations associated with the spectral resolution, and theoretically it allows the absorption function to be calculated for any spectral interval. In actual practice, however, as the spectral interval increases the computer time also increases. This happens, on one hand, because of the increasing number of lines to be taken into account and, on the other hand, this is caused by the increasing interval of integration. Therefore, the use of the line-by-line method in bulky computations for wide spectral intervals is not appropriate. This method provides a benchmark for testing various models. Nevertheless, even benchmark calculations face certain technical difficulties. That is why a number of recent papers[23–29] have been devoted to optimization of this method. Recent advances in the development of the effective models for calculating the transmittance with a low spectral resolution by use of series of exponential functions have been discussed in Refs. 30–42.

It is also worth noting the development of the so-called fast methods of calculation of the broadband absorption functions.[43–51] These methods are based on the use of absorption band models with the parameters found from calculation rather than from the fit to laboratory data.

The approximate models used for calculating thermal radiation fluxes can be conditionally subdivided into two groups: narrow-band models and broad-band models.[6]

In the narrow-band models, the entire spectral interval is divided into subintervals, within which the Planck function is assumed constant. In this case only the transmission function is integrated over the spectrum. For this case three approaches to determination of the transmission function can be used. The first one uses transmission functions described by analytical models with the parameters obtained by either calculation or fit to laboratory or LBL data.

In the second approach Laplace transformation is used. It allows the fast-oscillating function of the integrand to be replaced by a smooth monotonic function. As a result, the transmittance can be presented in the form of a short series of exponential functions. The advantage of this approach is the possibility of including molecular absorption into the scheme of multiple scattering calculations.

The third approach relies on the use of empirical functions similar to those used in the LOWTRAN model. The comparison with the LBL results showed that the narrow-band models give good results for CO_2 and H_2O at the interval width from 5 to 20 cm^{-1}. However, for $\Delta\nu$ less than 5 cm^{-1} or greater than 100 cm^{-1} the models can give large errors.

The broadband models of transmission are based on measurements, LBL calculations, or narrow-band models. In these models spectral averaging is conducted over wide intervals or even over the entire spectrum. One example is the model in which the integral emissivity is used instead of the transmission functions.[6] This model is widely used in climate studies. It was shown to describe well the 15-μm system of CO_2 bands. The main difficulty in the use of this model arises when considering overlapping bands of other gases or inhomogeneous paths.

Let us briefly characterize the narrow-band models of the transmittance.

2. Theoretical models of absorption spectra

Theoretical models are based on an idealized presentation of the absorption bands in the form of various models allowing their analytical description. These models are parametric; they have from two to four parameters, which are determined from the experimental data or calculated by the line-by-line method at different values of the thermodynamic parameters of the medium. The detailed description of the spectral models can be found in Refs. 22, 53, 54, and 55–60. Here we briefly describe only the principal results.

The following models have gained wide acceptance: (1) model of an isolated line, (2) Elsasser regular model of equidistant lines with the same intensity and halfwidth, (3) Plass statistical model (lines of equal intensity), (4) Goody statistical model (exponential distribution of intensities), and (5) Malkmus statistical model (modified exponential distribution of intensities).[59] The above-listed models are described below in Table 1.

The different models of the absorption function are shown in Fig. 2. Intercomparison among the models shows that they give different values of absorption with the given parameters β and $\tilde{o}$, and the discrepancy increases with increasing $\tilde{o}$ (at small $\tilde{o}$ all the models give almost the same value of absorption). It is clear from Fig. 2 that for any $\tilde{o}$ and β the inequality $A_{El} > A_{Pl} > A_G$ takes place, where El, Pl, and G denote respectively, the Elsasser, Plass, and Goody models.

As to the variability range of A_{Sl} and A_M, one can see that at small β the inequality $A_{El} > A_{Sl} > A_{Pl} > A_M$ takes place, whereas for large β $A_{Sl} < A_M < A_G$.

All these models use the absorbing mass W as the input information. It follows herefrom that all the considered models are two-parameter models with the parameters like $S/2\pi\gamma$ and $\beta = 2\pi\gamma/d$.

The models described above were constructed on the basis of the Lorentz shape of an absorption line. Then the models were generalized for the Doppler and Voigt shapes.[43,59]

In simulating the transmittance of a gas mixture, the so-called product rule

$$T_\Sigma = T_1\, T_2 \qquad (6)$$

is used, where T_i is the transmittance due to the absorption by the ith gas.

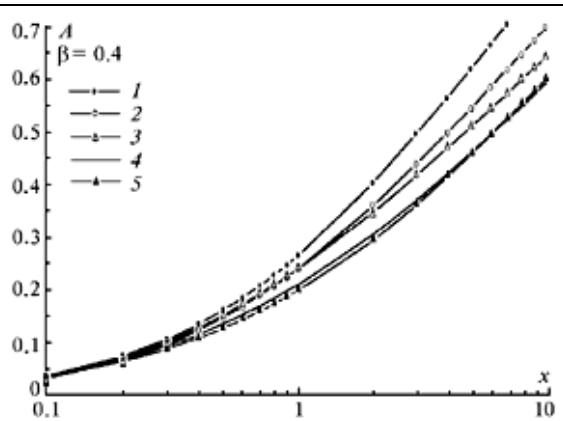
Table 1. Main absorption models and their approximations

Principal equation	Approximations		
	Weak line	Strong line	Non-overlapping line
Model of isolated line $A_{SI} = \frac{1}{\pi}\int_0^\pi \left[1 - \exp\left(-2\frac{x\beta^2}{t^2+\beta^2}\right)\right] dt;$ $\beta = 2\pi\gamma/\Delta\nu;\ x = SW/2\pi\gamma$	$A = \beta x$	$A = \sqrt{\pi}\, z\,[1 - \hat{O}(z)] + (1 - e^{-z^2});$ $z = \frac{2}{\pi}\sqrt{\frac{\beta^2 x}{2}}$	$A = \beta L(x)$
Elsasser regular model $A_{\text{Äl}} = \frac{1}{\pi}\int_0^\pi \left[1 - \exp\left(-\beta x\frac{\sinh\beta}{\cosh\beta - \cos t}\right)\right] dt;$ $\beta = 2\pi\gamma/d;\ x = SW/2\pi\gamma$	$A = 1 - \exp(-\beta x)$	$A = \hat{O}\left(\sqrt{\frac{\beta^2 x}{2}}\right)$	$A = \beta L(x)$
Plass statistical model $A_{\text{Ðl}} = 1 - \exp[-\beta L(x)];$ $\beta = 2\pi\gamma/d;\ x = SW/2\pi\gamma$	$A = 1 - \exp(-\beta x)$	$A = 1 - \exp\left(-\frac{2}{\pi}\sqrt{\frac{\beta^2 x}{2}}\right)$	$A = \beta L(x)$
Goody statistical model $A_G = 1 - \exp\left[-\frac{\beta x}{\sqrt{1+2x}}\right];$ $\beta = 2\pi\gamma/d;\ x = SW/2\pi\gamma$	$A = 1 - \exp(-\beta x)$	$A = 1 - \exp\left(-\sqrt{\frac{\beta^2 x}{2}}\right)$	$A = \frac{\beta x}{\sqrt{1+2x}}$
Malkmus statistical model $A_M = 1 - \exp\left\{-\frac{\sqrt{R}+1}{\sqrt{R}-1}\frac{\beta}{\pi}\times\right.$ $\left.\times\left[\sqrt{1+2\pi x\frac{\sqrt{R}}{\sqrt{R}+1}} - \sqrt{1+2\pi x\frac{1}{\sqrt{R}+1}}\right]\right\},$ At $R \geq 1$ $A_M = 1 - \exp\left\{\frac{\beta}{\pi}\left[\sqrt{1+2\pi x} - 1\right]\right\}$	$A = 1 - \exp(-\beta x)$	$A = 1 - \exp\left[-\frac{2}{\sqrt{\pi}}\sqrt{\frac{\beta^2 x}{2}}\right]$	$A = \frac{\beta}{\pi}\times$ $\times(\sqrt{1+2\pi x} - 1)$

Equation (6) becomes evident from the following physical reasoning. Assume that a given spectral interval $\Delta\nu$ involves absorption bands of two gases. Considering the bands as random objects, we can put forward the idea of correlation between them. If the bands do not correlate, then the mean transmittance of the gas mixture is equal to the product of the mean transmittances of each gas. Mathematically, this can be described in the following way. Let us introduce the density of joint distribution of the line positions ν_{1i} and ν_{2i} of the first and second gases – $P(\nu_{1i}, \nu_{2i})$. Then the mean transmittance of the gas mixture is

$$\bar{O}_\Sigma = \int_{\Delta\nu} Đ(\nu_{1i}, \nu_{2i})\, \dot{O}_1(\nu_{1i})\, \dot{O}_2(\nu_{2i})\, d\nu_{1i}\, d\nu_{2i}. \qquad (7)$$

If the spectra of two gases do not correlate, then $P(\nu_{1i}, \nu_{2i}) = P(\nu_{1i})\, P(\nu_{2i})$ and Eq. (6) follows directly from Eq. (7).



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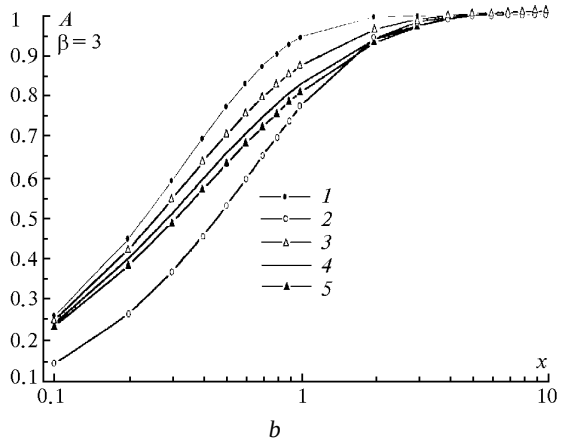

Fig. 2. Absorption functions calculated by different models: Elsasser model (*1*), model of isolated line (*2*), Plass model (*3*), Goody model (*4*), Malkmus model (*5*); β = 0.4 (*a*) and 3 (*b*).

The product rule (6) was studied experimentally in Refs. 61–63 and the following conclusions were drawn. The error of this approximation is low under the following conditions: (a) the interval Δν is wide enough to involve at least several lines of each gas; (b) line positions of two gases are random and not related by some functional dependence; (c) the partial pressure of the buffer gas is much higher than the partial pressure of absorbing gases.

It was found[6] that the error of approximation (6) is random with possible deviations toward both lower and higher values. The experience shows that application of narrow-band transmission functions with the subsequent spectral averaging minimizes this error.

The models described above can be applied to solution of the problems in optical radiation transfer along homogeneous paths in the case that temperature, pressure, and concentration of absorbing gases are constant along the path. As known, in the real atmosphere these parameters vary with altitude. The analytical methods can accurately take into account variations of meteorological parameters along the beam path only in the ideal case, if the absorption line intensities and halfwidths, as well as the relative content of an absorbing gas are coordinate independent. However, such a situation does not exit in the real atmosphere. That is why approximate methods are used for calculating the transmittance of the inhomogeneous atmosphere. The idea of the approximate methods is to reduce case of an inhomogeneous optical path to the corresponding problem for a homogeneous optical path. For this purpose either the method of reduced absorbing mass or the method of weighted mean pressure are usually used.[22,54, 64–66]

3. Combined technique for calculating transmittance

The combined technique for calculating transmission functions[22] was developed on the basis of the models of absorption spectra. This technique employs three models, namely, the Elsasser model, Plass statistical model, and Goody statistical model. Besides the principal equations given in the table, the combined technique uses the following approximations: Goody approximation of a strong line ($x = SW/2\pi\gamma \gg 1$), empirical model (for CO_2 in some spectral intervals), Elsasser approximation of a strong line, and others. The parameters of the models were determined, as a rule, from laboratory measurements of the transmission functions for different content of absorbing gases and different temperatures. In some cases the parameters were determined by fitting the calculated data.

4. Empirical methods for calculating transmission functions

Among the empirical methods, the LOWTRAN method developed in Cambridge for calculating atmospheric absorption has gained the widest acceptance.[18–20] This method allows calculation of the transmission function with resolution of 20 cm^{-1} to be made in the spectral region from 0.25 to 25.0 μm. The transmittance is described by some function

$$T = f(C(\nu)\cdot W),$$

where W is the equivalent absorbing mass,

$$W = \int \rho(z)\left[\frac{P(z)}{P_0}\left(\frac{T_0}{T(z)}\right)^{0.5}\right]^n dz;$$

$C(\nu)$ is the empirical coefficient depending on the frequency ν. The values of the parameters n and $C(\nu)$ and the form of the function f were determined by fitting laboratory data. First this method was realized in the form of nomograms.[18] Its further evolution was connected with the development of the corresponding software. The last version of this software is LOWTRAN 7.

The SOI (State Optical Institute) method is a three-parameter method. The transmittance by the SOI method is calculated as[12–14]:

$$T(\lambda) = \exp\{-\beta_\lambda (W)^{m_\lambda}\},\ W = \int \rho(z)\left[\frac{P(z)}{P_0}\right]^{n_\lambda} dz,$$

where $\rho(z)$ is the absorbing gas concentration, in $cm\cdot km^{-1}$; $P(z)$ is the air pressure, in atm; β_λ, m_λ, and n_λ are empirical parameters.

The SIAO (State Institute of Applied Optics) method. The transmittance is calculated by the equations[15–17]

$$T(\lambda) = \exp\{-\beta_\lambda\, w^{m_\lambda} P^{n_\lambda}\}.$$

Reference 17 gives the parameters β_λ, m_λ, and n_λ for the spectral region from 1 to 14 μm with the resolution $\Delta\lambda$ equal to 0.026–0.1 μm.

The MGO (Main Geophysical Observatory) method in its idea is close to the above methods. The particular equations and numerical data can be found in Ref. 21.

All the above methods of calculating the atmospheric absorption have a common limitation that restricts their practicability. This limitation is associated with the spectral resolution. These methods can be used for calculating the transmission function with the resolution not exceeding that for which the parameters entering the equations were obtained.

In this connection, it is worth notingh the methods of rapid calculation, which employ the ideas of model representation of the absorption spectra.[43–51] Spectral line parameters in these methods are determined from atlases of spectral lines. However, the accuracy of these methods should be checked for any particular spectral region and molecular species. In some cases, one has to refine of the parameters in order to obtain the needed accuracy.

5. Line-by-line method

The line-by-line method of calculating characteristics of the absorption and radiation is a benchmark for verification of various approximate models of transmission. It is also used for direct simulation of radiative transfer in molecular absorbing media. The main idea of this method consists in exact allowance for contribution of each line from a given frequency region $\Delta\nu$ to the total absorption. It has no limitations associated with the spectral resolution and allows one to calculate transmittance for monochromatic radiation. However, its operation takes a long computer time and therefore it is not used in climate modeling.

The low computational speed is caused by a giant number of spectral lines contributing to absorption. This number can achieve tens of thousand. Besides, the absorption coefficients is a rapidly varying function of the frequency ν. Therefore, for detailed description of the absorption spectrum, calculations should be performed with the frequency step comparable with the Doppler halfwidth of a spectral line (~0.0005 – 0.01 cm^{-1} depending on the spectral region). That explains why a great number of papers[23–29] have been devoted to the development of efficient line-by-line algorithms, although they started to be developed as in the 1960's as early (see Refs. 67–69).

5.1. Optimization of the line-by-line method

Various research groups try to shorten the time needed for transmittance computations using the line-by-line method. The main direction of these studies are the following[70]: (1) selection of absorption lines, (2) optimization of the frequency grid, (3) reduction of an inhomogeneous path to a homogeneous one, (4) cutting of the absorption line contour, (5) separation of computation of the selective and continuum absorption, (6) separation of the frequency and altitude dependence of the optical thickness in line wings for an inhomogeneous path, (7) optimization of the algorithm for calculating the Voigt profile. Below we describe the optimization methods which allow most essential reduction of the time needed for computation of the molecular absorption characteristics.[27–29, 71–73]

Selection of absorption lines

A given spectral region $\Delta\nu$ can involve absorption lines of a particular gas that have different intensities. The variability range of the line intensities is rather wide, and the number of lines can be very large. In the case of overlapping bands of different gases, the number of lines can be several hundred thousand (for example, in the 500 – 1300 cm^{-1} region the number of lines of the first six gases included in HITRAN91 (Ref. 74) is about 120 thousand). However, due regard of different content of these gases in the atmosphere, shows that only several thousand lines actually contribute to the absorption. Therefore, it is rather natural to take into account only significant lines in transmittance calculations. Other lines are excluded from the consideration. For this purpose the effective criteria for line selection are needed.

The current algorithms for selection of absorption lines[26,70,71] can be divided into several groups. The simplest algorithms reject the weakest lines with the intensity lower than some preset threshold value. More rigorous algorithms are based on evaluation of the absorption coefficients[26] or optical thickness.[70,71] All these algorithms have one significant drawback: they are inefficient in application to the upper atmosphere. In Refs. 27 and 28 the two-stage selection algorithm was proposed, which makes it possible to overcome this difficulty. At the first step, weak lines whose contribution to absorption is below some preset value are excluded. The second step is the altitude selection, i.e., for every line the altitude is estimated, above which the contribution of this line can be neglected.

Optimization of the frequency grid

When calculating the integral transmittance, one has to calculate spectral transmittance (integrand function) on some frequency grid determined by the quadrature formula. As a rule, a uniform grid is used, which can provide a high accuracy of integral transmittance. In this case computer time is inversely proportional to the grid step.

In recent years the algorithms employing grids with a nonuniform adaptive step responding to the oscillating behavior of the integrand function are widely used.[21,26,29,72,73] Let us consider one of the most effective algorithms – multigrid method proposed in Ref. 29. In this method the nonuniform grid crowding together in the vicinity of line centers is replaced with a series of uniform grids (from seven to twelve grids), whose step increases by the rule $h_l = h_0 2^l$, where h_0 is the step of the finest grid; l is the grid number. The value of $\gamma_V/4$ is used as h_0, where γ_V is the Voigt line halfwidth.

The absorption coefficient is calculated only at grid nodes. The grid number grows with distance off the line center. The values of the absorption coefficient between grid nodes are interpolated. The multigrid method provides for maximum reduction of the time needed for computation of the spectral transmittance without a loss in accuracy. Note that the multigrid method in its idea is close to the method used in the FASCOD algorithm.[75] In this algorithm, every line profile is split into three functions: "fast," "slow," and "very slow" ones. Then these functions are considered independently at three grids with the steps of $h/4$, h, and $4h$.

The multigrid algorithm is two to three times more rapid than the similar one implemented in FASCOD and ten to twenty times more rapid than the algorithm implemented in the GENLN2.

Reducing to a homogeneous path

Computation of integral transmittance of an inhomogeneous path takes a most part of time. In this case, N altitude integrals should be calculated for every grid node. For the Lorentz profile these integrals have the form

$$\tau(\nu, \nu_i) = \frac{1}{\pi\mu} \int_{z_1}^{z_2} \frac{S_i \gamma_i \rho \, dz}{(\nu - \nu_i)^2 + \gamma_i^2},$$

where $\tau(\nu, \nu_i)$ is the contribution of the ith line to the optical thickness at the frequency ν; N is the number of absorption lines. At the minimal step $h_0 = \gamma_d/4$ in the 10-μm spectral region and with the use of eleven grids ($l = 10$) the number of nodes is about 90 in the interval of $\Delta\nu = 1$ cm^{-1} wide. The largest step in this case was ~ 0.25 cm^{-1}. As the frequency interval $\Delta\nu$ was increased up to 10 cm^{-1}, the

number of nodes increased by 40 times. The number of altitude integrals in this case was about 130 *N*.

To decrease the computation time, the Curtis—Godson idea[64,65] is usually used. According to it, the inhomogeneous path is replaced by an equivalent homogeneous one. It is well known that two parameters appear in this case: the first parameter has the meaning of the absorbing mass W_i, and the second one has the meaning of the weighted mean pressure or the weighted mean halfwidth $\bar{\gamma}_i$. The Curtis—Godson scheme was modified in Refs. 28 and 112 so that the computational accuracy was improved to 0.5%.

In conclusion, it should be noted that the use of line selection is most effective if one needs to conduct repeated calculations in a given spectral region and different atmospheric conditions, since in this case lines are selected only once and then they are repeatedly used in the transmittance calculations.

By combining the multigrid algorithm, the two-stage selection of absorption lines, and the newly developed method of reducing inhomogeneous paths to the homogeneous ones in a unified computation scheme, a new very efficient rapid algorithm has been developed for computing the transmittance of a gas medium. It allows the computation time to be reduced by two to three orders of magnitude with the mean loss in accuracy no more than 0.5%.

5.2. Influence of uncertainties in spectroscopic information on accuracy of the line-by-line calculations of thermal radiation

The parameters of spectral lines in modern spectroscopic databases like HITRAN are known accurate to some error. This fact should be taken into account in simulations. Regardless of how accurate are the calculation methods we use, the errors in the spectroscopic parameters lead to uncertainties in the final results. For this reason one should consider how strong can be the influence of errors in spectroscopic parameters on the radiation characteristics.

Analysis made in Ref. 76 with CH_4 molecule taken as an example in the 1000–1400 cm^{-1} region showed that errors in calculation of absorption coefficients can be rather high and achieve tens percent. However, the error in transmission function with a 5 cm^{-1} wide square-shaped instrumental function did not exceed 1% provided that uncertainties in the line intensities and halfwidths can be considered as random values with a zero mean. The error in radiative fluxes in this case does not exceed 0.1 W/m^2. Thus, already at the spectral resolution of 5 cm^{-1} the random errors in the spectral line parameters can be neglected.

The situation is quite different if there are systematic errors in the spectral line parameters. In Ref. 77 it was noted that 5–10% systematic errors in the spectral data for strong H_2O absorption bands gives the error in the downwelling fluxes of 0.3 to 0.6 W/m^2. The total 10% systematic error in the selective absorption of CO_2, H_2O, and O_3 can give errors in the downwelling flux up to 1 W/m^2, what is less than 0.5% of the flux at the boundaries. Thus, the accuracy of spectroscopic data is sufficient for calculating the fluxes of thermal radiation accurate to within 0.5%, what corresponds to the capabilities of atmospheric experiments.

6. Method of *k*-distribution

The method called *k*-distribution is now widely used. The general approach was formulated by Lebedev in 1936. However, in practice this method has been being used only from the 1970's for describing the absorption by atmospheric gases in numerical schemes for calculation of solar radiation in the multiple scattering approximation. The term "*k*-distribution" was introduced by Arking and Grossman in Ref. 78, in which the transmission function of a homogeneous path was presented in the following form:

$$T(W) = \int_0^\infty f(k) \exp(-kW)\, dk, \tag{8}$$

and $f(k)$ was interpreted as the distribution of the absorption coefficient probability. The reasoning used by Arking and Grossman was as follows. The function

$$g(k) = \int_0^k f(k)\, dk \tag{9}$$

is monotonically increasing, and $g(\infty) = 1$, that is, $g(k)$ can be treated as a distribution function, and $f(k)$ can be considered as the distribution density. In Ref. 41 it was shown that this assumption is not fully justified. Nevertheless, the method of *k*-distribution has received rather wide use, and we also will use this terminology. The simplest interpretation of the method of *k*-distribution was given in Ref. 78, where it was proposed to divide the spectral interval $\Delta\nu$ into N subintervals $\Delta\nu_i$ in width, so that the absorption coefficient $k(\nu)$ within each subinterval is a smooth and monotonic function, and the derivative of this coefficient with respect to ν vanishes at the boundaries. Thus, for every interval we can construct the inverse function $\nu_i = k^{-1}(\nu)$ and change the variables:

$$T(W) = \frac{1}{\nu_2 - \nu_1} \sum_{i=1}^{N} \int_{\Delta\nu_i} \exp(-k(\nu)\, W)\, d\nu =$$

$$= \frac{1}{\nu_2 - \nu_1} \sum_{i=1}^{N} \int_{k_{i,\min}}^{k_{i,\max}} \exp(-kW) \left| \frac{d\nu_i(k)}{dk} \right| dk. \tag{10}$$

In Ref. 30 the stepwise functions of the form[79]

$$U_+(x) = \begin{cases} 0, & x \le 0 \\ 1, & x > 0. \end{cases}$$

were used. This allowed the integration limits in Eq. (10) to be extended from zero to infinity and the function $f(k)$ to be presented in the form

$$f(k) = \sum_{i=1}^{N} f_i(k) = \frac{1}{\nu_2 - \nu_1} \sum_{i=1}^{N} \left| \frac{d\nu_i(k)}{dk} \right| \times$$

$$\times [U_+(k - k_{i,\min}) - U_+(k - k_{i,\max})]. \tag{11}$$

The modulus in Eq. (11) arises for the equation to be universal for subintervals, where the function $k(\nu)$ can both increase and decrease. Because of this change Eq. (8) is used instead of Eq. (10).

From the formal point of view, this is quite correct. The integrand function has a limited number of breaks at the points where the derivative $dk(\nu)/d\nu$ is zero and, consequently, there is no contradiction in the existence of the integral in Riemann sense. However, a problem arises in

numerical implementation of this scheme. This problem is connected with the fact that the integral in Eq. (8) becomes improper, and the number of break points is proportional to the number of spectral lines and can be rather large.

Figures 3 and 4 exemplify the spectral dependence of the molecular absorption coefficient and the typical view of the function $f(k)$. The finite values of the function $f(k)$ at the break points are caused by the finite step of quantization when calculating the derivatives. At the first sight, it seems so that introduction of the function $f(k)$ does not simplify the computational scheme, but even complicates it. That is why this method was initially applied only to the models of absorption bands, in which the obtained $f(k)$ function was smooth with only two break points. Reference 78 describes the use of this method as applied to the model of an isolated line, Elsasser model, and Goody statistical model. In Ref. 30 this method was applied to the Malkmus statistical model, which then has gained wide acceptance until now.[31,32]

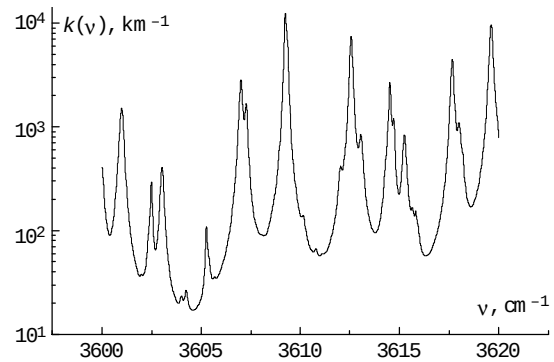

Fig. 3. Spectral dependence of the H_2O molecular absorption coefficient; meteorological model of midlatitudinal summer; altitude $h = 0$ km.

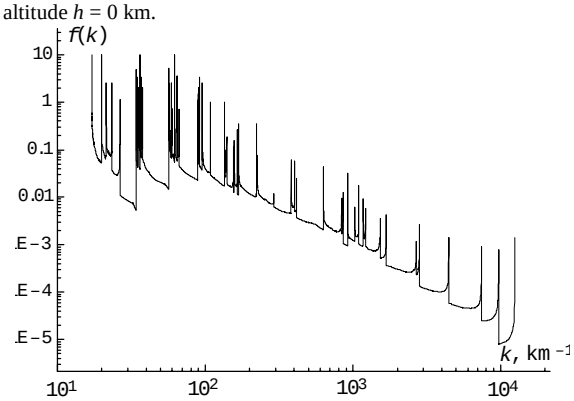

Fig. 4. Function $f(k)$ calculated from the spectral dependence of the H_2O absorption shown in Fig. 3.

In principle, the methods for calculating the integral of such a kind with the integrand function having singularities are developed rather well.[80,81] The integrand in such cases is presented as a product of two functions, one of which (singular) is declared to be the weighting function, while the other (smooth) is described by a power polynomial. The function $f(k)$ can be considered as a weighting function, and the exponent can be presented in the form of an interpolation polynomial. As a result, we obtain a series of exponential functions instead of Eq. (8). To find the coefficients C_i, we have to calculate numerically the integrals of the following form:

$$I_i = \int k^i f(k)\, \mathrm{d}k.$$

It can be shown that

$$I_i = \frac{1}{\Delta\nu} \int_{\nu_1}^{\nu_2} [k(\nu)]^i \, \mathrm{d}\nu,$$

and some of these integrals can be calculated analytically, for example

$$I_0 = 1, \; I_1 \cong \frac{1}{\Delta\nu} \sum_{k=1}^{N} S_k,$$

where N is the number of lines in the spectral interval $\Delta\nu$. Nevertheless, some integrals of the rapidly varying function $k(\nu)$ are to be calculated numerically. However, by this the task is not yet completed, since the next step is to construct a polynomial of the closest approximation to the exponential function with the variable k varying in a wide range. In principle, this problem is solvable for integral functions,[81] and the exponent belongs to this category. Nevertheless, the problem was not solved in such a form because of computational difficulties.

Further improvement of the method of k-functions is one more change of variables in the integral (8) in the form (9). This leads to the following equation[32]:

$$T(W) = \int_0^1 \exp(-k(g)\, W)\, \mathrm{d}g,$$

where $k(g)$ is the function inverse to $g(k)$. This is possible since the function $g(k)$ is monotonically decreasing. The typical view of $k(g)$ is shown in Fig. 5. These calculations used the same data as those for Figs. 3 and 4. In Ref. 32 it was noted that $k(g)$ can be easily obtained by sorting the absorption coefficients $k(\nu)$ calculated by the line-by-line method.

The Laplace transform allows the problem of parameterization of the transfer equation to be considered from a more general point of view.[33,41] Equation (8) can be considered as a Laplace transform,[30] if $T(W)$ is an analytic function in the half-plane $\mathrm{Re}W > s_0$ and vanishes at $|W| \to \infty$ in any half-plane $\mathrm{Re}W \ge a > s_0$ uniformly with respect to $\arg W$, and the integral $\int_{a-i\infty}^{a+i\infty} T(W)\, \mathrm{d}W$ converges absolutely. In this case $T(W)$ is the image of the function[82]:

$$f(k) = \frac{1}{2\pi i} = \int_{a-i\infty}^{a+i\infty} T(W) \exp\{kW\}\, \mathrm{d}W.$$

These conditions were proved to be met strictly only for the band models.[30,33] However, this does not reduce the general character of the conclusions. This approach is widely used for calculating the fluxes of thermal radiation thus providing, first, high accuracy comparable with that of the line-by-line method and, second, significantly shorter computation time.

One more advantage of this approach is that it allows the problem of parameterization of transmittance to be solved in a natural way by use of a series expansion over exponential functions.

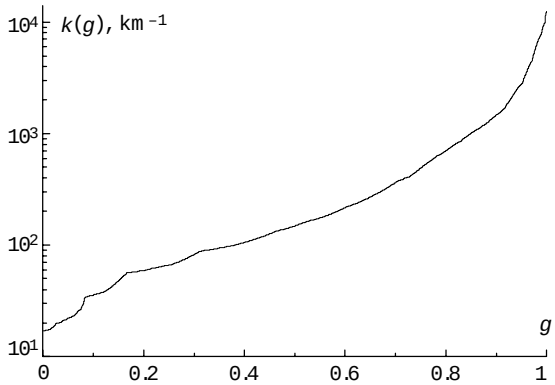

Fig. 5. H_2O absorption coefficient in the space of cumulative frequencies. Conditions are the same as mentioned in Fig. 3.

7. Expansion of transmission functions into a series over exponential functions

Presentation of transmission functions in the form of a series expansion over exponential functions has some advantages over the methods of models. These advantages are the following:

1. The series expansion over exponential functions allows the interaction of molecular absorption and scattering to be completely taken into account. They are most efficient when the transfer equation is solved by the Monte Carlo method, since in this case there is no need for use of the approximation of independent absorption and scattering processes. This statement will be explained below.

2. No one model can give an accuracy comparable with that given by this method. Thus, for example, Ref. 83 gives the scatter plots of the transmission functions calculated by the line-by-line method and different approximate methods. The maximum discrepancy is observed for the band method based on the fit of parameters to benchmark calculations, and the least discrepancy is observed for the method of series expansion over exponential functions, which is closest to the line-by-line method.

3. The multiplicative presentation of the transmission function is valid for exponents, as for the line-by-line method, but invalid for the method of models.

4. The parameters of the series over exponential functions can be readily and naturally calculated based on the line-by-line method. The parameters for the method of models are determined from more bulky model calculations of the transmission functions (see, for example, Ref. 84). The use of laboratory measurements to determine the parameters of the model of the transmission function is not always correct for calculating the radiation on atmospheric paths. Thus, for example, the radiative cooling rate calculated by the method of models can differ by two times from the highly accurate line-by-line calculations.[85]

7.1. Some mathematical aspects of the series expansion of transmission functions over the exponential functions

The transmission function for the plane-parallel atmosphere can be written as

$$T_\nu = \frac{\int\limits_{\Delta\nu} G(\nu') \exp\left\{-\int\limits_{z_1}^{z_2} \sum\limits_j k_j(\nu, z)\, \rho_j(z)\, dz\right\} d\nu'}{\int\limits_{\Delta\nu} G(\nu')\, d\nu'}, \qquad (12)$$

where $k_j(\nu, z)$ is the absorption coefficient of the jth gas at the frequency ν and altitude z; $\rho_j(z)$ is the concentration of the jth gas; $G(\nu')$ means either the instrumental function of a device or the function of an extraterrestrial source (for example, spectral intensity of the solar radiation). Atmospheric sources, in principle, can be taken into account as well, but then hard-to-solve problems arise in the parameterization.

By applying numerical methods for frequency integration of Eq. (12), we can readily obtain the series over exponential functions:

$$T_\nu = \sum_{n=1}^{N} C_n \exp\left\{-\int\limits_{z_1}^{z_2} \sum\limits_j k_j(\nu_n, z)\, \rho_j(z)\, dz\right\} + R_N. \qquad (13)$$

However, the error of the quadrature formula R_N is small only if the series is long enough. To ensure the 1% accuracy required in calculating the transmission functions about several thousand terms are, as a rule, needed in the series, if the width of the spectral interval is several tens of wavenumbers (cm^{-1}).

The up-to-date methods of parameterization of the transmission function allows it to be presented in the form of the series (13) with the number of terms not exceeding 10 and the error not exceeding 1%, except for the cases of overlapping absorption bands of different gases, which should necessarily be taken into account. In this case the error of parameterization can increase a little.[34,77] Such a serious reduction of the number of terms without significant loss in accuracy is possible if the Laplace transformation is applied to Eq. (12). Owing to this transformation, the rapidly oscillating integrand function can be replaced by a monotonic one. For details see Refs. 30, 33, 34, 41, and 77.

The further application of quadrature formulas gives a short series over exponential functions. The methods of numerical integration are well developed, and there are many modifications of the technique of parameterization of the transmission functions. Thus, for example, in Ref. 32 the method of rectangles with the adaptive step was used. The step was taken from some intuitive reasoning, what naturally cannot guarantee high accuracy of approximation especially if the series is short. A more rigorous approach was applied in Refs. 33, 36, 40, and 86, where the Chebyshev or Gauss quadratures were used. From the theory of numerical methods it follows that with the same number of terms in the series the Gauss quadrature gives higher accuracy than the Chebyshev quadratures does, since the former is accurate for integrand functions being polynomials of $(2n - 1)$ power, whereas the later is accurate only for polynomials of n power. Nevertheless, application of Chebyshev quadratures can be sometimes justified, if the integrand function is given with a random error (the coefficients C_k are of the same value and, consequently, the random error is minimal[87]).

Generally speaking, the problem on the possibility of using series expansion of the transmission function over

exponential functions can be solved by considering the system of exponential functions. There are two aspects here. The first is whether such an expansion exists or not, and the second is whether or not it is possible to describe the transmission function by a short series.

It is well-known that not every function can be approximated by a series over exponential functions, for example, it is not the case with a constant.[88] Therefore, we should determine whether or not the transmission functions belong to the class of functions which can be described by the complete system of exponential functions. This problem can be solved if power-law functions ($\{x^{n_i}\}_{i=1}^{\infty}$, $-1/2 < n_1 < n_2 < ...$), for which the Munts theorem exists,[89] are put in correspondence with the exponential functions. The Munts theorem states that if the series $\sum_{i=1}^{\infty} n_i^{-1}$ diverges, the necessary and sufficient conditions of completeness of the system of power-law functions in the space $C_2(0, 1)$ are fulfilled. The completeness of the system of functions guarantees fulfillment of the Parseval equality and convergence of the Fourier series. The system of exponential functions is definite in the space $C_2(0, \infty)$. The power-law functions can be put in correspondence with the exponential ones $x^{n_i} \leftrightarrow \exp(-m_i y)$ if the spaces $C_2(0, 1)$ and $C_2(0, \infty)$ are isomorphic.[90] To do this, one needs that the norm $\|x^{n_i}\|$ in the space $C_2(0, 1)$ to be equal to the norm $\|\exp(-m_i y)\|$ in the space $C_2(0, \infty)$. Any square-integrable function in the space $C_2(0, \infty)$ can be presented in the form of a series expansion over exponential functions, if the coefficients m_i satisfy the condition $0 < m_1 < m_2 < ...$ and the series of these coefficients $\sum_{i=1}^{\infty} m_i^{-1}$ diverges.

It can be readily shown that the transmission function is a square-integrable function in the space $C_2(0,\infty)$. For simplicity let us consider a homogeneous path. The norm of the transmission function is calculated through the absorption coefficients $k(\nu)$:

$$\|T(W)\|^2 = \int_0^{\infty} T^2(W)\, \mathrm{d}W = \frac{1}{(\Delta\nu)^2} \int_{\Delta\nu} \mathrm{d}\nu \int_{\Delta\nu} \frac{\mathrm{d}\nu'}{k(\nu) + k(\nu')}. \qquad (14)$$

Since $k(\nu) > 0$, it follows from Eq. (14) that $\|T(W)\| < \infty$. From this it follows that there exists the expansion of the transmission function into a series over exponential functions for the spectral regions where the absorption coefficient is not zero. In practice, absorption coefficients are sometimes set zero in the regions where absorption is low. However, the theory and practice show that this can be a source of problems arising in expanding the transmission functions into a series over the exponential functions.

Since the system of exponential functions is complete, we can construct the orthogonal basis, in terms of which the transmission function is expanded into a Fourier series. The details can be found in Ref. 40. The Parseval equality guarantees the uniform convergence of the series over exponential functions. Simulation showed that even for spectral intervals 1500 cm^{-1} as wide, six to seven terms of the series is sufficient to describe the transmission function accurate to 1%.

7.2. Application of exponential series to solution of the equation of short-wave radiative transfer by Monte Carlo method

The main advantage of the Monte Carlo method is its versatility. It suits inhomogeneous cases, horizontally and vertically inhomogeneous cloud layers, as well as non-plane-parallel atmospheres. Besides, this method allows molecular absorption to be taken into account almost exactly. However, the use of direct methods for taking into account molecular absorption is computationally very inefficient, since one first have to make calculations at every frequency and only then to average the results. The speed can be increased in this case by the approach described in Refs. 91 and 92. In this approach, when simulating the free paths of photons, their wavenumbers ν also form the random-size sample uniformly distributed on the interval $\Delta\nu$. In fact, to achieve the accuracy of 0.1% for the 0.2–100 μm spectral region, it is sufficient to use in calculations the mean frequency step of 1 cm^{-1}. In Ref. 93 the accuracy of frequency integration of radiative characteristics has been considered from the viewpoint of the probability theory, however, they obtained quite similar estimate.

Nevertheless, the line-by-line methods remains too cumbersome even with that rough step. More efficient ways of calculating molecular absorption require introduction of the transmission function and their following parameterization. The main problem in this case is connected with the fact that the transmission function is no longer the Bouguer exponent, since the transmittance algorithm nonlinearly depends on the path length even if the path is homogeneous. However, the presentation of the transmission function in the form of a series over exponential functions, as will be shown below, lifts this restriction.

It should be noted that recently some criticism has appeared in the literature[94] concerning the efficiency of application of the series expansion over exponential functions. However, the recent advances in the development of this method allowed the restrictions associated with the atmospheric inhomogeneity and overlapping of absorption bands to be removed. Besides, the numerical methods were developed for optimal presentation of the transmission functions by a series over exponential functions. This is considered in the given paper.

For further analysis it is convenient to use the transfer equation in the most general case of inhomogeneous scattering and absorbing atmosphere. We consider the standard problem, in which the underlying surface is a black body. Usually, the lower boundary is reflecting, but nevertheless a solution to this problem can be sought by solving the standard problem.[94] The equation for this was derived in Ref. 95. The integral transfer equation with the generalized kernel can be presented in the form[95,96]

$$Z(\mathbf{x}) = \int_X k(\mathbf{x}', \mathbf{x})\, Z(\mathbf{x})\, \mathrm{d}\mathbf{x}' + \Psi(\mathbf{x}), \qquad (15)$$

where $Z(\mathbf{x})$ is the sought function, which is defined as collision density related to the radiation intensity as

$$I(\mathbf{r}, \mathbf{\Omega}) = |\mu_\upsilon| S_\upsilon Z(\mathbf{r}, \mathbf{\Omega})/[\alpha(\mathbf{r})],$$

where X is the phase space of coordinates and directions, $X = (\mathbf{r}, \mathbf{\Omega})$; μ_0 is the secant of the solar zenith angle; S_υ is the solar constant; α is the extinction coefficient. The generalized kernel is described by the equation[95]

$$k(\mathbf{x}', \mathbf{x}) = \alpha(\mathbf{r}) \frac{\varpi(\mathbf{r}') f(\mathbf{r}, \mathbf{\Omega}, \mathbf{\Omega}') \exp\{-\tau(\mathbf{r}, \mathbf{r}')\}}{|\mathbf{r} - \mathbf{r}'|^2} \times$$

$$\times \delta\left(\Omega - \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}\right), \quad (16)$$

where $\varpi(\mathbf{r}')$ is the single scattering albedo; $f(\mathbf{r}, \mathbf{\Omega}, \mathbf{\Omega}')$ is the scattering phase function. The distribution density of sources $\Psi(\mathbf{x})$ for the standard problem is

$$\Psi(\mathbf{x}) = \alpha(\mathbf{r}) \exp\{-\tau(\mathbf{r}, \mathbf{r}_\infty)\} \delta(\mathbf{\Omega} - \mathbf{\Omega}_\upsilon). \quad (17)$$

The solution of the integral equation (15) can be presented by Neumann series

$$z = \sum_{i=1}^{\infty} K^i \Psi. \quad (18)$$

Some aspects concerning the existence of the solution are considered in Refs. 95 and 96. For a convenience let us present Eqs. (16) and (17) in the form

$$k(\mathbf{x}', \mathbf{x}) = \alpha(\mathbf{r}) \frac{\alpha_a(\mathbf{r}')}{\alpha(\mathbf{r}')} \exp\{-\tau_m(\mathbf{r}, \mathbf{r}')\} k_0(\mathbf{x}', \mathbf{x});$$

$$\Psi(\mathbf{x}) = \alpha(\mathbf{r}) \exp\{-\tau_m(\mathbf{r}, \mathbf{r}_\infty)\} \Psi_0(x),$$

where

$$k_0(\mathbf{x}', \mathbf{x}) = \frac{f(\mathbf{r}, \mathbf{\Omega}, \mathbf{\Omega}') \exp\{-\tau_a(\mathbf{r}, \mathbf{r}')\}}{|\mathbf{r} - \mathbf{r}'|^2} \times$$

$$\times \delta\left(\mathbf{\Omega} - \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}\right);$$

$$\Psi_0(\mathbf{x}) = \exp\{-\tau_a(\mathbf{r}, \mathbf{r}_\infty)\} \delta(\mathbf{\Omega} - \mathbf{\Omega}_\upsilon);$$

α_a is the aerosol scattering coefficient; τ_m and τ_a are the optical thickness due to molecular absorption and aerosol scattering, respectively. It is noteworthy that $\Psi_0(\mathbf{x})$ and $k_0(\mathbf{x}', \mathbf{x})$ do not include the molecular absorption characteristics.

Let us consider the first two terms of the series (18):

$$K\Psi = \int_X k(\mathbf{x}_1, \mathbf{x}) \Psi(\mathbf{x}_1) \, d\mathbf{x}_1 = \alpha(\mathbf{x}) \int_X k_0(\mathbf{x}_1, \mathbf{x}) \times$$

$$\times \Psi_0(\mathbf{x}_1) \alpha_a(\mathbf{r}_1) \exp\{-\tau_m(\mathbf{r}_1, \mathbf{r}_\infty) - \tau_m(\mathbf{r}_1, \mathbf{r})\} \, d\mathbf{x}_1, \quad (19)$$

$$K^2\Psi = \int_X \int_X k(\mathbf{x}_1, \mathbf{x}) k(\mathbf{x}_2, \mathbf{x}_1) \Psi(\mathbf{x}_2) \, d\mathbf{x}_1 \, d\mathbf{x}_2 =$$

$$= \alpha(\mathbf{x}) \int_X k_0(\mathbf{x}_1, \mathbf{x}) k_0(\mathbf{x}_2, \mathbf{x}_1) \Psi_0(\mathbf{x}_2) \alpha_a(\mathbf{r}_1) \alpha_a(\mathbf{r}_2) \times$$

$$\times \exp\{-(\tau_m(\mathbf{r}_2, \mathbf{r}_\infty) - \tau_m(\mathbf{r}_1, \mathbf{r}) - \tau_m(\mathbf{r}_2, \mathbf{r}_1))\} \, d\mathbf{x}_1 \, d\mathbf{x}_2. \quad (20)$$

When integrating Eq. (16) over frequency, we can isolate the transmission function due to molecular absorption. To do this, we have to select such spectral interval $\Delta\nu$, within which the solar constant and the scattering coefficients can be considered constant. In this case all factors not included into the optical thickness τ_m can be removed from the integrand function. With the allowance made for Eqs. (16), (19), and (20), we have the transmission function in the form

$$T = \frac{1}{\Delta\nu} \int_{\Delta\nu} \exp\{-\tau_m\} \, d\nu.$$

It is easy to make sure that the presentation of the transmission function as a series over the exponential functions

$$T = \sum_{i=1}^{n} C_i \exp\{-\tau_{m,i}\} \quad (21)$$

does not change the functional form of the solution.

It should be noted that the condition that the solar constant does not change within $\Delta\nu$ is not obligatory. To overcome this restriction, the transmission function can be re-defined:

$$T = \int_{\Delta\nu} S_\upsilon(\nu) \exp\{-\tau_m(\nu)\} \, d\nu \Big/ \int_{\Delta\nu} S_\upsilon(\nu) \, d\nu.$$

In this case the transmission function also can be presented in the form (21) (Refs. 34 and 76). Thus, for quite wide spectral intervals $\Delta\nu$, which can achieve 100 cm^{-1} and more, the transmission function can be described correctly using five to six terms of the series. The result obtained can be interpreted in the following way: the optical thickness in Eq. (21) is considered as a thickness at some specially selected frequency ν_i. In this case, to take into account molecular absorption in the spectral region $\Delta\nu$, one has to solve the transfer equation for these given frequencies and then to sum the solutions with the weights C_i. It should be emphasized that no assumptions on atmospheric homogeneity were used here.

8. Models of continuum absorption

Numerous experimental facts indicate that the line shape at large detuning from the resonance frequency has some features which manifest themselves in atmospheric transmission windows. Most important in calculation of the energy balance is the 8–12 μm atmospheric transmission window. The water vapor continuum absorption having its origin in wings of far lines contributes markedly to radiative processes.

To illustrate the role of continuum, Fig. 6 shows the difference between the upwelling flux at the upper atmospheric boundary and the downwelling flux at the ground level with and without the account of water vapor continuum.

One can see from Fig. 6 that the water vapor continuum absorption contributes significantly to the radiative balance of the atmosphere. The principal difference between the continuum absorption and selective one is that the sensitivity of radiative fluxes to small errors in the coefficients of continuum absorption is very high as compared to those in the coefficients of selective absorption. This is caused by the fact that saturation is observed in absorption bands, whereas the continuum

absorption, although being relatively low, contributes to a wide spectral window of 8–12 μm.

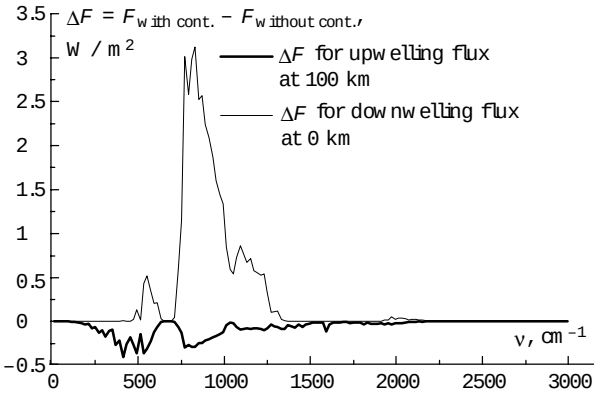

Fig. 6. Spectral contribution of water vapor continuum absorption to radiative fluxes. In calculations the absorption by H_2O, CO_2, O_3, CH_4, and N_2O was taken into account.

For these reasons the problem of taking into account the continuum absorption has long been discussed and is of interest until now. A number of papers have been devoted to theoretical and experimental aspects of this problem. The detailed description of the problem of continuum absorption can be found in Refs. 97 and 98. Here we only briefly present the most known approximations of continuum absorption, which are now in use in numerical simulation of the radiative transfer in the Earth's atmosphere.

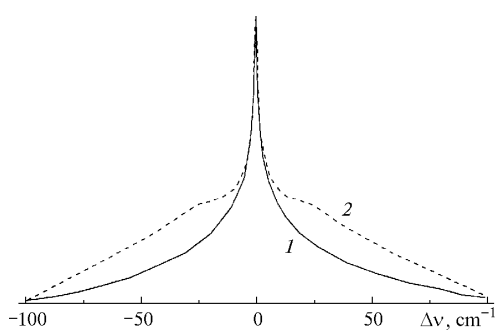

Fig. 7. H_2O line shape in the case of broadening by nitrogen molecules: Lorentz profile (*1*); profile according to the CKD2–2 model[37] (*2*).

According to current ideas, the H_2O absorption line profile near the center is well described by the Lorentz function. Then we observe an excess over the Lorentz profile and a fast exponential decay in the far periphery.[97,98] The typical absorption line profile is shown in Fig. 7.

It should be emphasized that the line shape used in Ref. 99 is based on empirical formulas, therefore it ignores some fine effects noticed in Refs. 97 and 98. In particular, from the theory of the line profile it follows that the line shape must be asymmetric. Another important fact established in Refs. 97 and 98 is that the temperature dependence of the absorption coefficients depends on detuning from the resonance frequency.

The continuum absorption coefficient is usually written as

$$k_{cont}(\nu) = k_{exp}(\nu) - k_L(\nu),$$

where $k_{cont}(\nu)$, $k_{exp}(\nu)$, and $k_L(\nu)$ are, respectively, the coefficient of continuum absorption, the experimentally measured coefficient, and that calculated using Lorentz profile. When calculating $k_L(\nu)$, the procedure of profile cutting at some detuning from the resonance frequencies (as a rule, it is equal to 10–25 cm^{-1}) is usually applied. This allows pre-calculation of $k_{cont}(\nu)$, which is a slowly varying function as compared with $k_L(\nu)$, to be made for the desired temperature and pressure ranges. This information on $k_{cont}(\nu)$ allows a significant economy of computation time in line-by-line calculations. As a result of such a procedure of determination of the continuum absorption coefficient, the fine structure of $k_{cont}(\nu)$ manifests itself in the absorption bands. This fact was first noticed in 1989 in Ref. 100, and in 1998 other investigators[101] also faced this problem in processing of high-resolution spectra. In the atmospheric transmission window, the relation between the selective and continuum absorption caused by the wings of strong H_2O rotational and 6.3-μm bands is significantly different, and the continuum absorption has a smooth spectrum.

Because of the complexity of the problem of describing the intermolecular interactions, all the current models of the line profile which describe the intensity distribution at far periphery are parametric, and their parameters are determined by fitting theoretical models to experimentally measured absorption coefficients. As a result, the quality of calculations depends on the quality of experimental information.

We have intercompared five models of continuum, three of which are generalizations of laboratory experiments[102–104] and others use the data of field measurements.[105,106] The models from Refs. 102–104 are defined only for the 8–12 μm, therefore the data were compared just in this interval (Fig. 8).

Figure 9 shows the radiative cooling rate for the same models as in Fig. 8.

It is seen from Fig. 9 that the radiative cooling rate calculated by the models from Refs. 102 and 105 is lower than that calculated by the other models.

Simulation was also conducted for the downwelling fluxes since they are most sensitive to continuum absorption. Comparison of the models from Refs. 102 and 105 assuming the conditions of midlatitudinal summer showed close results, whereas calculations by the models from Refs. 103 and 104 were close to each other but differed by roughly 4–5 W/m^2 from those by the models from Refs. 105 and 107 for summer.

The correction of the temperature dependence of the H_2O continuum proposed in Ref. 106 did not clarify the situation, because the differences even increased. The main difference of the model proposed in Ref. 106 from the others is caused by the stronger temperature dependence of the coefficients of continuum absorption.

It should be noted that correct measurement of the coefficients of continuum absorption at low temperature is now rather problematic, because of their low values. That is why the comparison of the calculated data with the field measurements is very important.

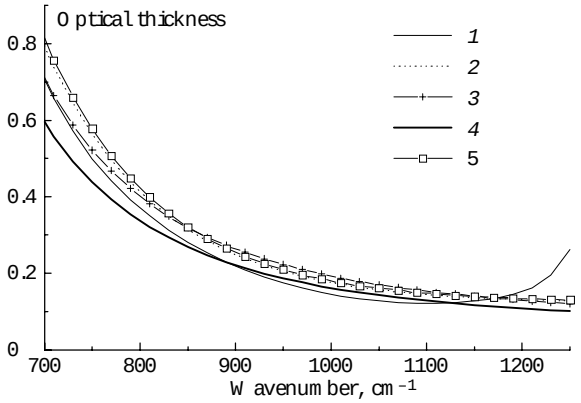

Fig. 8. Optical thickness of the ground layer as a function of wavenumber. Path of 1 km length, midlatitudinal summer meteorological model. Models of continuum: Ref. 102 (*1*), Ref. 103 (*2*), Ref. 104 (*3*), Ref. 105 (*4*), and Ref. 106 (*5*).

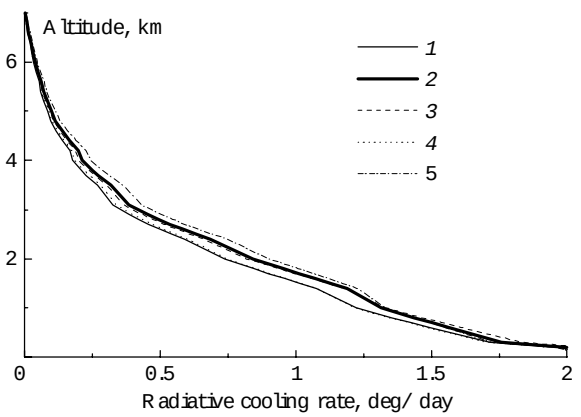

Fig. 9. Spectral component of radiative cooling rate of the atmosphere under conditions of midlatitudinal summer (with only the 8–12 μm spectral interval taken into account). Calculations were made for the same models as in Fig. 8.

Such a comparison was made in Ref. 107, where the calculated and experimentally measured downwelling longwave radiative fluxes were compared. This allowed Ellington[107] to conclude that the CKD2-2 model[99,101] ensures the rms deviation of the calculated data from the experimental ones to be at the level of 2 W/m^2. If this error is related to the uncertainty in the continuum absorption, then numerical estimates give the value of this uncertainty about 4–5% at positive air temperatures. Now this estimate is most realistic. A similar estimate has been obtained in Ref. 103. It should be noted that the error of 2 W/m^2, mentioned above, characterizes the rms deviation. At the same time, some errors were ±5 W/m^2 as high (Ref. 107), what is not that optimistic. Besides, from the histogram presented in Ref. 107 it is seen that errors do not obey normal distribution. This is indicative of the presence of unidentified factors, which, in our opinion, are mostly related to the continuum absorption.

The results described above indicate that the errors in spectral line parameters give a significantly smaller contribution to the uncertainty of calculation of downwelling fluxes as compared to the continuum absorption. Therefore, the error in calculation of fluxes is mostly caused by the uncertainty in the continuum absorption coefficients and their temperature dependence.

9. Intercomparison of radiative models

Models of the longwave radiation of the atmosphere were compared within the framework of the international work group.[6] Thirty eight research groups were involved in this project. Calculations were performed by the line-by-line method and with the use of various approximate models. The results of line-by-line calculations and experimental finding were compared as well.

To check the efficiency of radiative models, all the participants of the international work group were proposed to simulate the radiative characteristics for 55 different scenarios of the state in a clear sky atmosphere and six scenarios in the cloudy atmosphere. The LBL calculations made in the Geophysical Fluid Dynamics Laboratory were used as a benchmark.[6]

Some results of intercomparison of the radiative models borrowed from Ref. 47 are shown in Figs. 10 and 11. Figure 10*a* shows the distribution histogram of deviations from the LBL data for the downwelling longwave flux $F^{\downarrow}$ at the ground level. In calculations H_2O, O_3, and CO_2 were taken into account. The CO_2 content was taken equal to 300 ppmV. From Fig. 10 it is seen that 27 of 39 models (69%) for this scenario deviate from the benchmark calculations by ±2%; the rest models, except for one, fall within ±6%. The same results were obtained for ΔF at the level of tropopause and for $F^{\uparrow}$ at the top of the atmosphere.

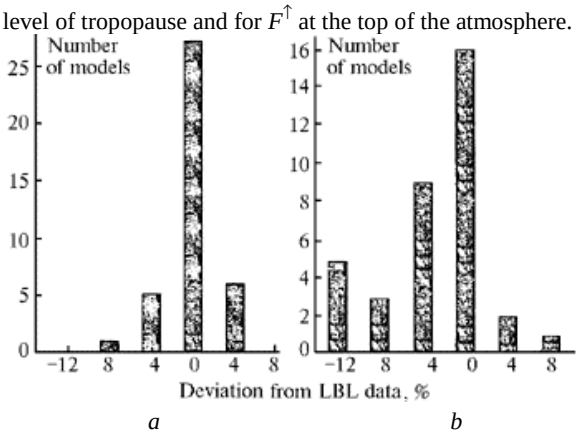

Fig. 10. Results of intercomparison. Atmospheric model of the midlatitude summer (H_2O, O_3) was used. The CO_2 concentration is equal to 300 ppmV, $F^{\downarrow}$(LBL) = 342 W/m^2: $F^{\downarrow}$ at the ground level (*a*); divergence of the flux ΔF_{net} in the troposphere (0–13 km), ΔF_{net}(LBL) = 193.7 W/m^2 (*b*).

Comparison of the calculated results for ΔF_{net} given in Fig. 10*b* shows that 16 of 36 models give the error as compared with the LBL data within ±2%, 27 models give the deviation within ±6%, 31 models fall within the ±10% error. Five models give the discrepancy more than 10%.

In Ref. 6 different methods were used to test the models. In particular, the models were compared with excluded absorption by CO_2 and H_2O continuum. In this case, even larger deviations between models were observed. On the whole, continuum and interfering gases hide wide differences between the models of gas absorption.

Figure 11 compares the accuracy characteristics of different algorithms for calculating thermal radiative fluxes at the level of tropopause with the effect from CO_2 doubled

content by the data of Ref. 6. From Fig. 11 it is seen that the rms deviation between fluxes calculated by the models significantly exceeds the effect of CO_2 doubling.

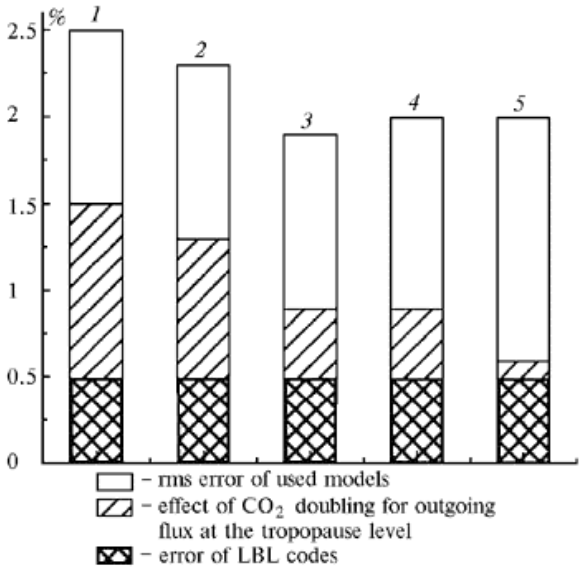

Fig. 11. Intercomparison of calculated deviations of the outgoing longwave radiative flux at the level of tropopause at doubled CO_2 concentration with the accuracy characteristics of the LBL codes and used models: tropics (*1*), midlatitude summer (*2*), midlatitude winter (*3*), polar summer (*4*), and polar winter (*5*).

To sum up the results of intercomparison of the radiative models, in Ref. 6 it was noted that once the procedure of altitude integration was improved, the difference between the narrow-band models and the LBL data was about ±2% for the fluxes at the atmospheric boundaries, ±5% for the flux divergence in the troposphere, and about 5% for the change ΔF at the tropopause level at doubling the CO_2 content.

The results of intercomparison among different models showed that high-resolution atmospheric measurements of the downwelling fluxes are needed. The results of comparison between the experimental and calculated data are given in Ref. 107, in which it was noted that improvement of the model of continuum absorption resulted in the close agreement between the line-by-line calculations and experimental data for the longwave downwelling fluxes (the rms deviation of 2 W/m^2 and maximum deviations of 5 W/m^2). This accuracy is acceptable for calculation of fluxes in climate problems. Comparison of the experimentally measured spectra of the solar radiation having passed through the atmosphere with the calculated data is given in Ref. 108. The measurements were conducted in the 2000–10000 cm^{-1} spectral region with the spectral resolution of 0.6 cm^{-1}. The deviation of the calculated data from the experimental ones did not exceed 1 W/m^2. For the solar zenith angles ~30° this value was about 0.3% of the net flux and increased roughly up to 1% for the large angles ~70°. This experiment showed that there is no excess absorption in the short-wave part of the spectrum for the direct solar radiation. It should be noted that tentative estimates[109] of the contribution of weak absorption lines to extinction of the short-wave radiation do not contradict these data. As the solar zenith angle increases (i.e., at the increase of the absorbing mass), the relative deviation of the calculated results from the experimental data[108] increases too.

The short-wave continuum is determined by fitting the calculated data to the experimental ones. That is why the absorption by weak lines which are absent in the current databases is considered as continuum absorption. The further development of the work started in Ref. 109 will probably refine the model of selective absorption and revise the model of continuum absorption.

In conclusion, it should be noted that development of the method of *k*-distribution allowed the problem of parameterization of the equation of radiative transfer in absorbing media to be solved. Thus, for example, the models described in Refs. 110 and 111 ensure very close agreement with the line-by-line calculations (the discrepancy in the net radiative fluxes not exceeding 0.3%).

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