Analysis of temperature dependence in cumulative spectra of rotational-vibrational absorption bands of atmospheric gases

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The lacunarity parameter characterizing fractal properties of optical spectra is shown to depend on the temperature of a medium. It can be used as a criterion of applicability of the exponential series when solving the radiative transfer equation for the case of inhomogeneous nonisothermal atmosphere.

Approximation of the atmospheric transmission function by exponential series (k-distribution method) allows high-efficiency calculation to be made of spectrally integral radiative characteristics, and it has received wide usage in solution of various problems in the global atmospheric circulation.[1,2] The method of k-distribution is based on the integral transformation

$$T = \frac{1}{\Delta\nu}\int\limits_{\Delta\nu}\exp[-k(\nu)L]\mathrm{d}\nu = \int\limits_0^1\exp[-k(g)L]\mathrm{d}g, \qquad (1)$$

where $k(\nu)$ is the molecular absorption coefficient; L is the path length; ν is the wavenumber; $k(g)$ can be interpreted as an absorption coefficient in the space of cumulative wavenumbers.[3] This transformation allows us to pass from fast-oscillating function $k(\nu)$ to the smooth function $k(g)$ (Fig. 1). Then, the transmission function can be presented by a short exponential series while keeping the same high accuracy of calculations (at the level of the line-by-line method).

It is a peculiarity of the k-distribution method that it is accurate in the case of a homogeneous isothermal atmosphere, while for an inhomogeneous path a model describing the dependence of the optical depth on local characteristics cannot be constructed without additional assumptions. By analogy with the line-by-line method, it is most natural to use the following formal definition of the optical depth τ in the space of cumulative wavenumbers g:

$$\tau(g, z_0, z) = \int\limits_{z_0}^{z} k(g,h)\rho(h)\mathrm{d}h, \qquad (2)$$

where $\rho(h)$ is the absorbing gas concentration at the height h, and $k(g, h)$ has the meaning of the "spectral" absorption coefficient at the height h. The parameter $k(g, h)$ can be calculated based on $k(\nu, h)$.

Equation (2) is heuristic and approximate. The estimates[4,5] showed that Eq. (2) gives an error at the level of 1% for H_2O, CO_2, and O_3 bands lying in the longwave spectral region under typical atmospheric conditions. It was also shown[5] that Eq. (2) is applicable to the isothermal atmosphere.

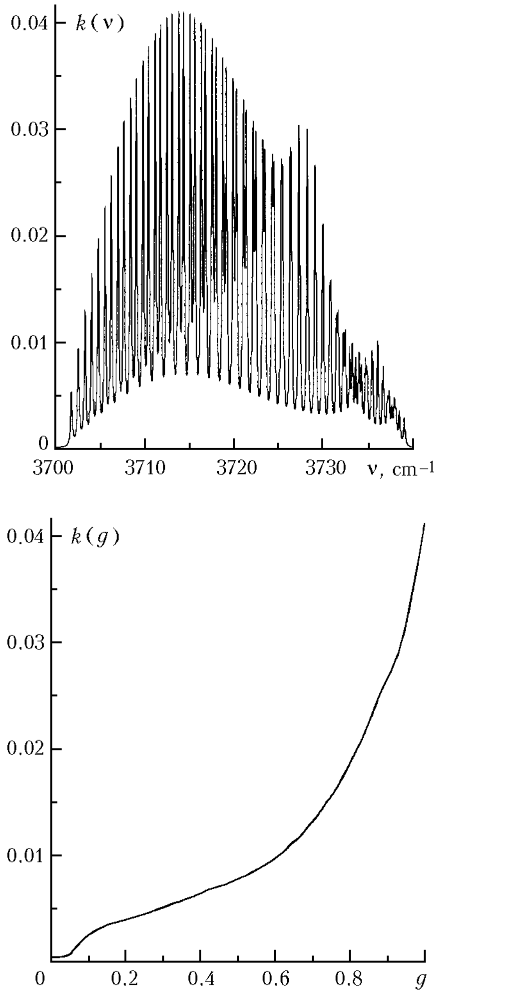

Fig. 1. Absorption spectrum of R-branch of the CO_2 11112–01101 band.

The inhomogeneous atmosphere usually is not isothermal, and, consequently, the use of Eq. (2) for calculation of radiation fluxes requires the applicability of this method to be evaluated. It should be noted that such calculations might give incorrect results for the significantly nonisothermal atmosphere. Let us consider, as a case study, a medium consisting of two layers

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(Fig. 2), which differ only in the temperature Θ_1 and Θ_2 ($\Theta_1 < \Theta_2$).

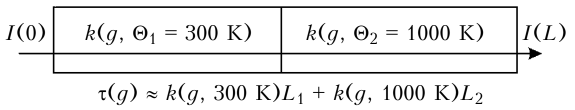

Fig. 2. Two-layer model of a gas medium.

Let the spectral range of interest $[\nu_1, \nu_2]$ include two lines centered at ν_1 and ν_2, one of which is due to a transition from the ground state and the other one being produced due to a transition from a highly excited state. Let the ratio between the line strengths S be such that $S_1(\Theta_1) = S_2(\Theta_2) = S$, $S_1(\Theta_1) \gg S_2(\Theta_1)$ and $S_1(\Theta_2) \ll S_2(\Theta_2)$. Assume that the absorption spectrum in each layer is formed only by one line, the absorbing mass W ($W = \rho L$, where L is the path length) is the same for both of the layers, lines have the Lorentz profile, and line widths are the same and temperature independent. Then the absorption coefficient in the ith layer has the form

$$k_i(\nu) = \frac{S}{\pi}\frac{\gamma}{(\nu - \nu_i)^2 + \gamma^2}. \qquad (3)$$

In the space of cumulative wavenumbers, we can obtain

$$k_i(g) = \frac{1}{(\Delta\nu)^2}\frac{S}{\pi}\frac{\gamma}{g^2 + (\gamma/\Delta\nu)^2}, \qquad (4)$$

where $0 \le g \le 1$, $\Delta\nu = (\nu_2 - \nu_1)$.

The total optical depth $\tau = \tau_1 + \tau_2$ (here τ_i is the optical depth of the ith layer), and the coefficients $k_i(g)$ are the same; therefore

$$\tau = \frac{1}{(\Delta\nu)^2}\frac{2SW}{\pi}\frac{\gamma}{g^2 + (\gamma/\Delta\nu)^2}. \qquad (5)$$

Equations (5) and (4) differ by only constant factor $2W$. Consequently, the absorption spectrum in the space of cumulative wavenumbers is such, as if the absorption lines have the same center in the space of cumulative wavenumbers, but actually, this is not the case.

This example describes a situation that is not typical of the Earth's atmosphere, but it shows that Eq. (2) is an approximation, which not always gives a good result, especially with the paths characterized by high temperature gradients.

Now there are no applicability criteria for the k-distribution method. The main cause for the errors in this method is variation of the structure of the aggregate band spectrum with the temperature variation. The aggregate spectrum has a complex quasirandom structure, and its temperature variations can be described with the use of a statistical approach. Let us demonstrate that the transmission function can be expressed through frequency distribution moments of the absorption coefficients.

The transmission function can be presented as (see, for example, Ref. 6):

$$T(L) = \int_0^\infty f(k)\exp(-kL)\mathrm{d}k. \qquad (6)$$

The function $f(k)$ has discontinuities of the first-kind, therefore it is declared a weighting function, and the exponent in the integrand can be approximated by the Legendre polynomial

$$\exp(-kL) = \sum_{m=1}^{N}\frac{\omega_N(k)}{(k - k_m)\omega'_N(k_m)}\exp(-k_m L), \qquad (7)$$

where

$$\omega_N(k) = (k - k_1)(k - k_2)\ \ldots\ (k - k_N), \qquad (8)$$

that is, the exponent is approximated by the polynomial of the power N:

$$\exp(-kL) = \sum_{m=1}^{N} a_m k^m \exp(-k_m L). \qquad (9)$$

Substituting Eq. (9) into Eq. (6), we obtain the exponential series

$$T(L) = \sum_{m=1}^{N} a_m \int_0^\infty f(k)k^m \mathrm{d}k \exp(-k_m L) = \sum_{m=1}^{N} C_m \exp(-k_m L). \qquad (10)$$

It can be shown that

$$\int_0^\infty f(k)k^m \mathrm{d}k = \frac{1}{\Delta\nu}\int_{\Delta\nu}[k(\nu)]^m \mathrm{d}\nu = M_m[k(\nu)]. \qquad (11)$$

It follows from Eq. (11) that the series parameters can be calculated by use of the distribution moments of the absorption coefficient. The first moments have known and rather clear meaning (mean and root-mean-square deviation). The change in the shape of the distribution at temperature variation affects the values of its first moments.

The parameter called lacunarity is used to describe properties of different distributions. One of the possible definitions of lacunarity Λ for a quasirandom function $s(R)$ has the following form:

$$\Lambda = \langle s^2 \rangle_s / \langle s \rangle_s^{\,2}, \qquad (12)$$

where averaging is carried out over all possible values of the function. Lacunarity characterizes the degree of deviation of the function values from the mean, and $\Lambda = 1$ means that the function is translation-invariant.

Practical calculation of lacunarity is connected with averaging of the initial function over some interval of the size δ. The lacunarity parameter is used for arbitrary distributions, but it should be noted that the dependence $\Lambda(\delta)$ is linear on the log–log scale for fractal and multifractal objects.[7,8]

For description of rotational-vibrational spectra, it is worth using the spectral dependence of the absorption coefficient as a function $s(R)$. In this case

$$\Lambda = M_2\{k(\nu)\}/[M_1\{k(\nu)\}]^2. \tag{13}$$

Since the lacunarity is defined through the first and second distribution moments of the absorption coefficient, the relation between the parameters of the exponential series of the transmission function and this spectral characteristic is obvious. It should be noted that higher lacunarity connected with higher moments is used along with Eq. (12).

Calculated results

We have carried out model calculations of the lacunarity parameter and the transmission function for a two-layer gas medium. The model of the medium and the method for calculation of the optical depth are shown in Fig. 2. In calculations of absorption spectra at different temperatures, we used the CDSD database of CO_2 line parameters.[9]

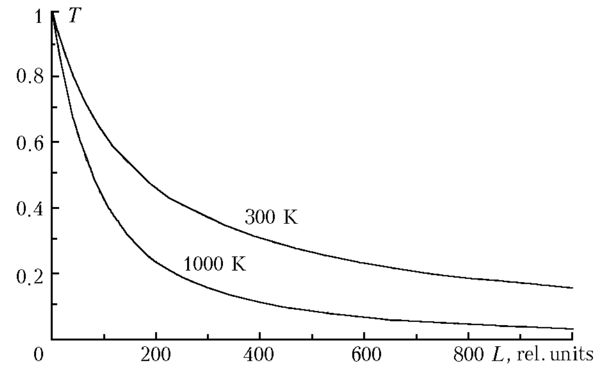

Fig. 3. Transmittance vs. path length at different CO_2 temperatures.

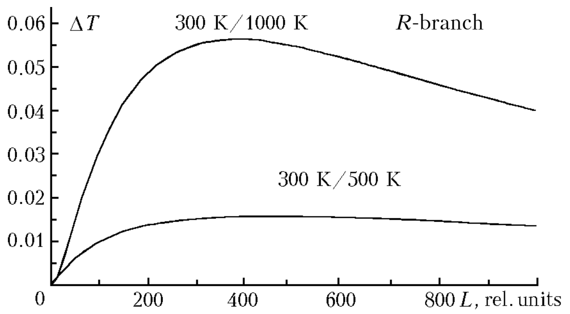

Fig. 4. Error in the transmission function calculated with the use of exponential series.

Figure 3 depicts the transmittance dependence on the path length for the individual layers, and Fig. 4 depicts the errors in the transmission functions calculated for the two-layer medium by Eq. (2). It can be seen that the error increases, as the temperature of one of the layers grows. Similarly, the lacunarity increases with the temperature growth (Fig. 5) because of the increasing inhomogeneity of the frequency distribution of the absorption coefficients. Thus, the lacunarity can serve a criterion of the k-distribution applicability.

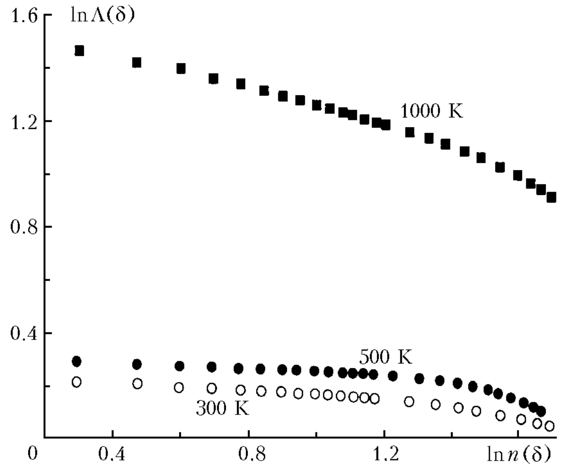

Fig. 5. Lacunarity of optical spectrum of the R-branch of the CO_2 11112–01101 band, where $n(\delta) = \Delta\nu\delta$.

It can be seen from the results presented that the dependence $\Lambda(\delta)$ approaches the linear one (on the log-log scale) as the temperature grows. This indicates that the above distribution begins to show the properties of scale invariance characteristic of fractal and multifractal distributions.

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