

# Allowing for Local Thermodynamic Non-Equilibrium in the Vibrational Bands of Carbon Dioxide Molecules in the Radiation Block of the Model of the General Circulation of Earth's Atmosphere

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**Abstract**—A way of calculating the field of solar radiation in Earth's atmosphere is described that considers the thermodynamic non-equilibrium in the vibrational bands of CO<sub>2</sub> and O<sub>3</sub>. The proposed technique allows calculations with high spectral resolution (line by line), along with parameterizations of the optical parameters of the Earth's upper atmosphere that can be used in calculating the field of solar radiation.

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## INTRODUCTION

To measure the heating of the atmosphere required for modeling the general circulation of the Earth's lower and middle atmosphere, we must consider the atmosphere's heating from its own IR radiation in the 10 to 2000 cm<sup>-1</sup> range of frequencies, and by solar radiation in the 2000 to 50000 cm<sup>-1</sup> range. Starting from a certain altitude, the lifetime of excited CO<sub>2</sub> and O<sub>3</sub> molecules becomes shorter than the mean free time between collisions, and the vibrational state population cannot be described by a Boltzmann distribution at atmospheric temperature. In other words, the vibrational local thermodynamic equilibrium (LTE) is no longer valid (it is a non-LTE), and the emission of atmospheric gases does not follow the Planck function.

Non-LTEs in CO<sub>2</sub> vibrational bands with wavelengths of ~15 μm form in Earth's atmosphere at altitudes greater than 75–80 km at night and above 70 km during the daytime. In vibrational bands with wavelengths of around 4.3 and 2.7 μm, it forms at altitudes over 70 km in both day and night. A non-LTE in O<sub>3</sub> vibrational bands with wavelengths of around 9.6 μm manifests strongly day and night at altitudes over 75 km.

When an LTE is not valid, the radiation transfer equation must be solved along with kinetic equations for the vibrational state populations [1–5]. Models for the formation of vibrational state populations of CO<sub>2</sub> under non-LTE conditions in terms of the vibrational

degrees of freedom of molecules (vibrational non-LTE) are being developed by different groups of researchers [3–12]. The most comprehensive theoretical analysis of ways of measuring non-LTE effects when solving the radiation transfer equation was presented in [1].

## NON-LTE RADIATION OF ATMOSPHERIC GAS

Let us assume that the atmosphere is flat and horizontally homogeneous. We consider the intrinsic radiation of the atmosphere with frequency  $\nu$ , which we assume depends only on altitude  $z$  and the angle between the direction of the photon momentum and the vertical direction (upward or downward, i.e., the zenith angle).

Let  $u$  be the zenith cosine;  $z_{max}$  is the height of the upper boundary of the atmospheric column for which the radiation field is calculated; and  $I(z, \nu, u)$  denotes the intensity of radiation with frequency  $\nu$  and zenith angle cosine  $u$ , at height  $z$ .  $K_{ab}(z, \nu)$  and  $K_{sc}(z, \nu)$  are the coefficients of the volume absorption and scattering of radiation with frequency  $\nu$  at height  $z$ .

The equation for the transfer of the atmosphere's own radiation is then written as

$$u \frac{dI(z, \nu, u)}{dz} = -(K_{ab}(z, \nu) + K_{sc}(z, \nu)) I(z, \nu, u) + W(z, \nu) + K_{sc}(z, \nu) S[I](z, \nu, u), \quad (1)$$

where  $W(z, \nu)$  is the radiation term;  $S[I](z, \nu, u)$  is the normalized density of the source of scattered radiation at frequency  $\nu$  and altitude  $z$ , with zenith angle cosine  $u$ . This density is determined by the equation

$$S[I](z, \nu, u) = \frac{1}{4\pi} \int_{-1}^1 I(z, \nu, u) \left( \int_0^{2\pi} \chi(z, \nu(w, u, \varphi)) d\varphi \right) dw,$$

where  $w$  and  $u$  are cosines of zenith angles before and after scattering;  $\varphi$  is difference between the azimuth angles of radiation before and after scattering;  $\nu(w, u, \varphi) = u w + \cos \varphi \sqrt{(1-u^2)(1-w^2)}$  is the cosine of the scattering angle; and  $\chi(z, \nu)$  is indicatrix of scattering for radiation with frequency  $\nu$  at height  $z$ , by an angle with cosine  $\nu$ .

When the LTE is valid, term  $W(z, \nu)$  is found via the Planck function

$$W(z, \nu) = K_{ab}(z, \nu) B(T(z), \nu),$$

$$B(T, \nu) = \frac{2h\nu^3}{c^2 (\exp(h\nu/(k_B T)) - 1)},$$

where  $h$  is Planck's constant;  $k_B$  is Boltzmann's constant;  $c$  is the speed of light; and  $T(z)$  is the temperature of the atmospheric gas at height  $z$ .

Let us consider a case where the atmospheric gas consists of a mixture of several gases and different types of aerosol particles, and when LTE is not valid for several absorption lines of some of the gases. The term in this case is the sum of the contributions from all gaseous components and aerosol particles:

$$W(z, \nu) = \sum_{\alpha} W_{\alpha}(z, \nu) + K_{aer,ab}(z, \nu) B(T(z), \nu), \quad (2)$$

where index  $\alpha$  denotes the type of molecule, and  $K_{aer,ab}(z, \nu)$  is the coefficient of the volume absorption of aerosol particles. Coefficient  $K_{ab}(z, \nu)$  is the sum of the coefficients of the volume molecular absorption of all gaseous components and aerosol particles:

$$K_{ab}(z, \nu) = \sum_{\alpha} n_{\alpha}(z) \sigma_{mol,ab,\alpha}(z, \nu) + K_{aer,ab}(z, \nu), \quad (3)$$

where  $n_{\alpha}(z)$  is the concentration of  $\alpha$  molecules, and  $\sigma_{mol,ab,\alpha}(z, \nu)$  is the absorption cross section of this molecule at height  $z$ . Along with frequency, this cross section also depends on the temperature and partial pressures of atmospheric gases and is conventionally calculated as the sum of all absorption lines of an  $\alpha$  molecule:

$$\sigma_{mol,ab,\alpha}(z, \nu) = \sum_i S_{\alpha i}(T(z)) F_{\alpha i}(z, \nu - \nu_{\alpha i}), \quad (4)$$

where  $i$  is the number of the absorption line of the  $\alpha$  molecule;  $\nu_{\alpha i}$  is the center frequency of this absorption line;  $S_{\alpha i}(T(z))$  is the intensity of this line; and

$F_{\alpha i}(z, \nu - \nu_{\alpha i})$  is the Voigt contour of this absorption line at height  $z$ . The intensity of the line is calculated using the equation

$$S_{\alpha i}(T) = S_{\alpha i}(T_{ref}) \times \frac{Q_{\alpha}(T_{ref}) \exp(-C_2 E_{\alpha i}/T) (1 - \exp(-C_2 E_{\alpha i}/T))}{Q_{\alpha}(T) \exp(-C_2 E_{\alpha i}/T_{ref}) (1 - \exp(-C_2 E_{\alpha i}/T_{ref}))},$$

where  $T_{ref} = 296$  K is a reference temperature;  $Q_{\alpha}(T)$  is the product of the rotational and vibrational partition functions of an  $\alpha$  molecule;  $E_{\alpha i}$  is the energy of the lowest transition level of this molecule ( $\text{cm}^{-1}$ );  $E_{\alpha i}$  is the energy of this molecule's transition, which corresponds to the absorption line with number  $i$  ( $\text{cm}^{-1}$ );  $C_2 = hc/k_B = 1.438769$  cm K is second radiation constant;  $c$  is the speed of light; and  $k_B$  is the Boltzmann constant.

Intensities  $S_{\alpha i}(T_{ref})$  of lines at the reference temperature and parameters  $E_{\alpha i}$ ,  $E_{\alpha i}$  for all lines are contained in the HITRAN 2012 database. Parameter  $Q_{\alpha}(T)$  for each type of molecule is calculated using the interpolation tables given in [13]. The procedure for calculating  $Q_{\alpha}(T)$  is included in the software package appended to the HITRAN database.

The HITRAN 2012 database was described in [14–17]. It contains spectroscopic parameters for 7400 447 spectral lines of 47 molecules. It can be downloaded from the official website at <http://www.cfa.harvard.edu/hitran>.

The Voigt contour is a convolution of Doppler and Lorentz contours and describes the experimental one quite well in the intermediate range of pressures. For the  $i$ -th line of an  $\alpha$  molecule at height  $z$ , this contour is given by the equations

$$F_{\alpha i}(z, \nu - \nu_{\alpha i}) = \frac{y}{a_D \pi \sqrt{\pi}} \int_{-\infty}^{\infty} \frac{\exp(-t)^2 dt}{y^2 + (x - t)^2}, \quad (5)$$

$$x = \frac{\nu - \nu_{\alpha i}}{a_D}, \quad y = \frac{a_L}{a_D},$$

where  $a_D$  is the width of the Doppler line and  $a_L$  is the half-width of the Lorentz contour line, which at height  $z$  is calculated with the formula

$$a_L = \left( \gamma_{\alpha i}^{\text{self}} \left( \frac{P_{\alpha}(z)}{P_{\text{ref}}} \right) + \gamma_{\alpha i}^{\text{air}} \left( \frac{P(z) - P_{\alpha}(z)}{P_{\text{ref}}} \right) \right) \left( \frac{T_{\text{ref}}}{T(z)} \right)^{\beta_{\alpha i}},$$

where  $\gamma_{\alpha i}^{\text{self}}$  is the coefficient of self-broadening of the  $i$ th line of an  $\alpha$  molecule (due to collisions between these molecules);  $\gamma_{\alpha i}^{\text{air}}$  is the coefficient of the air broadening of this line (due to collisions between these molecules and ones of other types); and  $\beta_{\alpha i}$  is the coefficient of the temperature dependence of this line,  $P_{\text{ref}} = 1$  atm.  $P_{\alpha}(z)$  is the partial pressure of  $\alpha$  molecules, and  $P(z)$  is the total pressure of atmospheric gas at altitude  $z$ .

Parameters  $\gamma_{\alpha i}^{\text{self}}$ ,  $\gamma_{\alpha i}^{\text{air}}$ , and  $\beta_{\alpha i}$  for all lines are contained in the HITRAN 2012 database. Parameter  $a_D$  at altitude  $z$  is given by the equation

$$a_D = \frac{v_{\alpha i}}{c} \sqrt{\frac{2RT(z)}{\mu_{\alpha}}},$$

where  $c$  is the speed of light,  $R$  is the universal gas constant, and  $\mu_{\alpha}$  is the molar mass of  $\alpha$  molecules.

Term  $W_{\alpha}(z, \nu)$  in Eq. (2) is calculated as the sum of contributions from all absorption lines of an  $\alpha$  molecule:

$$W_{\alpha}(z, \nu) = \sum_i n_{\alpha}(z) S_{\alpha i}(T(z)) F_{\alpha i}(z, \nu - \nu_{\alpha i}) J_{\alpha i}(z, \nu), \quad (6)$$

where  $J_{\alpha i}(z, \nu)$  is a function of the source of  $\alpha$  molecule radiation due to the  $i$ -th absorption line. At LTE,  $J_{\alpha i}(z, \nu) = B(T, \nu)$ .

Approximating a low population of the vibrational states of  $\text{CO}_2$  and  $\text{O}_3$  molecules and a two-level model approach to calculating the population of these states can be used for a non-LTE in Earth's atmosphere. In such an approach, function  $J_{\alpha i}(z, \nu)$  is given by the equation [1]

$$J_{\alpha i}(z, \nu) = \frac{L_{\alpha i}(z) + \varepsilon(z)B(T(z), \nu)}{1 + \varepsilon(z)}, \quad \varepsilon(z) = \frac{f_{\alpha i}(z)}{A_{\alpha i}}, \quad (7)$$

where  $A_{\alpha i}$  is the Einstein coefficient for the  $i$ th absorption line of an  $\alpha$  molecule, and  $f_{\alpha i}(z)$  is the frequency of deactivating collisions of excited  $\alpha$  molecules that correspond to the  $i$ -th absorption line:

$$L_{\alpha i}(z) = \frac{1}{2} \int_0^{\infty} \left( F_{\alpha i}(z, \nu - \nu_{\alpha i}) \int_{-1}^1 I(z, \nu, u) du \right) d\nu. \quad (8)$$

The procedure for calculating rate  $f_{\alpha i}(z)$  of collisions was described in [13].

Equations (2) and (6–8) show the intensity of radiation at certain frequencies depends on those at other frequencies. This greatly complicates calculations for the radiation field in Earth's atmosphere. However, Eq. (8) can be simplified considerably, for two reasons:

First, substantial deviation from the LTE is observed in the  $\text{CO}_2$  and  $\text{O}_3$  vibrational bands at altitudes above 70 km, where the absorption line contours become very narrow and virtually coincide with the Doppler contour.

Second, the main contribution to integral (8) for wavelengths of  $\sim 15$  and  $\sim 9.6$   $\mu\text{m}$  comes from upward atmospheric radiation, formed at altitudes below 20 km. This radiation is virtually constant for non-LTE absorption lines at altitudes of more than 40 km. For the indicated wavelengths, the contribution to integral (8) from direct and scattered radiation formed in the upper layers of the atmosphere is negligible.

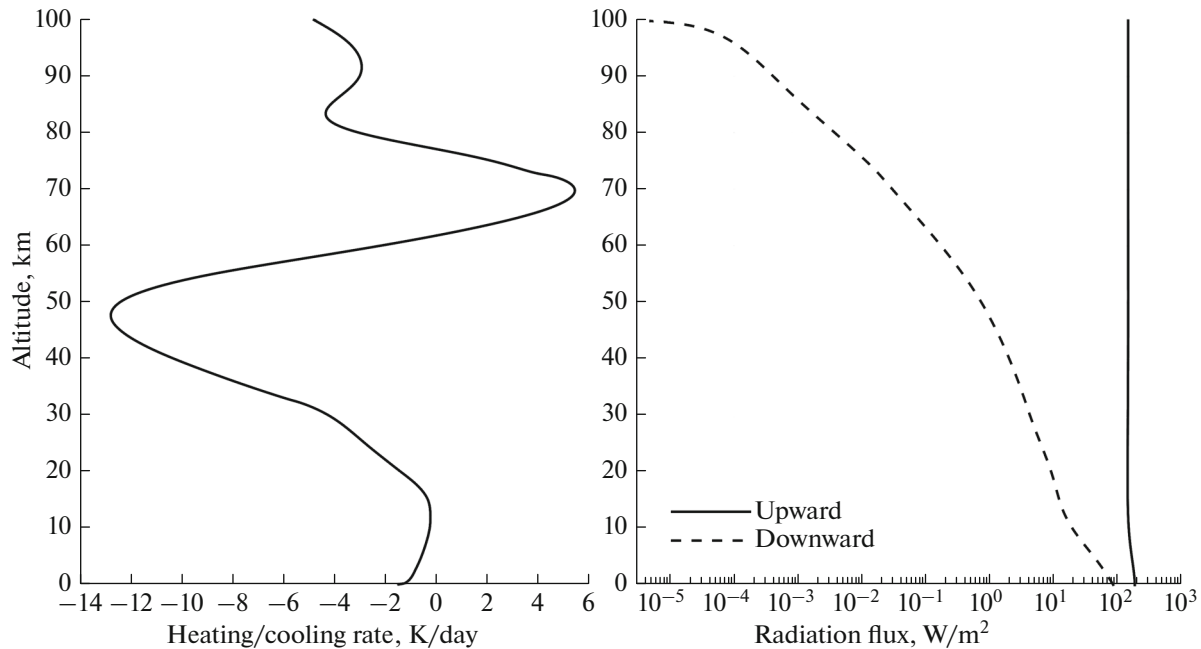
The main contribution to integral (8) for wavelengths of  $\sim 4.3$  and  $\sim 2.7$  mm was made by direct solar and scattered solar radiation of the atmosphere, which formed at altitudes below 20 km. This emission is also virtually constant over the range of the non-LTE absorption lines. The contribution to integral (8) from the solar radiation scattered by the upper layers of the atmosphere for the indicated wavelengths is negligible. Equation (8) for the vibrational bands of  $\text{CO}_2$  and  $\text{O}_3$  at altitudes of more than 70 km can thus be replaced with the formula

$$L_{\alpha i}(z) = \frac{1}{2} \int_{-1}^1 I(z, \nu, u) du. \quad (9)$$

Equations (2), (6), (7), and (9) allow us to calculate the radiation field in Earth's atmosphere by considering the non-LTE in  $\text{CO}_2$  and  $\text{O}_3$  vibrational bands independently for each frequency.

The authors performed reference calculations of the field of self-radiation of Earth's atmosphere with a frequency resolution of  $0.001 \text{ cm}^{-1}$  in the range of altitudes from the surface to 100 km in an approximation of a horizontally homogeneous atmosphere. The calculations were made as described above, allowing for the non-LTE in  $\text{CO}_2$  vibrational bands with wavelengths of around  $15 \mu\text{m}$ . A version of the technique of discrete ordinates that was described in detail in [18] was used to obtain a numerical solution to the radiation transfer equation. A uniform grid was used for altitude with a spacing of 200 meters and for zenith angles with an increment of less than  $9^\circ$ . Molecular and aerosol scattering were also taken into account. Vertical profiles of the temperatures and concentrations of the main atmospheric gases, calculated using the empirical NRLMSISE-00 model for July conditions over the North Atlantic at latitude  $55^\circ$ , were used in our calculations, along with vertical profiles of the volume fractions of minor gas components. The presence of three types of background aerosols (continental, marine, and stratospheric) was allowed for. The optical parameters of these aerosols were borrowed from [19].

Fluxes of upward and downward natural radiation in the  $500\text{--}1000 \text{ cm}^{-1}$  range of frequencies in a cloudless atmosphere (right image) and the rates of atmospheric heating/cooling due to these fluxes, obtained using reference calculations (left image), are presented in Fig. 1. As can be seen, the atmosphere cooled below 62 km, with the rate of cooling reaching  $\sim 13 \text{ K/day}$  at an altitude of 48 km. On the other hand, heating occurred at altitudes of 62 to 77 km, with the maximum heating rate of  $\sim 5.5 \text{ K/day}$  being reached at an altitude of  $\sim 70$  km. Cooling also occurred at altitudes of 77 to 100 km, where its rate did not exceed



**Fig. 1.** (Right) Upward and downward fluxes of natural radiation in the 500–1000 cm<sup>-1</sup> range of frequencies. (Left) Rate of heating/cooling of atmospheric gas due to these fluxes, obtained from reference calculations.

5.5 K/day. Our vertical profile of the heating/cooling rate of atmospheric gas is consistent with calculations by other authors, particularly the results presented in [1]. Calculations made without allowing for the non-LTE considerably overestimated the rate of heating at altitudes of more than 70 km.

## CONCLUSIONS

A way of calculating the function of a radiation source in the vibrational bands of CO<sub>2</sub> and O<sub>3</sub> that considers non-LTE conditions in Earth's upper atmosphere was proposed and substantiated. This technique allows calculations of the radiation field in Earth's atmosphere with high frequency (line by line) resolution independently for each frequency. It also allows us to parametrize the optical parameters of Earth's atmosphere to make quick and accurate calculations of the thermal and solar radiation fields in Earth's lower, middle, and upper atmospheres in light of scattering. The technique was tested using reference calculations and proved to be effective.

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