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Radiative transfer in a flat non-equilibrium mixture layer of CO_2–N_2 gases: numerical experiment

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Abstract—Infra-red radiative transfer in a non-equilibrium mixture of CO_2–N_2 gases is considered. A set of equations for vibrational temperatures is obtained. The set is solved by numerical methods for a flat gaseous layer and for the constant transitional–rotational temperature across the layer.

1. INTRODUCTION

THERE are many physical situations in which radiant energy and a polyatomic gas interacting with it are in a non-equilibrium state. This occurs in gas lasers, for example, in CO_2-lasers [1], and also in terrestrial atmospheres [2, 3]. In such cases, along with relaxation processes [4–6], of very great importance is radiation scattering in vibrational–rotational bands with redistribution over frequencies [4–6]. Here, the boundary conditions are also very important because they determine the overall balance between the absorbed and emitted radiant energy and that pumped by external energy sources. For this reason, it is necessary to take into account the interactions between the gas and the radiant energy of self-emission and external radiation. So, for a complete description of a non-equilibrium gas, it is necessary to have a set of kinetic equations for quantum distributional functions of molecules and photons.

For the first time, such a set was obtained in papers [7, 8] by the method of Zubarev's non-equilibrium statistical operator [9]. In many important cases it can be significantly simplified. Actually, as a result of collisions between molecules, an almost resonant exchange by vibrational energy takes place (VV-exchange) which leads to a fast transition to an equilibrium state in separate vibrational modes. Thus, each vibrational mode is described by its own vibrational temperature $T_i(\mathbf{r}, t)$.

In those cases when the characteristic times of macroscopic processes being described exceed the time of transition to an equilibrium state in separate vibrational modes, such an approach is justifiable [10, 11]. Moreover, since the time of rotational relaxation is very small [1], it can be assumed that rotational and translational degrees of freedom are in thermal equilibrium and can be described by the common temperature $T(\mathbf{r}, t)$. This situation is realized in CO_2-lasers [1] and also in the Earth atmosphere at high altitudes [11]. In this paper, all of the equations are presented which are required for a consistent description of a vibrationally non-equilibrium polyatomic gas interacting with its own and external radiation [12–14], as well as the results of numerical solution obtained for a CO_2–N_2 mixture plane layer in the case of free boundaries and a steady translational–rotational temperature.

2. SET OF EQUATIONS FOR VIBRATIONAL TEMPERATURES IN THE THEORY OF RESONANT SCATTERING IN MIXTURES OF NON-EQUILIBRIUM POLYATOMIC GASES

A consecutive description of the situation, when there is a partial disturbance of local thermodynamic equilibrium between different vibrational modes in a mixture of polyatomic gases interacting with its own and external radiation, is possible on the basis of a system of equations obtained in refs. [12–14]:

$$\left(\frac{\partial}{\partial t}+\mathbf{V}(\mathbf{r})\nabla\right)\cdot\varepsilon_i(\mathbf{r}) = \Gamma_i(\mathbf{r})$$
$$+\frac{1}{n(\mathbf{r})\cdot E_i}(\Psi_i(\mathbf{r})-4\pi W_i(\mathbf{r}))$$
$$+\frac{1}{n(\mathbf{r})\cdot E_i}\int_0^{\infty}\mathrm{d}\nu\int_v K_i(\nu,\mathbf{r})W(\nu,\mathbf{r}')$$
$$\times\frac{\exp(-\sigma(\nu,\mathbf{r},\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|^2}\,\mathrm{d}\mathbf{r}'+\frac{1}{n(\mathbf{r})\cdot E_i}\sum_l{}'\int_0^{+\infty}\mathrm{d}\nu$$
$$\times\int_v K_i(\nu,\mathbf{r})W^{\langle l\rangle}(\nu,\mathbf{r}')\frac{\exp(-\sigma(\nu,\mathbf{r},\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|^2}\,\mathrm{d}\mathbf{r}'. \quad (1)$$

Here, $\mathbf{V}(\mathbf{r}, t)$ and $n(\mathbf{r}, t)$ are the average velocity and number of molecules per unit volume of the gas component considered; E_i is the i-th independent mode vibrational quantum energy of the given type of molecules; $\varepsilon_i(\mathbf{r}, t)$ is the average number of the vibrational quanta of the i-th molecule mode; $\Gamma_i(\mathbf{r})$ is the relaxational term which describes the VV′ and VT pro-

NOMENCLATURE

c	speed of light, 2.9979×10^{10} cm s^{-1}
E_i	energy of i-th mode vibrational quantum of molecule [erg]
ε_i	average number of vibrational quanta in i-th molecule mode
g_κ	degeneracy of energy level
$\hbar$	Planck's constant, $h/2\pi = 1.055 \times 10^{-27}$ erg s
i	index from 1 to 4 designating symmetrical, deformational, asymmetric modes of CO_2 and vibrational mode of N_2
I_α	isotropical coefficient, $I_\alpha = 1$
K_B	Boltzmann's constant, 1.3806×10^{-16} erg K^{-1}
l	number of gas components
L	full number of independent vibrations in gas
m	mass of CO_2 molecule, 7.34×10^{-23} g
n	gas density [cm^{-3}]
P_{AB}	probability [s^{-1}]
Q_v	vibrational statistical sum at 296 K, 1.088
$\lvert R_\kappa^{\kappa'}\rvert^2$	matrix element square of vibrational–rotational transition dipole moment [erg cm^3]
$\mathbf{r}$	space vector [cm]
r_i	vibrational mode multiplicity
t	time [s]
$U_{jl}^{j'l'}$	rotational matrix elements
$\mathbf{V}$	average velocity of gas molecules [cm s^{-1}]
V	gas volume [cm^3].
Greek symbols	
π	3.14
κ	set of quantum numbers; for CO_2 $\kappa = (v_1, v_2, v_3, l, j)$.

cesses; $\Psi_i(\mathbf{r})$ the external source function; $W_i(\mathbf{r})$ and $W(v, \mathbf{r})$ the source functions associated with spontaneous radiation of molecules of the given species; $K_i(v, \mathbf{r})$ the spectral absorption coefficient of the i-th mode of molecules of the species considered; $\sigma(v, \mathbf{r}, \mathbf{r}')$ the optical depth of the mixture of gases at the frequency v along the beam connecting the points r and r'; V the volume of the emitting non-equilibrium gas.

According to refs. [12–14], the functions occurring in the system of equations (1) have the following form:

$$\varepsilon_i(\mathbf{r}) = \frac{1}{E_i}\sum_\kappa{}' E_{i\kappa} N_\kappa(\mathbf{r}), \tag{2}$$

$$\Psi_i(\mathbf{r}) = \int_0^{+\infty} \mathrm{d}v \int_{4\pi} K_i(v, \mathbf{r}) I_0(v, \mathbf{n}, \mathbf{r}_n) \times \exp\left[-\sigma(v, \mathbf{r}, \mathbf{r}_n)\right] \mathrm{d}\Omega_n, \tag{3}$$

$$W_i(\mathbf{r}) = \frac{8\pi^2 n(\mathbf{r})}{3\hbar c^3} \sum_{E'_\kappa > E_\kappa}{}' v_{\kappa'\kappa}^3 \times (E_{i\kappa'} - E_{i\kappa}) \lvert R_\kappa^{\kappa'}\rvert^2 N_{\kappa'}(\mathbf{r}), \tag{4}$$

$$W(v, \mathbf{r}) = \frac{16\pi^3 v n(\mathbf{r})}{3c^3} \sum_{E'_\kappa > E_\kappa}{}' \Phi_\kappa^{\kappa'}(v, \mathbf{r}) v_{\kappa'\kappa}^3 \lvert R_\kappa^{\kappa'}\rvert^2 N_{\kappa'}(\mathbf{r}),$$

$$K_i(v, \mathbf{r}) = \frac{2\pi n(\mathbf{r})}{3\hbar^2 c} \sum_{E'_\kappa > E_\kappa}{}' \Phi_\kappa^{\kappa'}(v, \mathbf{r})(E_{i\kappa'} - E_{ik}), \tag{5}$$

$$\lvert R_\kappa^{\kappa'}\rvert^2 \left(\frac{g_{\kappa'}}{g_\kappa} N_\kappa(\mathbf{r}) - N_{\kappa'}(\mathbf{r})\right), \tag{6}$$

$$\sigma(v, \mathbf{r}, \mathbf{r}') = \int_{[\mathbf{r}, \mathbf{r}']} \left(K(v, \mathbf{r}'') + \sum_l{}' K^{\langle l \rangle}(v, \mathbf{r}'')\right) \mathrm{d}s'' \tag{7}$$

$$K(v, \mathbf{r}) = \frac{4\pi^2 v n(\mathbf{r})}{3\hbar c} \sum_{E_{\kappa'} > E_\kappa}{}' \Phi_\kappa^{\kappa'}(v, \mathbf{r}) \times \lvert R_\kappa^{\kappa'}\rvert^2 \left(\frac{g_{\kappa'}}{g_\kappa} N_\kappa(\mathbf{r}) - N_{\kappa'}(\mathbf{r})\right). \tag{8}$$

Here $I_0(v, \mathbf{n}, \mathbf{r}_n)$ is the spectral intensity of external radiation; $N_\kappa(\mathbf{r})$ the generalized Treanor-type function [12]; $\lvert R_\kappa^{\kappa'}\rvert^2$ the squared module of the matrix element of the dipole vibrationally–rotational transition [15], $\Phi_\kappa^{\kappa'}(v, \mathbf{r})$ the spectral transition line contour described by the Voigt function normalized by unity:

$$N_\kappa(\mathbf{r}) = \frac{g_\kappa}{Q(\mathbf{r})} \times \exp\left[-\sum_i \frac{E_{i\kappa}}{K_B T_i(\mathbf{r})} - \frac{\left(E_\kappa - \sum_i E_{i\kappa}\right)}{K_B T(\mathbf{r})}\right] \tag{9}$$

$$Q(\mathbf{r}) = \sum_\kappa{}' g_\kappa \times \exp\left[-\sum_i \frac{E_{i\kappa}}{K_B T_i(\mathbf{r})} - \frac{\left(E_\kappa - \sum_i E_{i\kappa}\right)}{K_B T(\mathbf{r})}\right] \tag{10}$$

$$\lvert R_\kappa^{\kappa'}\rvert^2 = \frac{1}{g_{\kappa'}} \sum_{\sigma\sigma'} \left\lvert \left\langle \kappa', \sigma' \middle| \sum_s e_s \mathbf{r}_s \middle| \kappa, \sigma \right\rangle \right\rvert^2 \tag{11}$$

$$\int_0^\infty \Phi_\kappa^{\kappa'}(v, \mathbf{r})\, \mathrm{d}v = 1, \quad v_{\kappa'\kappa} = \frac{E_{\kappa'} - E_\kappa}{h}. \tag{12}$$

Here κ is a set of quantum numbers on which the vibrational–rotational energy of molecules E_κ depends; for example, for CO_2 $\kappa = (v_1, v_2, v_3, l, j)$; σ is a set complementary to κ so that $\alpha = (\kappa, \sigma)$ is the complete set of quantum numbers that characterize the state of the molecules of the given species; g_κ the degeneracy taking into account, in particular, nuclear degeneration; $E_{i\kappa}$ the harmonic part of the i-th mode vibrational energy of the molecules of a given species; $T_i(\mathbf{r}, t)$ the vibrational temperature of the i-th vibrational mode of a molecule; $T(\mathbf{r}, t)$ the translational–rotational temperature. It should also be noted that in formula (7) the integration is performed along the beam which connects the points $\mathbf{r}$ and $\mathbf{r}'$; $K^l(v, \mathbf{r})$ absorption coefficient of the l-th gas component the form of which is similar to equation (8), with the superscript l in the sum represented by equation (7) takes on the numbers of all the gas components except for the given one for which equations (1) are written out. The prime in front of the sums means that only the lowest vibrational states are summed up in order to eliminate the ascending branch [11] in the generalized Treanor distribution (9).

The contribution of resonant scattering of radiation from other gas components is taken into account in equation (1) by the expression

$$\frac{1}{n(\mathbf{r}) \cdot E_i} \cdot \sum_l{}' \int_0^\infty \mathrm{d}v \int_v K_i(v, \mathbf{r}) W^{\langle l \rangle}(v, \mathbf{r}') \times \frac{\exp[\sigma(v, \mathbf{r}, \mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|^2} \mathrm{d}\mathbf{r}' \quad (13)$$

in which the summation $\sum_l{}'$ extends over all the components except for the given one. The functions $W^l(v, \mathbf{r})$ have the form similar to that in equation (5), however, all the quantities here relate to the gas component numbered l. The explicit form of the relaxation term $\Gamma_i(\mathbf{r})$ in the most general form in a harmonic approximation was suggested in ref. [16] and is given in the next section. Note also that for the simplicity of formulation the time argument is omitted at the functions in all of the formulae. The system of equations (1) has a simple physical sense: a complete change in the main stored amount of vibrational quanta in the i-th mode of the given gas component is governed by collisions between the mixture molecules and also by the processes of multiple resonant scattering of photons in vibration–rotational bands associated with self-emission and external radiation. Here, the scattering processes are accompanied by the redistribution of scattered photons in frequencies.

3. RESONANT RADIATION SCATTERING IN A CO_2–N_2 MIXTURE FOR A GAS VOLUME HAVING THE GEOMETRY OF A PLANE LAYER

The description of the interaction between a mixture and the self-emission and external radiation on the basis of a system of non-linear equations (1) represents a very complex mathematical problem. The major problem is that in the vibrational–rotational spectrum of polyatomic molecules thousands of transitions should be taken into account [15, 17]. In addition to summation over all the transitions, in the system of integrodifferential equations (1) one should also perform integration over frequency, and this is fraught with great difficulties especially in the case of a spatially inhomogeneous gas. However, it is to be noticed that the entire volume occupied by the emitting gas can always be subdivided into regions in each of which the translational–rotational temperature can be approximately considered constant. By using this procedure, it is possible to significantly simplify the initial problem. Next, to be explicit, we shall consider a mixture of two gases, CO_2 and N_2. This mixture is of great interest since in all of sufficiently efficient CO_2-lasers use is made of nitrogen molecules as an additional channel for pumping energy into the asymmetric mode of CO_2 molecule vibrations [1]. Moreover, these are the basic components in modelling the terrestrial space [2, 3, 11].

We shall assume that the emitting gas volume has the geometry of a plane layer. This geometry is common for the upper layers of the atmosphere [2, 3, 18, 19] and, in the simplest case, it can model the optical resonator of a laser system [1]. Thus, assuming that the vibrational–rotational bands of molecules are described by a set of non-overlapping Doppler lines and that the gaseous mixture occupies the space bounded by two planes $z = 0$ and $z = z_0$, with $T = \text{const.}$, the system of equations (1) can be presented in the form

$$\frac{\partial}{\partial t} \varepsilon_i(z) = \Gamma_i(z) - \frac{32\pi^3}{3\hbar c^3} \sum_{E_{\kappa'} > E_\kappa} v^3_{\kappa'\kappa} \Delta^i_{\kappa'\kappa} \times |R^{\kappa'}_\kappa|^2 N_{\kappa'}(z) + \sum_{E_{\kappa'} > E_\kappa}{}' \int_0^{z_0} G^i_{\kappa'\kappa}(z, z') \times M(\sigma_{\kappa'\kappa}(z, z')) \, \mathrm{d}z' + \frac{\Psi_i(z)}{E_i n(z)} \quad (14)$$

where

$$G^i_{\kappa'\kappa}(z, z') = \frac{64\pi^4 n(z')}{9\hbar^2 c^4 d} \cdot v^3_{\kappa'\kappa} \Delta^i_{\kappa'\kappa} \cdot |R^{\kappa'}_\kappa|^4 \times \left(\frac{g_{\kappa'}}{g_\kappa} N_\kappa(z) - N_{\kappa'}(z) \right) \cdot N_{\kappa'}(z') \quad (15)$$

$$\sigma_{\kappa'\kappa}(z, z') = \frac{4\pi^{3/2}}{3\hbar c d} |R^{\kappa'}_\kappa|^2 \times \left| \int_{z'}^{z} \left(\frac{g_{\kappa'}}{g_\kappa} N_\kappa(s) - N_{\kappa'}(s) \right) \cdot n(s) \, \mathrm{d}s \right| \quad (16)$$

$$\Delta^i_{\kappa'\kappa} = \frac{E_{i\kappa'} - E_{i\kappa}}{E_i}, \quad d = \sqrt{\left(\frac{2K_\mathrm{B} T}{mc^2} \right)} \quad (17)$$

$$M(\xi) = \int_{-\infty}^{+\infty} E_1(\xi \exp(-\omega^2)) \cdot \exp(-2\omega^2) \, \mathrm{d}\omega \quad (18)$$

$$E_1(z) = \int_0^1 \exp\left(-\frac{z}{\mu}\right)\frac{d\mu}{\mu}. \qquad (19)$$

According to ref. [16], the relaxation term $\Gamma_i(z)$ in equation (14) describes all the possible relaxation channels in the population of vibrational levels on collision of molecules in a harmonic approximation has the form

$$\Gamma_i = \sum_{\langle l_s;\, l_j\rangle} Z_{AB}\cdot P_{AB}\begin{Bmatrix} l_s \to 0 \\ 0 \to l_j \end{Bmatrix} l_i \cdot \prod_{s=1}^{k}\binom{l_s+r_s-1}{l_s}$$
$$\times [r_s(r_s+\varepsilon_s^0)]^{-l_s}\prod_{j=k+1}^{L}(r_j\varepsilon_j^0)^{-l_j}\left\{\prod_{s=1}^{k}[\varepsilon_s^0(r_s+\varepsilon_s)]^{l_s}\right.$$
$$\times \prod_{j=k+1}^{L}[\varepsilon_j(r_j+\varepsilon_j^0)]^{l_j} - \prod_{s=1}^{k}[\varepsilon_s(r_s+\varepsilon_s^0)]^{l_s}$$
$$\left.\times \prod_{j=k+1}^{L}[\varepsilon_j^0(r_j+\varepsilon_j)]^{l_j}\right\}. \qquad (20)$$

Here Z_{AB} is the number of collisions of the molecule A with the molecules B per unit time, P_{AB} is the probability of the complex vibrational transition in the system A+B with one collision. Equation (20) describes relaxation in a binary mixture of gases A(CO_2) and B(N_2), with only those transitions being taken into account which are due to collisions A and B. This corresponds to the case when the CO_2 gas is a small admixture to N_2. Here L is the full number of independent vibrations in the gas. For the CO_2–N_2 mixture, $L = 4$. The arbitrary vibrational state of the system A+B is described by a set of vibrational numbers $(v_1, v_2, \ldots, v_L)$. Here all the possible relaxation channels on collision of A and B have the form [16]:

$$(v_1,\ldots,v_k;\, v_{k+1},\ldots,v_L)$$
$$\to (v_1 \pm l_1,\ldots,v_k \pm l_k;\, v_{k+1} \mp l_{k+1},\ldots,v_L \mp l_L).$$

Since here polyatomic molecules are modelled by a set of harmonic oscillators, the mean numbers of vibrational quanta in different modes are described by the formulae

$$\varepsilon_i = \frac{r_i}{\exp\left(+\dfrac{E_i}{K_B T_i}\right)-1}, \quad \varepsilon_i^0 = \frac{r_i}{\exp\left(+\dfrac{E_i}{K_B T_i}\right)-1}. \qquad (21)$$

By numbering from 1 to 4 the symmetric, deformational, and asymmetric modes of CO_2 and vibration of N_2, we shall have: $E_1/k_B = 2000$ K, $E_2/k_B = 960$ *K*, $E_3/k_B = 3380$ K, $E_4/k_B = 3353$ K, with $r_1 = r_3 = r_4 = 1$, $r_2 = 2$, since the deformation type of vibrations is two-fold degenerate. In numerical calculations, use was made of the basic relaxation channels in modes 1–4 being attributed to the following processes:

$$CO_2(00^01)+N_2 \to CO_2(03^10)+N_2$$
$$CO_2(00^01)+N_2 \to CO_2(11^10)+N_2$$
$$CO_2(00^01)+N_2(0) \to CO_2(00^00)+N_2(1)$$
$$CO_2(00^01)+N_2 \to CO_2(02^00)+N_2$$
$$CO_2(01^10)+N_2 \to CO_2(00^00)+N_2$$
$$CO_2(10^00)+N_2 \to CO_2(02^00)+N_2. \qquad (22)$$

The probabilities of the above processes were taken from refs. [2, 3]. In calculations, account was also taken of the effect of fast exchange by vibrational quanta between the symmetric and deformational modes of CO_2 due to Fermi resonance [1, 12–14] which in quasi-stationary problems leads to the equilibrium of the temperatures T_1 and T_2. In fact, the probability of the last process from the six indicated in set (22) greatly exceeds the remaining probabilities [16]. According to refs. [12, 14], this leads to a situation when in CO_2 molecules the coupled and antisymmetric modes of vibrations with the mean numbers of vibrational quanta $\varepsilon_c = 2\varepsilon_1 + \varepsilon_2$ and ε_3 are independent. In order to obtain an equation for the mean number of vibrational quanta in a coupled mode, it is necessary to multiply equation (14) for $i = 1$ by 2 and sum up with equation (14) for $i = 2$; consequently, the relaxation term Γ_c has the form: $\Gamma_c(z) = 2\cdot\Gamma_1(z)+\Gamma_2(z)$. In calculations an equilibrium state of N_2 was assumed, i.e. $T_4 = T$. Thus, the population distribution of the vibrational–rotational levels in the CO_2+N_2 mixture is described in this case by three different temperatures: $T_c = T_2$, T_3, and T. Since a stationary problem without external radiation sources with free escape of radiation through the boundaries $z = 0$ and $z = z_0$ was solved here, it is necessary to assume in equations (14) that $\partial\varepsilon_i/\partial t = 0$ and $\psi_i = 0$. The squares of the modules of matrix elements (11) were calculated with the help of the expression [15]:

$$|R_K^{K'}|^2 = (U_{JI}^{J'I'})^2 |V_{v_1 v_2^l v_3}^{v_1' v_2'^{l'} v_3'}|^2 \qquad (23)$$

where $U_{JI}^{J'I'}$ are the rotational matrix elements. The vibrational matrix elements in equation (23) can be determined with the help of the expression for the line strength [20]:

$$S_v^0 = \frac{4\pi^2 g I_\alpha v_0}{3hcQ_v}|V_{v_1 v_2^l v_3}^{v_1' v_2'^{l'} v_3'}|^2 \exp\left(-\frac{E_v}{K_B T_0}\right) \qquad (24)$$

where $Q_v = 1.088$ is the vibrational statistical sum at 296 K, $g = 1$ at $l \neq 0$, $g = 2$ at $l = 0$, $I_\alpha = 1$ is the isotropic coefficient, E_v the energy of the lower level.

4. NUMERICAL METHOD FOR SOLVING A SYSTEM OF INTEGRAL EQUATIONS THAT DESCRIBE RESONANT RADIATION SCATTERING IN A MIXTURE OF POLYATOMIC GASES

A system of equations (14) for a CO_2–N_2 mixture at a constant translational–rotational temperature was solved by the iteration technique. However, this method allows one to obtain a converging sequence of iterations only in the cases when the initial trial distributions of the vibrational temperatures $T_c(z) = T_1(z) = T_2(z)$ and $T_3(z)$ are rather close to the unknown exact solutions of system (14).

At large optical densities all of the vibrational temperatures are close to the translational–rotational temperature because of intense exchange between translational, rotational and vibrational degrees of freedom of the molecules. Therefore, in this case the initial distribution has the form: $T_c(x) = T_3(z) = T$. At low optical densities the integral term makes a small contribution, one may use the solution of the given system without allowance for scattering. However, of greatest interest is the distribution of vibrational temperatures for the intermediate optical densities. For this purpose, use is made of the method of parameter fitting. In the given problem, such a parameter is the gas density. The whole range of gas densities was subdivided into rather small regions, so that the solution from the neighbouring node can be taken as an initial approximation to solve the system of integral equations at the given intermediate density. The travel along the density was made both from the small to large values and in the reverse direction. In order to decrease the time of computation of the integral term, which describes multiple resonant scattering, use was made of an approximate factorization of nuclei $G^i_{\kappa'\kappa}(z, z')$ of system (14). This made it possible to perform the preliminary summation over j and to introduce several one-dimensional data files the number of which is determined by the number of different pairs of quanta numbers (l, l'). As a result, only summation over vibrational transitions remains in solution of the system.

According to equation (23), the matrix elements of vibrational–rotational transitions are factorized. Thereafter, in view of the weak dependence of the frequency of vibrational–rotational transition on the rotational quantum number, it is possible to write:

$$\nu_{\kappa',\kappa} \equiv \nu_{\langle v'l'j'\rangle\langle vlj\rangle} \simeq \nu_{\langle v'l'\rangle\langle vl\rangle}$$

and moreover

$$g_\kappa = g_{vl} \cdot g_j = g_{vJ}(2j+1), \quad v = (v_1, v_2, v_3).$$

Considering the expression for the level energy in the CO_2 molecule [15], the population difference has the form

$$\begin{aligned} N_\kappa - N_{\kappa'} &= \frac{1}{Q}\left(f_{vl}\exp\left(-\frac{B}{K_B T}\cdot j(j+1)\right)\right. \\ &\qquad \left. - f_{v'l'}\exp\left(-\frac{B}{K_B T}\cdot j'(j'+1)\right)\right) \\ &= \frac{1}{Q}\left(f_{vl}\exp\left(-\frac{B}{K_B T}\Delta j(j+j'+1)\right) - f_{v'l'}\right) \\ &\qquad \times \exp\left(-\frac{B}{K_B T} j'(j'+1)\right). \end{aligned} \tag{25}$$

The factor at f_{vl} in the last expression differs from unity only for the P and R branches; it decreases monotonically with an increase in j; however, for the values $j < 50$ it is equal to unity accurate to two decimal places. At the same time the contribution of rotational lines when $j > 50$ for translational–rotational temperatures being smaller than $T = 1000$ K is relatively insignificant. Thus, the factor at f can be assumed to be equal to 1. Taking equation (25), into account, the expression for $\sigma_{\kappa'\kappa}$ and $\sigma^i_{\kappa'\kappa}$ at a constant (over the layer) translational–rotational temperature can be written as

$$\begin{aligned} \sigma_{\kappa'\kappa}(z, z') &\simeq \sigma_n(z, z') \cdot \sigma^{j'l'}_{jl} \\ G^i_{\kappa'\kappa}(z, z') &\simeq G^i_n(z, z') \cdot G^{j'l'}_{jl} \end{aligned} \tag{26}$$

where n is the number of the vibrational transition $n = \{v, v'; l, l'\}$. As a result, the following approximate representation of the integral term obtains:

$$\sum_{E_{\kappa'} > E_\kappa}' \int_0^{z_0} G^i_{\kappa'\kappa}(z, z') \cdot M(\sigma_{\kappa'\kappa}(z, z'))\,\mathrm{d}z'$$

$$\simeq \sum_n \int_0^{z_0} G^i_n(z, z')\Phi_{l'l}(\sigma_n(z, z')) \tag{27}$$

$$\Phi_{l'l}(\sigma_n(z, z')) = \sum_{jj'} G^{j'l'}_{jl} M(\sigma_n(z, z')\sigma^{j'l'}_{jl}). \tag{28}$$

Equation (27) allows one to preliminarily calculate the function $\Phi_{l'l}(x)$ for each pair (l', l).

A similar approximation is applicable for the term which describes spontaneous emission.

In the case of numerical integration over z, it is necessary to consider the singularity of the function $M(\xi) \to \infty$ when $\xi \to 0$. In order not to lose the accuracy of computations, the integration in the vicinity of $z' = z$ was performed analytically, since for $z' \in (z-\varepsilon, z+\varepsilon)$

$$\sigma_{\kappa'\kappa}(z, z') \simeq \sigma_{\kappa'\kappa}(z)|z'-z|$$

the integration in the vicinity of $z' = z$ yields

$$\begin{aligned} &\int_{z-\varepsilon}^{z+\varepsilon} G^i_{\kappa'\kappa}(z, z') M(\sigma_{\kappa'\kappa}(z, z'))\,\mathrm{d}z' \\ &\quad = G_{\kappa'\kappa}(z, z') \int_{-\varepsilon}^{+\varepsilon} \mathrm{d}\xi \int_{-\infty}^{+\infty} \mathrm{d}\omega \cdot \mathrm{e}^{-2\omega^2} E_1(\mathrm{e}^{-\omega^2}\bar{\sigma}_{\kappa'\kappa}(z)|\xi|) \\ &\quad = 2G_{\kappa'\kappa}(z, z')\bar{\sigma}^{-1}_{\kappa'\kappa}(z)[-M_1(\bar{\sigma}_{\kappa'\kappa}(z)\varepsilon) \\ &\qquad + \varepsilon\bar{\sigma}_{\kappa'\kappa}(z) M(\bar{\sigma}_{\kappa\kappa}(z) \cdot \varepsilon) + \sqrt{\pi}] \end{aligned}$$

where

$$M_1(\xi) \equiv \int_{-\infty}^{+\infty} \mathrm{e}^{-\omega^2} \exp(-\xi\,\mathrm{e}^{-\omega^2})\,\mathrm{d}\omega.$$

Note that tables are available for $M(\xi)$, as well as asymptotics being known [21]. The expression for the integral term obtained in the vicinity of the $z' = z$ point can be factorized with respect to vibrational and rotational quantum numbers. This allows the summation to be made over the rotational quantum num-

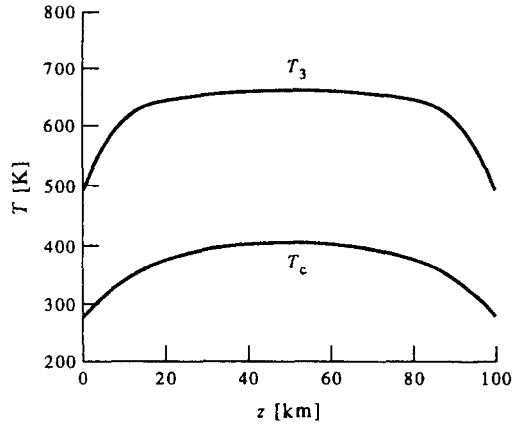

FIG. 1. Distribution of vibrational temperatures along a plane layer in the coupled and antisymmetric modes of CO_2 in a CO_2–N_2 mixture at $T = 1000$ K, $z_0 = 10^5$ m for the N_2 density equal to 3.45×10^{13} cm^{-3}.

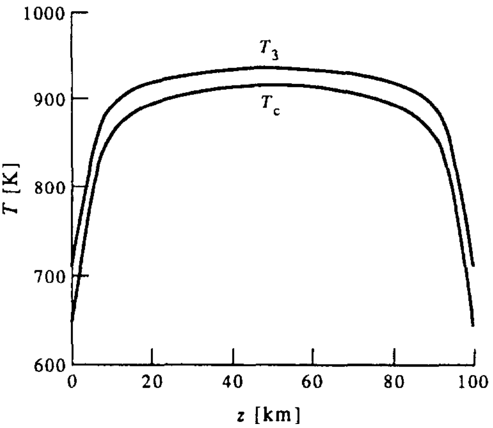

FIG. 3. Distribution of vibrational temperatures along a plane layer in the coupled and antisymmetric modes of CO_2 in a CO_2–N_2 mixture at $T = 1000$ K, $z_0 = 10^5$ m for the N_2 density equal to 3.04×10^{14} cm^{-3}.

ber. Thus, when solving the system of equations (14) the summation only over vibrational transitions remains.

5. RESULTS OF THE COMPUTATIONAL EXPERIMENT FOR A CO_2–N_2 MIXTURE

Figures 1–4 present the results of numerical solution of a system of equations (14) in a stationary case for different gas densities at $T = 1000$ K and CO_2 concentration equal to 0.031%. Here, it is supposed that a gaseous mixture fills a volume having the geometry of a plane layer, with radiation freely emitting from the boundaries; T_c and T_3 are the temperatures in the coupled and antisymmetric modes.

The dependence has a smooth monotonous character falling down to the boundaries of the layer. This is due to the free escape of radiation through the boundaries. At low densities the temperatures in the two modes are much smaller than the translational–rotational temperature because the emitted photons rarely undergo reabsorption. Conversely, at large densities all the temperatures tend to an equilibrium valve as a result of an intensive exchange by energy between the degrees of freedom at frequent collisions and re-absorptions.

With variation in the translational–rotational temperature as a parameter (from 500 to 1000 K) the solution of the system of equations (14) did not change its form appreciably.

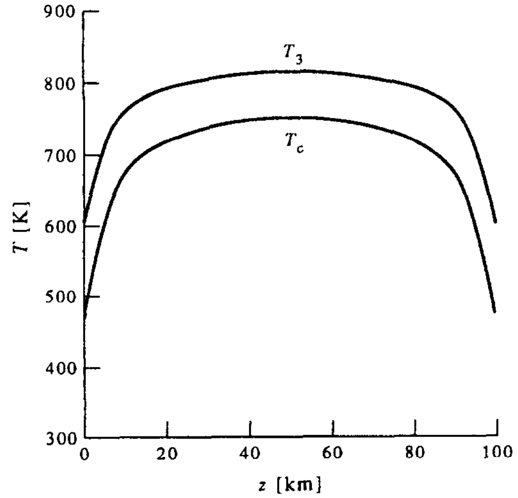

FIG. 2. Distribution of vibrational temperatures along a plane layer in the coupled and antisymmetric modes of CO_2 in a CO_2–N_2 mixture at $T = 1000$ K, $z_0 = 10^5$ m for the N_2 density equal to 1.20×10^{14} cm^{-3}.

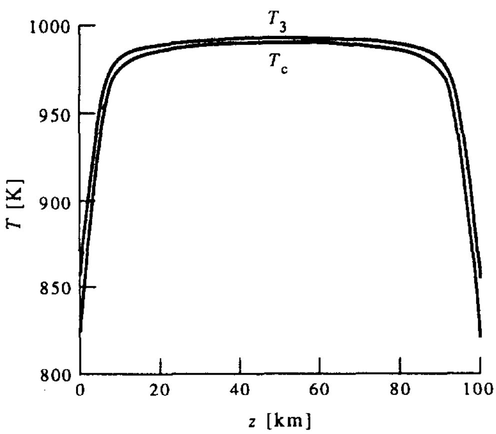

FIG. 4. Distribution of vibrational temperatures along a plane layer in the coupled and antisymmetric modes of CO_2 in a CO_2–N_2 mixture at $T = 1000$ K, $z_0 = 10^5$ m for the N_2 density equal to 1.0×10^{15} cm^{-3}.

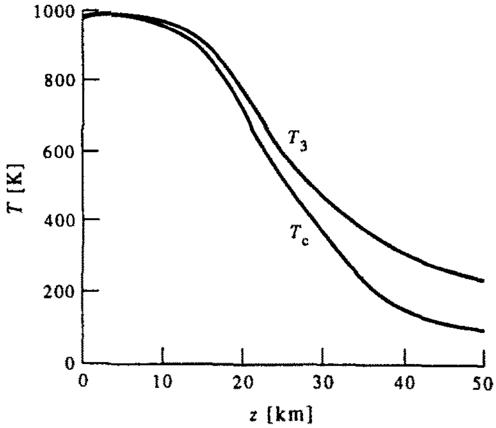

FIG. 5. Distribution of vibrational temperatures along a plane layer in the coupled and antisymmetric modes of CO_2 in a CO_2–N_2 mixture at $T = 1000$ K, $z_0 = 5 \times 10^4$ m for the density varying exponentially across the layer.

Figure 5 presents the solution of system (14) for an exponential distribution of mixture density across a plane layer.

In contrast to refs. [2, 3] the solutions obtained took into account a considerable quantity of vibrational transitons. The numerical solutions showed that the disregarding of weak transitions leads to considerable errors in the distribution of vibrational temperatures (on the order of hundreds of degrees).

Another distinction is due to the fact that the present work used not a two-level model, but rather a real multilevel system for a mixture of polyatomic gases.

Computer investigations showed that with specially selected parameters for polyatomic molecules (line strengths, exchange rates) qualitatively new effects can be obtained, such as non-specular distributed bistability and a non-monotonous distribution of vibrational temperatures.

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