Pergamon

Int. J. Heat Mass Transfer. Vol. 38, No. 1, pp. 163–173, 1995

0017-9310/95 $9.50+0.00

0017-9310(94)00113-8

Radiation transfer in vibrationally nonequilibrium gases

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(*Received* 7 *July* 1993)

Abstract—A technique is set out for calculating infrared radiation in vibrational–rotational bands of nonequilibrium molecular gases along nonuniform paths. The technique is based on the model of the random superposition of Elsasser bands applied to narrow spectral ranges. For determining the matrix elements of lines, use is made of the harmonic oscillator and rigid rotator approximation. At a reasonable sacrifice in accuracy, this allows one to apply the technique over a wide temperature range. For linear triatomic molecules, combining into groups of lines with almost identical lower-level energies is suggested. This considerably diminishes the expenditure of machine time when describing radiation transfer. A careful account of the changes in the contour of lines along the line of sight, including those associated with flow velocity, makes it possible to use the technique for highly nonuniform paths and supersonic flows. Testing was conducted on calculations for diatomic molecules and 2.7 and 4.3 μm CO_2 bands. The values of the constants needed are given. The comparison carried out allows one to recommend the technique for routine calculations in numerical simulation of a wide range of heat and mass transfer problems.

INTRODUCTION

The current interest in the problem under consideration has stimulated the development of a number of techniques for calculating radiation transfer in vibrational–rotational bands of molecular gases. Each of these techniques applies to a certain range of problems and has a limited applicability. Thus, to calculate burning jets, use is made of techniques based on one or other of the 'models of bands' [1–6] when mean parameters empirically found or predicted are introduced for the spectral range considered. These techniques are applied with success to radiation transfer in slightly nonisothermal equilibrium volumes of gases with impact broadening.

It is most expedient to employ 'line-by-line' calculations [7] in the problems of atmospheric optics for slightly heated gases. The use of such a technique at high temperatures is of little promise at the present time not only because of the lengthy calculations, but also because of the insufficient knowledge of the position and broadening parameters of 'hot' lines.

For calculating radiation transfer in the bands of simple molecules (diatomic, linear triatomic) methods are commonly used which are based on the assignment of the real structure of spectral lines and approximate description of their overlap [8–11]. The present technique also refers to this class. However, in contrast to those already available, the present authors suggest an approach which allows one to describe a wide range of experimental situations and at the same time to perform routine calculations with a smaller expenditure of machine time. The use of energy levels and matrix elements of the lines in their explicit form makes it possible to calculate radiation transfer in substantially nonequilibrium conditions.

EQUATION OF TRANSFER IN VIBRATIONALLY NONEQUILIBRIUM GASES

In vibrational–rotational bands radiation is formed in spectral lines, each of which originates as a result of the transition of a molecule from one quantum state k′ (upper level) to another state k″ (lower level). The radiative energy transfer equation, neglecting scattering, can be written as [12]

$$\frac{\mathrm{d}I_\nu}{\mathrm{d}x} = \sum_{\mathrm{k'k''}\,\mathrm{i}} f^i_{\mathrm{k'k''}}(\nu-\nu^i_{\mathrm{k'k''}})[A^i_{\mathrm{k'}}N^i_{\mathrm{k'}} + B^i_{\mathrm{k'k''}}N^i_{\mathrm{k'}}I_\nu - B^i_{\mathrm{k''k'}}N^i_{\mathrm{k''}}I_\nu] \quad (1)$$

where $A_{\mathrm{k'}}$ and $B_{\mathrm{k'k''}}$ are the Einstein coefficients for spontaneous and stimulated radiation; $B_{\mathrm{k''k'}}$ is the Einstein coefficient for stimulated radiation; $N_{\mathrm{k'}}$ and $N_{\mathrm{k''}}$ are the populations of the upper, k′, and lower, k″, levels, respectively; $f_{\mathrm{k'k''}}$ is the spectral line contour with the center at $\nu_{\mathrm{k'k''}}$.

In equation (1) summation is taken over all the mixture species i and over all the vibrational–rotational transitions k′k″ contributing to the radiation at frequency ν. Equation (1) is nothing more than the ordinary equation of spectral radiation transfer adapted to the linear structure of the spectrum. Contributions to the radiation at frequency ν come from all of the neighbouring lines, due to broadening. The number of molecules belonging to the vibrational–rotational line k′k″ and participating in the radiation at frequency ν is dictated by the popu-

NOMENCLATURE

$A_{k'}$	Einstein coefficient for spontaneous radiation
A_ν	spectral absorption of gas
$B_{k'k''}$	Einstein coefficient for stimulated radiation
$B_{k''k'}$	Einstein coefficient for stimulated absorption
B_ν	effective Planck function
c	speed of light
E_v	vibrational energy
F	Hermann–Wallis factor
F_j	rotational energy
$f_{k'k''}$	spectral line contour
g_k	degeneracy of k level
h	Planck's constant
I_ν	spectral intensity of radiation
j	rotational quantum number
k	Boltzmann's constant
l	angular moment quantum number
N_k	population of k level
P	gas pressure
Q	statistical sum
S	integral absorption index of spectral line
$S(j, l)$	squared matrix element for rotational transition
T	temperature
T_ν	spectral transmittance of gas
U	gas flow velocity
v	vibrational quantum number
x	geometric path length in gas.

Greek symbols

α	integral index of band absorption
β^2	squared matrix element of vibrational transition
γ	spectral line half-width
κ_ν	spectral absorption coefficient
μ	molecular weight
ν	frequency
σ	relative efficiency of optical collisions
ω	effective (optical) length.

Subscripts

k	number of quantum state
v	vibrational characteristic
r	rotational characteristic
ν	spectral characteristic.

Superscripts

$'$	refers to upper-level characteristics
$''$	refers to lower-level characteristics.

lations of the k′ and k″ levels, and by the line contour $f_{k'k''}$.

The value

$$\kappa_\nu = \frac{T}{300} \sum_{k'k''i} f^i_{k'k''}(\nu - \nu^i_{k'k''}) B^i_{k''k'} N^i_{k''} \times \left(1 - \frac{B^i_{k'k''} N^i_{k'}}{B^i_{k''k'} N^i_{k''}}\right) \quad (2)$$

is nothing but the spectral absorption coefficient expressed in cm^{-1}. In order for the absorption coefficient to be dependent only on the properties of the molecule, a factor before the coefficient is used which is proportional to the number of molecules per unit volume. The dimensionality of κ_ν varies, depending on the dimensionality of the factor. In equation (2), the STP system has been selected, i.e. the absorption coefficient reduced to normal conditions ($P = 1$ atm, $T = 300$ K). Summation in equation (2) is taken over all the mixture components and all the vibrational–rotational transitions.

The value of $B^i_{k''k'} N^i_{k''}$ is proportional to the line force $S^i_{k''k'}$ for the transition from the k″ to the k′ levels, whereas the value

$$e^i_{k''k'} = \frac{B^i_{k'k''} N^i_{k'}}{B^i_{k''k'} N^i_{k''}} = \frac{g^i_{k''} N^i_{k'}}{g^i_{k'} N^i_{k''}}$$

determines the ratio (taking into account the degeneration of the levels $g_{k''}$ and $g_{k'}$) of the populations of the upper and lower vibrational–rotational levels that determine the line. Thus

$$\kappa_\nu(x) = \sum_{k'k''i} (1 - e^i_{k''k'}) S^i_{k''k'} f^i_{k''k'} (\nu - \nu^i_{k''k'}). \quad (3)$$

The value

$$A_\nu(x) = \sum_{k'k''i} f^i_{k''k'} (\nu - \nu^i_{k''k'}) A^i_{k'k''} N^i_{k'}$$

is a source function. Using the relationship between the Einstein coefficients

$$A_{k'k''} = C_1 B_{k'k''}; \quad C_1 = \frac{2h\nu^3}{c^2}$$

the source function will be rewritten in the form

$$A_\nu(x) = \kappa_\nu(x)\, B_\nu(x)$$

$$B_\nu = C_1 \frac{\sum\limits_{k'k''i} e^i_{k''k'} S^i_{k''k'} f^i_{k''k'} (\nu - \nu^i_{k''k'})}{\sum\limits_{k'k''i} (1 - e^i_{k''k'}) S^i_{k''k'} f^i_{k''k'} (\nu - \nu^i_{k''k'})}. \quad (4)$$

Here $B_\nu(x)$ is the extension of the equilibrium Planck function to the case of the arbitrary population of the vibrational–rotational levels. In the case of thermodynamic equilibrium in the medium the value $e_{k''k'}$, which is equal to

$$e_{k''k'} = \exp\left(-\frac{C_2\nu}{T}\right); \quad C_2 = \frac{h}{K}$$

does not depend on the position of the levels and

$$\kappa_\nu(x) = (1-e_{k''k'}) \sum_{k'k''i} S^{i}_{k''k'} f^{i}_{k''k'}(\nu-\nu^{i}_{k''k'}) \tag{5}$$

$$B_\nu = C_1 \frac{e_{k''k'}}{1-e_{k''k'}}. \tag{6}$$

To shorten representation, the geometric length x will be replaced by the effective length ω using the relation

$$\mathrm{d}\omega = P\frac{300}{T}C\,\mathrm{d}x \tag{7}$$

and the equation of transfer will be rewritten in the form

$$\frac{\mathrm{d}T_\nu}{\mathrm{d}\omega} = \kappa_\nu(B_\nu - I_\nu). \tag{8}$$

Solution of equation (8) with allowance for the designation adopted in equation (7) will be written as

$$I_\nu = I_{\nu_0}\exp\left(-\int_0^{\omega^*}\kappa_\nu\,\mathrm{d}\omega\right) + \int_0^{\omega^*} B_\nu(\omega)\exp\left(-\int_\omega^{\omega^*}\kappa'_\nu\,\mathrm{d}\omega'\right)\kappa_\nu\,\mathrm{d}\omega \tag{9}$$

where I_{ν_0} is the incident radiation, and ω^* is the effective length up to the observation point.

Often, for the $\omega-\omega^*$ layer the following quantities are introduced:

$$T_\nu = \exp\left(-\int_\omega^{\omega^*}\kappa'_\nu\,\mathrm{d}\omega'\right); \quad A_\nu = 1 - T_\nu \tag{10}$$

called the transmittance and absorptance of the $\omega-\omega^*$ layer, respectively. In the absence of incident radiation, solution (9) can be presented in the form

$$I_\nu = \int_0^{\omega^*} B_\nu(\omega)\left(\frac{\mathrm{d}T_\nu}{\mathrm{d}\omega}\right)\mathrm{d}\omega. \tag{11}$$

Formula (11) formally fully solves the problem of spectral radiation transfer calculation in vibrational–rotational bands of nonequilibrium and nonuniform layers of molecular gases if the following quantities are prescribed: $S_{k''k'}(\omega)$, the forces of the lines that contribute to the radiation at frequency ν; $\nu_{k''k'}$, the position of the line center; $f_{k''k'}(\nu-\nu_{k''k'})$, the contour of each spectral line; $N_{k'}$ and $N_{k''}$, populations of the upper and lower vibrational levels in transition between which there originates a line.

A MODEL FOR CALCULATING THE MEAN SPECTRAL RADIATION

The present paper considers a class of problems in which it is necessary to calculate not the spectral radiation, but that averaged over a certain frequency range ($\Delta\nu \sim 10\ \mathrm{cm}^{-1}$) and defined as

$$I_\nu = \frac{1}{\Delta\nu}\int_{\nu-\Delta\nu/2}^{\nu+\Delta\nu/2} I_{\nu'}\,\mathrm{d}\nu' \tag{12}$$

where I_ν is the solution of spectral problem (11). Basic difficulties are manifested in performing practical calculations. As seen from equations (3) and (4), the absorption coefficients and the source function values depend linearly on the populations of the levels and the line forces. Therefore, the requirements imposed on the accuracy of specification for the position of the levels and matrix element transitions are not strong. However, in order to calculate the spectral characteristics, it is necessary to indicate the position of the line centers with the accuracy determined by the halfwidth of these lines. For relatively low pressures, these are values of the order of 10^{-3}–$10^{-4}\ \mathrm{cm}^{-1}$. Only the positions of a small number of lower levels is known with such accuracy. At high temperatures, when it is necessary to take into account the transitions between high-lying levels, the attainment of the required accuracy for solving spectral problems becomes virtually impossible. Moreover, the line contour is well known only at a distance from the center smaller than, or equal to, 10 half-widths. Thus, the description of many real situations by using spectral calculations with direct selection of all the lines is not only cumbersome, but is also not possible in principle at the present time. The remedy is to apply the models of bands that do not require rigorous assignment of the line positions. A variety of such models have been developed for different molecules and physical situations [5, 13–16].

When describing vibrationally nonequilibrium diatomic and linear triatomic molecules, including those for the 4.3 and 2.7 μm CO_2 bands, it seems advisable to use the following model. The range of averaging incorporates the lines that belong to a variety of different vibrational transitions. For each vibrational transition the lines occurring in the interval selected (of the order of $10\ \mathrm{cm}^{-1}$) are almost equally spaced and the line force varies little within this interval; therefore, the application of the Elsasser model is quite justifiable [8]. The positions of the lines belonging to different transitions do not correlate in any way between themselves; therefore, in order to take into account their overlapping, one can use the statistical model of refs. [1, 5]. Within the framework of this model, the solution of the equation of transfer for a nonuniform path, without allowance for the incident radiation, can be written in the form

$$I(\nu)|_{x=R} = \int_0^R \left(\sum_k B_k \frac{\partial \ln \tau_k}{\partial x}\right)\tau\,\mathrm{d}x \tag{13}$$

where

$$B_k = C_1\frac{e_k}{1-e_k} \tag{14}$$

is the equivalent of the Planck function for the vibrational transition from the k to the k+1 level at frequency ν; e_k is the ratio of the populations of the upper and lower levels. Formula (14) results from equation (4) if one assumes that source function is independent of the frequency over the averaging interval and there is weak overlapping between different transitions. In the case of the Boltzmann distribution over vibrational levels, the Planck function has the form

$$B_k(\nu) = \frac{2hc^2\nu^3}{\exp\left(\frac{kE_{v'}}{T_{v'}} - \frac{kE_{v''}}{T_{v''}}\right)\exp\left[\frac{k(\nu-\nu_k)}{T_0}\right]-1}. \tag{15}$$

According to the statistical model for the overlapping of different transitions, the transmittance of the layer, τ, is expressed as the product

$$\tau = \prod_k \tau_k \tag{16}$$

where τ_k is the 'transmittance' for one transition in the Elsasser approximation:

$$\tau_k = \int_{-d/2}^{d/2} \mathrm{d}\nu \exp\left[-\int_X^R S \sum_{n=-\infty}^{n=+\infty} f(\nu - nd)\,\mathrm{d}\omega\right]. \tag{17}$$

Equation (17) uses an assumption of approximate equality between the forces of vibrational–rotational lines falling into the considered interval $\Delta\nu$ and belonging to one transition.

Equations (13)–(17) determine the adopted model. The internal accuracy of the model depends on the situation considered. The assumption about the Elsasser structure inside the vibrational transition is better, the narrower the averaging range and the smaller the optical depth of the absorbing layer. The accuracy of the statistical model for the overlapping of different transitions is higher, the larger the number of transitions that contribute to the interval considered (the higher the temperature) and smaller, the larger the optical depth [4]. However, the errors which may occur in calculations by this model are due not only to internal errors, which, in principle, can be evaluated for each specific case, and not only for the errors in the model parameters, which can be improved if required, but mainly for the difference of the real molecule from its model representation. These errors can be found only by comparing model predictions with experiment. Some of such comparisons will be given below.

CALCULATION PROCEDURE

The model considered above leads to the following scheme for the calculation of the radiation at frequency ν along the line of sight.

An inhomogeneous layer is divided into a series (N) of homogeneous zones, for each of which all the thermodynamic parameters are prescribed; thereafter, radiation is calculated from the finite formula

$$I(\nu) = \sum_{n=1}^{N} B_\nu(n)\,(T_\nu(n-1) - T_\nu(n))\,;\; T_\nu(0) = 1. \tag{18}$$

The effective Planck function $B_\nu(n)$ and the transmission function $T_\nu(n)$ involved in the above formula are determined by the contribution of all the vibrational transitions of the lines which fall into the frequency range $\nu \pm \Delta\nu/2$. In this case, all the molecules (isotopes) and all the band branches should be taken into account. The full transmittance of zone n is determined as a product of the transmittances of separate transitions:

$$T_\nu(n) = \prod_k T_{\nu,k}(n). \tag{19}$$

The mean spectral transmittance diminishes from zone to zone following the law

$$T_{\varphi,k}(n) = T_{\nu,k}(n-1) - D[T_{\nu,k}(n)]. \tag{20}$$

In this case, the effective Planck function is expressed as

$$B_\nu(n) = \frac{\sum B_{\nu,k}(n)\,D(T_{\nu,k}(n))}{\sum D(T_{\nu,k}(n))}. \tag{21}$$

The change in transmittance in zone n, $D(T_{\nu,k}(n))$, is determined in the Elsasser approximation as

$$D(T_{\nu,k}(n)) = \int_{-d/2}^{d/2} \mathrm{d}\nu \exp\left[-\sum_{i=1}^{n-1} \omega(i)\,F_{k,i}(\nu)\right] \times (1 - \exp[-\omega(n)\,F_{k,n}(\nu)]) \tag{22}$$

where $\omega(i) = \rho C_i(300/T)\Delta x$ is the effective zone width, and $F_{k,n}(\nu)$ is the Elsasser absorption coefficient determined from the prescribed mean force of the line, line contour and space between the lines. It is esential in this case that the effective space between the lines and the squared matrix element is independent of the zone.

Thus, calculations are reduced to a successive selection of vibrational transitions, for each of which the following quantities should be found: mean spacing between the lines, mean square of their matrix element, and populations of their upper and lower levels. For each zone the sums $\sum_k B_{\nu,k}(n)D(T_{\nu,k}(n))$ and $\sum_k D(T_{\nu,k}(n))$, and the product $\prod_k T_{\nu,k}(n)$, are accumulated. The selection should be continued until new transitions cease to make a noticeable contribution to the accumulated quantities.

PARAMETERS OF THE MODEL FOR CERTAIN MOLECULES

The spectroscopy of vibrational–rotational bands of the simplest molecules is based on the separation of vibrational and rotational motions. The energy of the level is written down in the form of a sum of vibrational energy which is usually described as the approximation of harmonic or anharmonic oscillators, rotational energy, in the rigid rotator approximation, and the additions for vibrational–rotational interaction and centrifugal stretch. The values of the energy levels of simple molecules (diatomic, linear triatomic) are determined by the Danhem formula [5]. The constants incorporated into this formula are determined from experimental data according to the position of the vibrational–rotational lines. Their values, adopted in the present paper, are given in ref. [5].

An attribute of a CO_2 molecule is the presence of the Fermi resonance originating between vibrational levels with the same angular moment due to the close equality of one quantum of symmetric vibration to two quanta of bending vibration, and leading to a substantial shift in the energy levels. Allowance for the Fermi resonance when determining the position of vibrational levels can be done by the method given in ref. [17]. There are tables of vibrational energy levels for the majority of simplest molecules [18, 19] which can be used directly in calculations. However, any tables have limitations on the number of levels. Therefore, it is more convenient to use computational formulae, the more so because their accuracy is no worse than $\pm 0.5\ \mathrm{cm}^{-1}$ for not very high levels.

The 4.3 μm CO_2 band is formed by transitions in which the third quantum number V_3 varies by 1, whereas the 2.7 μm band is formed by transitions in which V_3 varies by 1 and V_1 varies by 1 or V_2 varies by 2. To describe radiation characteristics in these bands it is convenient that all the diversity of vibrational levels be represented as a set of levels of anharmonic oscillators, each of which is characterized by certain values of the first and second vibrational quantum numbers. The population of the level of such an oscillator is proportional to $\exp(-kE_{\mathrm{v}_1\mathrm{v}_2^l0}/T_{\mathrm{v}'})$, and the quantities characterizing the energy levels of the anharmonic oscillator are calculated as functions of the first and second quantum numbers from the formula

$$\begin{aligned}E(V_1, V_2, l, 0) &\\ &= V_1[\omega_1 + V_1(X_{11} + V_1 Y_{111}\\ &\quad + V_2 Y_{112}) + V_2(X_{12} + V_2 Y_{122})]\\ &\quad + V_2[\omega_2 + V_2(X_{22} + V_2 Y_{222})] + g_{22} l^2.\end{aligned}$$

One other simplification can be made to provide the accuracy which is claimed by this technique. When describing the structure of vibrational levels of CO_2, the transitions between which make a contribution in the 4.3 μm band, viz. for the groups of levels having approximately the same energy in the first and second modes, mean parameters can be introduced. For the levels in the 2.7 μm CO_2 band such unification of levels cannot be performed, since transitions take place with variations in the first or second quantum numbers, so that only unification of the levels with different angular moments l is possible. Then each group represents the specified number R of identical anharmonic oscillators. Allowance for the decrease in the number of lines for transitions with $l = 0$ will be made by summing them with the weight equal to 0.5. Thus, R may also acquire half-integer values. The frequency of the vibrational transition between excited levels will be determined in terms of the mean frequency of the transition $0 \rightarrow 1$ for the ν_{0_R} group and the mean value of anharmonism following the formula

$$\nu_{\mathrm{v_R}} = \nu_{0_\mathrm{R}} - 2D_\mathrm{R}{}^* V_3.$$

The vibrational energy of excited levels for the group is determined in terms of the mean energy of the lower state, E_{0_R}:

$$E_{\mathrm{v_R}} = E_{0_\mathrm{R}} + V_3[\nu_{0_\mathrm{R}} - (V_3 - 1)D_\mathrm{R}].$$

The rotational structure for the group is determined in terms of the mean rotational constant of the lower level B_{0_R} and constants of vibrational–rotational interaction α_R:

$$B_{\mathrm{v_R}} = B_{0_\mathrm{R}} - \alpha_\mathrm{R} V_3.$$

The transmittance for the entire group is the transmittance of one oscillator with mean values of the parameters raised to the power R.

The spectroscopic values needed for the calculation by the scheme described are listed in Table 1. Table 1 contains the values of averaged constants for 31 groups of oscillators for the 4.3 μm band (including the isotope) and 27 groups for the 2.7 μm band of a CO_2 molecule, as well as the values of constants for CO, NO and HCl molecules. For oscillators in the 2.7 μm band, for each value of the vibrational energy of the lower state, the values of the frequencies ν_{0_R} are given for two types of vibrational transitions:

$$V_1 V_2^l 0 \rightarrow (V_1 + 1) V_2^l 1 \quad \text{and} \quad V_1 V_2^l 0 \rightarrow V_1 (V_2^l + 2) 1.$$

For not very high temperatures ($T \leqslant 3000$ K) and moderate pressures ($P \leqslant 1$ atm), when calculating the force of the vibrational–rotational line the approximation of the harmonic oscillator and rigid rotator can be employed with an accuracy sufficient for the purposes of the present work. In nonequilibrium media the population of each of the energy levels should be specified from outside, but in many practically important cases [20–22] one can see that in the interior of each vibrational degree of freedom there is the Boltzmann distribution over vibrational levels with characteristic temperatures T_1, T_2, and T_3 (in the case of a molecule with three vibrational degrees of freedom, for example CO_2) and T_v (in the case of diatomic molecules, for example CO) different, generally speaking, from the rotational temperature which is close to the translational temperature, $T_\mathrm{r} = T$. In this approximation, the following

Table 1

	E_{0_R}	R	ν_{0_R}	ν_{0_R}	B_{0_R}	
1	0.00	0.5	2349.16		0.3902	$C^{12}O_2^{16}$
2	667.40	1.0	2336.67		0.3910	
3	1335.96	2.0	2325.60		0.3910	4·3 μm
4	2004.00	3.0	2313.60		0.3916	
5	2672.00	4.5	2302.40		0.3917	
6	3341.00	6.0	2291.00		0.3922	$\alpha_{0\to 1} = 2448$
7	4009.00	8.0	2279.00		0.3923	
8	4677.00	10.0	2268.00		0.3928	$D_R = 12.58$
9	5345.00	12.5	2256.00		0.3930	
10	6014.00	15.0	2244.00		0.3940	$\alpha_R = 0.00309$
11	6681.00	18.0	2233.00		0.3940	
12	7350.00	21.0	2222.00		0.3940	
13	8018.00	24.5	2210.00		0.3940	
14	8686.00	28.0	2198.00		0.3950	
15	9354.00	32.0	2187.00		0.3950	
16	10 029.00	36.0	2169.00		0.3950	
17	10 689.00	40.5	2165.00		0.3950	
18	11 355.00	45.0	2156.00		0.3960	
19	12 039.00	50.0	2161.00		0.3960	
20	12 719.00	55.0	2130.00		0.3960	
21	13 375.00	60.5	2118.00		0.3960	
22	0.00	0.5	2283.00		0.3755	$C^{13}O_2^{16}$
23	648.70	1.0	2270.00		0.3755	
24	1297.70	2.0	2258.00		0.3755	4.3 μm
25	1947.00	3.0	2245.00		0.3755	
26	2597.00	4.5	2233.00		0.3755	
27	3247.00	6.0	2221.00		0.3755	$\alpha_{0\to 1} = 26.65$
28	3898.00	8.0	2208.00		0.3755	
29	4550.00	10.0	2196.00		0.3755	$D_R = 11.87$
30	5203.00	12.5	2184.00		0.3755	
31	5856.00	15.0	2172.00		0.3755	$\alpha_R = 0.00283$
32	0.00	0.5	3714.81	3612.89	0.3888	$C^{12}O_2^{16}$
33	667.40	1.0	3723.27	3580.38	0.3896	
34	1335.14	1.0	3726.64	3552.94	0.3903	
35	1285.41	0.5	3692.31	3568.47	0.3903	
36	1388.17	0.5	3711.47	3589.55	0.3875	2.7 μm
37	1967.89	2.0	3713.83	3535.52	0.3911	
38	2076.83	1.0	3713.67	3556.02	0.3883	
39	2601.75	2.5	3703.10	3517.27	0.3918	$\alpha_{0\to 1} = 44.9$
40	2715.75	1.5	3695.39	3542.49	0.3891	
41	2796.97	0.5	3705.95	3550.95	0.3863	$\alpha_{0\to 1} = 32.2$
42	3254.38	3.0	3703.49	3495.55	0.3926	
43	3390.67	2.0	3698.44	3513.75	0.3898	
44	3514.81	1.0	3688.75	3509.37	0.3870	$D_R = 12.58$
45	3880.98	3.5	3693.67	3478.84	0.3934	
46	4024.07	2.5	3682.19	3498.45	0.3906	$\alpha_R = 0.00309$
47	4130.30	1.5	3685.95	3513.30	0.3878	
48	4224.59	0.5	3688.07	3510.45	0.3850	
49	4530.71	4.0	3691.30	3459.09	0.3941	
50	4689.61	3.0	3684.42	3474.03	0.3913	
51	4821.38	2.0	3684.46	3486.07	0.3886	
52	4937.63	1.0	3690.55	3488.04	0.3858	
53	5183.82	4.0	3688.89	3439.74	0.3949	
54	5350.42	3.5	3637.71	3425.76	0.3921	
55	5458.44	2.5	3616.76	3465.38	0.3893	
56	5559.59	1.5	3563.23	3417.41	0.3865	
57	5196.74	4.5	3480.44	3284.01	0.3949	
58	5666.58	0.5	3682.37	3471.99	0.3838	
59	0.00	1.0	2143.27		1.9225	CO $\alpha_{0\to 1} = 260$ $D_R = 13.295$ $\alpha_R = 0.01754$
60	0.00	1.0	1875.72		1.6954	NO $\alpha_{0\to 1} = 132$ $D_R = 13.97$ $\alpha_R = 0.0178$
61	0.00	1.0	2880.64		10.44	HCl $\alpha_{0\to 1} = 113.1$ $D_R = 52.05$ $\alpha_R = 0.3019$

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† The dimensions of the quantities given are cm^{-1}; the dimension of $\alpha_{0\to 1}$ is $\text{atm}^{-1}\ \text{cm}^{-2}$.

expression will be written down for the line force of the harmonic oscillator:

$$S_{\mathrm{v''j''}\to\mathrm{v'j'}}(T,T_{\mathrm{r}},T_{\mathrm{v'}},T_{\mathrm{v''}})=\alpha_{\mathrm{v''}\to\mathrm{v'}}(T,T_{\mathrm{r}},T_{\mathrm{v'}},T_{\mathrm{v''}})\frac{1}{Q_{\mathrm{r}}}$$

$$\times\exp\left(-\frac{kF_{\mathrm{v}}(j)}{T_{\mathrm{r}}}\right)\frac{\nu_{\mathrm{v''j''}\to\mathrm{v'j'}}}{\nu_{\mathrm{v''}\to\mathrm{v'}}}S(j'',l'')\,F_{\mathrm{v'j'}}^{\mathrm{v''j''}}$$

$$\times\frac{1-\exp\left[-\left(\frac{kE_{\mathrm{v'}}}{T_{\mathrm{v'}}}-\frac{kE_{\mathrm{v''}}}{T_{\mathrm{v''}}}\right)\right]\times\exp\left[-\frac{k}{T_{\mathrm{r}}}\left(\nu_{\mathrm{v''j''}\to\mathrm{v'j'}}-\nu_{\mathrm{v''}\to\mathrm{v'}}\right)\right]}{1-\exp\left[-\left(\frac{kE_{\mathrm{v'}}}{T_{\mathrm{v'}}}-\frac{kE_{\mathrm{v''}}}{T_{\mathrm{v''}}}\right)\right]}\qquad(23)$$

where

$$\alpha_{\mathrm{v''}\to\mathrm{v'}}(T,T_{\mathrm{r}},T_{\mathrm{v'}},T_{\mathrm{v''}})=\alpha_{\mathrm{v''}\to\mathrm{v'}}(T_0)\frac{T_0}{T}\frac{Q_{\mathrm{v}}(T_0)}{Q_{\mathrm{v}}(T_i)}$$

$$\times\frac{1-\exp\left[-\left(\frac{kE_{\mathrm{v'}}}{T_{\mathrm{v'}}}-\frac{kE_{\mathrm{v''}}}{T_{\mathrm{v''}}}\right)\right]}{1-\exp\left[-\frac{k}{T_0}\nu_{\mathrm{v''}\to\mathrm{v'}}\right]}$$

$$\times\exp\left[-\left(\frac{kE_{\mathrm{v''}}}{T_{\mathrm{v''}}}-\frac{kE_{\mathrm{v''}}}{T_0}\right)\right].\qquad(24)$$

The squared matrix element for a purely rotational transition $S(j'',l'')$ will be written down in the form:

for diatomic molecules

$$S(j'',l'')=\begin{cases}j+1 \text{ for the } R\text{-branch, } \Delta j=+1\\ j \text{ for the } P\text{-branch, } \Delta j=-1\end{cases}$$

for triatomic molecules

$$S(j'',l'')=\begin{cases}(j+1)-\dfrac{l^2}{j+1}\text{ for the } R\text{-branch, } \Delta j=+1\\ j-\dfrac{l^2}{j}\text{ for the } P\text{-branch, } \Delta j=-1\\ \dfrac{l^2}{j}+\dfrac{l^2}{j+1}\text{ for the } Q\text{-branch, } \Delta j=0;\quad j\neq 0\end{cases}.$$

The line force correction for the vibrational–rotational interaction is determined by the Herman–Wallis F-factor ($F_{\mathrm{v'j'}}^{\mathrm{v''j''}}$) which can be expressed in terms of the rotational quantum number function. Usually, this coefficient differs very little from unity and its dependence on the quantum rotational number j can be neglected when calculating the mean spectral radiation. The vibrational statistical sum Q_{v} can be calculated with sufficient accuracy in the harmonic oscillator approximation using the temperatures of the modes T_1, T_2, and T_3 for CO_2, and T_{v} for diatomic molecules. For the rotational statistical sum it is possible to use the expression for a rigid rotator with correction for centrifugal stretch [10].

The integral absorption index of excited transitions $\alpha_{\mathrm{v''}\to\mathrm{v'}}(T_0)$, entering into formula (24), can be expressed in terms of the experimentally measured integral absorption index of the basic transition $\alpha_{0\to1}(T_0)$. For this purpose, it is possible to use the dependence of the squared matrix element of vibrational transition $\beta^2_{\mathrm{v'}\to\mathrm{v''}}$ on the vibrational quantum number in the harmonic approximation [2]:

$$\alpha_{\mathrm{v''}\mathrm{v'}}=\alpha_{0\to1}\frac{\nu_{\mathrm{v'}\to\mathrm{v''}}}{\nu_{0\to1}}\frac{g_{l,\mathrm{v'}\to\mathrm{v''}}}{g_{l,0\to1}}\frac{\beta^2_{\mathrm{v'}\to\mathrm{v''}}}{\beta^2_{0\to1}}$$

$$\times\exp\left[-\frac{k(E_{\mathrm{v''}}-E_0)}{T_0}\right]\frac{1-\exp\left[-\frac{k\nu_{\mathrm{v'}\to\mathrm{v''}}}{T_0}\right]}{1-\exp\left[-\frac{k\nu_{0\to1}}{T_0}\right]}\qquad(25)$$

where

$$g_l=\begin{cases}1, & \text{at } l=0\\ 2, & \text{at } l\neq 0\end{cases}.$$

In the harmonic approximation $\beta^2_{\mathrm{v'}\to\mathrm{v''}}$ is proportional to $(\mathrm{v''}+1)$ for the basic bands of diatomic molecules, to (v''_3+1) for the 4.3 μm CO_2 band, and to $(\mathrm{v}''_1+1)(\mathrm{v}''_3+1)$ for the 2.7 μm CO_2 band [2].

In the non-equilibrium case, the effective temperature of the population of levels $T_{\mathrm{v}_1\mathrm{v}_2^l\mathrm{v}_3}$ in formula (23) can be expressed in terms of the temperature of the modes by means of the division of energies belonging to different types of vibrations:

$$\frac{E_{\mathrm{v}_1\mathrm{v}_2^l\mathrm{v}_3}}{T_{\mathrm{v}_1\mathrm{v}_2^l\mathrm{v}_3}}=\frac{E_{\mathrm{v}_1\mathrm{v}_2^l\mathrm{v}_3}-E_{0\mathrm{v}_2^l\mathrm{v}_3}}{T_1}+\frac{E_{0\mathrm{v}_2^l\mathrm{v}_3}-E_{00^0\mathrm{v}_3}}{T_2}+\frac{E_{00^00}}{T_3}.\qquad(26)$$

Some notes should be made regarding the question of the contour of spectral lines. According to general concepts [5, 23], the form of the vibrational–rotational line is determined by simultaneous action of the collisional and Doppler mechanisms of broadening. The Doppler broadening associated with the thermal motion of molecules leads to the Gaussian form of the line with the half-width equal to

$$\gamma_g=\frac{\nu_0}{C}\sqrt{\frac{2RT\ln 2}{\mu}}.\qquad(27)$$

There are experimental situations for which it is necessary to also take into account the Doppler shift of the centers of lines due to the translational motion of a gas. In this case the Doppler displacement of the center of the line, $\Delta\nu_{\mathrm{D}}$, is determined by the projection of the gas velocity U to the line of sight:

$$\Delta\nu_{\mathrm{D}}=\nu-\nu_0=\nu_0\frac{U}{C}.\qquad(28)$$

There is a large volume of literature devoted to the problems of collisional broadening. Shock broadening leads to the Lorentzian line contour. The theory of shock broadening predicts only the linear dependence of the Lorentzian half-width on pressure, whereas, in order to find the values of γ_L and their dependence on temperature, an analysis of experimental data is required. According to ref. [5], the value of γ_L for the ith gas in a mixture of gases is determined as

$$\gamma_L = \frac{P}{P_0}\left(\frac{T_0}{T}\right)^{0.5} \gamma_{L_0}\left(C_i\left(\frac{T_0}{T}\right)^{0.5} + \sum_{j=1} C_j\alpha_{i,j}\right) \quad (29)$$

where γ_{L_0} is the half-width in the resonance interaction of the ith gas molecules between themselves, and $\alpha_{i,j}$ is the relative efficiency of optical collisions in the interaction of the ith gas molecules with the jth gas molecules.

In a general case the line contour is described by the Voigt profile [24]. For such a countour the summation of lines for the Elsasser transition in equation (16) can be made analytically:

$$\sum_{n=-\infty}^{n=+\infty} f(v-nd) = \frac{1}{\sqrt{\pi}\, d}\int_{-\infty}^{+\infty} \exp(-y^2) \times \frac{\mathrm{sh}\,\beta}{\mathrm{ch}\,\beta - \cos S}\,\mathrm{d}y \quad (30)$$

where

$$\beta = \frac{2\pi\gamma_L}{d} \quad S = \frac{2\pi\left(v - v_0 - \frac{y\gamma_L^2}{\ln 2}\right)}{d}. \quad (31)$$

In the calculations, the main time is spent in calculating transmittance for the Elsasser transition. It was performed by means of direct integration of equation (22) following the standard program of integration with an automatic selection of steps. When calculating the absorption coefficient, use was made of the following approximations. In the case when $\gamma_L/\gamma_D > 3$ or $(v-v_0)/\gamma_D > 4$, only the Lorentzian broadening of lines was taken into account:

$$F_k = \frac{S_k}{d_k}\frac{\mathrm{sh}\,\beta}{\mathrm{ch}\,\beta - \cos S} \quad (32)$$

where

$$\beta = \frac{2\pi\gamma_L}{d} \quad S = \frac{2\pi(v-v_0)}{d}.$$

When $\gamma_D > 10^{-4}\gamma_L$, a purely Doppler contour was calculated:

$$F_k = S_k \exp\left[-\frac{(v-v_0)^2 \ln 2}{\gamma_D^2}\right]. \quad (33)$$

In intermediate cases the coefficient was calculated in the approximation of isolated lines with the help of expansions given in [2]. If one designate $\gamma_L/\gamma_D = A$ and $(v-v_0)/\gamma_D = y$, the calculation of the contour can be reduced to the summation of the following, rather quickly converging series:

$$F = \frac{1}{\sqrt{\pi d}} \sum_{n=1}^{\omega} S_n \exp(-y) \quad (34)$$

in which the coefficients S_n are determined from the recurrent relations

$$U_1 = \exp(A^2)\,\mathrm{erfc}(A)$$

$$R_1 = 1 \quad R_{n+1} = R_n + 1$$

$$C_1 = 1 \quad C_{n+1} = C_n \frac{Y}{R_n}$$

$$U_{n+1} = A\left(\frac{1}{\sqrt{\pi}} - AU_n\right)\Big/(R_n - 0.5)$$

$$S_n = C_n U_n. \quad (35)$$

In conclusion, the following circumstances should be emphasized once again. In principle, it is possible to formulate the means of calculating nonequilibrium radiation in the vibrational–rotational bands of molecules along a nonuniform beam with any, *a priori* specified accuracy. However, at present its practical realization is hindered not only by technical difficulties in view of cumbersome computations, but also by the necessity to accurately specify the position of the lines and their contours. The latter circumstance does not allow one to hope that, at the present time, one could manage to create a technique for calculating radiation which would guarantee the specified accuracy over a wide range of parameters. An alternative approach is the use of the models for taking into account the overlapping of lines. At present, a great number of techniques for calculating radiation have been suggested which involve different models of bands. As soon as the accurate description of the spectrum structure is substituted by its model representation, the accuracy of calculation ceases to fully characterize the accuracy of the real object description. In this case, the only reliable criterion for applying one technique or another in the prescribed ranges of parameters is the widest possible comparison with experimental data.

COMPARISON WITH EXPERIMENTAL DATA AND CALCULATIONS OF OTHER AUTHORS

The final evaluation of the accuracy and reliability of a computational scheme can be obtained only after comparison with experimental data or independent calculations by other techniques. In this case, not only the applicability of the selected model is verified, but also the absence of technical errors in the means used to realize it.

For testing the technique suggested, an attempt has been made by the present authors to use all the materials accessible. A wide comparison of the present calculations with the experimental data and calculations of other authors available in the literature has been performed. Some of the results obtained are given below.

Figure 1 gives a comparison with experimental data on the transmittance of CO_2 in the 4.3 μm band, and Fig. 2 a comparison with line-by-line calculations

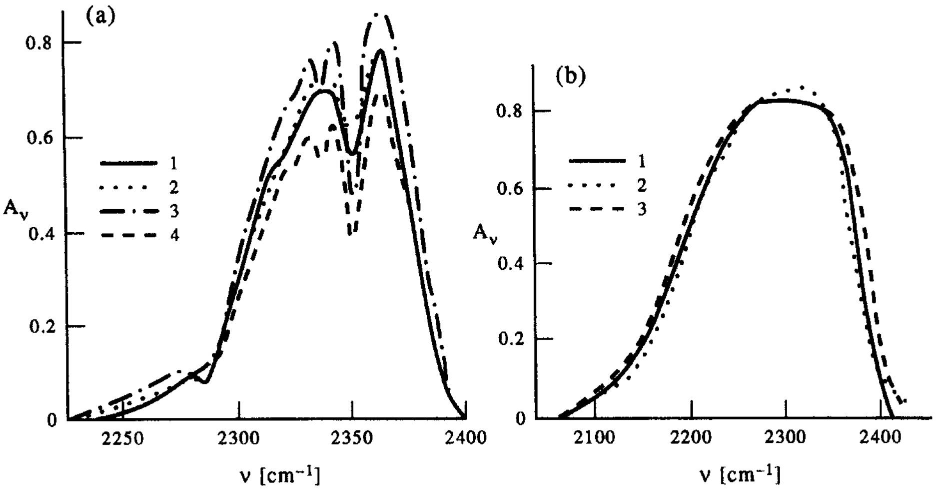

Fig. 1. (a) Spectral absorption of CO_2 layer having the parameters: $P = 1.32 \times 10^4$ Pa; $x = 121$ m; $r_{CO_2} = 2.5 \times 10^{-5}$; $T = 296$ K. (1) Calculation in the present work; (2) experiment; (3) calculation by the Elsasser model; (4) calculation by the statistical model from ref. [27]. (b) Spectral absorption of CO_2 layer with the parameters: $P = 10^5$ Pa; $x = 3.1$ cm; $r_{CO_2} = 0.23$; $T = 1800$ K. (1) Calculation in the present work; (2) experiment; (3) calculation from ref. [28].

from the bank of spectral lines [25] in the 2.7 μm CO_2 band. Figure 3 presents the results of calculations of the spectral intensity of CO_2 radiation in the 4.3 μm region for three absorbing masses. Figure 4 shows the deformation of the CO_2 spectral absorption in the 2.7 μm band, depending on the temperature of the unified (symmetric and deformational) mode T_{12} and the asymmetric mode temperature T_3. As already noted above, an accurate account of the changes in the contour of lines along the line of sight allows one to use the technique for extremely inhomogeneous paths and supersonic flows. In Fig. 5 the effect of the heated CO_2 flow velocity on the radiation spectrum in the 4.3 μm band is demonstrated when observed through an atmospheric layer. The radiation and absorption spectra of the vibrational–rotational CO_2 for the case of a nonuniform path in the zone of excitation of an elec-

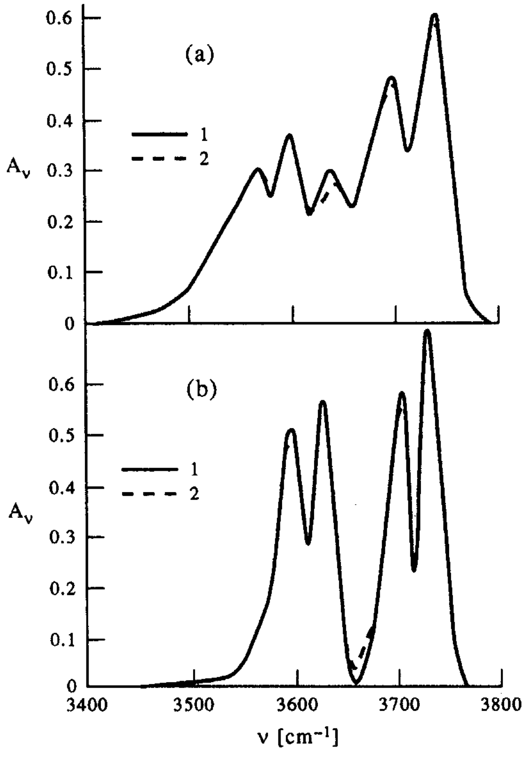

Fig. 2. Spectral absorption of CO_2 layer with the parameters: $P = 5 \times 10^4$ Pa; $x = 1$ m; $r_{CO_2} = 0.1$; $T = 750$ K (a). $P = 10^5$ Pa; $x = 100$ m; $r_{CO_2} = 0.0003$; $T = 300$ K (b). (1) Calculation by the procedure described; (2) line-by-line calculation.

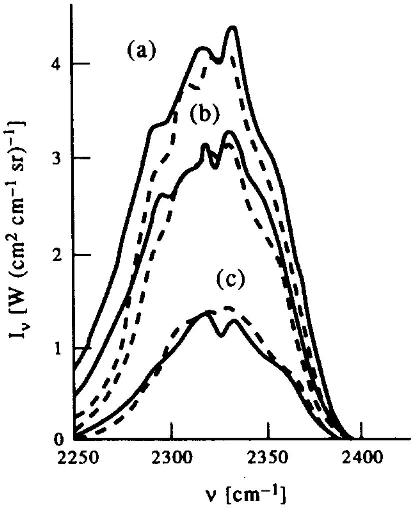

Fig. 3. Spectral intensity of radiation of the CO_2 layer with the parameters: $P = 10^3$ Pa; $x = 0.9$ (a); 4.5 (b); 8 cm (c); $r_{CO_2} = 1$; $T = 300$ K, $T_2 = 500$ K, $T_3 = 1500$ K. (---) Calculation by the statistical model from ref. [29].

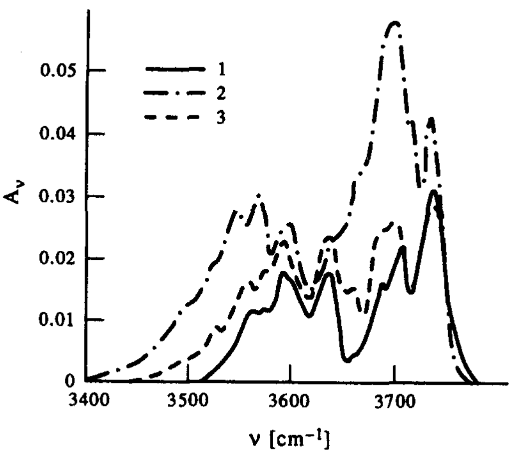

Fig. 4. Spectral absorption of the CO_2 layer with the parameters: $P = 10^3$ Pa, $x = 1$ m, $r_{CO_2} = 0.2$ depending on vibrational temperatures: $T = 400$, $T_{12} = 400$, $T_3 = 400$ K (1); $T = 400$, $T_{12} = 1000$, $T_3 = 1500$ K (2); $T = 400$, $T_{12} = 400$, $T_3 = 1500$ K (3).

tric-discharge laser (Fig. 6) were employed to experimentally determine the vibrational temperature of the asymmetric CO_2 mode. The values of the temperature T_3 obtained coincided with those calculated theoretically from the excitation energies [26].

We will not discuss here the reliability and accuracy of the experimental data given as well as the comparative merits of this or other techniques depending on the range of parameters. We note only that, within the framework of reasonable consideration, the technique suggested in the present work without any adaptation to the experimental conditions satisfactorily describes the averaged spectral characteristics of radiation transfer in linear tri- and diatomic molecules in the range of temperatures from 200 to 3000 K and pressures up to 2 atm.

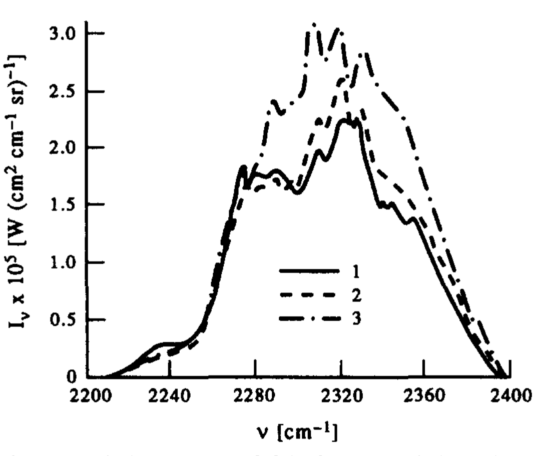

Fig. 5. Radiation spectra of CO_2 flow passed through the atmosphere vs the flow velocity $u = 0$ (1), 1000 (2), 3000 m s^{-1} (3). The flow parameters: $P = 10^3$ Pa, $x = 1$ m; $r_{CO_2} = 0.1$; $T = 400$ K, $T_{12} = 500$ K, $T_3 = 800$ K. Parameters of the atmosphere: $P = 10^3$ Pa, $x = 500$ m; $r_{CO_2} = 0.0003$; $T = 300$ K.

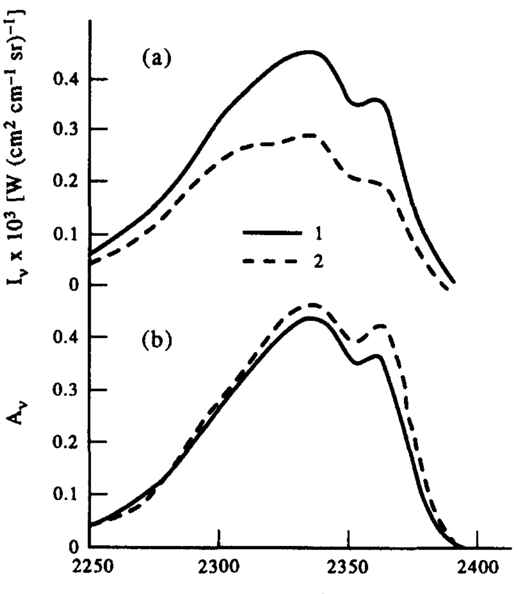

Fig. 6. Radiation (a) and absorption (b) spectra of homogeneous (1) and inhomogeneous (2) CO_2 layers with the following parameters: $P = 6 \times 10^3$ Pa, $x = 90$ cm, $r_{CO_2} = 0.03$; $T = 300$ K, $T_3 = 1200$ K.

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