INFRA RED RADIATION AND INVERSION POPULATION OF CO₂ LASER LEVELS IN VENUSIAN AND MARTIAN ATMOSPHERES

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Formation mechanisms of nonequilibrium 10 μm CO₂ molecule radiation and the possible existence of a natural laser effect in the upper atmospheres of Venus and Mars are theoretically studied. An analysis is made of the excitation process of CO₂ molecule vibrational-band levels (with natural isotropic content) induced by direct solar radiation in bands 10.6, 9.4, 4.3, 2.7 and 2.0 μm. The model of partial vibrational-band temperatures was used in this case. The problem of IR radiation transfer in vibrational-rotational bands was solved in the "radiation escape" approximation. High-altitude profiles of the vibrational-band temperatures and CO₂ (100) and CO₂ (001) level populations were defined from the numerical calculations. An effect of direct (without participation of other translational degrees of freedom) transformation of the solar radiation absorbed in the near IR spectral region (λ ≤ 4.3 μm) into natural atmospheric radiation was found in bands 10.6 and 9.4 μm. It was found that in the planetary atmospheres illuminated by the sun there is a layer of nonequilibrium IR radiation which with sighting on the planetary limb has a maximum at altitude Z = 108 km for Venus and Z = 60 km for Mars with intensity at the subsolar point of respectively -2300 and -320 erg cm⁻² x sec⁻¹. It is indicated that at altitudes Z ≥ 115 km for Venus and Z ≥ 70 km for Mars, there exists an inversion population of levels 001 and 100, which yields a radiation intensification coefficient (1 - 4) x 10⁻⁹ cm⁻¹. With sighting in a tangential direction this guarantees radiation intensification of (10 - 40) percent in one pass. Thus, Venus and Mars can be classified as the first natural lasers of the IR range known to us.
INFRARED RADIATION AND INVERSION POPULATION OF CO$_2$
LASER LEVELS IN THE VENUSIAN AND MARTIAN ATMOSPHERES

B. F. Gordiyets and V. Ya. Panchenko*

I. Introduction

It is common knowledge that upper planetary atmospheres, rarefied gases exposed to corpuscular electromagnetic solar radiation, are non-equilibrium molecular media (in chemical composition, component temperatures, and populations of excited states). The nonequilibrium nature of infrared radiation in vibrational-rotational transitions is also a manifestation of nonequilibrium in vibrational degrees of freedom. This radiation plays an extremely important role in the thermal regime of upper atmospheres, and can provide important information regarding the processes in these media. Considerable attention [1 - 13] has recently been focused on a theoretical study of the population of molecular vibrational levels and IR radiation in vibrational-rotational transitions in the mesosphere and thermosphere of the Earth. This, however, cannot refer to the atmospheres of other planets. The processes of gas cooling by IR radiation in the 15$\mu$m CO$_2$ band and its heating because of absorption by CO$_2$ molecules of solar radiation in the near IR spectral region ($\lambda \leq 4.3$ $\mu$m) have only been analyzed in great detail for the upper Venusian atmosphere in publication [14] based on a numerical solution to the equation of radiation transfer.

In addition to studies of the 15 $\mu$m and IR bands in the region $\lambda \leq 4.3$ $\mu$m for the Venusian and Martian atmospheres, it is also very important to analyze IR radiation in the 10.6 and 9.4 $\mu$m CO$_2$ bands. It is our opinion that this interest is due to the features of IR radiation capture which, as will be shown in this work, results in a "transfer" of energy from the bands of the near IR region ($\lambda \leq 4.3$ $\mu$m) into the 10.6 and 9.4 $\mu$m bands. In addition, since the widely known laboratory CO$_2$ laser

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**Numbers in margin indicate pagination in original foreign text
operates on the 10.6 μm band lines, it is extremely important to study the Venutian and Martian atmospheres as possible active media for natural IR range lasers.

It should be noted that these questions have not yet been theoretically studied. At the same time there are experimental data on IR radiation of Venus and Mars in individual vibrational-rotational 10.6 μm CO₂ band lines which were obtained with the help of a surface infrared telescope-spectrometer using measurements in the transparency windows of the Earth's atmosphere [15 - 17]. In this case publication [17] found inversion population of levels 00°1→10°0 of CO₂ molecules for the Martian atmosphere.

The purpose of this work is to theoretically study the nonequilibrium populations of CO₂ vibrational levels in the Venutian and Martian atmospheres, to analyze IR radiation in the 10.6 and 9.4 μm CO₂ bands, and to study the atmospheric properties as active laser media which intensify IR radiation in the transition 00°1→10°0 of CO₂ molecules.

II. Model and Analysis Method

This work will study the altitude area 80 - 130 km for Venus and 35 - 120 km for Mars. The lower boundary of these regions approximately corresponds to the level where the condition of local thermodynamic equilibrium will cease to be fulfilled for the vibrational states of the asymmetric CO₂ molecule mode (i.e., their population begins to deviate from the equilibrium values which correspond to the gas temperature). In these altitude intervals, the main mechanisms for excitation and deactivation of the vibrational CO₂ levels are absorption of infrared solar radiation, spontaneous radiation vibrational-rotational transitions (with regard for possible capture of energy) and vibrational transitions during collisions. Evaluations indicate that even at the upper boundary of the studied regions of altitudes, the most rapid among all of these processes is vibrational-vibrational exchange of energy during collisions (VV-processes). This makes it possible to simplify the problem of finding
the populations of different vibrational levels, by reducing it to
determination of energy (or the average reserve of vibrational quanta)
of different CO₂ vibrational modes.

Strong captivation of IR radiation in the main 4.3 μm CO₂ band
(transitions 00°0 → 00°1 in the main isotope component \(^{12}C^{16}O_2\)) results in
the fact that for correct determination of the reserve of vibrational
quanta in the asymmetric CO₂ mode and population of level 00°1 it is
necessary to take into consideration the optical excitation and radiation
breakdown of vibrations of the CO₂ asymmetric mode, and through weaker
bands 2.7 and 2 μm, a number of hot bands (i.e., transitions between
excited vibrational states) and transitions in small isotope admixtures.
In order to find the energy reserve of the asymmetric CO₂ mode, this work
examined five isotope modifications of a CO₂ molecule (see Table 1) and
17 infrared bands in each isotope component.

| Table 1. Isotope Modifications "j" of CO₂ Molecules and Their Relative
| Content "Yj"
<table>
<thead>
<tr>
<th>j</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td>(^{12}C^{16}O_2)</td>
<td>(^{12}C^{16}O_2)</td>
<td>(^{12}C^{16}O_2)</td>
<td>(^{12}C^{16}O_2)</td>
<td>(^{12}C^{16}O_2)</td>
</tr>
<tr>
<td>Yj</td>
<td>1</td>
<td>1.2×10^-9</td>
<td>4.0×10^-7</td>
<td>7.4×10^-5</td>
<td>4.6×10^-3</td>
</tr>
</tbody>
</table>

Some characteristics of the analyzed bands are presented in Table 2. The transition energies indicated there (in cm\(^{-1}\)) and the strengths
of the bands for the first 15-m of the bands are taken from publication
[14]. The data of Table 2 were used for all the isotope modifications
of CO₂ molecules. It was assumed in the calculations that the individual
vibrational-rotational lines in all the bands (and the total quantity of
the examined bands is 5 × 17 = 85) are not covered. This assumption is
correct for the studied altitude regions.

We note that with the exception of bands 00°0 → 00°1, 10°0 → 00°1 and
02°0 → 00°1, the other IR bands included in the analysis guarantee direct
excitation and deactivation of different combined levels \((V_1, V_2^1, l)\), and not level 00^01 of the asymmetric mode. Excitation and deactivation of the latter in these bands occurs indirectly, by means of rapid collision processes of vibrational-vibrational energy-exchange type \((V_1, V_2^1, l) + (00^00) \rightarrow (V_1, V_2^1, 0) + (00^01)\). Rapid vibrational exchange of energy between the asymmetric mode levels of the isotope molecule also guarantees the establishment of quasiequilibrium between these modes. If we ignore the isotope shift in level energy, then the presence of

<table>
<thead>
<tr>
<th>Wave-length</th>
<th>No. of</th>
<th>Transition</th>
<th>Trans. freq. (v_i) (cm(^{-1}))</th>
<th>Strength (S_{V_i I})</th>
<th>(n_i)</th>
<th>(m_l)</th>
<th>(\Delta E_i^1) (K)</th>
<th>(\Delta E_i^2) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3 (\mu)</td>
<td>1</td>
<td>00^00-00^01</td>
<td>2349</td>
<td>2324</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>01^10-01^1I</td>
<td>2337</td>
<td>2996</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>02^20-02^2I</td>
<td>2327</td>
<td>3640</td>
<td>2</td>
<td>2</td>
<td>-60</td>
<td>-60</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>10^00-10^01</td>
<td>2327</td>
<td>2223</td>
<td>2</td>
<td>2</td>
<td>+60</td>
<td>+60</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>02^10-02^1I</td>
<td>2324</td>
<td>8726</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.7 (\mu)</td>
<td>6</td>
<td>00^00-10^01</td>
<td>3715</td>
<td>47.1</td>
<td>0</td>
<td>2</td>
<td>+60</td>
<td>+60</td>
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<tr>
<td></td>
<td>7</td>
<td>00^00-02^1I</td>
<td>3613</td>
<td>37.5</td>
<td>0</td>
<td>2</td>
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<td>-60</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>01^10-11^1I</td>
<td>3723</td>
<td>40.6</td>
<td>1</td>
<td>3</td>
<td>+106</td>
<td>+106</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>01^10-03^1I</td>
<td>3590</td>
<td>33.9</td>
<td>1</td>
<td>3</td>
<td>-102</td>
<td>-102</td>
</tr>
<tr>
<td>2.1 (\mu)</td>
<td>10</td>
<td>00^00-12^2I</td>
<td>4976</td>
<td>1.04</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>00^00-04^4I</td>
<td>6190</td>
<td>0.38</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>-177</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>00^00-20^8I</td>
<td>4654</td>
<td>0.28</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>+182</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>01^10-23^6I</td>
<td>4608</td>
<td>0.26</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>+240</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>01^10-13^4I</td>
<td>4955</td>
<td>0.88</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>01^10-05^2I</td>
<td>5123</td>
<td>0.67</td>
<td>1</td>
<td>6</td>
<td>0</td>
<td>-226</td>
</tr>
<tr>
<td>10.6 (\mu)</td>
<td>16</td>
<td>10^00-00^01</td>
<td>961</td>
<td>6.87</td>
<td>2</td>
<td>0</td>
<td>+60</td>
<td>0</td>
</tr>
<tr>
<td>9.4 (\mu)</td>
<td>17</td>
<td>02^00-00^01</td>
<td>1064</td>
<td>5.47</td>
<td>2</td>
<td>0</td>
<td>-60</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE 2. CHARACTERISTICS OF INFRARED BANDS OF THE C\(^{12}\)O\(^{16}\)\(_2\) MOLECULE
quasiequilibrium means equality for all isotopes of the mean reserve of vibrational quanta for one molecule (this is equivalent to the equality of vibrational-band temperatures of the asymmetric isotope modes).

Despite these simplifications, it is still an extremely complicated problem to find the populations of CO₂ vibrational levels in the Venutian and Martian atmospheres, since this generally requires solution of the associated system of IR radiation transfer equations in different bands. The situation is extremely simplified, however, if in order to describe the radiation capture we use the known approximation of "radiation escape" [8, 14]. One can show that in this case the stationary average reserve \( \alpha \) of vibrational quanta in the asymmetric CO₂ mode can be approximately described by the equation

\[
\frac{d\alpha}{dt} = 0 - P_{\text{c}}(\alpha^0) + \sum_{j=1}^{5} \sum_{i=1}^{17} \frac{A_i M_i(t_{ij})}{E_{ij}} \exp\left(-\frac{m_i E_{\text{cm}}}{kT_{\text{DI}}} \frac{\Delta E_i}{kT'} \right) \frac{d_{ij}}{1+d_{ij}}
\]

(1)

Here the first term in the right side describes the collision relaxation, the second term describes excitation because of absorption of solar IR radiation in different bands and different isotope components, the third term describes the spontaneous radiation transitions (with regard for radiation capture). The quantity \( \alpha^0 \) is an equilibrium value \( \alpha \), which corresponds to gas temperature \( T \);

\[
d_{ij} = e^{-\frac{E_{ij}}{kT}} \frac{E_{ij}}{kT - E_{ij}}
\]

\( E_{010} \) and \( E_{001} \) - level energy \( 01^0 \) and \( 00^0 \); \( P_{\text{c}} \) - probability of collision deactivation of level \( 00^1 \); \( \gamma_{ij} \) - relative contents of isotope CO₂ molecules (see Table 1); \( A_i \) - probabilities of spontaneous radiation transition bands indicated in Table 2; \( V_i \) - probabilities of level excitation because of solar radiation absorption in these bands (for an optically thin medium). The quantities \( V_i \) and \( A_i \) are linked by the Einstein ratio
\[ V_i = \beta A_i \frac{\exp(-E_i/kT)}{1 - \exp(-E_i/kT)} \]  

(2)

where \( E_i \) --transition energy, \( T_0 = 5800^\circ K \)--solar radiation temperature, \( \beta \)--dilution factor. For Venus \( \beta = 1.04 \times 10^{-5} \), and for Mars \( \beta = 2.34 \times 10^{-6} \). The probabilities \( A_i \) are linked to the corresponding forces of bands \( S_i \) presented in Table 2 by the known ratio

\[ A_i [\ell] = 2.8 \times 10^{-5} V_j^2 \frac{g_H}{g_B} S_i \]  

(3)

where \( g_B, g_H \)--statweights of the upper and lower transition level, \( V_j \)--transition frequency in cm\(^{-1}\), while \( S_i \) is expressed in cm\(^3\) x atm\(^{-1}\). The exponential multipliers with \( V_i \) and \( A_i \) determine the relative populations correspondingly of the lower and upper vibrational levels for the IR bands.

These combination levels include different states of symmetrical and deformational CO\(_2\) modes. The energy of these states has been presented by us in the form \( n_i E_{010} + \Delta E'_i \) (for the lower band levels) or \( m_i E_{010} + \Delta E''_i \) (for the upper band levels) where \( n_i, m_i \)--whole numbers. The values \( n_i, \Delta E'_i, m_i, \Delta E''_i \) are indicated in Table 2. The levels form systems of multiplets, and the multiplets differ from each other by the value of the number \( n_i \) (or \( m_i \)) and the levels within the multiplet differ by the value \( \Delta E'_i \) (or \( \Delta E''_i \)). According to [18] in this system of levels with collisions of molecules, because of the rapid VV-processes and the transition between the components of one multiplet, a so-called Trinorovskiy distribution of populations is established. It is characterized for the centers of multiplets by Boltzmann distribution with a certain (generally speaking different from gas) temperature \( T_{010} \), and within the multiplet, by a Boltzmann distribution with gas temperature \( T \) (see below [19]). This fact is also reflected by the exponential multipliers in (1). In this case in the terms which contain \( A_i \), the product

\[ \exp(-m_i E_{010} - \Delta E''_i) \]  

would be...
determines the relative population of the levels.

The functions $M(\tau_{ij})$ and $L(\tau_{ij})$ in equation (1) in the framework of the employed "radiation escape" approximation take into consideration the decrease in probable excitation of levels by IR solar radiation and the probable radiation breakdown of them because of capture of the radiation in the vibrational-rotational bands. In this case $\tau_{ij}$ is the optical mass for absorption by the $j$-th isotope component of IR radiation in the $i$-th band, and $\tau_{ij}^{Q}$ is the similar optical mass for absorption of solar radiation.* The appearance of the function $M(\tau_{ij})$ and $L(\tau_{ij})$ depends on the shape of the spectral vibrational-rotational lines. With a Foight contour of these lines, one can consider with accuracy satisfactory for us that

$$L(\tau) = \begin{cases} L_{\text{dop}}(\tau) + L_{\text{for}}(\tau), & \text{with } L_{\text{dop}}(\tau) L_{\text{for}}(\tau) < 1 \\ 1, & \text{with } L_{\text{dop}}(\tau) L_{\text{for}}(\tau) \geq 1 \end{cases}$$

$$M(\tau) = \begin{cases} M_{\text{dop}}(\tau) + M_{\text{for}}(\tau), & \text{with } M_{\text{dop}}(\tau) M_{\text{for}}(\tau) < 1 \\ 1, & \text{with } M_{\text{dop}}(\tau) M_{\text{for}}(\tau) \geq 1 \end{cases}$$

*We note that in the subsequent use of the "radiation escape" approximation in equation (1) with the function $L(\tau)$ another multiplier 1/2 must figure. However consideration for this multiplier which is justified for optically dense gas ($\tau \ll 1$) in the limiting case of an optically thin medium ($\tau \rightarrow 0$) produces values of effective probable radiation breakdown of the level which is two-fold underestimated. Since, as the analysis indicated, the radiation breakdown of level 00°1 in the studied
here $M_{\text{dop}}(\tau)$, $L_{\text{dop}}(\tau)$ and $M_{\text{lor}}(\tau)$ and $L_{\text{lor}}(\tau)$ are values of the functions $M$ and $L$ respectively with purely Doppler and purely Lorentz line contours. The quantities $M_{\text{dop}}(\tau)$ and $L_{\text{dop}}(\tau)$ for the CO₂ bands are tabulated in [8], while their asymptotic expressions for $\tau \gg 1$ are presented in [6]. One can approximate the data of publication [6, 8] with the following expressions with accuracy no worse than $\pm 15\%$:

\[
L_{\text{dop}}(\tau) = \begin{cases} 
1 - 4\tau + 10\tau^2 & \text{with } 0 \leq \tau \leq 0.4 \\
0.7 - 0.5\tau^2 & \text{with } 0.4 < \tau \leq 0.7 \\
0.2/\tau & \text{with } \tau > 0.7
\end{cases}
\] (6)

\[
M_{\text{dop}}(\tau) = \begin{cases} 
1 - 0.336\tau & \text{with } 0 \leq \tau \leq 2.5 \\
0.4/\tau & \text{with } \tau > 2.5
\end{cases}
\] (7)

We note that with large $\tau$, $M_{\text{dop}}(\tau) \approx 2 \times L_{\text{dop}}(\tau)$. With the Lorentz line contour with the help of asymptotic expressions (6), one can approximately write the functions $L_{\text{lor}}(\tau)$ and $M_{\text{lor}}(\tau)$ by the formulas

\[
L_{\text{lor}}(\tau) \approx \begin{cases} 
1 & \text{with } 0 < \tau < 0.2a_a \\
\left(\frac{0.2a_a}{\tau}\right)^{1/2} & \text{with } \tau > 0.2a_a
\end{cases}
\] (8)

\[
M_{\text{lor}}(\tau) = \begin{cases} 
1 & \text{with } 0 < \tau < \left(\frac{3}{2}\right)^2 0.2a_a \\
\frac{3}{2} \left(\frac{0.2a_a}{\tau}\right)^{1/2} & \text{with } \tau > \left(\frac{3}{2}\right)^2 0.2a_a
\end{cases}
\] (9)

Region of altitudes is determined by the transitions $00^\circ 1 - 10^\circ 0$, $00^\circ 1 - 02^\circ 0$, for which the Venutian and Martian atmospheres are optically thin media at altitudes respectively greater than $\sim 85$ and $\sim 40$ km, then the multiplier $1/2$ is omitted in equation (1). This permits more accurate calculation of the quanta reserve.
Here a is the parameter which is determined by the ratio of the Lorentz $\Delta \nu_{\text{lor}}$ and the Doppler $\Delta \nu_{\text{dop}}$ widths of the vibrational-rotational lines in the band center: $a = \frac{\Delta \nu_{\text{lor}}}{\Delta \nu_{\text{dop}}}$. For pure CO$_2$ gas, $a = 3.5 \times 10^{-15} [\text{cm}^{-1}]$. Where $v_i$ is the frequency of transition in the band center (in cm$^{-1}$), while the CO$_2$ molecule concentration is expressed in cm$^{-3}$.

The optical thicknesses $\tau_{ij}$ can be determined from the following ratio with accuracy satisfactory for us

$$\tau_{ij} \approx \Theta_{ij}[\text{CO}_2] H_{\text{CO}_2} \gamma_j \exp \left( \frac{-n_i E_0}{kT_0} - \frac{AE_j}{kT} \right)$$

(10)

where $H_{\text{CO}_2}$ -- height of the uniform atmosphere for CO$_2$; the quantity $[\text{CO}_2]_i \gamma_j \exp \left( \frac{-n_i E_0}{kT_0} - \frac{AE_j}{kT} \right)$ is the CO$_2$ molecule concentration on the lower vibrational transition level; $\sigma_i$ -- section of radiation absorption in the center P and R--branches of the band i:

$$\Theta_{ij}[\text{cm}^2] = \frac{2 \pi \lambda^2}{h} \frac{B_e}{v_i} 5 \times 10^{-15} \frac{\sigma_i}{v_i}$$

(11)

Here $B_e$ -- rotational constant of the molecule in °K, the transition frequency $v_i$ is expressed in cm$^{-1}$, gas temperature T in °K, and the strength of the $S_i$ band in cm$^3$ atm (see Table 2).

In order to find the average reserve $\alpha$ of vibrational quanta in the asymmetric CO$_2$ mode, and also to analyze the intensities of different IR radiation bands and to study the possible intensification of IR radiation in the transition 00°1 - 10°0, it is necessary to generally solve equation (1) jointly with the equations for vibrational-band temperature $T_{010}$, gas temperature T and gas density $\rho$ at the given altitude. This work, however, considered T and $\rho$ to be known, and in order to find their altitude profiles in the Venumian atmosphere, a daily average model of Dickinson [14]
was used, and in the Martian atmosphere, the model on moderate temperature recommended by COSPAR [20]. In addition, in order to reveal possible variations in the calculation results, models were analyzed in which the temperature at all the studied altitudes differed from the temperature of the main profile by ±20° for Venus and ±10° for Mars. In the case of Mars, this temperature deviation corresponds to the COSPAR recommendations to obtain "hot" and "cold" atmospheric models [20].

The equation for vibrational-band temperature $T_{010}$ in this work was also not especially analyzed, and in order to find $T_{010}$, the results of publication [14] were used to calculate the source function for the fundamental band 15 μm (transition 00°0 → 0110) in the Venutian atmosphere. According to the magnitude of deviation presented there (Figure 7 in [14])

$$\Delta \mathcal{J}_0 = \exp(-\frac{E_0}{kT_0})/\exp(-\frac{E_0}{kT})$$

of this source function from its equilibrium value, we immediately define the temperature we need $T_{010}$ in the Venutian atmosphere. For Mars, we additionally used publication [21], according to which when there is a radiation decomposition and collision relaxation, the level in the optically dense medium

$$\Delta \mathcal{I} \approx \left[1 + \frac{A}{P} L(T)\right]^{-\frac{A}{P}}$$  \hspace{1cm} (12)

where $A$ and $P$--probabilities of radiation (formula (3)) and collision deactivation of the level 0110, $L(T)$--function (4).*

With regard for [12], the quantities $\Delta \mathcal{I}_0$, $\Delta \mathcal{I}_0$, $\Delta \mathcal{I}_2$, for Mars and Venus on the level where the CO$_2$ concentrations are the same, are linked by the ratio

*Results of [21] were formally obtained for an individual line, however one can successfully use them also for vibrational-rotational bands by using a modified expression for $L(T)$ of the type (4), (6), (8). This fact follows because as indicated in [6, 8, 22] transfer of radiation in the band can formally be described by an equation which is similar to the radiation transfer equation in an individual line.
\[
\Delta x_{\sigma} = \Delta x_\phi \left[ (1 - \beta) \Delta x_\phi^2 + b \right]^{\frac{1}{\beta}},
\]

where 
\[
\beta = \frac{\Delta x_\phi}{(k T)^{\frac{1}{2}}} \quad \text{---dimensionless multiplier for which we adopted} \quad 0.57.
\]

Formula (13) was also used to find \( \Delta x_{\sigma} \) (and the temperature \( T_{010} \) associated with it) from the values \( \Delta x_\phi \) presented in [14].

III. Nonequilibrium Populations of Vibrational Levels and IR Radiation in the 10.6 and 9.4 \( \mu \)m CO\(_2\) Bands

With regard for what has been said, formulas (1) - (13) were used to calculate the average reserve \( \alpha \) of vibrational quanta in the asymmetrical CO\(_2\) mode and vibration-band temperature \( T_{001} \) of this mode associated with \( \alpha \) by the ratio

\[
P_{10} = \frac{1}{\exp\left(\frac{E_{\text{rot}}}{k T_{001}}\right) - 1}
\]

In these calculations, the following expressions were used for the probability \( P_{10} \) of collision deactivation of level 00\(^0\)1:

\[
P_{10}(\text{CO}_2-\text{CO})[\tau] \approx 1.3 \times 10^{-5} \exp\left(\frac{7.495}{T_{1/2}} - \frac{63.1}{T_{1/2}} \frac{2240}{T_{1/2}}\right) [\text{cm}]^{-1}
\]

\[
P_{10}(\text{CO}_2-0)[\tau] \approx 2.1 \times 10^{-5} [24] \quad [23]
\]

\[
P_{10}(\text{CO}_2-\text{H}_2)[\tau] \approx 3.1 \times 10^{-5} T^{2/3} [\text{H}_20] \quad [19, 23]
\]

The high-altitude profile of atomic oxygen concentration needed to calculate \( P_{10} \) was taken for Venus from publication [25], and for Mars from [26]. The relative content of \( \text{H}_2\text{O} \) vapors at all altitudes was assumed to be constant and equal to \( 10^{-5} \). All the calculations were conducted for the zenith solar angle \( \theta = 0^\circ \) (subsol point).

Jointly with temperatures \( T \), \( T_{010} \) and CO\(_2\) molecule concentration,

\*The accuracy of this method of evaluating \( T_{010} \) for Mars in our task is quite sufficient, for it turns out (see below) that in the greater and the most interesting part of the studied region of altitudes (35 - 105 km for Mars and 80 - 125 km for Venus) \( T_{010} = T \), i.e., for level 01\(^0\)0 a local thermodynamic equilibrium occurs.
the quantity α (or temperature $T_{001}$) determines the population of any vibrational CO$_2$ levels and intensity of different IR radiation bands. Some results of calculation are presented in Figures 1, 2. Figures 1a and 2a show the altitude of profiles of temperatures $T$, $T_{010}$ and $T_{001}$, while Figures 1b and 2b show the profiles of level population 00°1 and 10°0, and the total CO$_2$ molecule concentration. It is apparent from

![Venus Diagram](image.png)

**Figure 1.** Altitude Course of Gas Temperature $T$, Vibrational-Band Temperatures $T_{010}$, $T_{001}$ of CO$_2$ Molecules (Figure a), as Well as Populations $N_{100}$, $N_{001}$ of Levels 10°0, 00°1 and Total CO$_2$ Molecule Concentration (Figure b) in the Atmosphere of Venus at the Subsolar Point for the Model with "Temperate" Temperature.
Figure 1a, 2a, that at the lower boundary of the studied altitude region for the asymmetric mode, the local thermodynamic equilibrium begins to be disrupted, so that T_{001} \succ T_{100}. \ T \ occurs, \ and \ the \ separation \ of \ T_{001} \ from \ T \ rises \ monotonically \ with \ altitude \ all \ the \ way \ to ~125 \ km \ for \ Venus \ and ~105 \ km \ for \ Mars. \ The \ rise \ in \ T_{001} \ results \ in \ the \ fact \ that \ despite \ the \ decrease \ with \ altitude \ in \ the \ total \ CO_2 \ concentration, \ the \ 00^\circ l \ level \ population \ not \ only \ does \ not \ decrease, \ but \ even \ rises, \ and \ has \ a \ maximum \ at \ Z = 110 \ km \ for \ Venus, \ and ~80 \ km \ for \ Mars (Figure 1b, 2b). \ One \ of \ the \ reasons \ for \ the \ rise \ in \ T_{001} \ is \ decrease \ with \ altitude \ in \ the \ optical \ thicknesses \ \tau_{ij}. \ \ This \ results \ in \ an \ increased \ probability \ of \ excitation \ W_{ij} \ of \ the \ vibrational \ quanta \ in \ the \ CO_2 \ asymmetric \ mode \ by \ the \ solar \ IR \ radiation \ in \ many \ j \ bands, \ i.e., \ increase \ in \ the \ components \ in \ the \ sum \ which \ comprises \ the \ second \ term \ in \ the \ right \ side \ of \ (1). \ In \ this \ case \ one \ should \ note \ that \ absorption \ of \ solar \ radiation \ in \ the \ IR \ bands \ 2.7 \ and 2. \ \mu \ m \ of \ the \ main \ component \ C^{12}_0^{16}_2 \ (including \ in \ certain \ hot) \ as \ well \ as \ in \ bands \ 4.3 \ and \ 2.7 \ \mu \ m \ of \ the \ isotope \ molecules - small \ admixtures \ plays \ an \ extremely \ important \ role \ in \ excitation. \ This \ fact \ is \ illustrated \ in \ Figures \ 3a \ and \ 4a, \ where \ high-altitude \ profiles \ of \ different \ probabilities \ of \ vibrational \ quanta \ excitation \ of \ the \ asymmetric \ mode \ which \ are \ calculated \ according \ to \ formulas \ (2) - (13) \ are \ presented: \ the \ total \ probability \ of \ excitation \ W_{\text{total}} = \sum_{j} W_{ij} \ (i.e., \ the \ second \ term \ in \ the \ right \ side \ of \ (1)).

probability \ W_{\text{4.3 \ \mu \ m}} = \sum_{x} W_{ix} \ of \ excitation \ of \ the \ main \ isotope \ component \ C^{12}_0^{16}_2 \ in \ the \ 4.3 \ \mu \ m \ bands \ (including \ hot \ transitions), \ probability \ W_{2.7 \ \mu \ m} = \sum_{x} W_{ix} \ (i.e., \ the \ second \ term \ in \ the \ right \ side \ of \ (1)) \ excitation \ C^{12}_0^{16}_2 \ in \ 2.7, \ 2 \ and \ 10 \ \mu \ m \ bands \ (including \ hot \ transitions), \ and \ finally, \ probability \ W_{\text{total}} = \sum_{j} W_{ij} \ of \ excitation \ in \ all \ bands \ of \ all \ isotope \ molecules - small \ admixtures. \ It \ is \ apparent \ from \ Figures \ 3 \ a \ and \ 4a \ that \ at \ altitudes \ 105 - 135 \ km \ for \ Venus \ and \ 65 - 130 \ km \ for \ Mars, \ solar \ radiation \ absorption \ in \ the \ 4.3 \ \mu \ m \ bands \ of \ the \ main \ isotope \ component \ C^{12}_0^{16}_2 \
Mars

Figure 2. The Same as in Figure 1 but for Mars

only guarantees -10 - 20% of the total excitation rate.

Figures 3b and 4b present high-altitude profiles of other important parameters which determine the magnitude $\alpha$ (or $\Theta_0$) and intensity of the IR radiation band of the atmospheres. The total effective probability of deactivation of the vibrational quanta are presented here

$$A^2 P_{20} = \sum_{\nu=1}^{12} A_{\nu} P_{\nu 20}, \quad A_{\nu} = A(\nu, j) \exp \left(-\frac{\nu E_{\nu}}{kT_{\text{av}}} + \delta_{\nu}\right) \Lambda_{\nu}$$
probability of collision deactivation $P_{10}$, as well as effective probabilities

$$A^{30} = \sum A_{i0}, \quad A^{20} = \sum \sum A_{i0}$$

of deactivation of the vibrational quanta in an asymmetric mode because of radiation transition respectively in 5 bands, 4.3 μm (including hot transitions) of the main isotope component $\text{Cl}_2\text{O}_1\text{H}_2$, bands 2.7, 2 and 10 μm (including hot transitions) of the main component $\text{Cl}_2\text{O}_1\text{H}_2$, and in all 17 bands of the isotope molecules-small admixtures. It is apparent that the effective probability $A^{10.0}$ in contrast to the probabilities $A^{4.3}$, $A^{2.7}$, $A^{2.0}$ and $A^{15}$ above ~90 km for Venus and ~45 km for Mars ceases to depend on the altitudes. This is explained by the fact that the planetary atmosphere here for transfer of IR radiation vertically upwards in the bands 10.6 and 9.4 μm become optically thin media. The independence of the probability $A^{10.0}$ on altitude and its important contribution to the total probability of deactivation also guarantees jointly with the increasing total excitation probability $W$ (see Figures 3a, and 4a) a rise in $T_{001}$ with altitude (see Figure 1a, 2a).

The relative values of effective probabilities presented in Figures 3b and 4b also provide important information about the energy dissipation channels of the CO$_2$ asymmetric mode. It is apparent that all the way to altitude ~120 km for Venus, and ~105 km for Mars, the probability $A^{10.0}$ is the greatest among the effective radiation probabilities of deactivation. In the range 110-120 km for Venus and 70-100 km for Mars, it provides over 50% of the contribution to the total deactivation probability. It follows from here that the 10.6 and 9.4 μm IR bands are the most intensive among the examined bands. If one also takes into consideration that excitation of the CO$_2$ asymmetric mode of vibrations occurs by IR solar radiation absorption in 2.2, 2.7 and 4.3 μm bands (see Figures 3a and 4a), then this also means that the Venunian and Martian atmospheres have an intensive effect: direct (without participation of the forward stages
Figure 3. High-Altitude Course of Excitation Probabilities $W$ (Figure a) and Deactivation $A$ and $P_{10}$ (Figure b) of the Asymmetric Mode of the CO$_2$ Molecule in the Venusian Atmosphere with "Temperate" Temperature. Indexes 2.0, 2.7, 4.3, 10.0 correspond to the IR Bands 2.0, 2.7, 4.3 and 10 and 10.6-9.4 $\mu$m (including hot transitions) in the Main Isotope Component C$^{12}$O$^{16}$$_2$. The index 1S corresponds to all bands in all small isotope components; the index r corresponds to the total ratio of probabilities. $P_{10}$ corresponds to the probability of collision deactivation of the level 0001.
of freedom of gas) transformation of the solar radiation absorbed in the near-IR spectral region ($\lambda \leq 4.3$ m) into natural atmospheric IR radia-

tion in the spectral region $\lambda > 10$ m. This effect is governed by the following physical factors: rapid collision resonance process of vibra-
tional-vibrational energy exchange of the type $(V_1, V_2^4, 1) + (00^00) + (V_1, V_2^4, 0) + (00^01)$ transferring the molecules to lower vibrational
levels, and subsequent de-excitation from these levels respectively in the 15 $\mu$m and 10 $\mu$m bands, where de-excitation from the level 00$^01$ in the 4.3 $\mu$m band is ineffective because of the strong capture of radia-
tion. We note here that publication [14] in studying the thermal regime of the Venutian atmosphere has already discussed transformation of solar
energy absorbed in the 2 and 2.7 $\mu$m bands into IR atmospheric radiation
in the 4.3 and 15 $\mu$m bands, however it did not take into consideration
the important, and at the altitudes 110 - 120 km (as is apparent from Figures 3b and 4b) the main channel for dissipation of the absorbed energy because of de-excitation in the 10.6 and 9.4 μm bands in the transition 00°1 → 10°0 and 00°1 → 02°0. Since, as follows from [14], at the indicated altitudes energy absorption of the sun in the near IR spectral region \( \lambda \leq 4.3 \mu m \) is the main source of atmospheric heating, then consideration for IR radiation in the 10.6 and 9.4 \( \mu m \) bands must noticeably influence the results [14], and in particular reduce the calculated temperature in the mesopause region when \( Z = 113 \) km.

In light of the important role of 10.6 and 9.4 \( \mu m \) bands in the thermal and radiation regime of the Venutian and Martian atmospheres, we also calculated the IR radiation streams in these bands for two directions: 1) on the planet limb, i.e., with sighting from space on the tangent with the perigee of the sighting line at altitude \( Z \); 2) in a vertical direction upwards into space from the atmospheric column with lower \( Z \) at altitude \( Z \). The first case is important for possible comparison with the broad-band measurements, and provides information about the high-altitude course of atmospheric parameters, while the second determines the energy of the atmospheric column. The calculation results are presented in Figures 5a and 6a. It is apparent that with sighting on the tangent, the stream has a maximum at altitude -107 km for Venus and -60 km for Mars with value respectively -2300 and -315 erg/cm² x sec. The presence of this luminescent IR layer is explained by the fact that above its maximum, the number of excited \( \text{CO}_2 \) molecules (00°1) diminishes in the horizontal column, and below the maximum, as the altitude \( Z \) diminishes, the role of radiation capture rises. The stream of IR radiation vertically upwards from the column with lower base at altitude \( Z \), as is apparent from Figures 5a and 6a, with a decrease in \( Z \) initially rises fairly drastically, and below -85 km for Venus and 40 km for Mars, it practically ceases to change. It comprises a quantity respectively -80 and -18 erg/cm² x sec. These constant values are reached because of the influence of radiation capture. For a vertical direction it begins to play a role at the lower boundary of the studied altitude region (this is apparent even from the high-altitude course A10.0 in Figures 3b and 4b).
Effective transformation of the solar energy absorbed in the near IR spectral region $\lambda \leq 4.3$ $\mu$m into natural IR radiation of the planets in the 10.6 and 9.4 $\mu$m bands results in the fact that the intensity of this nonequilibrium radiation significantly exceeds the equilibrium value corresponding to the conditions where the vibrational-band temperature $T_{001}$ equals the gas temperature $T$. This fact is illustrated in Figures 7 and 8, where the ratios of true intensities to their equilibrium values are presented for sighting on the tangential directions. It is apparent that for models of "cold" atmospheres, the true intensity can be $-10^3$-fold greater than the equilibrium for Venus, and $-10^4$-fold for Mars.

Figure 5a. Flow of IR Radiation in the 10.6 and 9.4 $\mu$m CO$_2$ Bands in the Venusian Atmosphere with "Temperate" Temperature.

Key:
- $Q^{10}_h$: flow on the planetary limb, i.e. with horizontal sighting from space

(Key continued on next page)
Figure 5a key continued:

\[ \text{Q}^v_{10} \quad \text{vertical flow into space from the atmospheric column with} \]
\[ \text{base at altitude } Z \]

Figure 5b. Power of Laser Generation in the 10.6 um line in the Venustian Atmosphere with "Temperate" Temperature Depending on the Altitude \( Z \) of the Laser Axis Above the Surface and with Three Values of the Loss Coefficient on Mirrors.

\[
\begin{array}{c}
\text{Mars} \\
\end{array}
\]

\[ \text{Figure 6. The Same as in Figure 5, but for Mars} \]

In concluding this section we will compare our calculations with the experimental data of publications [15 - 17]. They used a surface infrared telescope-spectrometer which has high spectral resolution to sight the planetary disc illuminated by the sun and to measure the intensity and shape of the individual vibrational-rotational line of the 10.6 um band.
Figure 7. Ratio of True IR Radiation Intensities in Bands 10.6 and 9.4 μm CO₂ and Their Equilibrium Values in the Venusian Atmosphere. Calculation made for IR radiation streams on the planetary limb, i.e., with horizontal sighting from space, for atmosphere with "temperate" temperature, and also for "cold" and "hot" atmospheres.
falling into the transparency window of the earth's atmosphere. The measured width of the line was used to define the effect of gas temperature in the emitting atmospheric column. The author used the intensity of one line through summation on the rotational levels to determine the total energy flow in all lines belonging to the 10.6 and 9.4 μm bands. For the subsolar point, this experimental flow was 80 erg/cm² x sec for Venus [15] and 18 erg/cm² x sec for Mars [17]. These data coincide with our calculated values of vertical flow from the column with lower base at altitudes Z, smaller -40 km for Mars and -85 km for Venus.* The authors of publication [15] proposed to explain the measured nonequilibrium radiation flow for Venus by the absorption of solar radiation of the near IR spectral region by water vapors with subsequent transfer of energy from H₂O to CO₂. However, the good agreement between theory and experiment that we obtained indicated that the observed intensities are provided by absorption by the CO₂ molecules themselves.

The authors of [17] also used the measured IR radiation intensities to define the quantity of excited CO₂ (00°1) molecules and the vertical column of the Martian atmosphere where the observed radiation is formed in lines. Their experimental value equal to -2.2 x 10¹⁴ cm⁻² also coincided with our calculated quantity which corresponds to the column with base altitude Z =40 km.

IV. Inversion Population and Intensification of Radiation 10.6 μm in the Transition 00°1 -10°0

Exceeding of the vibrational-band temperature Tₐ₀₁ over T₀₁₀ results in yet another important effect in Venusian and Martian atmospheres: development of inversion population of vibrational levels 00°1 and 10°0, 02°0 and intensification of radiation in the vibration-rotational lines of bands 10.6 and 9.4 μm. It is apparent from Figures 1b and 2b that for "standard" atmospheres, the Nₐ₀₁/N₁₀₀ ratio of level population 00°1

*From the deeper atmospheric layers, the cause of radiation capture in the center of the line, the contribution to total radiation intensity of the 10.6 and 9.4 μm bands will be made essentially only by the distant wings of the individual lines. The authors of [15, 17] did not take this contribution into consideration.
Figure 8. The same as Figure 7, but for Mars.
and \(10^\circ\) becomes greater than 1 at altitudes 116 km for Venus and 70 km for Mars. The magnitude of inversion population \(\Delta N = N_{001} - N_{100}\) has maximum values \(2 \times 10^7 - 2.8 \times 10^8\) cm\(^{-3}\) for Venus (and 3.2 - 5.3) \(\times 10^7\) cm\(^{-3}\) for Mars at altitudes respectively at 113 - 130 and 80 - 88 km. These magnitudes \(\Delta N\) provide coefficients of intensification \(\varepsilon\), which although they are small are already accessible for experimental detection. Among the different vibrational-rotational transitions, the maximum \(\varepsilon\) value is realized in the P-branch of the transition \(00^\circ I \rightarrow 10^\circ 0\) with rotational level \(J = \sqrt{2B} (\text{Be} = \text{rotational constant in °K})\); and with the Doppler line contour equal to

\[
\varepsilon_{\text{max}} \left[\text{cm}^{-1}\right] = \frac{7.5 \times 10^{-16}}{T} \Delta N, \tag{15}
\]

where \(\Delta N\) is expressed in cm\(^{-3}\), \(T\) in °K.

The high-altitude profiles with \(\varepsilon_{\text{max}}\) which are calculated with the use of (15) are presented in Figures 9a and 10a. It is apparent that in the region of the maximum, the intensification coefficient can reach values \(-5 \times 10^{-9}\) cm\(^{-1}\) for Venus and \(-2 \times 10^{-9}\) x cm\(^{-1}\) for Mars. These quantities already provide a noticeable radiation intensification on the visual beam. Figures 9b and 10b present high-altitude profiles of intensification \(G\) on the visual beam (in one pass) for sighting in tangential directions. It is apparent that the intensification has a maximum at altitudes 110 - 125 km for Venus and 70 - 80 km for Mars, and reaches at these maximums values of 3 - 50% for Venus and 5 - 15% for Mars. This intensification is quite sufficient for experimental detection of it. It is important in this case to note the similar magnitudes of intensification on one pass are very typical even for laboratory CO\(_2\) lasers (of course, with length of the active medium \(~10^6\)-fold smaller). For a vertical direction, the total intensification in the column where an inversion population exists, according to calculations for standard Venutian and Martian atmospheres, is respectively 0.16 and 0.26%. Publication [17] from an experiment for Mars obtained intensification values 0.14 - 0.27% which were close to our calculated data.
Figure 9. High-Altitude Course for the Coefficient of IR Radiation Intensification $\alpha_{\text{max}}$ for a Unit of Length (Figure a) and Intensification $G$ in one Pass with Horizontal Sight- ing (Figure b) on the Transition 00°1 + 10°0 in the Venusian Atmosphere. The calculation was made for an atmospheric model with "tem- perate" temperature, as well as for "cold" and "hot" atmospheres.
Figure 10. The Same as Figure 9, but for Mars

As a future project one can suggest that lasers be created in the Venusian and Martian atmospheres, after mirrors which form a laser resonator system are installed on two artificial satellites of these planets and are oriented in the proper manner. The orbital altitude of these satellites and the distance between them must be selected so that the line which connects the mirror axes passes at altitudes where the intensification is the maximum. After defining losses on the mirrors, one can calculate the power generated by these lasers. Figures 5b and 6b present the results of this calculation depending on the altitude $Z$ of the laser axis above the planetary surface. The calculation was made for standard atmospheres and different values of the coefficient of mirror loss on the assumption that one mirror is opaque, and the losses on the second are due to the transmission necessary to remove the radiation
from the resonator. It is apparent that the generation power for the
Venutian laser must be $\geq 1 \times 10^{-4}$ W/cm$^2$, and for the Martian $\geq 4 \times 10^{-5}$
W/cm$^2$. In this case the area of the mirrors which determines the total
generation power can be more than 100 km$^2$.

We note that these lasers would become gas lasers with solar exci-
tation of the medium under natural conditions. The creation of labora-
tory gas solar lasers has been suggested in [27].

We note the following in conclusion. Astrophysics is currently well
aware of the natural space objects which intensify electromagnetic radi-
ation in the centimeter wavelength range. These are masers on OH and H$_2$O
molecules (see for example, [28, 29]) which are very widespread among
distant space objects. However, until recently there have been no known
natural lasers of the infrared and visible range. Publication [1] has
examined the possibility of laser intensification of infrared radiation
in the Earth's mesosphere. This indicated the existence of inversion
population on vibrational-rotational OH transitions because of the $H +$
$O_3 \rightarrow OH^* + O_2$ reaction which governs the well known hydroxyl mesospheric
emission. However, the intensification coefficients were extremely small.
From the data of publication [8, 12] which calculated the vibrational-
band temperature $T_{001}$ of the CO$_2$ asymmetric mode in the mesosphere and
lower thermosphere of the Earth, one can also conclude that inversion
population of the levels 00$^i$-10$^o$ exists at altitudes 85 - 95 km.
However even in this case because of the low CO$_2$ concentration, the in-
tensification is negligible. Thus, as follows from this publication and
measurements [17], Venus and Mars can be classified as the first natural
laser objects of the IR range known to us.

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