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INFRARED RADIATION AND INVERSION POPULATION OF CO_2 LASER LEVELS IN VENUSIAN AND MARTIAN ATMOSPHERES

B.F. Gordiyets and V. Ya. Panchenko

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Formation mechanisms of nonequilibrium 10 μm CO_2 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 CO_2 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 CO_2 (100) and CO_2 (001) level populations were defined from the numerical calculations. An effect of direct (without participation of ... translational degrees of freedom) transformation of the solar radiation absorbed in the near IR spectral region ($\lambda \lesssim 4.3$ m) 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 $Z \approx 108$ km for Venus and $Z \approx 60$ km for Mars with intensity at the subsolar point of respectively ~ 2300 and ~ 320 ergcm^{-2} x sec^{-1}. It is indicated that at altitudes $Z \gtrsim 115$ km for Venus and $Z \gtrsim 70$ km for Mars, there exists an inversion population of levels 001 and 100 which yields a radiation intensification coefficient $(1 - 4) \times 10^{-9}$ cm^{-1}. With sighting in a tangential direction this guarantees radiation intensification of $\sim(10 - 40)$ percent in one pass. Thus, Venus and Mars can be classified as the first natural lasers of the IR range known to us.

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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 /3**

It is common knowledge that upper planetary atmospheres, rarefied gases exposed to corpuscular electromagnetic solar radiation, are nonequilibrium 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 μm CO_2 band and its heating because of absorption by CO_2 molecules of solar radiation in the near IR spectral region ($\lambda \leq 4.3$ μm) 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 μm and IR bands in the region $\lambda \leq 4.3$ μm for the Venusian and Martian atmospheres, it is also very important to analyze IR radiation in the 10.6 and 9.4 μm 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 ($\lambda \leq 4.3$ μm) into the 10.6 and 9.4 μm bands. In addition, since the widely known laboratory CO_2 laser /4

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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 CO_2 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 CO_2 molecules for the Martian atmosphere.

The purpose of this work is to theoretically study the nonequilibrium populations of CO_2 vibrational levels in the Venutian and Martian atmospheres, to analyze IR radiation in the 10.6 and 9.4 μmCO_2 bands, and to study the atmospheric properties as active laser media which intensify IR radiation in the transition 00°1 →10°0 of CO_2 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 CO_2 molecule mode (i.e., their population begins to deviate from the equilibrium values which correspond to the gas temperature). /5
In these altitude intervals, the main mechanisms for excitation and deactivation of the vibrational CO_2 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

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the populations of different vibrational levels, by reducing it to determination of energy (or the average reserve of vibrational quanta) of different CO_2 vibrational modes.

Strong captivation of IR radiation in the main 4.3 μm CO_2 band (transition 00°0 → 00°1 in the main isotope component $C^{12}O^{16}_2$) results in the fact that for correct determination of the reserve of vibrational quanta in the asymmetric CO_2 mode and population of level 00°1 it is necessary to take into consideration the optical excitation and radiation breakdown of vibrations of the CO_2 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 CO_2 mode, this work examined five isotope modifications of a CO_2 molecule (see Table 1) and 17 infrared bands in each isotope component.

TABLE 1. ISOTOPE MODIFICATIONS "j" OF CO_2 MOLECULES AND THEIR RELATIVE CONTENT "γ_j"

j	1	2	3	4	5
Molecule	$C^{12}O^{16}_2$	$C^{13}O^{16}_2$	$C^{12}O^{16}O^{18}$	$C^{12}O^{16}O^{17}$	$C^{13}O^{16}O^{18}$
γ_j	1	$1,12.10^{-2}$	$4,08.10^{-3}$	$7,42.10^{-4}$	$4,6.10^{-5}$

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 CO_2 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 x 17 = 85) are not covered. This assumption is correct for the studied altitude regions. /6

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

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TABLE 2. CHARACTERISTICS OF INFRARED BANDS OF THE $C^{12}O^{16}_2$ MOLECULE

Wave-length	No. of band i	Transition	Trans. freq. ν_i (cm^{-1})	Band strength S_i ($cm^{-2}atm^{-1}$)	n_i	m_i	$\Delta E_i'$ (°K)	$\Delta E_i''$ (°K)
4,3 μm	I	00^00-00^0I	2349	2924	0	0	0	0
	2	$0I^I0-0I^II$	2337	2896	I	I	0	0
	3	02^00-02^0I	2327	3640	2	2	-80	-80
	4	$I0^00-I0^0I$	2327	2223	2	2	+80	+80
	5	02^20-02^2I	2324	5726	2	2	0	0
2,7 μm	6	00^00-I0^0I	3715	47,I	0	2	0	+80
	7	00^00-02^0I	3613	37,5	0	2	0	-80
	8	$0I^I0-II^II$	3723	40,5	I	3	0	+I06
	9	$0I^I0-03^II$	3580	33,9	I	3	0	-I02
2 μm	I0	00^00-I2^0I	4978	I,04	0	4	0	0
	II	00^00-04^0I	5I00	0,38	0	4	0	-I77
	I2	00^00-20^0I	4854	0,28	0	4	0	+I82
	I3	$0I^I0-2I^II$	4808	0,26	I	5	0	+240
	I4	$0I^I0-I3^II$	4965	0,88	I	5	0	0
	I5	$0I^I0-05^II$	5I23	0,57	I	6	0	-226
I0,6 μm	I6	$I0^00-00^0I$	96I	6,57	2	0	+60	0
9,4 μm	I7	02^00-00^0I	I064	5,47	2	0	-60	0

excitation and deactivation of different combined levels $(V_1, V_2^{\ell}, 1)$, and not level 00°1 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 $(V_1, V_2^{\ell}, 1) + (00°0) \rightarrow (V_1, V_2^{\ell}, 0) + (00°1)$. Rapid vibrational exchange of energy between the asymmetric mode levels of the isotope molecule also guarantees the establishment of quasiequilibrium between these modes. /8 If we ignore the isotope shift in level energy, then the presence of 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 CO_2 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 α of vibrational quanta in the asymmetric CO_2 mode can be approximately described by the equation

$$\frac{d\alpha}{dt}=0=P_{10}(\alpha^0-\alpha)+\sum_{j=1}^{5}\gamma_j\sum_{i=1}^{17}V_i M(\tau_{ij}^{0})\exp\left(-\frac{n_i E_{010}}{kT_{010}}-\frac{\Delta E_i'}{kT}\right)$$
$$-\sum_{j=1}^{5}\gamma_j\sum_{i=1}^{17}A_i L(\tau_{ij})\exp\left(-\frac{m_i E_{010}}{kT_{010}}-\frac{\Delta E_i''}{kT}\right)\frac{\alpha}{1+\alpha} \qquad (1)$$

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 α^0 is an equilibrium value α, /9
which corresponds to gas temperature T: $\alpha = e^{-E_{001}/kT}\cdot(1-e^{-E_{010}/kT})^{-1}$

E_{010} and E_{001}--level energy 01°0 and 00°1; P_{10}--probability of collision deactivation of level 00°1; γ_j--relative contents of isotope CO_2 molecules (see Table 1); A_i--probabilities of spontaneous radiation transitional 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

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$$V_i = \beta A_i \cdot \frac{\exp(-E_i/\kappa T_\theta)}{1 - \exp(-E_i/\kappa T_\theta)} \qquad (2)$$

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

$$A_i\left[\frac{1}{c}\right] = 2.8 \cdot 10^{-8} \cdot \nu_j^2 \frac{g_H}{g_B} \cdot S_j \qquad (3)$$

where g_B, g_H--statweights of the upper and lower transition level, ν_j--transition frequency in cm^{-1}, while S_j is expressed in cm^2 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 /10 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 $\exp\left(-\frac{m_i E_{010}}{KT_{010}} - \frac{\Delta E''_i}{KT}\right) \cdot \frac{\alpha}{1+\alpha}$

determines the relative population of the levels.

The functions $M(\tau^{\odot}_{ij})$ 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 τ_{ij} is the optical mass for absorption by the j-th isotope component of IR radiation in the i-th band, and $\tau^{\odot}_{ij}$ is the similar optical mass for absorption of solar radiation.* The appearance of the function $M(\tau^{\odot}_{ij})$ and $L(\tau_{ij})$ /11
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

$$L(\tau) = \begin{cases} L_{dop}(\tau) + L_{lor}(\tau), & \text{with } L_{dop}(\tau) + L_{lor}(\tau) < 1 \\ 1, & \text{with } L_{dop}(\tau) + L_{lor}(\tau) \geq 1 \end{cases} \tag{4}$$

$$M(\tau) = \begin{cases} M_{dop}(\tau) + M_{lor}(\tau), & \text{with } M_{dop}(\tau) + M_{lor}(\tau) < 1 \\ 1, & \text{with } M_{dop}(\tau) + M_{lor}(\tau) \geq 1 \end{cases} \tag{5}$$

*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 ($\tau \to 0$) 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

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here $M_{dop}(\tau)$, $L_{dop}(\tau)$ and $M_{lor}(\tau)$ and $L_{lor}(\tau)$ are values of the funct... M and L respectively with purely Doppler and purely Lorentz line con... The quantities $M_{dop}(\tau)$ and $L_{dop}(\tau)$ for the CO_2 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 ~15%: /12

$$L_{dop}(\tau) \approx \begin{cases} 1 - 4\tau + 10\tau^2 & \text{with } \tau \le 0.2 \\ 0.7 - 0.5\tau & \text{with } 0.2 < \tau \le 0.4 \\ 0.2/\tau & \text{with } \tau > 0.4 \end{cases} \quad (6)$$

$$M_{dop}(\tau) \approx \begin{cases} 1 - 0.336\tau & \text{with } \tau \le 2.5 \\ 0.4/\tau & \text{with } \tau > 2.5 \end{cases} \quad (7)$$

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

$$L_{lor}(\tau) \approx \begin{cases} 1 & \text{with } \tau < 0.202 \cdot a \\ \left(\frac{0.202 \cdot a}{\tau}\right)^{1/2} & \text{with } \tau > 0.202\, a \end{cases} \quad (8)$$

$$M_{lor}(\tau) \approx \begin{cases} 1 & \text{with } \tau < \left(\frac{3}{2}\right)^2 \cdot 0.202 a \\ \frac{3}{2}\left(\frac{0.202 \cdot a}{\tau}\right)^{1/2} & \text{with } \tau > \left(\frac{3}{2}\right)^2 \cdot 0.202 a \end{cases} \quad (9)$$

region of altitudes is determined by the transitions 00°1 → 10°0, 00°1 → 02°0, for which the Venutian and Martian atmospheres are optically thin media at altitudes respectively greater than ~85 and ~40 km, then the multiplier 1/2 is omitted in equation (1). This permits more accurate calculation of the quanta a rese...e.

Here a is the parameter which is determined by the ratio of the Lorentz $\Delta\nu_{lor}$ and the Doppler $\Delta\nu_{dop}$ widths of the vibrational-rotational lines in the band center: $a = \frac{\Delta\nu_{lor}}{\Delta\nu_{dop}} (\ln 2)^{1/2}$. For pure CO_2 gas, $a \approx 3.5 \times 10^{-15}$ $[CO_2] \frac{1}{\nu_i}$, where ν_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 optic thicknesses τ_{ij} can be determined from the following ratio with accuracy satisfactory for us /13

$$\tau_{ij} \approx \sigma_i [CO_2] \cdot H_{CO_2} \cdot \gamma_j \cdot \exp\left(-\frac{n_i E_{010}}{kT_{010}} - \frac{\Delta E_j'}{kT}\right) \quad (10)$$

where H_{CO_2}--height of the uniform atmosphere for CO_2; the quantity $[CO_2]$ x $\gamma_j \exp\left(-\frac{n_i E_{010}}{kT_{010}} - \frac{\Delta E_j'}{kT}\right)$ is the CO_2 molecule concentration on the lower vibrational transition level; σ_i--section of radiation absorption in the center P and R--branches of the band i:

$$\sigma_i [cm^2] = \sqrt{\frac{225}{T}} \sqrt{\frac{B_e}{T}}\, 5.1 \cdot 10^{-15} \frac{S_i}{\nu_i} \quad (11)$$

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

In order to find the average reserve α 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 ρ at the given altitude. This work, however, considered T and ρ to be known, and in order to find their altitude profiles in the Venusian 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 variatons 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]. /14

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 $00^00 \rightarrow 01^10$) in the Venutian atmosphere. According to the magnitude of deviation presented there (Figure 7 in [14]) $\Delta X_{♀} = \exp\left(-\frac{E_{010}}{kT_{010}}\right) / \exp\left(-\frac{E_{010}}{kT}\right)$ 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

$$\Delta X \simeq \left[1 + \frac{A}{P} L(\tau)\right]^{-1/2} \tag{12}$$

where A and P--probabilities of radiation (formula (3)) and collision deactivation of the level 01^10, $L(\tau)$--function (4).*

With regard for [12], the quantities $\Delta x_{♂}$ and $\Delta x_{♀}$ 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 $L(\tau)$ 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.

$$\Delta x_{♂} = \Delta x_{♀}\left[(1-b)\Delta x_{♀}^{2} + b\right]^{-1/2}, \tag{13}$$

where $b = \frac{L^{♂}(T)}{L^{♀}(T)}\frac{p^{♀}}{p^{♂}}$ --dimensionless multiplier for which we adopted /15

the value 0.57. Formula (13) was also used to find $\Delta x_{♂}$ (and the temperature T_{010} associated with it) from the values $\Delta x_{♀}$ presented in [14].*

III. Nonequilibrium Populations of Vibrational Levels and IR Radiation in the 10.6 and 9.4 μm CO_2 Bands

With regard for what has been said, formulas (1) - (13) were used to calculate the average reserve α of vibrational quanta in the asymmetrical CO_2 mode and vibration-band temperature T_{001} of this mode associated with α by the ratio $\alpha = [\exp(E_{001}/kT_{001}) - 1]^{-1}$. In these calculations, the following expressions were used for the probability P_{10} of collision deactivation of level 00°1:

$$P_{10}(CO_2\text{-}CO_2)[\tfrac{1}{c}] \approx 1.36\cdot10^{-16}\cdot T\exp\left(4.14 + \frac{7495}{T^{1/3}} - \frac{631}{T^{2/3}} + \frac{2240}{T}\right)[CO_2] \quad [23]$$

$$P_{10}(CO_2\text{-}O)[\tfrac{1}{c}] \approx 2.1\cdot10^{-13}\cdot[O] \quad [24] \tag{14}$$

$$P_{10}(CO_2\text{-}H_2O)[\tfrac{1}{c}] \approx 3.1\cdot10^{-15}\cdot T\cdot[H_2O] \quad [19,23]$$

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 H_2O vapors at all altitudes was assumed to be constant and equal to 10^{-5}. All the calculations were conducted /16 for the zenith solar angle $Z^{\odot} = 0°$ (subsolar 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) $T_{010} \approx T$, i.e., for level 01°0 a local thermodynamic equilibrium occurs.

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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

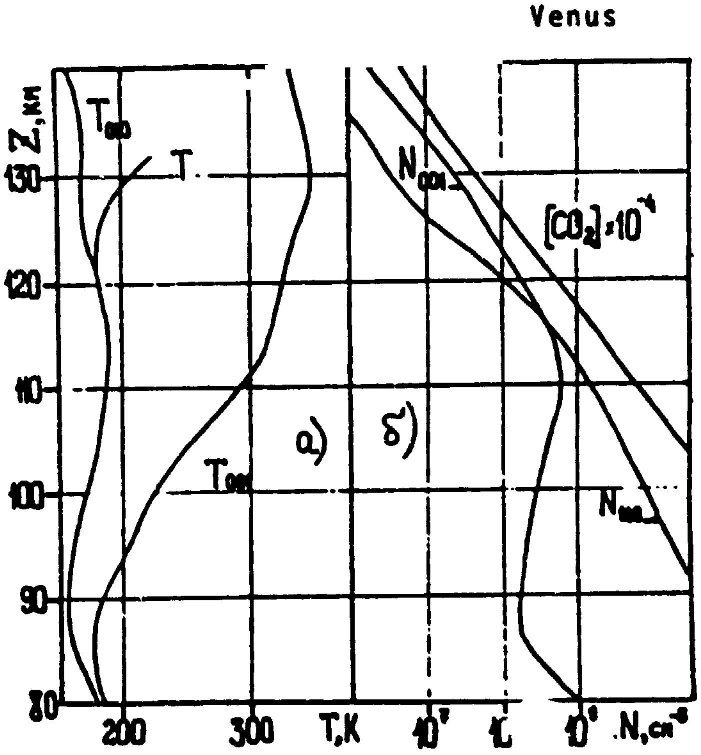

Figure 1. Altitude Course of Gas Temperature T, Vibrational-Band Temperatures T_{010}, T_{001} of CO_2 Molecules (Figure a), as Well as Populations N_{100}, N_{001} of Levels 10°0, 00°1 and Total CO_2 Molecule Concentration (Figure b) in the Atmosphere of Venus at the Subsolar Point for the Model with "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 $T_{001} > T_{100}$, 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°1 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 τ^{θ}_{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

$$W_{ij} \equiv \chi_{ij} V_i M(\tau^{\theta}_{ij}) \exp\left(-\frac{K_i E_{010}}{K T_{010}} - \frac{\Delta E_i}{KT}\right)$$

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 µm of the main component $C^{12}O^{16}_2$ (including in certain hot) as well as in bands 4.3 and 2.7 µm 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 $W^{\Sigma} = \sum_{j=1}^{5}\sum_{i=1}^{12} W_{ij}$ (i.e., the second term in the right side of (1)), /19

probability $W^{4.3} = \sum_{i=1}^{5} W_{i1}$ of excitation of the main isotope component $C^{12}O^{16}_2$ in the 4.3 µm bands (including hot transitions), probability $W^{2.7} = \sum_{i=6}^{9} W_{i1}$; $W^{2.0} = \sum_{i=10}^{12} W_{i1}$ and $W^{10.0} = \sum_{i=16}^{11} W_{i1}$ excitation $C^{12}O^{16}_2$ in 2.7, 2 and 10 µm bands (including hot transitions), and finally, probability $W^{IS} = \sum_{j=2}^{5}\sum_{i=1}^{11} W_{ij}$ 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 µm bands of the main isotope component $C^{12}O^{16}_2$

Mars

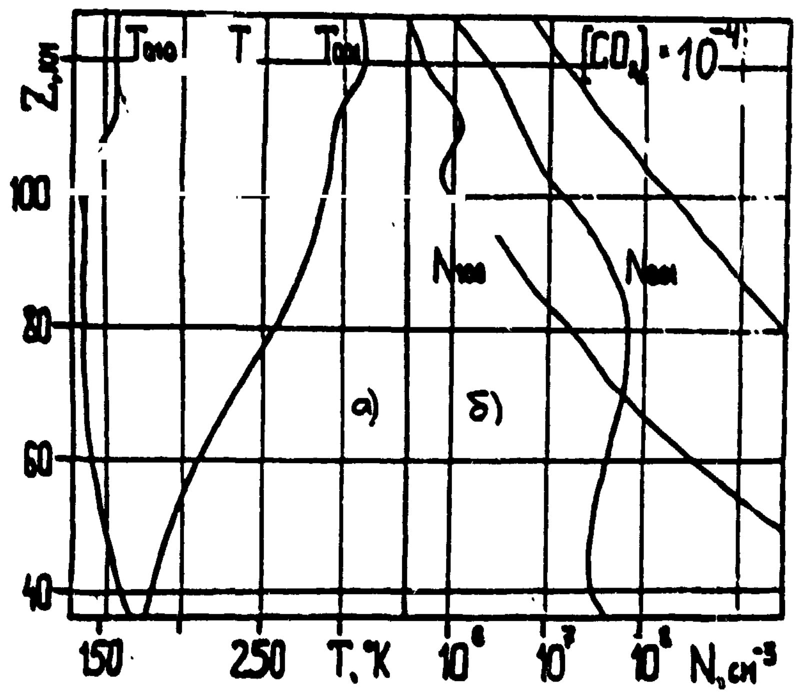

Figure 2. The Same as in Figure 1 but for Mars

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 α (or T_{001}) and intensity of the IR radiation band of the atmospheres. The total effective probability of deactivation of the vibrational quanta are presented here

$$A^{\Sigma} \cdot P_{10} = \sum_{j=1}^{5} \sum_{i=1}^{n} A_{ij} \cdot P_{10}, \text{ where } A_{ij} = \gamma_{ij} L(\tau_{ij}) \exp\left(-\frac{m_i E_{010}}{kT_{010}} - \frac{\Delta E_{ij}''}{kT}\right) A_i,$$

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probability of collision deactivation P_{10}, as well as effective probabilities

$$A^{4.3} \equiv \sum A_{1l}, \quad A^{2.7} \equiv \sum A_{1l}$$

$$A^{2.0} \equiv \sum A_{1l}, \quad A^{10.0} \equiv \sum A_{1l}, \quad A^{IS} \equiv \sum \sum A_{ij}$$

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 $C^{12}O^{16}_2$, bands 2.7, 2 and 10 μm (including hot transitions) of the main component $C^{12}O^{16}_2$, 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^{IS} 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 m 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^{Σ} (see Figures 3a, and 4a) a rise in T_{001} with altitude (see Figure 1a, 2a). /22

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, 2.7 and 4.3 μm bands (see Figures 3a and 4a), then this also means that the Venusian and Martian atmospheres have an intensive effect: direct (without participation of the forward stages

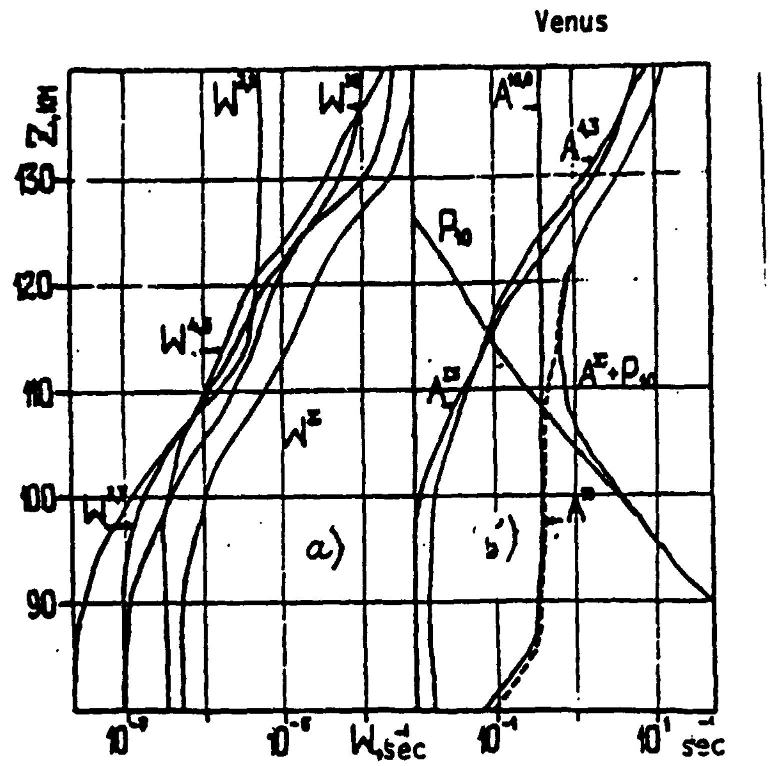

Figure 3. High-Altitude Course of Excitation Probabilities W (Figure a) and Deactivation A and P_{10} (Figure b) of the Asymmetric Mode of the CO_2 Molecule in the Venusian Atmosphere With "Temperate" Temperature. Indexes 2.0, 2.7, 4.3, 10.0 Correspond to the IR Bands 2.0, 2.7, 4.3 and 10 and 10.6-9.4 μm (including hot transitions) in the Main Isotope Component $C^{12}O^{16}{}_2$. The index IS corresponds to all bands in all small isotope components; the index Σ corresponds to the total ratio of probabilities. P_{10} corresponds to the probability of collision deactivation of the level 00°1.

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- /23

Mars

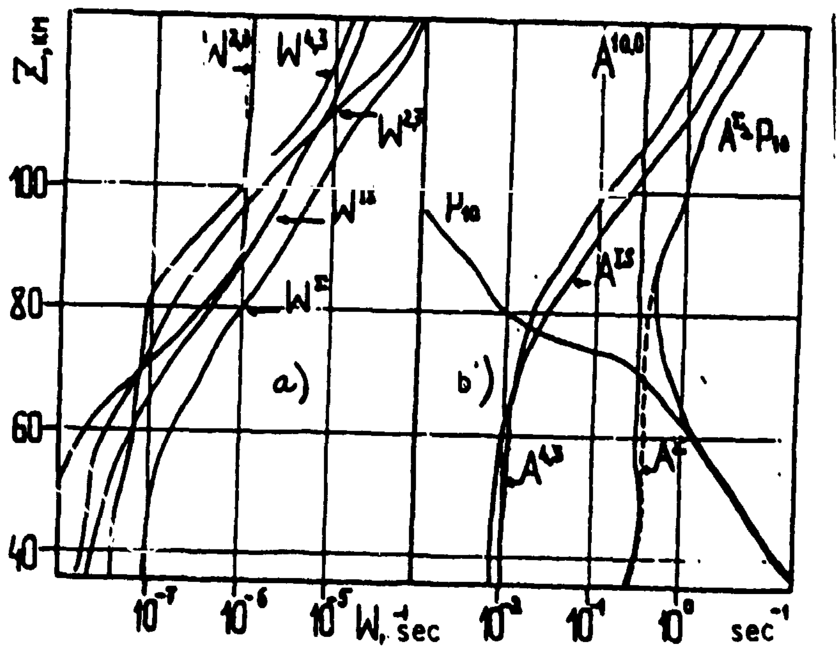

Figure 4. The Same as in Figure 3, but for Mars

tion in the spectral region $\lambda \geq 10$ m. This effect is governed by the following physical factors: rapid collision resonance process of vibrational-vibrational energy exchange of the type $(V_1, V^{\ell}_2, 1) + (00^\circ0) \rightarrow (V_1, V^{\ell}_2, 0) + (00^\circ1)$ transferring the molecules to lower vibrational levels, and subsequent de-excitation from these levels respectively in the 15 μm and 10 μm bands, where de-excitation from the level 00°1 in the 4.3 μm band is ineffective because of the strong capture of radiation. 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 μm bands into IR atmospheric radiation in the 4.3 and 15 μm bands, however it did not take into consideration

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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 $\lambda \leq 4.3$ m is the main source of atmospheric heating, then consideration for IR radiation in the 10.6 and 9.4 μm bands must noticeably influence the results [14], and in particular reduce the calculated temperature in the mesopeak region when Z = 113 km.

In light of the important role of 10.6 and 9.4 μm 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 base 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 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 $A^{10.0}$ in Figures 3b and 4b).

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Effective transformation of the solar energy absorbed in the near IR spectral region $\lambda \leq 4.3$ μm into natural IR radiation of the planets in the 10.6 and 9.4 μm 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 ~ 4.10³-fold greater than the equilibrium for Venus, and ~ 4.10⁴-fold for Mars. /27

Venus

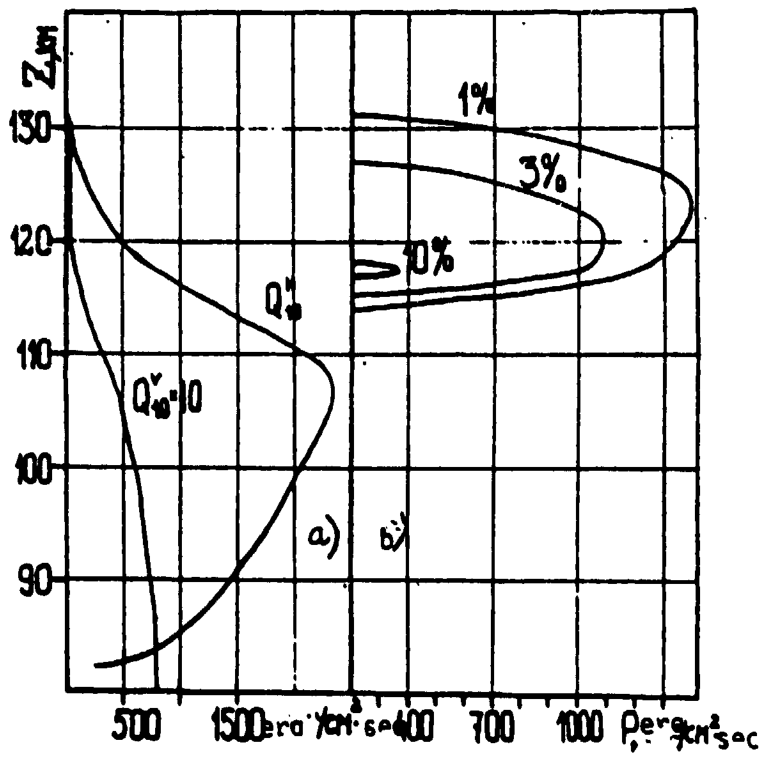

Figure 5a. Flow of IR Radiation in the 10.6 and 9.4 μm CO_2 Bands in the Venusian Atmosphere with "Temperate" Temperature.

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

(Key continued on next page)

Figure 5a key continued:

Q^v_{10}. vertical flow into space from the atmospheric column with base at altitude Z

Figure 5b. Power of Laser Generation in the 10.6 μm line in the Venutian 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.

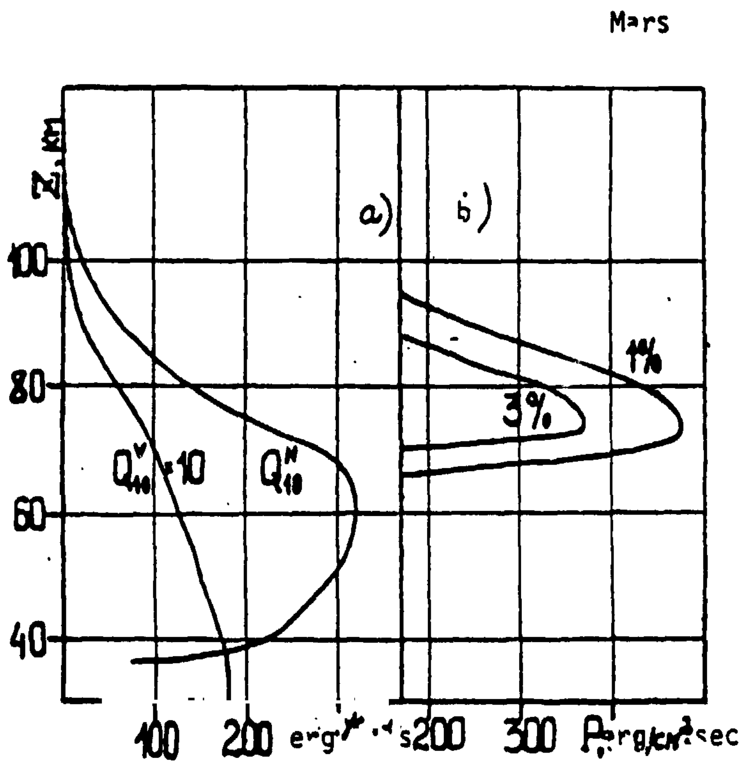

Figure 6. The Same as in Figure 5, but for Mars

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

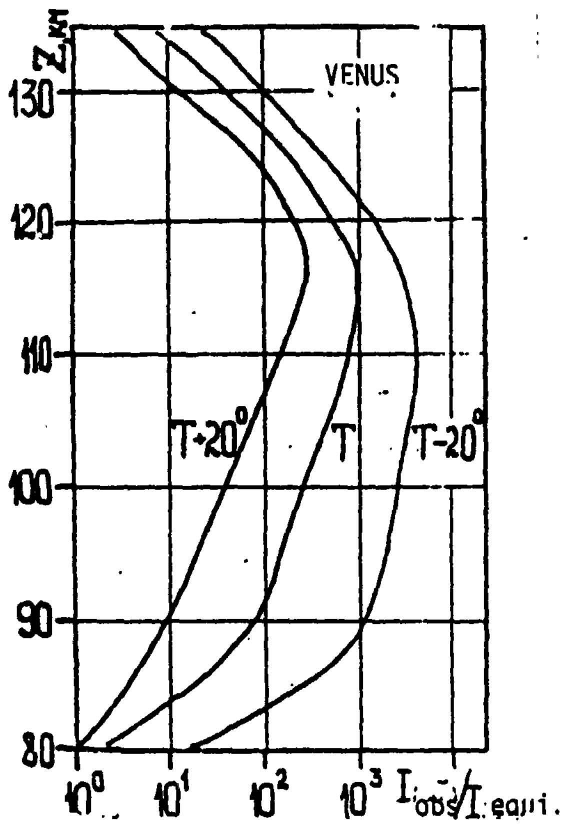

Figure 7. Ratio of TrueIR Radiation Intensities in Bands 10.6 and 9.4 μm CO_2 and Their Equilibrium Values in the Venusian Atmosphere.
Calculation made for IR radiation streams on the planetary limb, i.e., with horizontal sighting from space, for atmosphere with "temperate" temperature, and also for "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 /30
the near IR spectral region by water vapors with subsequent transfer of energy from H_2O to CO_2. However, the good agreement between theory and experiment that we obtained indicated that the observed intensities are provided by absorption by the CO_2 molecules themselves.

The authors of [17] also used the measured IR radiation intensities to define the quantity of excited CO_2 (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 10^{14} 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 T_{001} over T_{010} 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 N_{001}/N_{100} 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.

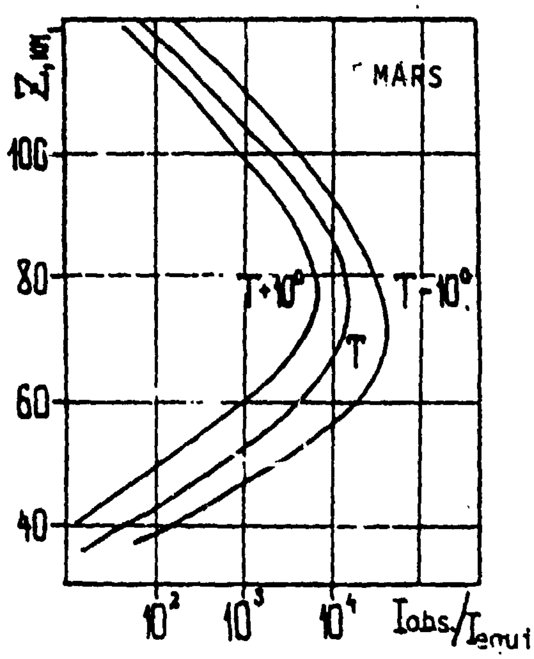

Figure 8. The Same as Figure 7, but for Mars.

and 10°0 becomes greater than 1 at altitudes 116 km for Venus and 70 km for Mars. /31 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 ΔN provide coefficients of intensification $\varkappa$, which although they are small are already accessible for experimental detection. Among the different vibrational-rotational transitions, the maximum $\varkappa$ value is realized in the P-branch of the transition 00°1 $\rightarrow$ 10°0 with rotational level $j = \sqrt{\frac{T}{2Be}}$ (Be--rotational constant in °K) and with the Doppler line contour equal to

$$\varkappa^{max}\left[\frac{1}{cm}\right] \simeq \frac{7.5\cdot 10^{-16}}{T}\cdot \Delta N, \qquad (15)$$

where ΔN is expressed in cm^{-3}, T in °K.

The high-altitude profiles with $\varkappa^{max}$ which are calculated with the use of (15) are presented in Figures 9a and 10 a. It is apparent that in the region of the maximum, the intensification coefficient can reach values $\sim 5 \times 10^{-9}$ cm^{-1} for Venus and $\sim 2 \times 10^{-9} \times cm^{-1}$ 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 $\sim 10^6$-fold smaller). For a vertical /34 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.

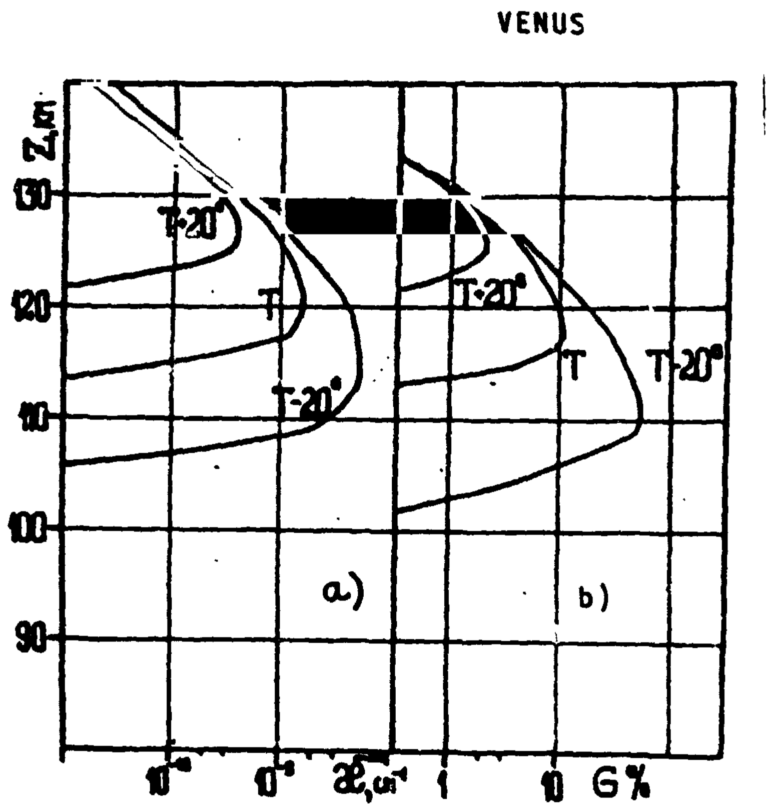

Figure 9. High-Altitude Course for the Coefficient of IR Radiation Intensification $\varkappa^{max}$ for a Unit of Length (Figure a) and Intensification G in one Pass with Horizontal Sighting (Figure b) on the Transition 00°1 → 10°0 in the Venusian Atmosphere. The calculation was made for an atmospheric model with "temperate" temperature, as well as for "cold" and "hot" atmospheres.

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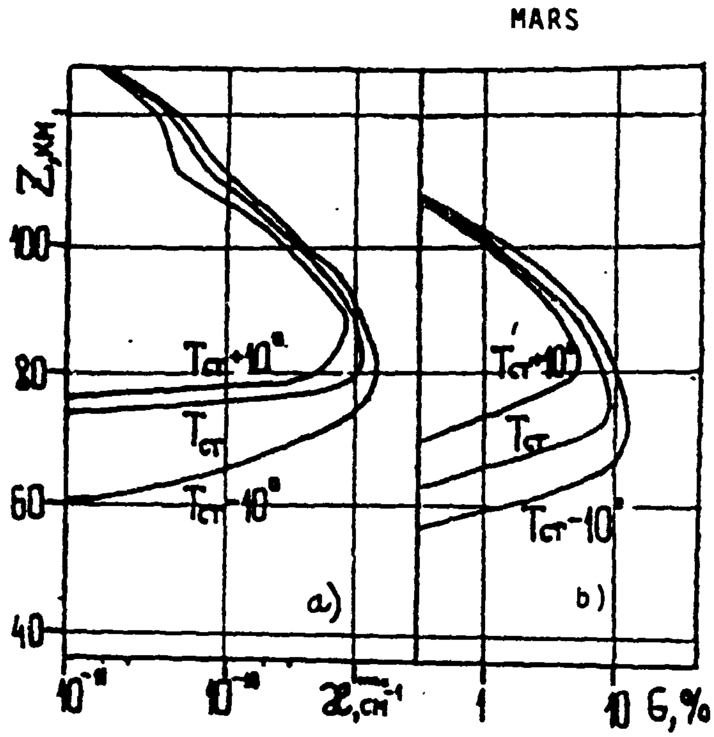

Figure 10. The Same as Figure 9, but for Mars

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 areinstalled 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

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from the resonator. It is apparent that the generation power for the Venutian laser must be $\geq 1 \times 10^{-4}$ W/cm², and for the Martian $\geq 4 \times 10^{-5}$ W/cm². In this case the area of the mirrors which determines the total generation power can be more than 100 km².

We note that these lasers would become gas lasers with solar excitation of the medium under natural conditions. The creation of laboratory gas solar lasers has been suggested in [27]. /35

We note the following in conclusion. Astrophysics is currently well aware of the natural space objects which intensify electromagnetic radiation in the centimeter wavelength range. These are masers on OH and H_2O 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°1 - 10°0 exists at altitudes 85 - 95 km. However even in this case because of the low CO_2 concentration, the intensification 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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