NON-THERMAL 10μm CO_2 EMISSION LINES IN THE ATMOSPHERES OF MARS AND VENUS*

M.A. Johnson, A.L. Betz, R.A. McLaren[†], E.C. Sutton[#]
and C.H. Townes

Department of Physics, University of California, Berkeley
Berkeley, California 94720

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ABSTRACT

Mechanisms are examined for excitation of strong 10μm CO_2 emission lines seen on Mars and Venus. Line absorption of near IR solar flux directly by CO_2 or by H_2O with collisional transfer of energy to CO_2 are proposed as likely excitation mechanisms. Altitudes for peak 10μm emission are estimated to be near 80 km for Mars and 120 km for Venus.

[#] National Science Foundation Fellow.

[†] NATO Postdoctoral Fellow 1974-75
Present address: Department of Astronomy, University of Toronto, Toronto, Canada M5S 1A7

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I. Introduction

A 10μm infrared heterodyne spectrometer with 5 MHz (1.7×10^{-4} cm^{-1}) resolution has been used to measure line profiles of CO_2 in the atmospheres of Mars and Venus. Unexpectedly strong emission has been observed (Betz et al. 1976) from both planets at the line centers of the $00°1 - [10°0 - 02°0]_I$ vibration-rotation band of $^{12}C^{16}O_2$. The emission lines have a Gaussian shape with a width corresponding to kinetic temperatures of about 170K for Mars and 200K for Venus. The strength of the emission, however, exceeds the flux emitted from a blackbody at these temperatures by factors ranging from 5 to 15. Some characteristics of these lines and possible excitation mechanisms are examined below.

II. Observations

The observations were made at Kitt Peak National Observatory** during 1975, November and December.

The spectrometer is described in an accompanying paper (Betz et al. 1976).

(a) Mars

Emission features at the P12 through P28 transitions of the $00°1 - [10°0 - 02°0]_I$ band of $^{12}C^{16}O_2$ were observed in the atmosphere of Mars. Kinetic temperatures derived from the linewidths ranged from 150K to 200K. Rotational

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temperatures determined from the relative line strengths were also in this range. The absolute line strengths, however, were two to ten times greater than emission from a gas in LTE at temperatures derived from the linewidth. Shown in Figure 1 is the central portion of the 950 cm^{-1} P(14) line seen from a region on the planet producing the maximum continuum signal. This region corresponded approximately to the subsolar point, near 290° west longitude and 0° latitude. The emission line occurs in the central core of a broad absorption feature which has been removed in plotting the figure. These absorption features have been observed in detail and will be described in a subsequent paper.

(b) Venus

In the case of Venus a systematic study was made of the emission strength across the face of the planet, which was near a phase of .65. The emission was approximately constant along lines of equal solar illumination and increased very sharply toward the subsolar limb. No emission was detected from the dark half of the planet, nor was any seen in the center of the $^{13}C^{16}O_2$ absorption lines. Shown in Figure 2 are two line profiles from Venus; the stronger emission is from the subsolar limb and the weaker is from near the terminator. The sharp rise in emission near the limb may occur over a region substantially smaller than our 4 arc sec beam diameter. Even so, the observed linewidth is 0.63 of the minimum width expected from a gas in LTE emitting the observed amount of radiation at line center.

III Emission Mechanisms

Two facts suggest an emission mechanism tied closely to the solar flux in the emitting region of the atmosphere: (1) the emission from Venus is substantially stronger than that from Mars, and (2) the Venus emission strength depends strongly on the solar illumination at the observed region.

Several apparently likely emission mechanisms can be quickly ruled out by general arguments. Resonant scattering of 10μm solar radiation cannot produce the observed emission because the incident solar flux within the observed linewidth at 10μm is about 200 times smaller than the emission. Similarly, electronic excitation by solar XUV continuum is ruled out as an energy source for the emission because the total solar XUV energy flux from 5Å to 1600Å is barely comparable to the total emitted energy flux of 20 $\mathrm{erg/cm^2/sec}$ in the 10μm lines and it seems likely that only a very small fraction of the XUV energy could be converted to these emission lines. Solar excitation of CO_2 in any of the strong 4μm transitions, such as directly from the ground state to 00°1 level, is also ruled out by the relatively low solar flux at 4μm. Absorption of the solar flux in the near IR region ($\lambda < 3\mu m$), however, is adequate to explain the emission if the absorbed energy can be used to populate the 00°1 level.

In contrast to production of the linewidth solely by thermal velocities, the very narrow widths observed might in principle be produced by a population inversion causing gain narrowing of the stimulated emission. At 10μm, however, such narrowing would occur only for gains high enough to produce a line several hundred times stronger than observed.

A comparison of the relative time scales for the relaxation of kinetic, vibrational and rotational energy in pure or nearly pure CO_2 shows the special nature of the 00°1 level, the upper level of the observed 10μm transition. At 200K in LTE the fractional population of this level is only 5×10^{-8}. Molecules excited to this level radiate spontaneously either to the ground state in about 2×10^{-3} seconds or to the 10°0 - 02°0 states in 1.5 seconds, the latter producing the observed 10μm radiation. At a density of 10^{13} cm^{-3}, which is, as will be shown, relevant to emission mechanisms, the average time between CO_2-CO_2 kinetic collisions is about 4×10^{-4} seconds and at least one of the colliding molecules is almost certainly in the ground vibrational state. Several kinetic collisions are sufficient to equilibrate both the kinetic and rotational energies, but Stephenson and Moore (1970) have shown that the cross section for collisional de-excitation of the 00°1 vibrational level is about 10^{-4} of the kinetic cross section. The 10μm radiative transition therefore competes favorably with collisional de-excitation at densities of 10^{13} cm^{-3} or less. Finzi and Moore (1975) have also shown that the many CO_2 levels with one or more quanta of the asymmetric stretch vibration, ν_3, interchange these quanta with a collision cross section almost equal to the kinetic cross section. Since the 00°1 level is the lowest level containing any ν_3 quanta, virtually every kinetic collision involving a molecule in a state containing one or more ν_3 vibrational quanta leaves a molecule in the 00°1 state. Once in this state, energy cannot easily be lost from deep in the atmosphere by radiative decay to the ground state because in this strong 4μm absorption the photon mean free path is not more than a few meters for a density of 10^{13} cm^{-3}, and the 4μm radiation is therefore resonantly trapped.

We propose two possible mechanisms for absorption of solar radiation and subsequent re-emission at 10μm: (1) direct line absorption of near IR radiation by CO_2, and (2) line absorption of near IR by H_2O with collisional transfer of energy to CO_2. The calculations will be illustrated for the case of Mars, rather than Venus, because the solar flux and the line of sight to Mars were colinear, simplifying the analysis.

(a) Line absorption by CO_2

Using the observed intensity of the strongest line, the total 10μm emission from a single rotational level of the 00°1 vibrational state of CO_2 was calculated to be 2×10^{13} photons/cm^2/sec at the source on the basis of three assumptions: (1) that the emission is unpolarized, (2) that the unobserved 00°1 $-[10°0 - 02°0]_{II}$ band at 1050 cm^{-1} emits a flux comparable to the observed 00°1 $-[10°0 - 02°0]_{I}$ band at 950 cm^{-1}, and (3) that the emitting region is optically thin and emits istropically rather than as a Lambertian source. Failure of any one of these assumptions to be true decreases the calculated emission by about a factor of two. The expected solar absorption of the strongest line in each of a number of CO_2

bands was calculated assuming an isothermal upper Martian atmosphere at a temperature of 170K. A Voigt line profile was integrated through an exponential density distribution between the limits of 10^9 and 10^{17} cm^{-3} for a scale height of 10 km. Population in the upper level of the absorbing transition was assumed to be transferred with unit efficiency to the 00°1 level by the rapid exchange of ν_3 vibrational quanta in CO_2 - CO_2 collisions. The fraction of molecules in the 00°1 state which radiate at 10μm was taken equal to the ratio of the 10μm spontaneous radiation rate to the sum of this rate and the collisional de-excitation rate. Resonant trapping of the 4μm radiation from the 00°1 level was also assumed. The following expression gives the maximum expected number of 10μm photons emitted from a column of unit area:

$$N(10\mu m)\ cm^{-2}sec^{-1} = N_s \int \frac{dW}{dh} (1+n/n')^{-1} dh \qquad (1)$$

where W is the equivalent width (cm^{-1}) of the absorbing transition, calculated as a function of the height $\underline{h}$(cm); N_s is the solar spectral density striking Mars at the absorption frequency (cm^{-2} sec^{-1}/cm^{-1}); $\underline{n}$ is the density of CO_2 molecules (cm^{-3}); and $\underline{n'}$ is given by

$$n' = \frac{A}{\sigma\bar{v}} = 1.4 \times 10^{14}\ cm^{-3} \qquad (2)$$

where A is the sum of Einstein A coefficients for all 10μm transitions having a common upper level in the 00°1 vibrational state and is calculated from measured band strengths to be 0.6 sec^{-1}; σ is the cross section for quenching of the 00°1 level by collision and is taken to be $1.5 \times 10^{-19} cm^2$ (Stephenson and Moore, 1970); and $\bar{v}$ is the average molecular velocity at 170K. The strongest line in each of the eight strongest near IR $^{12}C^{16}O_2$ absorption bands ($\lambda < 3\mu m$) was selected (McClatchy et al, 1973), and the expected 10μm emission was calculated from equation (1) to be within 20% of the observed amount. Inclusion of the estimated contributions due to the weaker lines in strong bands of $^{12}C^{16}O_2$ and to the stronger lines of rare isotopic species increased the total expected emission to about 4 times the observed amount. Heavy saturation of the strong lines required inclusion of a range of 10^4 in line strengths.

Shown in Figure 3 is the calculated distribution of the emission versus density for the sum of the eight lines explicitly calculated. The emission from the weaker and the isotopic lines is expected to peak at densities near 3×10^{14} cm^{-3}, lowering somewhat the altitude for maximum emission shown in Figure 3. The effect of non-zero optical depth in the emitting transition has been included for densities greater than 10^{15} cm^{-3}. The fact that the emission is a maximum for densities greater than 10^{13} cm^{-3} justifies the assumption that collisions redistribute the ν_3 vibration quanta to the 00°1 level with unit efficiency. Finzi and Moore (1975) have measured the cross section for exchange of ν_3 quanta as 2.4×10^{-15} cm^2 at 295K and Moore (1976) has suggested a

T^{-1} dependence for this cross section. At a density of 10^{13} cm^{-3} and a temperature of 170K the rate per excited molecule for collisional transfer of ν_3 quanta to molecules initially in the ground vibrational state is about 10^3 sec^{-1}, considerably faster than most radiative transitions in CO_2. The lack of observed emission from $^{13}C^{16}O_2$ can be explained by a normal $^{13}C/^{12}C$ abundance ratio of 0.011 and rapid interchange of ν_3 quanta between the two isotopic species of CO_2. The emission from carbon-13 is thus expected to be about 100 times weaker than that from carbon-12.

(b) Absorption by H_2O and collisional transfer to CO_2

In spite of the low fractional abundance of H_2O in the atmosphere of Mars, the large number of near infrared lines in the H_2O spectrum absorb an amount of solar flux comparable to that absorbed by CO_2. In addition,the three strong H_2O resonance bands 100, 001, and 011 have band centers which coincide to within 40 cm^{-1} or less with the $[10^\circ 1 - 02^\circ 1]_{II}$, $[10^\circ 1 - 02^\circ 1]_{I}$, and 01^12 levels of CO_2, respectively. Using an approximation to the curve of growth (Rodgers and Williams, 1974) in the absence of pressure broadening and a table of H_2O line strengths (McClatchey et al, 1973), the equivalent widths of these three H_2O bands were calculated as functions of column density of H_2O. Equation 1 was then used to calculate the expected 10μm emission for various fractional abundance ratios of H_2O to CO_2. A numerical abundance of 1 part in 2800 is sufficient to explain all the observed 10μm emission if the transfer of ν_3 vibrational quanta from H_2O to CO_2 and then to the 00°1 level of CO_2 has unit efficiency. The cross section for the resonant transfer from H_2O to CO_2 is probably within an order of magnitude of the kinetic cross section and is therefore expected to dominate over radiative losses, as is also true for transfer of ν_3 vibrational quanta among CO_2 molecules. Barker et al. (1970) have found column densities for Mars as high as 60μm of precipitable H_2O, corresponding to an abundance by number of about 1/450 if uniformly mixed with a 10 km scale height. The water vapor content in the Martian atmosphere is known to change with season and it may be possible to determine the importance of water vapor to the 10μm emission process by observing seasonal variations in the emission. The dashed line in Figure 3 shows the calculated dependence on density of the 10μm emission if the excitation mechanism is H_2O absorption alone and H_2O has an abundance of 1 part in 2800 by number.

(c) Emission from Venus

The strongest 10μm emission line from Venus is approximately 6 times stronger than the strongest line from Mars. We attribute this increase over the Martian emission in part to the 4-fold increase in solar flux on Venus compared to Mars. The remaining increase is most likely due to the fact that the angle between the line of sight and the direction of illumination was about 90° for Venus but near zero for Mars. In the case of Venus the area of illumination could therefore be much larger than the observed area for a particular volume of gas. The energy flux in the 10μm emission from the subsolar region of Venus is expected to be about 4 times that from Mars, or about 80 erg/cm^2/sec. The strong increase in emission observed toward the subsolar limb suggests that the radiation temperature for directions nearly tangent to the sunlit surface should be still higher than what is observed here. However, while some population inversion probably occurs, even in these tangential directions amplification is expected to be unimportant.

The fact that the calculated emission was based on a 10 km scale height Venus has no important influence on the density range on Venus for which maximum emission occurs because the density at which absorption takes place is relatively independent of scale height. The water vapor content of Venus atmosphere may be much lower than that of Mars; Barker (1975) and Young (1975) have reported a fractional abundance of 10^{-5} to 10^{-6}, but it is known to fluctuate greatly.

Radiative equilibrium processes in the upper atmosphere of Venus have been discussed by Dickinson (1972); observation of these 10μm emission lines provides direct evidence of conditions at this rarely observed altitude, as well as a measure of radiative losses for this wavelength region.

IV. Concluding Remark

It is clear that the intense, narrow CO_2 emission lines discussed here are excited by sunlight and represent a deviation from LTE. Near infrared absorption in both CO_2 and H_2O appear to be responsible for the excitation, and further observation of variations in the line intensities may allow evaluation of the relative importance of these two proposed excitation mechanisms. Minor atmospheric constituents other than H_2O may also transfer excitation energy to CO_2, but at least on Mars the abundance of H_2O makes it the most likely source of excitation other than CO_2 itself. Since the emission lines are both narrow and intense they provide through their Doppler velocities a good means of measuring and monitoring high altitude winds on Venus and Mars (Betz et al. 1976). In addition, for regions in the atmospheres with a density near 10^{14} cm^{-3}, the linewidths give kinetic temperatures of about 170K for Mars and 200K for Venus.

We appreciate informative discussions with C.B. Moore and M.J.S. Belton.

Figure Captions

Figure 1 An emission line profile seen in the Martian atmosphere after 24 minutes of integration. The curve is a Gaussian fit to the data and has a width corresponding to a kinetic temperature of 172K. T_{RJ}, the Rayleigh-Jeans temperature, is equal to the received spectral power density divided by Boltzman's constant and referenced to the top of the earth's atmosphere. Emission from an optically thick gas at 172K corresponds to $T_{RJ} = 0.49$K. The continuum radiation appearing outside the absorption feature (not shown) from the surface of the planet at 275K has $T_{RJ} = 9.6$K.

Figure 2 Two emission profiles seen in the atmosphere of Venus after 16 minutes of integration. Filled circles show emission near subsolar limb; open circles, near the terminator at the center of the planet. Solid curves are Gaussian profiles fit to the data. The width of the larger profile corresponds to 203K; the smaller, to 182K. Radiation from a blackbody at 203K has $T_{RJ} = 1.6$K. The dashed curve is a line profile for a gas in LTE at 414K with an optical depth at line center of 0.63. For a gas in LTE this is the minimum width profile having the observed central intensity. Continuum radiation with a Rayleigh-Jeans temperature, T_{RJ}, of 2K has been removed.

Figure 3 Calculated relative emission vs density. Solid curve is for excitation by CO_2 absorption alone; dashed curve, for H_2O absorption only. Altitude estimates are based on isothermal upper atmospheres at 170K for Mars, 200K for Venus.

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A.L. Betz, Department of Physics, University of California,
Berkeley, California 94720

M.A. Johnson, Department of Physics, University of California,
Berkeley, California 94720

R.A. McLaren, Department of Astronomy, University of Toronto,
Toronto, Canada M5S 1A7

E.C. Sutton, Department of Physics, University of California,
Berkeley, California 94720

C.H. Townes, Department of Physics, University of California,
Berkeley, California 94720.

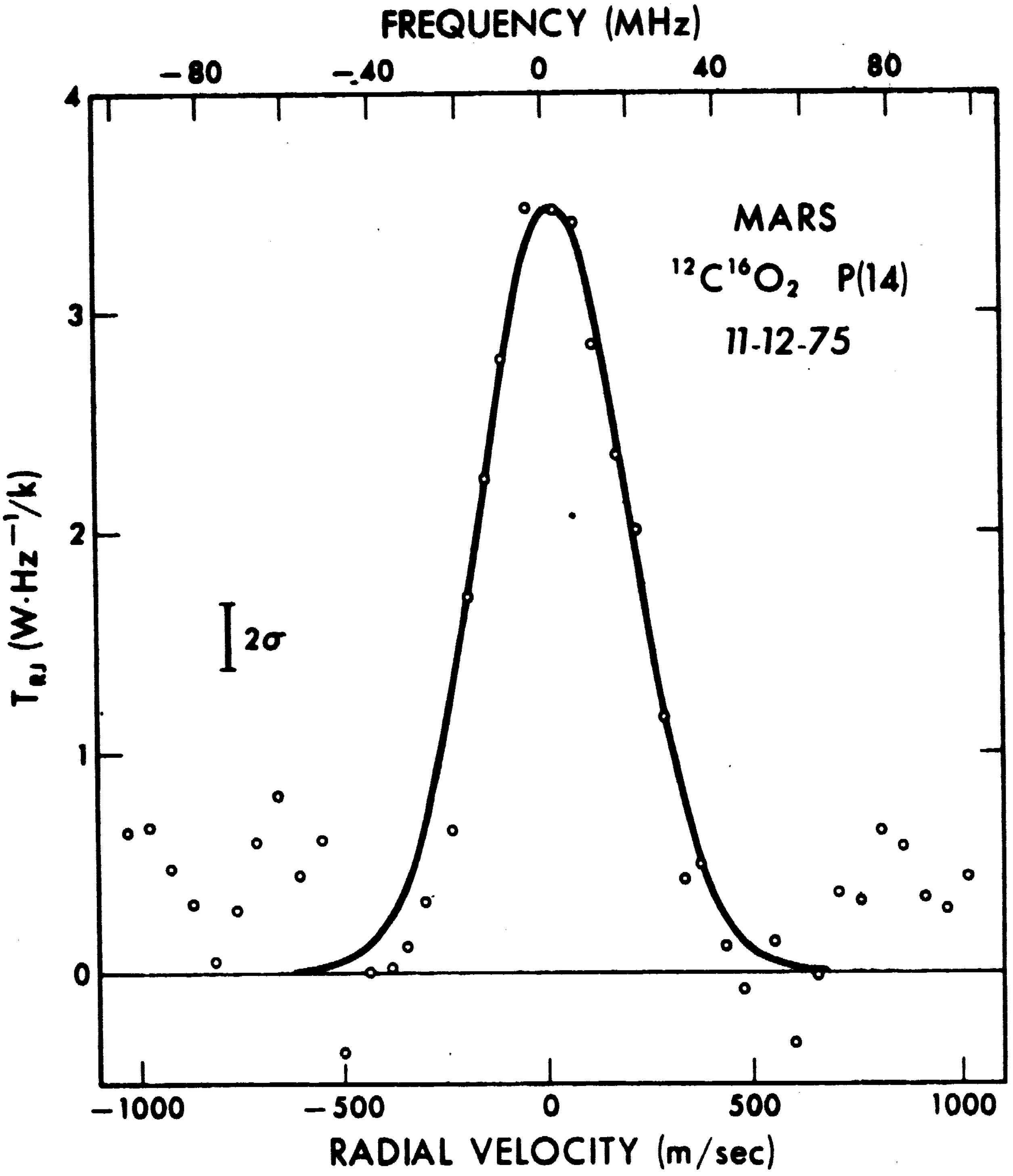

FIGURE 1

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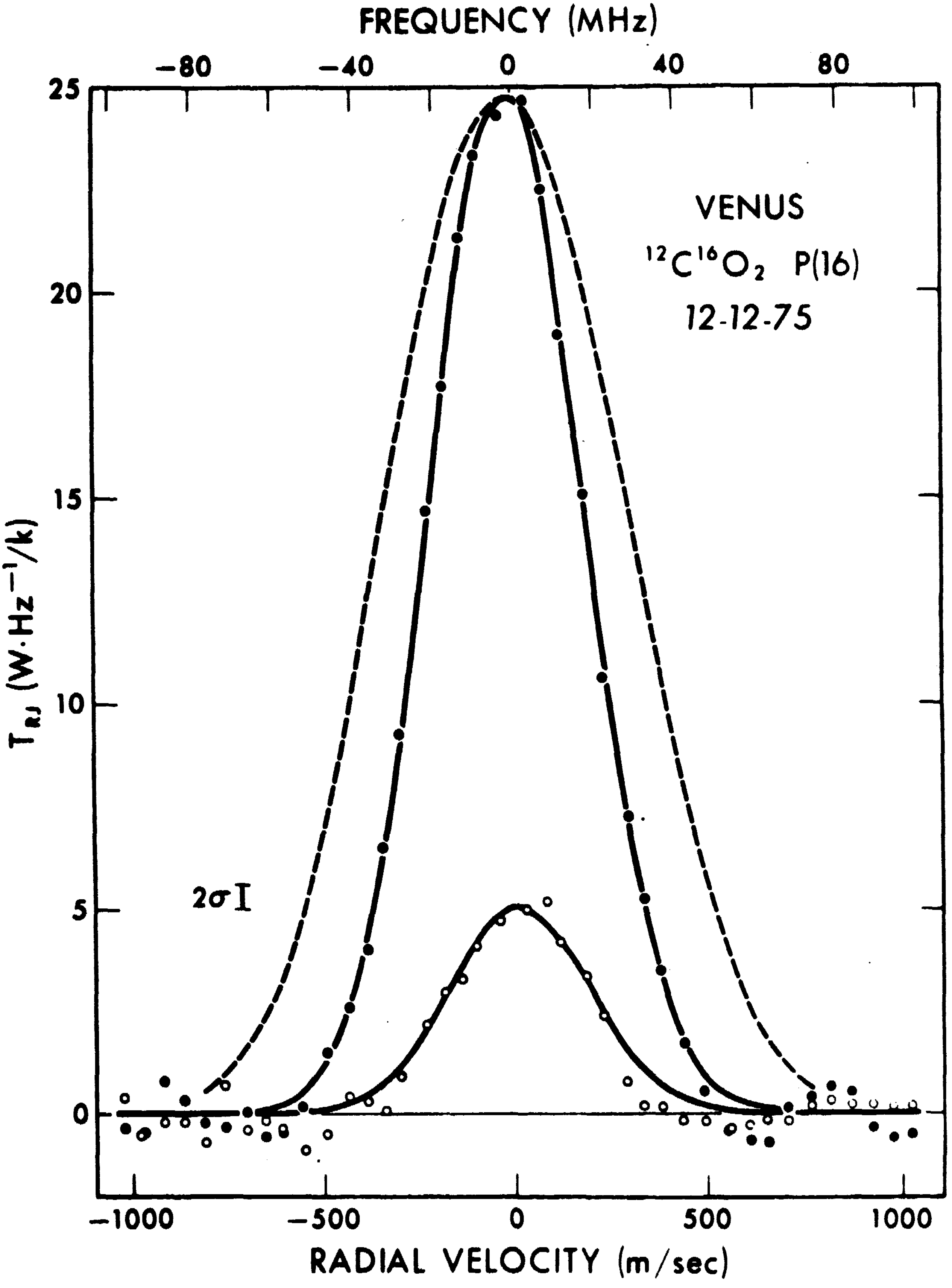
FREQUENCY (MHz)
−80
−40
0
40
80
25
20
15
10
5
0
T_{RJ} (W·Hz^{-1}/k)
VENUS
$^{12}C^{16}O_2$ P(16)
12-12-75
2σ I
−1000
−500
0
500
1000
RADIAL VELOCITY (m/sec)

FIGURE 2

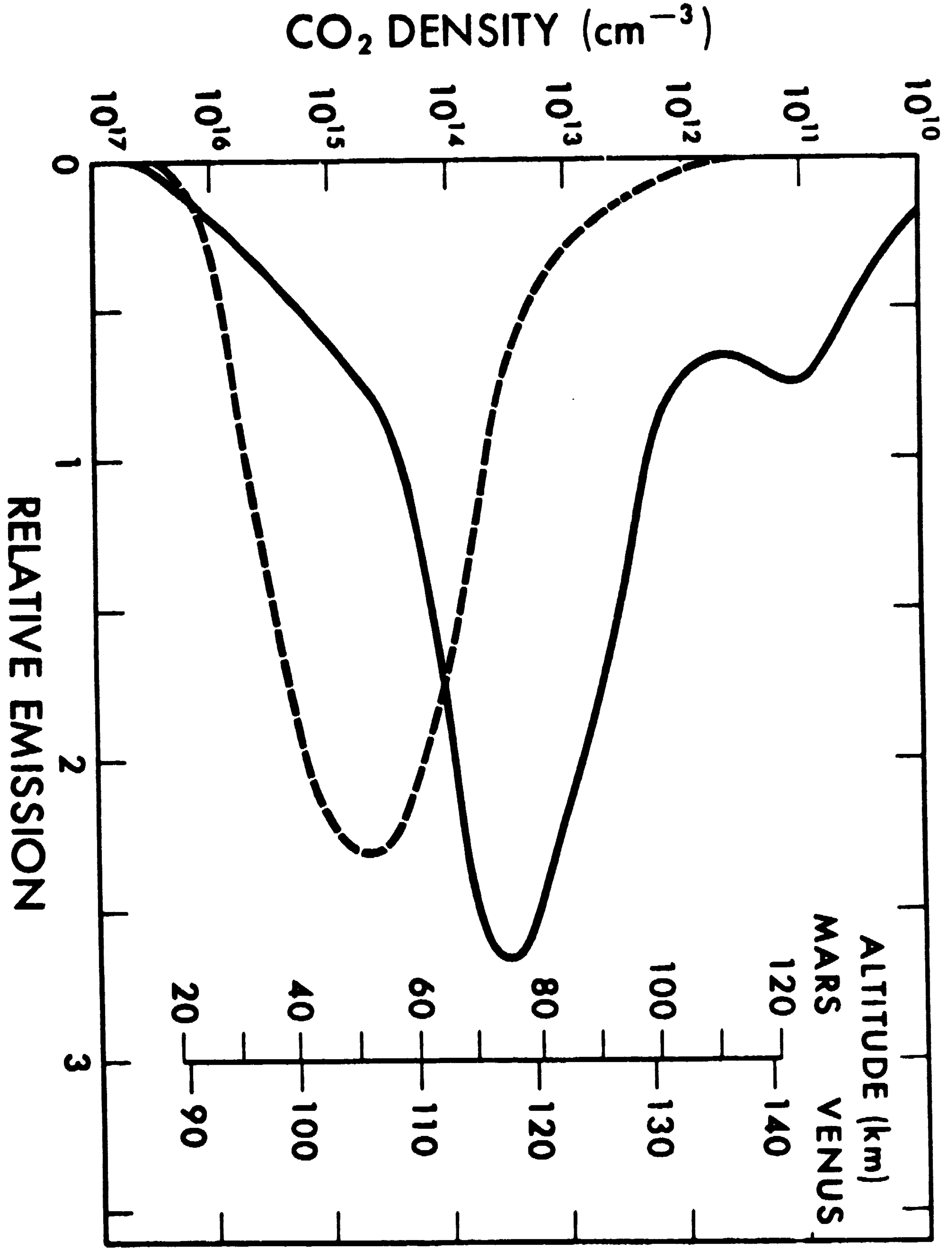
CO₂ DENSITY (cm⁻³)
10¹⁷
10¹⁶
10¹⁵
10¹⁴
10¹³
10¹²
10¹¹
10¹⁰
0
1
2
3
RELATIVE EMISSION
ALTITUDE (km)
MARS
VENUS
120
100
80
60
40
20
140
130
120
110
100
90

FIGURE 3