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RADIATIVE TRANSFER WITHIN THE MESOSPHERES OF VENUS AND MARS

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ABSTRACT

A simplified formulation is presented for radiative transfer within the mesosphere of a carbon dioxide atmosphere. This includes radiative contributions due to hot bands, minor isotope bands, and departures from vibrational equilibrium. It is shown that radiative transfer within the mesosphere is completely independent of other regions of the atmosphere. The analysis, when applied to predict the global mean radiative-equilibrium temperature profile for Venus, gives excellent agreement with the more detailed calculations of Dickinson. With respect to Mars, a temperature minimum is found to occur at a pressure of 30 μb, consistent with the suggestion of a temperature minimum near 20 μb by the *Mariner 9* television experiment.

Inclusion of non-LTE emission by hot bands in the 4.3-μ and 10-μ spectral regions indicates that such emission probably plays a minor role. Vibrational energy exchange between isotopes, however, is shown to be significant within the upper mesosphere. Qualitative consideration is also given to dynamics induced by diurnal changes in solar heating.

Subject headings: atmospheres, planetary — infrared — Mars — Venus

I. INTRODUCTION

Calculations concerning the radiative-equilibrium thermal structure within the mesospheres of Venus and Mars, whose atmospheres consist primarily of carbon dioxide, have been performed by McElroy (1967, 1968*a*, *b*, 1969), although his interest mainly involved thermospheric structure. More recently Dickinson (1972) has presented a global mean temperature profile for Venus, with particular emphasis upon the mesosphere, by employing a numerical line-by-line integration of the equation of transfer. As his results illustrate, when Doppler broadening predominates, the radiative heating or cooling by a given vibration-rotation band is quite insensitive to both band intensity and partial pressure, such that weak bands and minor isotopes may contribute significantly to the heat budget of the mesosphere. Furthermore, at low pressures characteristic of the mesosphere, vibrational non-equilibrium significantly influences net radiative transport.

In view of the numerical complexities involved in Dickinson's procedure, it would seem useful to investigate the possibility of a simplified formulation for radiative transfer within a carbon dioxide mesosphere, employing Dickinson's results as a standard for comparison. Also, because of the short response time relative to rotation time for the Venusian mesosphere, it is reasonable to expect diurnal variations in radiative heating or cooling, which would be accompanied by thermally induced motions. A simplified formulation for radiative transfer would greatly facilitate the study of such dynamics.

The present paper gives an approximate analytical formulation for radiative transfer within a carbon dioxide mesosphere. This formulation is then employed to investigate the mesospheric thermal structure for Venus, which is shown to be in excellent agreement with the more exact calculations of Dickinson (1972); and it is also applied to the mesosphere of Mars. The simplicity of the formulation allows other possible radiative processes to be readily incorporated, such as non-LTE emission by the 10-μ and 4.3-μ hot bands, as well as vibrational energy transfer between isotopes.

II. ANALYTICAL MODEL

a) *Radiative Heating Equation*

Consider first the case for which net radiative heating is due solely to the $^{12}C^{16}O_2$ ground-state bands, with infrared transmission occurring within the 15-μ band, while solar absorption results from the near-infrared bands. This is the governing radiative-transfer process within the stratospheres of Venus and Mars; and, as discussed by Cess and Ramanathan (1972), the physical process consists of a transition from strong overlapping lines within the lower stratosphere to strong nonoverlapping lines in the upper stratosphere, with pressure broadening being the dominant line broadening mechanism throughout the entire stratosphere.

Following Cess and Ramanathan (1972), we let

$$\xi = \beta u_1 , \qquad u_i = \frac{3S_i}{2A_{0i}} \int_y^\infty P dy , \qquad \beta = \frac{2\gamma_0 P}{d} ,$$

where A_0 denotes the bandwidth parameter and S the band intensity, while P is pressure, y a vertical coordinate measured upward within the atmosphere, γ_0 the mean Lorentz line width per unit pressure, and d the mean line spacing. The subscript i refers to the specific band, with $i = 1$ denoting the 15-μ band, whereas $i \geq 2$ refers to the near infrared solar absorption bands, and N represents the total number of bands. The divergence of the radiative flux vector, q_R, appropriate to the upper stratosphere, may be obtained by letting $\xi \to 0$ within equation (8) of Cess and Ramanathan (1972), with the result that

$$\frac{dq_R}{du_1} = \mu\alpha \sum_{i=2}^{N} e_{\omega i}(T_s) \frac{d}{du_1} A\left(\frac{2u_i}{3\mu}\right) - J_{\omega 1} \frac{d}{du_1} A(u_1) , \tag{1}$$

where T_s is the effective blackbody temperature of the Sun, μ is the cosine of the solar zenith angle, $e_{\omega i}$ is Planck's function at the center of band i, $J_{\omega 1}$ is the 15-μ source function ($J_{\omega 1} = e_{\omega 1}$ for LTE), and $\alpha = (R_s/L)^2$, where R_s is the radius of the Sun and L the distance between the planet and the Sun. The quantity $A(u_i)$ represents the total band absorptance for band i, and equation (1) applies when the pressure-broadened lines are nonoverlapping, for which $A(u_i) = 2A_{0i}(\beta u_i)^{1/2}$ (Cess and Ramanathan 1972).

Equation (1) clearly illustrates that radiative heating within the upper stratosphere is independent of events occurring elsewhere within the atmosphere, since radiative exchange integrals are absent. The reason for this is that in the strong nonoverlapping limit for pressure-broadened lines, the band absorptance varies as a linear function of pressure, and consequently this portion of the atmosphere is mathematically analogous to, although physically quite different from, the optically thin limit for a homogeneous gas. A more detailed discussion on this point is given by Cess and Ramanathan (1972). In the following we will assume that equation (1) is also valid when the lines are Doppler broadened, although the foregoing explanation concerning the absence of exchange integrals is strictly applicable only when the Doppler lines are in the linear limit. In view of Dickinson's (1972) discussion concerning the importance of the exchange integrals, however, this would appear to be an appropriate assumption.

If equation (1), when suitably modified to account for other radiative processes, is indeed applicable throughout the mesosphere, then the fact that net radiative heating is strictly a local process means that the mesosphere may be treated independently of other regions of the atmosphere, i.e., the stratosphere and thermosphere. We will, in fact, show that the stratosphere-mesosphere thermal structure may be determined by asymptotically matching independent stratosphere and mesosphere solutions.

In addition to transmission in the 15-μ regions, carbon dioxide has near-infrared bands in the 4.3-, 2.7-, 2.0-, 1.6-, 1.4-, and 1.2-μ regions. Previous application of equation (1) to the stratosphere has incorporated only the ground-state bands of $^{12}C^{16}O_2$, and the first step in extending applicability to the mesosphere involves the inclusion of weaker overlapping bands at each spectral location. These bands comprise both hot bands and isotope bands; and if it is assumed that the individual lines of a given band do not overlap with those of another band, then the extension of equation (1) consists of simply summing the individual bands within a given spectral location.[1] We will apply equation (1) separately to each isotope. If we let the subscript m denote the isotope, then the net radiative heating due to each isotope is expressed as

$$\frac{dq_{Rm}}{du_1} = \sum_{i=2}^{7} \sum_{k=1}^{N_i} \Theta_{ik} - J_{\omega 1} \sum_{k=1}^{N_1} \frac{d}{du_1} A(u_{1k}) , \tag{2}$$

where we neglect the small differences in wavenumber at the centers of the overlapping bands, $J_{\omega 1}$ is taken to be the same for all 15-μ bands following assumption (i) of the next section, and

$$\Theta_{ik} = \mu\alpha e_{\omega i}(T_s) \frac{d}{du_1} A\left(\frac{2u_{ik}}{3\mu}\right) , \qquad u_{ik} = \frac{3S_{ik}f_m}{2A_{0i}} \int_y^\infty P dy . \tag{3}$$

The subscript i again refers to the spectral location of the band, k denotes a particular band within each spectral location with $k = 1$ representing the ground-state band and $k \geq 2$ the hot bands, N_i is the number of overlapping bands, and f_m is the isotope mixing ratio. The bandwidth parameter is assumed to be independent of k, while in accord with earlier nomenclature $u_1 = u_{11}/f_m$.

b) *Formulation for Vibrational Nonequilibrium*

The final extension of equation (1) involves the incorporation of vibrational nonequilibrium. The CO_2 molecule has three modes of vibration: symmetric stretch, bending, and asymmetric stretch, denoted by ν_1, ν_2, and ν_3, respectively. Absorption of solar near-infrared photons excite higher vibrational states, and upon collision the excited molecules relax by transferring part of their excited vibrational energy to vibrational energy of the colliding molecule and the rest to translational energy. At sufficiently low pressures, however, the molecules can loose energy by reradiation (non-LTE emission), and a non-LTE formulation of the radiative-transfer problem is necessary.

Since it is intended to compare the present model with the numerical solution of Dickinson (1972), the same assumptions as made by Dickinson in formulating the non-LTE problem are initially employed, while further

[1] The same result may be achieved by employing the multiplicative property of the mean transmission function (Goody 1964).

discussion regarding some of these assumptions will be given later. Quoting Dickinson, these assumptions are:[2]

"(i) Cooling by the 15-μ hot bands depends only on the populations of the fundamental 15-μ levels as calculated from a two-level NLTE theory.

(ii) The 15-μ overtone vibrations excited by absorption of near-infrared combination bands populate directly $\nu_2 = 1$, $\nu_3 = 0$ states and only increase hot band emission according to (i).

(iii) The collisional exchange of overtone levels in (ii) occurs before the 4.3-μ level of the combination band radiates and, consequently, only a ground-state 4.3-μ photon can be reradiated after a near-infrared absorption."

Molecules in the $\nu_3 = 1$ state relax by transferring vibrational energy into vibrational energy of the bending mode or by reradiating in the 4.3-μ ground-state band. The net energy in the $\nu_2 = 1$ bending mode is either converted into kinetic energy by collisional relaxation or reradiated in the 15-μ ground-state band.

The problem reduces to that of estimating the source function for the 15-μ bands after accounting for energy which has been converted from the $\nu_3 = 1$ level to the $\nu_2 = 1$ level. A general formulation for the source function has been given by Goody (1964), while Tiwari and Cess (1971) have reformulated this in terms of the band absorptance, and the source function $J_{\omega 1}$ for the $\nu_2 = 1$ level may be expressed as

$$\pi J_{\omega 1} = e_{\omega 1}(T) + \epsilon_{11} dq_R/du_1 , \tag{4}$$

where

$$\epsilon_{ik} = \frac{3}{8}\frac{\eta_{ik}}{\phi_{ik} f_m A_{01}}$$

and η_{ik} and ϕ_{ik} are the vibrational relaxation time and radiative lifetime, respectively. Recall that $k = 1$ denotes the ground-state band.

Again following Dickinson (1972), we assume no vibrational exchange between isotopes (discussion of this is given later) such that combination of equations (2) and (4) for each isotope yields

$$\frac{dq_{Rm}}{du_1} = \left[1 + \epsilon_{11}\sum_{k=1}^{N_1}\frac{d}{du_1}A(u_{1k})\right]^{-1}\left[\sum_{i=3}^{7}\Gamma_i\sum_{k=1}^{N_i}\Theta_{ik} + Q_{4.3} - e_{\omega 1}(T)\sum_{k=1}^{N_1}\frac{d}{du_1}A(u_{1k})\right], \tag{5}$$

where Γ_i is the ν_2 fraction of solar energy in the combination bands. The net vibrational energy which is transferred from the $\nu_3 = 1$ level to ν_2 vibrations is denoted by $Q_{4.3}$, so that the 4.3-μ band ($i = 2$) is excluded from the summation over i. Following the same procedure as employed in arriving at equation (5), and neglecting collisional population of the $\nu_3 = 1$ level from the ground state at these temperatures, we obtain

$$Q_{4.3} = \left[1 + \epsilon_{21}\left(\frac{S_{11}}{S_{21}}\right)\frac{d}{du_1}A(u_{21})\right]^{-1}\left[\sum_{k=1}^{N_2}\Theta_{2k} + \sum_{i=3}^{7}(1 - \Gamma_i)\sum_{k=2}^{N_i}\Theta_{ik}\right]. \tag{6}$$

In subsequent applications of equations (5) and (6), the relaxation times and radiative lifetimes, η_{ik} and ϕ_{ik}, will be taken directly from Dickinson (1972).

c) Band Absorptance Correlations

It remains to express the band absorptance, $A(u)$, for use in equations (5) and (6). We employ an approximation similar to that of Goody and Belton (1967), which consists of Lorentz-to-Doppler matching of the band absorptance. Dickinson (1972), on the other hand, has utilized the correct Voigt line profile.

In accord with previous discussion, the band absorptance for Lorentz lines is given as

$$A(u) = 2A_0(\beta u)^{1/2} . \tag{7}$$

This physically corresponds to nonoverlapping lines, a condition which is satisfied within the upper stratosphere and mesosphere. The corresponding expression for nonoverlapping Doppler lines is given by Cess (1973) as

$$A(u) = A_0 u(1 - 0.18u/\delta) , \qquad u/\delta \le 1.5 ; \tag{8a}$$

$$A(u) = 0.753 A_0 \delta\{[\ln(u/\delta)]^{3/2} + 1.21\} , \qquad u/\delta \ge 1.5 ; \tag{8b}$$

where $\delta = \pi^{1/2}\gamma_D/d$, and γ_D is the Doppler half-width. Since equations (5) and (6) employ the derivative of the band absorptance, the Lorentz-Doppler matching of the band absorptance is performed at the level for which

$$\left.\frac{dA}{du_1}\right|_{\text{Lorentz}} = \left.\frac{dA}{du_1}\right|_{\text{Doppler}} .$$

The band intensities, for use in equations (7) and (8), are taken from Dickinson (1972), while the mean Lorentz

[2] These assumptions require collisional equilibrium between the excited ν_2 levels, which is consistent with the non-LTE model of Tripodi and Vincenti (1971).

half-width per unit pressure, γ_0, is from Cess and Ramanathan (1972). Values of the bandwidth parameter A_0 are from Cess and Ramanathan (1972) for the 15-μ and 4.3-μ bands, while for the remaining near-infrared bands they have been deduced from Houghton's (1963) correlation incorporating the temperature dependence $A_0 \sim T^{1/2}$. The mean line spacing, d, has been taken to be 4 times the rotational constant for all bands except those of the asymmetric isotopes and bands of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ which have no Σ spin in either the upper or lower states. The mean line spacing is twice the rotational constant for these bands.

d) *Radiative Equilibrium*

Terrestrial abundances of five isotopes ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{16}O^{18}O$, $^{12}C^{16}O^{17}O$, $^{13}C^{16}O^{18}O$) are included in the present analysis, with the band intensities of the minor isotopes taken to be the same as those of $^{12}C^{16}O_2$ (Dickinson 1972). Equation (5) applies to each isotope, and the total heating function is given by

$$\frac{dq_R}{du_1} = \sum_{m=1}^{5} \frac{dq_{Rm}}{du_1} . \tag{9}$$

For illustrative purposes, we consider the state of radiative equilibrium, for which $dq_R/du_1 = 0$, such that from equation (5) the mesosphere temperature profile is described by

$$e_{\omega 1}(T) = \sum_{m=1}^{5}\left[1 + \epsilon_{11}\sum_{k=1}^{N_i}\frac{d}{du_1}A(u_{1k})\right]^{-1}\left[\sum_{i=3}^{7}\Gamma_i\sum_{k=1}^{N_i}\Theta_{ik} + Q_{4.3}\right]\Bigg/\left\{\sum_{m=1}^{5}\left[1 + \epsilon_{11}\sum_{k=1}^{N_i}\frac{d}{du_1}A(u_{1k})\right]^{-1}\left[\sum_{k=1}^{N_i}\frac{d}{du_1}A(u_{1k})\right]\right\}, \tag{10}$$

with $Q_{4.3}$ given by equation (6).

The actual evaluation of equation (10) requires an iterative solution, since the hot-band intensities, S_{ik} for $k \geq 2$, depend upon the number densities of the excited vibrational states, and for non-LTE these are influenced by the radiative-transfer process. The iterative procedure consists of assuming initial values of the source function, $J_{\omega 1}$, for each isotope, from which the number densities of the excited vibrational states are determined as discussed by Dickinson (1972). Equation (10) then describes $e_{\omega 1}(T)$ at a given atmospheric level, and combination of equations (4) and (5) for each isotope yields new values for the source functions. The process is repeated until convergence of the source functions is achieved. The procedure is quite straightforward if one starts at the stratopause for which LTE prevails and $J_{\omega 1} = e_{\omega 1}(T)$. As one progresses to higher levels within the mesosophere, the initial choices for the source functions are in turn governed by the corresponding values at the previous level.

e) *Non-LTE Emission by 10-μ Bands*

A radiative process which has not been considered by Dickinson (1972) consists of non-LTE emission by the 10-μ hot bands, and the present formulation affords a convenient means of investigating the possible influence of such emission. There are two bands in the 10-μ region; the (02^00–001) band at 1064 cm^{-1} and the (100–001) band at 961 cm^{-1}, with band intensities of 0.045 cm^{-1} (cm-atm)$^{-1}$ and 0.023 cm^{-1} (cm-atm)$^{-1}$ at NTP, respectively (Burch, Gryvnak, and Williams 1962).

There are many possibilities by which the ν_3 vibrations can relax into ν_2 vibrations (Houghton 1969; Taylor and Bitterman 1969), and it is not clear which of these dominate the relaxation process. For present purposes it suffices to write the kinetic equation for the population of the $\nu_3 = 1$ levels as

$$\frac{Q_{21}}{hc\omega_2} + \frac{Q_{81}}{hc\omega_3} + \frac{Q_{82}}{hc\omega_8} = \frac{n(\gamma_3 = 1)}{\eta_{21}} , \tag{11}$$

where $n(\gamma_3 = 1)$ is the number density, Q_{ik} denotes the net heating in a given band, $i = 8$ refers to the 10-μ bands, the wavenumber difference of the centers of the 10-μ bands has been neglected, and h and c denote Planck's constant and the speed of light.

The left side of equation (11) represents the net rate of increase in the population of the $\nu_3 = 1$ level due to absorption minus emission, neglecting production by collisional processes, while the right side is the rate at which the excited molecules are collisionally deactivated. Again representing the net vibrational energy which is transferred from the $\nu_3 = 1$ level to ν_2 vibrations by $Q_{4.3}$, we obtain $Q_{4.3} = Q_{21} + Q_{81} + Q_{82}$.

Expressing the number density $n(\nu_3 = 1)$ in terms of the source function $J_{\omega 2}$ for the 4.3-μ region, neglecting solar absorption in the 10-μ bands, and employing the same procedure used in arriving at equation (6) yields

$$Q_{4.3} = \left[1 + \sigma + \epsilon_{21}\left(\frac{S_{11}}{S_{21}}\right)\frac{d}{du_1}A(u_{21})\right]^{-1}(1 + 0.57\sigma)\left[\sum_{k=1}^{N_2}\Theta_{2k} + \sum_{i=3}^{7}(1 - \Gamma_i)\sum_{k=1}^{N_i}\Theta_{ik}\right], \tag{12}$$

where

$$\sigma = \frac{3S_{11}\eta_{21}}{8f_m A_{01}}\left[\frac{1}{\phi_{81}S_{81}}\frac{d}{du_1}A(u_{81}) + \frac{1}{\phi_{82}S_{82}}\frac{d}{du_1}A(u_{82})\right].$$

Inclusion of non-LTE emission by the 10-μ hot bands thus consists of simply replacing equation (6) by equation (12). The only additional information required is the bandwidth parameter for each of the 10-μ bands, and these have been taken from Edwards and Sun (1964).

III. RESULTS

Mesospheric temperature profiles, employing equation (10), will be presented for both Venus and Mars, and if a constant scale height, H, is assumed within the mesosphere, then $u_{ik} = 3S_{ik}f_m HP/2A_{0i}$, such that equation (10) describes temperature as a function of total pressure. At sufficiently high pressures Doppler broadening, non-LTE, minor isotope bands, and hot bands are all negligible; and from equation (7), equation (10) reduces to

$$e_{\omega 1}(T_0) = \alpha\mu^{1/2}\sum_{i=2}^{N} e_{\omega i}(T_s)\left(\frac{2S_i A_{0i}}{3S_1 A_{01}}\right)^{1/2}, \tag{13}$$

where the temperature T_0 defined by the above expression is independent of pressure. Equation (13) is identical to equation (10) of Cess and Ramanathan (1972) for the upper stratosphere, and T_0 represents an overlap solution between the mesosphere and stratosphere. The entire stratosphere-mesosphere thermal structure may thus be determined by additive composition (Van Dyke 1964), i.e., by adding independent mesosphere and stratosphere solutions and subtracting the common overlap solution T_0. For this purpose the stratosphere results of Cess (1972) are employed for both Venus and Mars.

a) *Venus*

We first consider Venus, for which Dickinson (1972) has presented results for global mean radiative equilibrium. In figure 1 we compare his revised temperature profile (Dickinson 1973) with the present analysis as given by equations (6) and (10), but with the solar heating term Θ_{ik} replaced by its global mean counterpart $\langle\Theta_{ik}\rangle$ expressed in

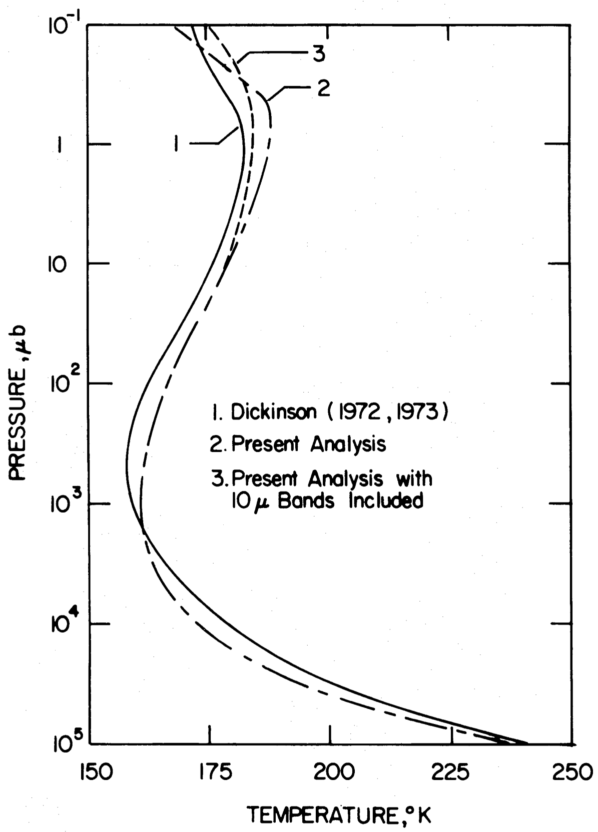

FIG. 1.—Comparison of calculated temperatures within the atmosphere of Venus for global mean radiative equilibrium

the Appendix by equation (17) for pressure-broadened bands and by equation (18) for Doppler-broadened bands. The pressure level at the tropopause, which is required in order to determine the temperature profile within the stratosphere (Cess 1972), was taken to be 240 millibars (mb) (Dickinson 1972). We have retained the convention proposed by Dickinson in defining stratopause (temperature minimum), mesopeak (temperature maximum), and mesopause (transition between mesosphere and thermosphere).

The agreement of the present model (curve 2) with Dickinson's calculations (curve 1) is within 6° K for pressures greater than 0.1 microbars (μb), and this certainly confirms the applicability of the present approximate procedure. Both ultraviolet heating and thermal conduction become important at higher altitudes, i.e., within the thermosphere. These contributions have not been included in the present analysis. As previously discussed, however, the temperature structure of the thermosphere does not influence that of the mesosphere.

The net solar heating by $^{12}C^{16}O_2$ within each spectral location is given in table 1 as a percentage of total solar heating by $^{12}C^{16}O_2$. Further detailed discussions concerning comparative heating and cooling rates are given by Dickinson (1972).

The effect of non-LTE emission by the 10-μ hot bands, which is included by employing equation (12) rather than equation (6) within equation (10), is illustrated in figure 1 by comparing curves 2 and 3. Incorporating the 10-μ bands reduces the temperature by about 4° K at the 1-μb level, while the temperature is increased by roughly 8° K at 0.1 μb. This increase in temperature at the lower pressures due to non-LTE emission is not as contradictory as it might seem. In the vicinity of 0.1 μb the 4.3- and 10-μ bands are all in non-LTE, and when a molecule emits in the 10-μ bands it still retains two quanta of ν_2 photons which are thermalized since the 15-μ band is in LTE. On the other hand, a molecule emitting through the 4.3-μ bands loses all the emitted energy. Effectively then, the fraction of energy which goes into ν_2 vibrations is increased due to the 10-μ bands. This is not the case at higher pressures ($\simeq 1$ μb), for which the 4.3-μ bands are in LTE. The 10-μ bands are included in subsequent calculations, although their influence is not large.

Differential solar heating within the mesosphere can be expected to induce meridional winds, the strength of which depends upon temperature differences between the polar and equatorial mesosphere. To estimate these temperature differences, it is sufficient to consider diurnally (longitudinally) averaged temperature profiles. Such profiles are representative of actual temperature profiles, even if solar heating induces a strong diurnal variation of temperature, since thermally induced day-to-night side winds would reduce these temperature differences. A further discussion of diurnal variations is given in § IV.

Diurnally averaged temperature profiles are illustrated for three latitudes in figure 2, where the tropopause has been located at 58 km (Cess 1972), and Θ_{ik} in equations (10) and (12) has been replaced by a longitudinal average as given by equations (19) and (20). Temperature is more strongly dependent upon latitude above 100 km, with a temperature difference between 0° and 85° latitude of roughly 50° K in the vicinity of the mesopeak. The reason for this is that the bands are Doppler broadened at these altitudes, and for Doppler broadening the heating is almost linearly proportional to the cosine of latitude angle, whereas a square-root proportionality exists for pressure broadening. The mesopeak correspondingly shifts to lower altitudes with increasing latitude. The strong latitudinal temperature differences could, of course, be modified by thermally induced meridional winds.

b) *Mars*

Two diurnally averaged thermal profiles for Mars, employing directly previous stratosphere results at latitudes of 4° and 58° (Cess 1972), are illustrated in figure 3 for altitudes above the 100-μb level. The stratopause is seen to be located at a pressure of roughly 30 μb, which corresponds to an approximate altitude of 45 km.

The 30-μb level for the stratopause is quite interesting in light of the *Mariner 9* television experiment as reported by Leovy *et al.* (1972), in which a well-defined thin haze layer was observed over most of the planet. This layer is located at approximately 20 μb, and it is estimated to be about 2 km thick. Leovy *et al.* tentatively conclude that it is composed of condensate particles forming at a persistent temperature minimum. Water ice is a probable candidate for the condensate material. The profiles presented in figure 3 certainly support their conclusion of a temperature minimum near the 20-μb level.

TABLE 1

SOLAR HEATING IN INDIVIDUAL SPECTRAL REGIONS AS A PERCENTAGE OF TOTAL HEATING FOR $^{12}C^{16}C_2$

Spectral Region (μ)	Pressure				
	10^3 μb	10^2 μb	10 μb	1 μb	10^{-1} μb
4.3	78%	62%	40%	21%	10%
2.7	14	17	25	42	40
2.0	6.5	8	20	27	46
1.6–1.2	1.5	13	15	10	4

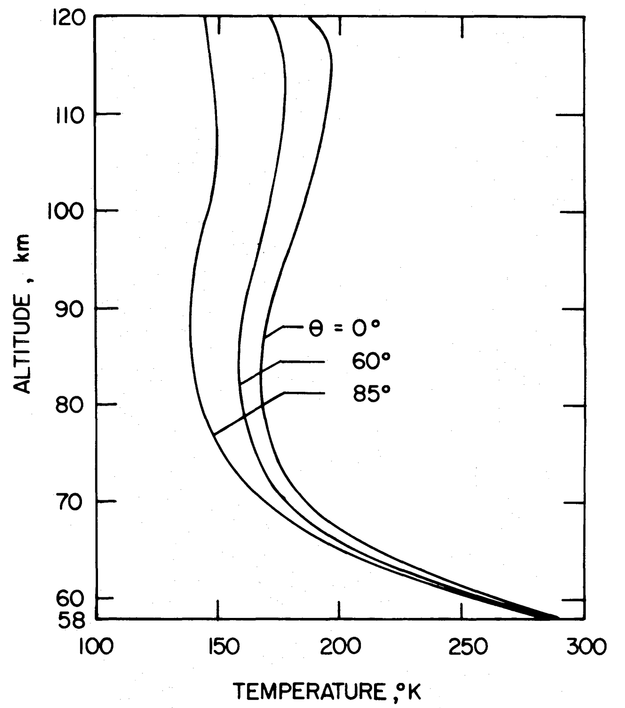

FIG. 2.—Diurnally averaged temperature profiles for Venus at different latitudes

The strength of the temperature inversion within the mesosphere of Mars is much less than that for Venus, which is a direct consequence of the smaller insolation on Mars. Instead of a well-defined mesopeak for Mars, there is a nearly isothermal region extending from 2 μb to 0.3 μb. This is largely due to the loss of energy by non-LTE emission in the 10-μ bands, which reduces the temperature within this region while increasing the temperature at altitudes above the 0.3-μb level. Indeed, calculations which have been performed neglecting the 10-μ bands produce a well-defined mesopeak at 0.4 μb.

IV. DISCUSSION OF RESULTS

a) *Diurnal Variations*

It has clearly been shown that the thermal structure within the mesosphere is independent of other regions of the atmosphere, and consequently any diurnal change of temperature within the mesosphere must be due to the time dependence of local solar heating. Employing the unsteady energy equation, Cess and Ramanathan (1972) have derived a parameter ϵ, appropriate to the stratopause, which represents the ratio of the thermal response time of the atmosphere to the rotation time of the planet. Making use of equation (5), and following the same procedure, one has for the mesosphere

$$\epsilon = \left(\frac{C_p\Omega}{3S_{11}TR}\frac{dT}{de_{\omega 1}}\right)\sum_{m=1}^{5}\left\{\left[1 + \epsilon_{11}\sum_{k=1}^{N_l}\frac{d}{du_1}A(u_{1k})\right]\Big/\left[\sum_{k=1}^{N_l}\frac{d}{du_1}A(u_{1k})\right]\right\}, \tag{14}$$

where R is the gas constant, C_p the specific heat at constant pressure, and Ω the rotational velocity of the planet. For $\epsilon \gg 1$ the atmosphere does not respond to time-dependent solar heating, whereas for $\epsilon \ll 1$ there is a strong response. This latter situation should, however, result in thermally induced winds, which would in turn reduce the diurnal temperature variation.

For Venus, $\Omega = 6.2 \times 10^{-7}$ s^{-1} based upon a solar day, and ϵ decreases from a value of 0.04 at the stratopause to 0.003 at 0.1 μb. Dickinson (1973) predicts significant diurnal temperature variations between the 1-μb and 0.1-μb levels, but negligible variations at altitudes below the 100-μb level due to modification of the day-to-night temperature variation by thermally induced winds. His dynamical model consists of motion from the subsolar to the antisolar points and employs the linear energy equation for which vertical adiabatic cooling is balanced by radiative heating. At the 100-μb level he estimates a diurnal temperature variation of approximately 1° K. On the other hand, employing the nonlinear energy and momentum equations, and adopting the fluid dynamical model proposed by Schubert (1969) and Malkus (1970), Ramanathan and Cess (1974) estimate a 13° K diurnal variation at 100 μb together with a 200 m s^{-1} zonal wind. No diurnal effects would be expected below the 5×10^3 μb level, which is consistent with the *Mariner 5* data (Cess and Ramanathan 1972).

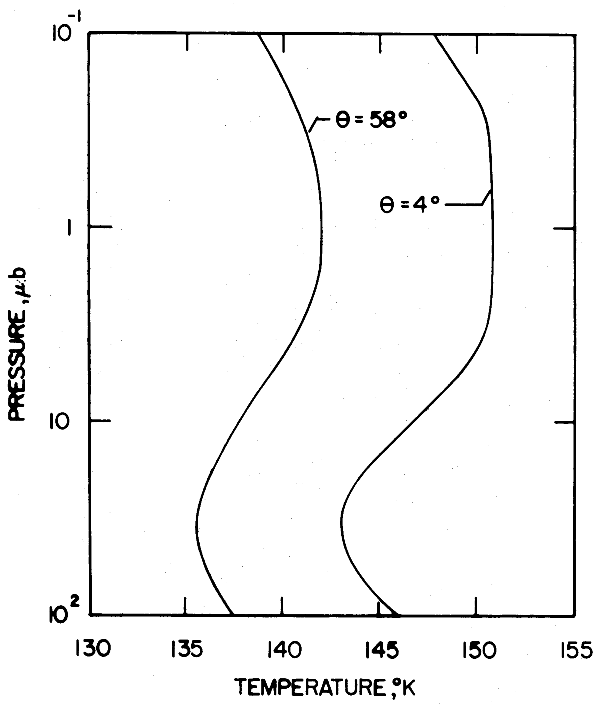

FIG. 3.—Diurnally averaged temperature profiles for Mars at different latitudes

The rotational velocity of Mars is $7.1 \times 10^{-5}\ s^{-1}$, and ϵ decreases from a value of 9 at the stratopause to 0.8 at the $10^{-1}\ \mu b$ level. This would appear to preclude the possibility of strong diurnally induced motions within the Martian mesosphere.

b) *Non-LTE Emission in the 4.3-μ Hot Bands*

As previously stated, collisional depopulation of the ν_2 levels of the combination bands has been assumed to be so rapid that non-LTE emission takes place only through the 4.3-μ ground-state band. If this process is not sufficiently rapid, the ν_3 levels of the combination bands may reradiate through the 4.3-μ hot bands.

In order to estimate the possible influence of this effect, we have employed an overall rate constant α $(= 1/\eta_{ik}P)$ for the collisional depopulation of the ν_1 and ν_2 levels in all the combination bands. Equation (12) for $Q_{4.3}$ was then modified to account for non-LTE emission in the 4.3-μ hot bands, and this hot band emission was found to be negligible for $\alpha > 2 \times 10^9\ s^{-1}\ atm^{-1}$, while for $\alpha = 2 \times 10^8\ s^{-1}\ atm^{-1}$ the atmospheric temperature for Venus was reduced by 8° K at the 0.1-μb level and by 5° K at the mesopeak, whereas it was unchanged at altitudes below the 2-μb level.

Rhodes, Kelley, and Javan (1968) have attempted to experimentally determine the rate for the reaction

$$CO_2(02^00) + CO_2(00^00) \rightarrow CO_2(00^00) + CO_2(10^00) + 102\ cm^{-1}\ ,$$

but the reaction is so rapid that they could only set a lower bound of $7.6 \times 10^8\ s^{-1}\ atm^{-1}$. For the reaction

$$CO_2(02^00) + CO_2(00^00) \rightarrow 2CO_2(01^10) - 46\ cm^{-1}$$

they determine $\alpha = 3.0 \times 10^8\ s^{-1}\ atm^{-1}$. These values, together with the foregoing discussion, suggest that non-LTE emission by the 4.3-μ hot bands probably plays a minor role within the mesospheres of Venus and Mars. Because of the scarcity of data, however, it is impossible to be more quantitative on this point.

c) *Vibrational Energy Transfer Between Isotopes*

Exchange of vibrational energy between isotopes has been neglected thus far. Stephenson, Wood, and Moore (1968), and Stephenson and Moore (1972) have measured rate constants for the near resonant vibrational exchange process

$$^{12}C^{16}O_2(00^01) + X(00^00) \rightarrow {}^{12}C^{16}O_2(00^00) + X(00^01) + \Delta E\ ;$$

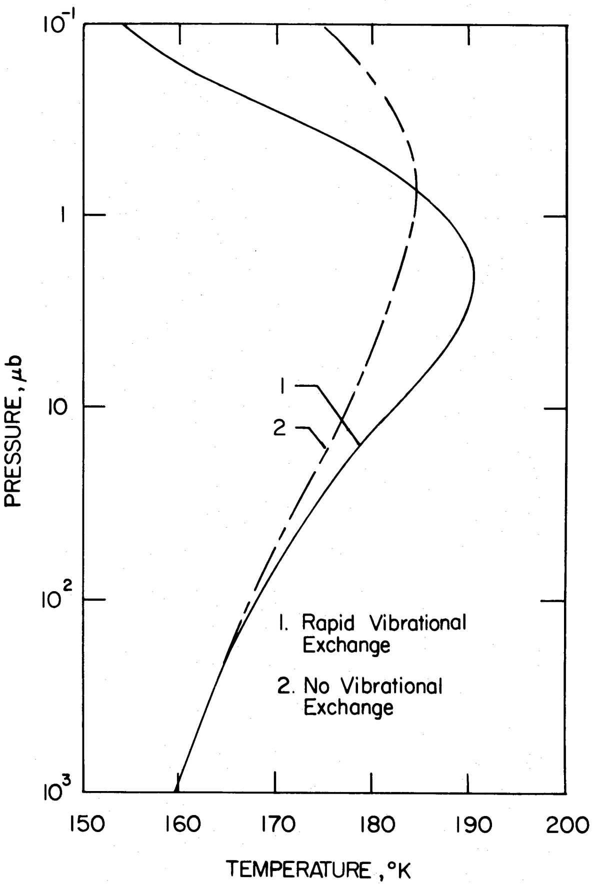

FIG. 4.—Comparison of limiting assumptions for vibrational exchange between isotopes. Results are for global mean radiative equilibrium within the atmosphere of Venus.

and denoting the rate constant for the above reaction by α_m, they give

$$\alpha_m = 3.0 \times 10^9 \text{ s}^{-1} \text{ atm}^{-1} \quad \text{for} \quad X = {}^{12}C^{16}O^{18}O\,,$$
$$\alpha_m = 1.2 \times 10^9 \text{ s}^{-1} \text{ atm}^{-1} \quad \text{for} \quad X = {}^{13}C^{16}O_2\,.$$

It is easily shown that if $\alpha_m f_m/\alpha \gg 1$, where α is the relaxation rate of the $\nu_3 = 1$ level ($\alpha \simeq 10^5$ s^{-1} atm^{-1}), then the ν_3 levels will be exchanged between isotopes before they can relax into ν_2 levels. Since $f_m = 1.1 \times 10^{-2}$ and 4.1×10^{-3} for $^{13}C^{16}O_2$ and $^{12}C^{16}O^{18}O$, respectively, the foregoing condition is clearly met for these isotopes. We need not consider $^{12}C^{16}O^{17}O$ and $^{13}C^{16}O^{18}O$, since they do not contribute significantly at altitudes for which vibrational exchange between isotopes may be important ($\simeq$0.1 μb). Rate constants for the exchange of ν_2 levels between isotopes are not available, but they can reasonably be expected to be of the same order of magnitude, since the ν_2 levels are also in near resonance.

It has previously been assumed that there is no vibrational exchange between isotopes, while from the foregoing discussion it would appear more appropriate to consider the opposite extreme of rapid exchange of vibrational energy between isotopes. The global mean radiative-equilibrium profiles for Venus, as evaluated employing both of these limiting assumptions, are compared in figure 4. For rapid exchange between isotopes, the temperature at the 0.1-μb level is reduced by 21° K, while the mesopeak is shifted to the 2-μb level with an increase in temperature of 6° K. Dickinson (1972) has also considered the rapid-exchange limit. He quotes a comparable reduction in temperature at the 0.1-μb level, although he prefers the no-exchange limit. In view of previous discussion, however, we believe that the rapid-exchange limit is more representative of reality.

For rapid exchange of vibrational energy between isotopes, the source function is the same for all isotopes, and the iterative procedure described in § II*d* is greatly simplified. Cooling by isotopes other than $^{12}C^{16}O_2$ is enhanced, but for pressures greater than 1 μb this increased cooling is more than compensated by an increase in near infrared heating. For pressures less than 1 μb, the 4.3-μ contribution to near-infrared heating is in non-LTE, resulting in a net decrease in temperature relative to the no-exchange limit. For Mars the difference between the two limiting assumptions will be much less than for Venus, due to the smaller insolation.

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APPENDIX

AVERAGING PROCEDURES FOR SOLAR ABSORPTION

The solar absorption term in the radiative heating equation is given by equation (3), and we wish to express both global and longitudinal (diurnal) averages of this quantity. For pressure broadening, combination of equations (3) and (7) yields

$$\Theta_{ik}(\mu) = \alpha e_{\omega i}(T_s)\left(\frac{2A_{01}}{3S_{11}}\right)\left(\frac{2\gamma_0 A_{0i} S_{ik} f_m}{Hd}\right)^{1/2}\mu^{1/2}, \quad (15)$$

while equation (8) for Doppler broadening gives

$$\Theta_{ik}(\mu) = \alpha e_{\omega i}(T_s)\left(\frac{2S_{ik}f_m A_{01}}{3S_{11}}\right)\left(1 - \frac{0.24\mu_{ik}}{\delta\mu}\right), \quad u_{ik}/\delta\mu \leq 9/4; \quad (16a)$$

$$\Theta_{ik}(\mu) = 1.13\alpha e_{\omega i}(T_s)\left(\frac{\delta A_{0i}\mu}{u_1}\right)\left[\ln\left(\frac{2u_{ik}}{3\delta\mu}\right)\right]^{1/2}, \quad u_{ik}/\delta\mu \geq 9/4. \quad (16b)$$

Consider first the global average, given by

$$\langle\Theta_{ik}\rangle = \frac{1}{2}\int_0^1 \Theta_{ik}(\mu)d\mu,$$

and for pressure broadening

$$\langle\Theta_{ik}\rangle = \tfrac{1}{3}\Theta_{ik}(1). \quad (17)$$

The procedure is not as straightforward for Doppler broadening, but a suitable approximation is simply

$$\langle\Theta_{ik}\rangle = \tfrac{1}{2}\Theta_{ik}(\bar{\mu}) \quad (18)$$

with $\bar{\mu} = \frac{1}{2}$.

For diurnal averaging we consider only the equinox, for which $\mu = \cos\theta\cos\phi$, with θ denoting latitude while ϕ is longitude measured from the subsolar point. Equations (15) and (16) thus describe $\Theta_{ik}(\theta, \phi)$ for the dayside, while $\Theta_{ik} = 0$ on the nightside. The diurnal average is expressed by

$$\bar{\Theta}_{ik}(\theta) = \frac{1}{2\pi}\int_0^{2\pi} \Theta_{ik}(\theta, \phi)d\phi,$$

and for pressure broadening

$$\bar{\Theta}_{ik} = 0.382\,\Theta_{ik}(\theta, 0), \quad (19)$$

while an appropriate approximation for Doppler broadening is

$$\bar{\Theta}_{ik} = \tfrac{1}{2}\Theta_{ik}(\theta, \bar{\phi}) \quad (20)$$

with $\cos\bar{\phi} = 2/\pi$.

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