Infrared Radiative Emission in the Venustian Mesosphere

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ABSTRACT

A model is developed for the NLTE infrared radiative transfer in a CO₂ atmosphere at low pressure. This model is used to determine the source function for CO₂ 15 μm vibrational levels and the radiative equilibrium temperature for the atmosphere of Venus above cloud level. The most significant improvement in the radiative transfer model over previous efforts is the inclusion of vibrational-vibrational (V-V) exchange between 15 μm levels. The exchange is especially important for determining isotopic and hot band source functions. This rate is introduced parametrically by assuming it is the same for all transitions, and 10, 100 or 1000 times as rapid as the relaxation rate for the 15 μm fundamental level. We analyze in detail the rates of photon escape to space in the various CO₂ bands. Over much of the Venustian mesosphere, significantly more photons escape to space in the hot and isotopic bands than in the CO₂ fundamental band. However, the latter is essentially in LTE to significantly lower pressure than the other bands and is insensitive to the V-V transition rates. Hence remote sensing of temperature from the infrared radiances would require smallest corrections for NLTE and be least sensitive to V-V rates if only radiances from the latter band were measured. With this band, the assumption of LTE is valid up to the 1 μb level. Sufficient thermal excitation exists up to 0.01 μb for a NLTE temperature inversion to be practical. Detection of hot bands or isotopic band emission from around 0.1 μb in conjunction with a known temperature would allow deduction of the band source functions and hence inference as to the V-V rates.

1. Introduction

In the last decade we have seen the development of procedures for determining vertical temperature profiles in a planetary atmosphere from satellite observations of its infrared emission. Instrumental techniques are now available that permit observation of 15 μm CO₂ emissions from regions of such low pressure that they are determined not simply by thermal excitation, but rather by detailed balancing of the various collisional and radiative processes responsible for excitation or de-excitation of each CO₂ energy level of importance. The application of these techniques to Venus have recently been discussed by Houghton and Taylor (1975). The emissions that would be detected in attempting remote sensing of the temperature of a planetary atmosphere are intimately linked to the processes determining the global mean radiative equilibrium temperature. Consequently, a complete radiative equilibrium model can provide much valuable insight as to the limitations on remote temperature sensing imposed by the nonlocal thermodynamic equilibrium processes (NLTE).

We previously developed a global mean radiative equilibrium model for the upper atmosphere of Venus (Dickinson, 1972; hereafter referred to as Paper I). This model treated in much greater detail than earlier attempts, the energetics of CO₂ vibrational levels responsible for infrared emissions. However, the model contained some arbitrary assumptions which might introduce significant error in the predictions of infrared emissions from a given temperature profile.

A given vibrational level of a CO₂ molecule may be collisionally excited or deexcited not only by exchange with the kinetic energy of the colliding molecule but also by exchange of a vibrational quantum with the other molecule. These two possibilities are referred to as vibrational-translational (V-T) or vibrational-vibrational (V-V) exchange, respectively. The basic collisional excitation of the fundamental 15 μm (ν₂ = 1) level is necessarily a V-T transition. This rate is now well known from laboratory studies. However, if CO₂ is a major constituent, the higher levels (ν₂ = 2, ν₂ = 3, etc.) are primarily excited by V-V transitions resulting from collision of two excited molecules.

The basic reason for this dominance of V-V over V-T exchange, if V-V exchange is possible, is that V-V transitions per collision are much more probable than V-T transitions. However, there is little laboratory evidence as to numerical values of the V-V rates for various important 15 μm transitions. Consequently, we previously assumed that the V-V transitions connecting higher 15 μm levels to ν₂ = 1 occurred instantaneously. It was recognized that V-V transitions between different isotopes of CO₂ might also be significant but these were neglected.
The previous assumptions as to V-V rates were made not only because of the absence of laboratory values but also because they appeared necessary for the formulation to be adequately tractable to numerical calculation. However, we have now developed a new formulation for the energetics of CO₂ molecules with finite and non-zero V-V rates that is not significantly more complicated than the previous formulation.

We have also been encouraged by what appears to be the first unambiguous measurement of a V-V transition between 15 μm levels. The CO₂ vibrational energy states are shown schematically in Fig. 1. Bulthuis (1973) has excited the ν₁=1 level (which has essentially the same energy as and is believed closely coupled to the ν₂=2 level) with a CO₂ laser and measured its relaxation rate to the ν₂=1 level. The actual measurement was of the sum of this relaxation rate and the V-T relaxation rate of ν₂=1. He speeded up the latter transition by addition of increasing amounts of water vapor until it became faster than the V-V rate. (Traces of H₂O greatly accelerate V-T transitions of CO₂.) The rate of coupling of ν₁=1 to the other ν₂=2 levels was, consequently, not indicated by the experiment. He found the V-V transition to be 150 times faster than the V-T relaxation rate of ν₂=1 given by collision with other CO₂ molecules. This measured V-V rate is an order of magnitude slower than the previous value inferred by Rhodes et al. (1968).

To properly include V-V transitions, we would not only have to know individual rates for transitions between each of the levels in the 15 μm system shown in Fig. 1, but also the rates at which ν₂=1 quanta of CO₂O₁⁸ are exchanged with all the other CO₂ isotopes whose ν₂=1 emission is important, that is, CO₂O₁⁶, CO₂O¹⁸O¹⁸ and CO₂O¹⁷O¹⁷. These rates are not known, but we believe that general information as to the sensitivity of emissions to such rates can be gained by a simple parameter study. In the present paper, we assume all V-V rates are the same except that the various individual states of essentially equal energy of the higher excited levels are in thermal equilibrium. It is assumed, for example, that there is only one ν₂=2 level whose population defines the strength of all hot bands with the (0₂⁰0) or (0₂⁻⁰) or (100) states as lower levels. Emission from all of these sublevels consequently depletes the ν₂=2 “level.” For further simplicity we have specified the single assumed V-V rate to be a constant multiple of the ν₂=1, V-T relaxation rate. In particular, we use factors of 10, 100 and 1000.

In the next section, we shall formulate the NLTE model with the single assumed V-V rate. A particular objective is to express the NLTE source functions in terms of contributions from various distinguishable processes, i.e., (i) thermal excitation, (ii) radiative exchange between layers, (iii) V-V exchange with other isotopes, and (iv) V-V exchange with hot bands. In the subsequent section, these contributions are evaluated for the different assumed V-V rates and global mean radiative equilibrium temperature profiles are derived using these V-V rates. Finally, we discuss the implications of these results for future attempts at remote sensing of the temperatures in the Venusian (or Martian) mesosphere.

2. Formation of the energetics of CO₂ molecules

a. Population of the ν₂=1 levels

We consider transitions between ground state molecules of a particular isotope and the corresponding first excited level. The concentrations of these two states are denoted n₀ and n₁, respectively. The balance equation for the excited level can be written as

\[(A₁₀+C₁₀+D₁₀)n₁ = (B₀₁I+C₀₁+D₀₁+S⁺-H⁺)n₁ (1)\]

where the left-hand side of (1) describes processes whereby n₁'s are lost and the right-hand side describes processes by which n₁'s are gained. These exchanges are with the ground state, higher levels, or other isotopes. The terms in (1) have the following meaning:

\[A₁₀\]  Einstein A coefficient for spontaneous emission
\[C₁₀\]  rate of V-T collisional deexcitation to the ground state
\[D₁₀\]  rate of V-V loss to other isotopes
\[B₀₁I\]  rate of V-T collisional excitation from the ground state
\[C₀₁\]  rate of V-V excitation by other isotopes
\[S⁺\]  net rate of V-V excitation from hot bands due to absorbed solar photons
$H^B$ net rate of V-V deexcitation to hot bands to supply hot band emission that would occur in the absence of solar photons.

The first three of the above terms are transition rates per first excited level molecule, the last five are transition rates per ground state molecule.

These terms are evaluated as follows. First, $A_{10}$ is a constant proportional to the strength of the vibrational-rotational band. The rate $A = 1.504 \text{ s}^{-1}$ is adequately known for $\text{C}^{18}\text{O}_2^{16}$ and taken to have the same value for all other isotopes. (Isotopic abundances of CO$_2$ are inferred from the standard terrestrial fractional concentrations of C$^{18}$, O$^{18}$ and O$^{17}$.) The collisional relaxation rates are given by

$$
C_{10} = n_0 \lambda_{VT}$$
$$C_{01} = n_0 \lambda_{VT} \cdot 2 \exp\left(-960/T\right),
$$

(2)

where $T$ is temperature and $\lambda_{VT}$ is the V-T relaxation rate per molecule for $v_2 = 1$, evaluated as in Paper I. The rate $C_{10}$, for example, is 0.3 s$^{-1}$ at the 10 $\mu$m level. This rate is adequately known for $\text{C}^{18}\text{O}_2^{16}$ at room temperature and above through measurements by several different techniques, but at the temperatures below 200 K appropriate to the Venusian mesosphere, it may be uncertain by as much as a factor of 2. The exponential term is a Boltzmann factor for 15 $\mu$m vibrations. Other isotopes of CO$_2$ are assumed to have the same V-T rate.

As derived in Paper I, the radiative excitation term is given by

$$
B_{01} = \frac{1}{2}A \int \frac{n_1(z')}{n_0(z')} dP(z,z'),
$$

(3)

where $dP(z,z')$ is the increment per increment of $z'$ of the band and angular averaged factor $P(z,z')$, which defines the probability of a photon emitted at $z$ reaching $z'$. Note that this term is proportional to the derivative of the term usually referred to as transmission in atmospheric problems. It is calculated with an assumption of nonoverlapping lines with a crude overlap factor applied at lower levels.

The terms for hot band and isotopic exchange are proportional to the V-V transition rates, denoted $\lambda_{VV}$, which, as previously mentioned, are assumed to take the same value for all transitions. As in Paper I, we neglect the small difference in energy of different 15 $\mu$m transitions. The most important V-V exchange of energy between the $i$th and the $j$th isotopes is the reaction

$$
\text{CO}_2^{i}(v_2 = 1) + \text{CO}_2^{j}(v_2 = 0) \leftrightarrow \text{CO}_2^{i}(v_2 = 0)
+ \text{CO}_2^{j}(v_2 = 1).
$$

(4)

Superscripts $i$ and $j$ are used on terms to refer to a particular isotope. These superscripts are omitted when only a single isotope is referred to. The rates $D_{01}$ and $D_{10}$ are determined for a particular $i$th isotope by

$$
D_{10} = \lambda_{VV} \sum_{j \neq i} n_j (v_2 = 0) \cdot (n_i - n_j) \cdot \exp\left(-960/T\right),
$$
$$
D_{01} = \lambda_{VV} \sum_{j \neq i} n_j (v_2 = 0) \cdot (n_i - n_j) \cdot \exp\left(-960/T\right),
$$

(5)

where superscript $t$ refers to total concentration of a given level. Evidently, determination of $D_{01}$ requires knowledge of the relative populations of the first excited level of all the other isotopes.

The most significant V-V hot band state exchanges occurring between molecules of the same isotopic form are

$$
\text{CO}_2^{i}(v_2 = m) + \text{CO}_2^{j}(v_2 = 0) \leftrightarrow \text{CO}_2^{i}(v_2 = m - 1)
+ \text{CO}_2^{j}(v_2 = 1).
$$

(6)

These hot band exchanges are represented in (1) by $S^H$ and $H^B$. The excitation $S^H$ results from energy transfer from all $v_2 = m$ levels significantly populated by near IR solar photon absorption and represents the only path in our calculations for solar near IR energy which is to be eventually realized as kinetic energy of molecules. Collisional V-V deexcitation of the $v_2 = 1$ level represented by $H^B$ in (1) populates hot bands. The only significant deexcitation terms of this kind involve the transitions

$$
\text{CO}_2^{i}(v_2 = 1) + \text{CO}_2^{j}(v_2 = 1) \rightarrow \text{CO}_2^{i}(v_2 = 0)
+ \text{CO}_2^{j}(v_2 = 2),
$$

(7)

$$
\text{CO}_2^{i}(v_2 = 1) + \text{CO}_2^{j}(v_2 = 2) \rightarrow \text{CO}_2^{i}(v_2 = 0)
+ \text{CO}_2^{j}(v_2 = 3).
$$

(8)

For isotopes other than C$^{18}$O$_2^{16}$ only the $v_2$ exchange in (7) gives non-negligible deexcitation.

As in Paper I, it is quite convenient to redefine the radiative exchange terms to measure not the radiative exchange with other levels but rather the net exchange or difference between exchange with other levels and the exchange of the other levels with the given level, i.e., a molecule undergoes a net exchange of quanta with other molecules at a rate $AE(z)$, where

$$
E(z) = \frac{1}{2} \int [x(z') - x(z)] dP(z,z'),
$$

(9)

using $x(z)$ to be the relative excitation of the first level of the $i$th isotope, i.e.,

$$
x(z) = \frac{n_i(z)}{n_0(z)}.
$$

(10)

This formulation assumes no radiative exchange between different bands. An additional term useful to introduce is the net isotopic exchange term per ground state $i$th molecule, which is given by the difference between the two terms in (5) normalized by division.
by \( n_0^e \). This term is denoted \( I^F \), i.e.

\[
I^F = \lambda_{VV} \sum_j \left( \frac{n_j^e}{n_0^e} \right) [\chi^j(z) - \chi^i(z)].
\]

(11)

As in Paper I, we rearrange (1) to obtain

\[
\chi(z) = \frac{(F/\lambda)[S^H - H^0 + I^F + A E(z)]}{1 + 2\lambda \exp(-960/T)},
\]

(12)

where \( F \) is the NLTE reduction factor in the cool-to-space approximation,

\[
F = \frac{1}{1 + \frac{1}{2} (A/\lambda) P(z, \infty)},
\]

(13)

and we use \( \lambda = n_0^e \lambda_{VT} \). The term \( F \) in (13) represents the ratio of radiative emission to LTE emission neglecting all terms except V-T excitation-deexcitation and radiative exchange to space. This term can differ greatly from the factor \( \lambda/(A + \lambda) \) that would be appropriate for optically thin conditions, in that it is essentially unity to much higher levels since \( P(z, \infty) \), the probability of photon escape to space, is much less than unity for strong CO2 bands in the Venusian mesosphere. (See Paper I for further discussion.) The term \( F \) has an additional significance in the determination of the source function and net heating rates. That is, it gives the fraction of quanta entering (or leaving) the \( v_2=1 \) level from V-V transfer that are thermalized. Likewise \((1-F)\) gives the fraction of quanta entering (or leaving) the \( v_2=1 \) level from V-V transfer that are lost to space by enhanced (or reduced) \( v_2=1 \) emission. We may thus interpret terms such as \( S^H, -H^0, I^F \) as giving the “heating” of the \( v_2=1 \) level in photon units and \( FS^H, -FH^0, FI^F \) as giving the actual conversion to molecular kinetic energy.

For comparing various terms, it is convenient to write (12) so that all terms are normalized relative to LTE thermal emission, i.e.,

\[
\chi(z) = 2 \exp(-960/T) [F + \psi^S - \psi^H + \psi^I + \psi^E].
\]

(14)

where if we denote the LTE population factor, \( 2 \exp(-960/T) \), by \( B \), then

\[
\psi^S = F S^H / (\lambda B),
\]

(15a)

\[
\psi^H = F H^0 / (\lambda B),
\]

(15b)

\[
\psi^I = F I^F / (\lambda B),
\]

(15c)

\[
\psi^E = F A E / (\lambda B).
\]

(15d)

represent the ratio to LTE thermal emission of the radiative emission of a 15 \( \mu \)m fundamental level due to net excitation respectively by solar heating, hot band cooling, net V-V exchange with other isotopes, and net radiative exchange with other levels.

\[ b. \) Higher level populations \]

Higher vibrational levels are excited by the absorption of near-infrared photons and by collisional excitation from lower energy levels. Depopulation occurs by collision and radiative emission. Let \( n_m^i \) denote the number concentration of the \( m \) level of the \( i \)th isotope, and \( n_m \) the concentration of the \( m \)th level for all isotopes. Then the appropriate approximate balance equation for the \( m+1 \) level is written

\[
(A_{m+1,m} + \lambda_{VV} n_0)n_{m+1} = (B_{m+1,m} n_m + S_{m+1,m}^H)n_m + \lambda_{VV} \sum_{j=0}^{m-1} n_{m-j} n_{j+1}.
\]

(16)

Here \( A_{m+1,m} \) is the rate of radiative deexcitation from \( m+1 \) to \( m \), \( B_{m+1,m} \) the rate of photon absorption for the \( i \)th isotope per \( m \)th level molecule, and \( S_{m+1,m}^H \), the rate at which \( m+1 \) level quanta of this isotope are generated by absorption of solar energy per \( m \)th level molecule. We have neglected deexcitation by collision with other excited molecules.

Again we define a net exchange term \( E_m(z) \) analogous to (9) by the difference between radiation gained from other levels and that which other levels gain from level \( z \). Then (16) can be rearranged into a form similar to (11):

\[
\frac{n_{m+1}^i}{n_m^i} = \frac{S_{m+1}^H + \frac{\lambda_{VV}}{\lambda} \sum_{j=0}^{m-1} n_{m-j} n_{j+1} + A_{m+1,m} E_m(z)}{n_0 \lambda_{VV} + B_{m+1,m} P(z, \infty)}.
\]

(17)

Here \( P(z, \infty) \) is the probability of escape to space in the \( m \)th level hot band of that isotope. Eq. (17) is an integral equation since the radiative exchange term \( E_m(z) \) involves \( n_{m+1}^i \). However, experience with the ground-state bands indicates that this term may be neglected without serious error. With the approximation \( E_m \approx 0 \), we use (17) to derive NLTE populations of all the \( v_2>1 \) excited levels.

\[ c. \) The solar excitation term \]

The solar excitation terms in (12) and (17) are determined as follows. It is only possible here to describe the barest details of a rather complicated calculation. Absorption of solar energy in the 4.3, 2.7, 2.0, 1.6, 1.4 and 1.2 \( \mu \)m bands is calculated as in Paper I. The energy absorbed is partitioned between excitation of 15 \( \mu \)m \( (v_2) \) and 4.3 \( \mu \)m \( (v_3) \) vibrational levels. The bands at 4.3, 1.4 and 1.2 \( \mu \)m are assumed to absorb only 4.3 \( \mu \)m quanta. The \( v_2=3 \) excitation of the latter two bands is assumed by V-V exchange to instantaneously put three molecules into the \( v_2=1 \) state. The \( v_2=1 \) states either are collisionally relaxed to \( v_2=0 \) or re-radiate as \( v_2 \) bands which have \( v_2=m \) where \( m \) is less than or equal to that of the original excitation. If \( v_2>0 \), these are referred to
as hot bands. The $\nu_2$ photon much more readily escapes to space in these hot bands than does in the 4.3 $\mu$m fundamental. The rate at which new photons are emitted per upper level molecule is given under optically thick conditions by $\frac{1}{2}A_{m-1}P_m(s, \infty)$, i.e., the fraction $[1 - \frac{1}{2}P_m(s, \infty)]$ of photons emitted represent "old" photons originally emitted elsewhere. Thus, for optically thick conditions we refer to $2[\frac{1}{2}A_{m-1}P_m(s, \infty)]$ as the effective radiative lifetime of a state. The ratio of the collisional quenching lifetime ($\tau_{qVV}$) to the effective radiative lifetime determines the ratio of loss to space by 4.3 $\mu$m emission in a particular band ($\nu_2 = m$) to conversion to a lower energy state. (We are ignoring the possibility of emission of photons carrying two or more 15 $\mu$m quanta or a 4.3 $\mu$m quantum and 15 $\mu$m quanta. Such "combination bands" including those absorbing solar radiation have much longer lifetimes than the lifetimes for emission of individual quanta.)

The number of $\nu_2$ or $\nu_3$ vibrons excited by absorption of energy partitioned into those vibrations in a particular band is determined by the energy absorbed divided by the energy carried per photon. This rule is applied to determining the number of $\nu_2 = 3$ photons created by $\nu_3 = 1$ collisional relaxation (so that any direct conversion to molecular kinetic energy is neglected). The $\nu_2 = 1$ ground-state quanta ($\nu_2 = 0$) are allowed not only to radiate at 4.3 $\mu$m or to relax to the $\nu_2 = 3$ level, but also to radiate at 10 $\mu$m down to a $\nu_2 = 2$ lower level (Ramanathan and Cess, 1974). In terms of Fig. 1, the (001) state at the top right converts either to one of the (030), (030), (110) by a V-V transition or to one of the (020) or (100) levels by emitting a 10 $\mu$m photon. These latter weak bands can make some contribution to the loss of $\nu_2 = 1$ ground-state quanta because of the great optical thickness in the ground-state 4.3 $\mu$m band. They are, however, negligible compared to 4.3 $\mu$m emission for states with $\nu_2$ excitation.

The rate of 15 $\mu$m excitation is determined as follows. A particular solar IR combination band absorbs $\nu_2 = m$ quanta, where $m = 2$ for 2.7 $\mu$m, $m = 4$ for 2.0 $\mu$m, and $m = 6$ for 1.6 $\mu$m. Similarly, collisional relaxation of 4.3 $\mu$m levels generates $m = 3$ $\nu_2$ quanta whereas 10 $\mu$m emission from $\nu_2 = 2$ generates $m = 2$ quanta. The vibrational energy in the mth level relaxes to the m-1 level either by emitting a hot-band 15 $\mu$m photon escaping to space, or by a V-V transition with a ground-state molecule resulting in excitation of this molecule to the $\nu_2 = 1$ level. Thus the rate of mth level excitation determines an equal rate of m-1 level excitation with some additional fraction of this excitation going into $\nu_2 = 1$. For $\nu_2 \leq 3$, we use the ratio of the optically thick effective radiative lifetime to the quenching lifetime to define this fraction going into $\nu_2 = 1$ by a V-V transition.

In summary, the rate of excitation of each $\nu_2 > 1$ level is given by the sum of all solar near-IR photons absorbed with sufficient energy partitioned into $\nu_2$ vibrons to excite that or higher $\nu_2$ levels plus the rate of additional transfer of $\nu_2$ quanta from the 4.3 $\mu$m levels into that or a higher $\nu_2$ level. The $\nu_2 = 1$ levels are also excited according to this prescription but with additional excitation by V-V transfer from all the higher levels.

3. New heating rates and radiative equilibrium calculation

We have carried out global mean radiative equilibrium calculations as in Paper I, except that our IR rates have now been modified on the basis of the inclusions of finite V-V exchange as described in the previous section. Our UV solar heating rates have also been modified as a result of arguments for a lower heating efficiency than that which we used in Paper I. A more detailed discussion of the changed radiative heating rates and their effect on global mean temperatures is given in Dickinson (1976). A brief outline of the changes is given here.

The net infrared radiative heating for a fundamental-band is still described by Eq. (33) of Paper I, provided the V-V exchange term "$S_{\nu_1}$" now includes $S^{H}$, $-H^{B}$ and $I^{B}$, i.e., the rate of excitation by near-IR solar absorption, hot-band cooling, and V-V exchange with other isotopes. The excitation of $\nu_2 = 1$ by near-IR photons determines the net near-IR heating whereas the sum of the other excitation terms mentioned above gives the net 15 $\mu$m cooling. Hot-band cooling is calculated as it would be in LTE except that emission is proportional to the NLTE hot-band source functions determined according to (17) and the net cooling is multiplied by the NLTE reduction factor (13). This factor, as described earlier, gives the compensating reduction in the $\nu_2 = 1$ level cooling resulting from the loss of quanta to hot-band cooling. Hot-band cooling is reduced from that derived in Paper I by the assumption of NLTE hot-band emission, but there is also an increase of the 15 $\mu$m cooling due to the exchange between isotopes and there is less near-IR heating because of the emission to space of more of the 15 $\mu$m quanta absorbed in near-IR solar bands. The net effect is a significant reduction in the mesosphere's radiative equilibrium temperature from that derived in Paper I with coldest temperatures found for smallest values of $\lambda_{VV}$. The reason that NLTE hot-band cooling rates (unlike fundamental-band cooling rates) are proportional to the source function is a consequence of the absence of a significant exchange of energy with translation in the former but not the latter case.

The previous prescription for UV heating was adopted from Stewart (1972) who inferred a heating efficiency of 0.3 for EUV ($\lambda < 1080$ $\AA$) assuming that the chemical energy of O$(^{3}D)$ generated by dissociation of CO$_2$ ($\lambda < 1670$ $\AA$) would be collisionally quenched. It now appears that the O$(^{3}D)$ terms should be largely quenched by excitation of CO$_2$ vibrations. At levels where EUV heating is significant, the CO$_2$ vibrational
quantum so excited would mostly escape to space. The quenching of \( O(1D) \) also contributes significantly to Stewart's 0.3 efficiency for \( \lambda < 1080 \text{Å} \). Much of the remainder of the energy assumed thermalized must come from hot atoms or molecules which carry off the chemical energy released in ionic dissociative recombination. In particular, \( O_2^+ + e \rightarrow 20 + 5.1 \text{ eV} \) provides much of Stewart's heating efficiency. Much of this kinetic energy should excite CO\(_2\) vibrations rather than add to the kinetic energy of \( \text{CO}_2 \) (Dickinson, 1975). We infer 0.10 as a likely value for the EUV heating efficiency in a \( \text{CO}_2 \) thermosphere (with a few percent of zero). Thus, the calculations reported here have been extended to the top of the thermosphere using a 10% heating efficiency for \( \lambda < 1080 \text{Å} \) and assuming the \( O(1D) \) energy excited at longer wavelengths is lost. Solar fluxes are the same as used in Paper I. This revised UV heating is only significant over the top few scale heights of the region discussed in this paper. The inferred global mean exospheric temperature is now reduced to the order of 300 K.

We do not include the excitation of IR vibrations by UV absorption in the calculation of IR emission. At the levels of interest here, the total near-IR energy absorbed into \( \text{CO}_2 \) vibrations exceeds the total UV energy absorbed by more than an order of magnitude. The UV excitation should be relatively negligible in determining vibrational excitation and infrared emission below the \( 10^{-3} \mu b \) level, but high in the thermosphere it should make a contribution comparable to that of solar IR absorption.

Other details of the infrared calculations are as in Paper I. In particular, each band is represented by 10 equivalent lines, each of which is assigned an effective strength and number of lines considered to have that strength by averaging over the correct line distribution of a band. Cooling and NLTE sources are determined with Voigt line profiles using an approximation to the Voigt escape to space and transfer between layer functions. A partial description of this formulation was attempted in the Appendix of Paper I, but unfortunately the details given there contain some errors. A correct and more detailed description is to be published elsewhere. In the meanwhile, the author would be happy to communicate these to anyone who may need them. We have again allowed for all weak lines of any significance and have included the five most abundant isotopes of \( \text{CO}_2 \). At the high pressures in the stratosphere, line overlap has been accounted for as described in Paper I. The calculation uses 100 layers of 0.25 width in log pressure and extends from a lower boundary at 120 mb to an upper boundary at the \( 2.8 \times 10^{-5} \mu b \) level. The region to be discussed between 0.1 mb and \( 5 \times 10^{-3} \mu b \) is at least seven scale heights from both of the boundaries so that boundary effects are believed to be entirely negligible. The 0.25 grid width as discussed in Paper I is considered to give (barely) adequate resolution for the IR radiative transfer as calculated here and on length scales greater than one scale height.

### 4. Discussion of the various contributions to radiative emission

Frequently in considering radiative emission from \( \text{CO}_2 \), it has been implicitly assumed that the radiation originates from a single ground-state band, presumably that of \( \text{C}^{18}\text{O}_2 \). Emission from isotopic and hot bands has been regarded as of secondary importance to be included with minor correction factors. Such a viewpoint is definitely erroneous as regards the 15 \( \mu m \) emission from the Venusian mesosphere. One of the conclusions of the present study is that the number of photons escaping to space from an altitude in the Venusian mesosphere is greater for isotopic and hot bands in total than for the \( \text{C}^{18}\text{O}_2 \), \( \nu_2 = 1 \) level over a wide range of altitudes.

Significant NLTE effects on the radiative emission extend to lower altitudes in the weak bands. Consequently, the conclusion that weak-band emission is important implies that NLTE processes would have to be accounted for to lower latitudes than if the fundamental band alone were important in order to derive a temperature profile from measurements of emission.

All our numerical results are referred to a \( \log_e (p_0/p) \) vertical scale, where \( p \) is pressure, with \( z = 0 \) defined by the \( p_0 = 5 \times 10^{-3} \mu b \) level. We consider a range of 10 scale heights \( (z = -10 \text{ to } z = 0) \) to essentially span the Venusian mesosphere. For convenient reference, we give approximate correspondences between pressure and these coordinates in Table I. Present technology would allow remote sensing of the 15 \( \mu m \) radiative emissions throughout this range of pressures. The question we are interested in, then, is what determines such emission and what limitations do NLTE processes impose on the inversion of the emission for temperatures.

We shall now first consider the results of our model with \( \lambda_{VT} = 100 \lambda_{VT} \). Differences resulting from larger or smaller assumed values of \( \lambda_{VT} \) will subsequently be discussed. Fig. 2 shows the calculated source functions, i.e., rates of radiative emission normalized by LTE emission, for the fundamental bands of the five isotopes of possible significance. A similar plot was previously given, i.e., Fig. 7 of Paper I. As before, the most abundant isotopes remain near LTE to lowest pressures, with \( \text{C}^{14}\text{O}^{18} \) significantly not in LTE for \( p < 10 \mu b \).

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but C\textsuperscript{18}O\textsubscript{16} near LTE up to \( p = 0.1 \) \( \mu b \). Nevertheless, the isotopic bands are much closer to LTE over this pressure range than obtained previously because of the now included processes of V-V exchange between isotopes. The ratio of excitation of \( v_2 = 1 \) to LTE excitation as given by (13) remains near unity provided the ratio of the rate of collisional excitation (\( n_n \lambda_{VT} \)) to rate of escape to space [\( \frac{3}{2} AP(z, \infty) \)] remains large. Hence the major reason for the more abundant isotopes remaining in LTE to lower pressures is that \( P(z, \infty) \) is smaller for the more abundant isotopes (e.g., Fig. 4 of Paper I). Fig. 3 shows the contribution to the source functions by thermal excitation as defined by the term \( F \) given by (13). The total source functions of the less-abundant isotopes follow more closely the C\textsuperscript{18}O\textsubscript{16} thermal excitation term than they do their own thermal excitation term, indicating the importance of V-V exchange for maintaining the populations of the isotopic levels in the Venusian mesosphere.

Hot-band source functions for the \( v_2 = 2 \) and \( v_2 = 3 \) bands of C\textsuperscript{18}O\textsubscript{16} normalized relative to LTE are shown in Fig. 4. We show for the first hot-band level (\( v_2 = 2 \)) the source function both with and without absorption of solar IR photons. Clearly, solar absorption makes a major contribution to all hot-band source functions, and for the second hot bands, provides over several scale heights a much larger number of molecules excited to \( v_2 = 3 \) than would be available in LTE. The population of levels \( \nu > 3 \) is overwhelmingly dominated by solar absorption in the Venusian mesosphere and above. Recall that the three \( v_2 = 2 \) and three \( v_2 = 3 \) levels, whose populations relative to LTE values are given in Fig. 4, have been combined into single effective levels by the assumption that the sublevels are closely coupled by collision.

In the next three figures, we shall consider the contribution of various bands to the global-mean emission rate that would be seen from space. We give these contributions as the rate of photon emission per total CO\textsubscript{2} molecule so that emission per unit volume simply follows by multiplication by the total molecular concentration at a given level. These rates for each band have been obtained by multiplying the local rate of photon emission per molecule by the angular average proba-
bility of a photon escaping from that level to space. Practical remote sensing would generally see photons emitted at a particular angle relative to the vertical. The present results correspond closest to a zenith angle of 60°. The escape-to-space probabilities vary by less than a factor of 2 with other “downward” viewing geometries. In a limb-viewing geometry they decrease by an order of magnitude at some levels but the relative differences between bands still change but little.

A further complication in remote sensing not allowed for here is that it is not possible to detect emissions from a single level but rather only over altitude ranges determined by the “weight” functions defined by the atmospheric emission and instrument design. Emissions that would actually be sensed can be inferred from the following figures by multiplying the values by total number densities, and by some instrument filter function, by integrating over the vertical coordinate, and by multiplying by the fraction of the upward hemisphere subtended by the instrument and, if energy units are required, by multiplying by the energy per photon. Such a calculation would necessarily be specific to a given instrument. Our definition of emission rates seems most appropriate for making general inferences regarding difficulties in the interpretation of such observations.

We show in Fig. 5 the rates of emission to space of the C\(^{18}\)O\(_2\) fundamental band in comparison with the sum of the hot-band and the sum of the isotopic-band contributions. For a given band this emission is given by the product of the LTE rate at which photons escape to space and the relative NLTE source functions such as shown in Figs. 2 and 4. At pressures near 0.1 mb,

the isotopic- and hot-band contributions are both only order of 20% of the C\(^{18}\)O\(_2\) emission. However, at \(\rho = 10\) \(\mu\)b, the total rate of emission of the hot and isotopic bands together nearly matches that of C\(^{18}\)O\(_2\), \(\nu_s = 1\). At pressures much less than 10 \(\mu\)b, the hot-band emission dominates over the fundamental-band emission. Indeed for C\(^{18}\)O\(_2\) the emission from \(\nu_s = 2\) and \(\nu_s = 3\) reaching space exceeds the emission to space from \(\nu_s = 1\) by nearly an order of magnitude at pressures between 1 and 0.1 \(\mu\)b and the total emission of isotopic bands reaching space also exceeds that of the C\(^{18}\)O\(_2\), \(\nu_s = 1\) band between the 1 and 0.1 \(\mu\)b levels. Further comparison can be made of the contributions of individual bands. Fig. 6 shows the rates of emission to space of the individual isotopic bands. It is seen that at some level each of the three isotopes C\(^{16}\)O\(_2\)\(^{16}\)O\(_2\), C\(^{16}\)O\(_2\)\(^{16}\)O\(_2\), C\(^{18}\)O\(_2\)\(^{18}\)O\(_2\) contributes more to emission than does C\(^{18}\)O\(_2\). Indeed, between 1 and 0.1 \(\mu\)b, all these isotopes give essentially as large or larger an emission to space as does C\(^{18}\)O\(_2\). Only the contribution of C\(^{16}\)O\(_2\)\(^{16}\)O\(_2\) is relatively small (\(\leq\) 10% of that of C\(^{18}\)O\(_2\)). Yet rarer isotopes would naturally be yet more negligible.

As indicated by Fig. 2, the local emission rates per isotopic molecule for all the isotopes are within a factor of 2 of each other. The dominant factor determining the importance of the isotopic bands is the rapid increase of the probability of escape to space \(P(z, \infty)\) with decreasing molecular concentration. At levels where line centers are optically thick but escape rates are nearly independent of pressure (as seen in Fig. 6 for C\(^{18}\)O\(_2\) for \(z < -5\), for C\(^{18}\)O\(_2\) for \(z < -7\), C\(^{18}\)O\(_2\) for \(z < -8\), and C\(^{18}\)O\(_2\) for \(z < -9\)), the cooling is from Voigt-Lorentz wings, whereas at higher levels where the escape rate increases rapidly with decreasing pressure, cooling is from Doppler wings. At the highest levels (seen only for isotopic bands in Fig. 6) the bands become optically thin at line centers and the escape rate again varies only

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**Fig. 5.** Rate at which photons escape to space for the different band systems per CO\(_2\) molecule: solid line, C\(^{18}\)O\(_2\); \(\nu_s = 1\) fundamental band emission; dotted line, sum of the fundamental band emissions of all the other isotopes (\(\nu_s = 1\) isotopic bands); dashed line, emission of the hot bands (\(\nu_s \geq 2\)). This rate gives the average over angle of the contribution of a given level to the radiance an unfiltered broadband detector in space would see. Same model assumptions as Fig. 2.

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**Fig. 6.** As in Fig. 5 except that the emission to space of the different \(\nu_s = 1\) isotopic bands is given separately, labelled as in Fig. 2.
The contributions of the 1st through 5th hot bands to emission to space is shown in Fig. 7. The above discussion regarding the reasons for the importance of the weak isotopic bands also applies to the hot bands, but the interpretation of the hot-band escape rates at the higher levels ($z > -6$) depends also on consideration of their excitation by solar near-IR photons. The excitation of $ν = 6$ is by absorption of these quanta by the 1.6 μm solar absorption band which is optically thin in the mesosphere. Therefore the excitation rate is constant over the altitudes shown. The $ν = 5$ is only excited by the $ν = 6$ states relaxing through collisions or emission to that level and so has the same rate of excitation as $ν = 6$ since it gains no additional photons by solar absorption. The 15 μm hot bands with upper levels $ν ≥ 4$ are also optically thin in line centers throughout the mesosphere and thermal excitation is negligible. The rate of radiative emission and V-V collisional deexcitation for these bands are comparable near $z = -2$. Hence above this level, the solar excitation of $ν = 5$ or 6 levels results in 15 μm emission proportional to the excitation rate and so also independent of altitude.

Absorption of solar energy at 2.0 μm provides the primary excitation of the $ν = 4$ level. This excitation also dominates the $ν = 3$ level population above $z = -3$. Between $z = -5$ and $z = -3$, relaxation of 4.3 μm is the primary source of $ν = 3$ quanta whereas collisional excitation dominates at lower levels (cf. also Fig. 4). Finally, the excitation of the $ν = 2$ levels is primarily thermal up to $z = -3$ as seen in Fig. 4. This excitation at higher levels is dominated by the absorption of solar radiation in the 2.7 μm bands. These bands only become optically thin above $z = 0$ so that the excitation and hence emission rate of $ν = 2$ is seen to increase upward to the top of Fig. 7.

In summary, only the 1st (upper level of $ν = 2$) and 2nd (upper level of $ν = 3$) hot-band emission is significant relative to that of the fundamental band in the Venusian mesosphere. At pressures $p < 1$ μb where the hot bands contribute significantly more photons to space than does the fundamental band, the emission of these bands depends in part on solar excitation processes. This excitation will vary with solar zenith. The present calculation gives day-night average excitation. Solar excitation will, of course, be zero on the nightside and roughly double that indicated here on the dayside. The rate of hot-band emission near the 0.1 μb level is also quite sensitive to the assumed rate of V-V transitions so that its measurement could perhaps better establish the appropriate value of $λ_{VV}$ to be used for calculations such as these.

We now examine the relative magnitude of the various terms that determine the fundamental band NLTE source functions of the various isotopes. In Fig. 8, we show $ψ_8$, the contribution of global mean solar heating function. These terms defined by Eq. (15a) are
normalized to an LTE source function and so show directly the contributions of solar excitation to the NLTE source functions shown in Fig. 2. All such excitation terms include the factor \( F \) of Eq. (13) [and Fig. 3] whose difference from unity represents, as previously discussed, a reduction of the effect of a given excitation process by leakage of \( \nu_2 = 1 \) photons to space. This factor is unity to higher levels for the more abundant isotopes and so accounts for the increase of \( \psi^S \) with increasing abundance up to \( \text{C}^{18}_4 \text{O}^{16}_4 \). On the other hand, for \( \text{C}^{13}_4 \text{O}^{18}_4 \), \( \psi^S \) peaks at the lowest pressure, its largest value being \( \sim 0.5 \) or less than the \( \psi^S \approx 0.65 \) for \( \text{C}^{18}_4 \text{O}^{16}_4 \). This difference results from the large optical thickness of the \( \text{C}^{18}_4 \text{O}^{16}_4 \) 2.7 \( \mu \)m solar absorption bands at the peak level of \( \psi^S \) in contrast to the isotopic 2.7 \( \mu \)m bands which are essentially optically thin at levels where the factor \( F \) becomes less than unity. The altitude below which \( \psi^S \) does not contribute significantly to the source function also increases with increasing isotopic abundance. This term is important for \( \text{C}^{18}_4 \text{O}^{16}_4 \) only for \( \rho < 1 \mu \)b but for the other isotopes it is important down to \( \rho = 10 \mu \)b. The solar excitation of \( \text{C}^{18}_4 \text{O}^{16}_4 \), \( \nu_2 = 1 \) for various solar zeniths is shown in Fig. 9. It is more than twice the global mean values near the subsolar point, where this solar excitation alone generates greater \( \nu_2 = 1 \) emission than that of LTE. In general, in view of this zenith dependence and of the sensitivity of the hotband emission rates to solar excitation, we would expect a large day-to-night decrease of 15 \( \mu \)m emission at pressures lower than 0.1 \( \mu \)b even without any temperature variation. It would be necessary to correct for this solar-excited emission to be able to derive the variation of temperature from day to night at these levels.

Next we consider \( \psi^T \) defined by Eq. (15c), the contribution of V-V exchange between isotopes to the NLTE source functions again normalized relative to the LTE source. Fig. 10 shows this term. The most abundant isotope \( \text{C}^{18}_4 \text{O}^{16}_4 \) transfers quanta to all the other isotopes because its source function remains closer to unity than any of the others as seen in Fig. 2. This transfer leads to peak excitation of the other isotopes at a level increasing in pressure with decreasing abundance, again because the drop-off of the \( F \) of Fig. 3 and Eq. (13) is at higher pressure for smaller abundance. Largest de-excitation of \( \text{C}^{18}_4 \text{O}^{16}_4 \) occurs near the 0.1 \( \mu \)b level where transfer rates are large and the \( F \) factor has just begun to decrease from unity. The effect of isotopic exchange of quanta on \( \text{C}^{18}_4 \text{O}^{16}_4 \) is generally considerably less than it is on the other isotopes. Because of the low mixing ratios of the other isotopes \( \text{C}^{18}_4 \text{O}^{16}_4 \) collides much less frequently with molecules capable of this exchange than do the other isotopes. At the \( z = -2.5 \) level where
Finally, we show in Fig. 12 the contribution of hotband excitation to the \( v_2 = 1 \) source functions. Only the three most abundant isotopes are included. This term is small compared to the contribution of other terms for isotopes other than \( ^{18}\text{C}^{30}\text{O}_2 \) for which deexcitation, \( \sim \frac{1}{5} \) of the LTE source function, occurs near \( \rho \approx 0.1 \mu b \).

In conclusion, the various relative contributions to the source functions are important for \( ^{18}\text{C}^{30}\text{O}_2 \) at lower pressures than any of the other isotopes as illustrated by Fig. 13 which compares on the same graph the various terms contributing to the \( ^{18}\text{C}^{30}\text{O}_2 \) and \( ^{16}\text{C}^{30}\text{O}_2 \) source functions. For \( ^{16}\text{C}^{30}\text{O}_2 \) the largest contributions are by solar excitation, \( \sim \frac{1}{5} \) (global mean); isotopic exchange, \( \sim \frac{1}{5} \); and net radiative exchange and hotband excitation, both \( \sim \frac{1}{5} \). Further implications of these terms for attempts to measure temperature from IR emissions will be discussed in the conclusions.

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Our model has been integrated for V-V relaxation rates assumed to be an order of magnitude either slower and/or faster than our standard case. The resulting differences are best illustrated by considering the source functions so derived. Fig. 14 compares $\nu_2 = 1$ source functions for the four most abundant isotopes and for $\lambda_{VV} = 10, 100, 1000 \lambda_{VT}$. Evidently, the $^{12}$O$_2$ hot source function changes but insignificantly, whereas the source functions of the other less abundant isotopes change by a factor of 2 at pressures less than 0.1 $\mu$b in ranging between the assumed extreme values for $\lambda_{VV}$. The $^{12}$O$_2$ hot-band source functions also differ signifi-

![Graphs showing source functions for various isotopes and values of $\lambda_{VV}$.](image)

**Fig. 13.** Contribution of the various terms to the source function of Fig. 2 for a) $^{12}$O$_2^{16}$ and b) $^{12}$O$_2^{16}$. Solid line, global mean near-IR photon absorption; dashed line, net V-V exchange with other isotopes; dot-dashed line, net radiative exchange between layers; dotted line, V-V exchange with hot bands.

**Fig. 14.** Source functions for the various isotopes and three values of $\lambda_{VV}$: solid line, $\lambda_{VV} = 100 \lambda_{VT}$; dotted line, $\lambda_{VV} = 10 \lambda_{VT}$; dashed line, $\lambda_{VV} = 1000 \lambda_{VT}$. 
stantly at low pressures over the assumed values of \( \lambda_{VV} \) as shown in Fig. 15. In particular, significant NLTE effects occur at a scale height or two lower with the assumed slow V-V rates than with the assumed fast V-V rates.

The global-mean temperature profiles calculated for the three cases are given in Table 2. [Refer to Table 1 of Dickinson (1972) for corresponding pressure level and approximate altitude.] A temperature difference of several degrees or more occurs at some levels between the various profiles. Decreasing the V-V rates decreases 15 \( \mu \)m cooling due to hot bands or to isotopes but it also decreases the amount of solar radiation that is thermalized. The latter effect apparently dominates at lower levels and the former effect at higher levels. The temperatures reported previously in Paper I increased from \( \sim 160 \) K near the stratosphere (\( \sim 1 \) mb pressure) to temperatures in excess of 180 K in the middle of the mesopause. Now the global mean mesospheric temperatures are nearly isothermal (\( \sim 160 \) K), primarily as a result of a factor of 2 reduction in peak solar IR heating rates with the present finite V-V relaxation rates.

The dependence on V-V transfer of the rates at which photons from various bands escape to space is evident from previous figures. In particular, since (see Fig. 14) the \( ^{16} \text{C}^{36} \text{O}_2 \), \( \nu_2 = 1 \) source function is rather insensitive to the assumed V-V rates, the emission to space of this band will vary largely with the Boltzmann emission factor \( \exp(-960/T) \). This factor varies by at most 10% for the variations in temperature of Table 2. On the other hand, the emission of the isotopic bands is dominated by source function variations which as we indicated may vary by a factor of 2 from the assumption of slow to that of fast V-V rates. The hot-band emission at levels where NLTE effects are large increases slightly with decreasing V-V rates. In other words, the decrease of thermal emission is more than compensated for by the resulting increase of absorbed solar energy that is reradiated rather than absorbed. At levels sufficiently high that \( n_0 \lambda_{VV} < A \), the hot-band emission rates approach constant values depending only on the absorption of solar radiation.

5. Conclusions

Solutions have been obtained for the NLTE infrared radiative transfer in the upper atmosphere of Venus and for the corresponding radiative equilibrium temperature profile. Significant but largely unknown parameters in the calculation are the rates at which quanta are transferred between the different 15 \( \mu \)m vibrational energy levels of \( \text{CO}_2 \) including such transfers between different isotopes. These rates were introduced parametrically by assuming them to be 10, 100 and 1000 times as large as the vibrational-translational relaxation rate of the fundamental 15 \( \mu \)m level.

The NLTE source functions for the various 15 \( \mu \)m \( \text{CO}_2 \) bands have been derived. The V-V transfer from \( ^{16} \text{C}^{36} \text{O}_2 \) maintains the source functions of the less abundant isotopes much closer to LTE than would otherwise be the case. Furthermore, the uncertainties as to appropriate V-V rates introduce significant uncertainties in the isotopic source functions. By contrast, the \( ^{18} \text{C}^{36} \text{O}_2 \) source function is rather insensitive to the magnitude of the V-V rates.

We examined the relative contributions to the NLTE fundamental-band source functions by solar excitation, isotopic exchange, hot-band exchange, and net radiative exchange between layers. All these processes contribute a significant fraction of LTE excitation to the source functions at some levels. Largest contributions by non-thermal excitation occurs at lower pressure with increasing isotopic abundance. Hot-band source functions were also derived. Solar absorption greatly modifies the NLTE hot-band source functions. In particular, the \( \nu_2 \geq 3 \) levels over some region have populations significantly greater than LTE values. The details of the hot-band source functions also depend significantly on the assumed V-V rates.
The emission to space of the various bands is compared. Over much of the Venusian mesosphere the net emission to space from hot bands and isotopic bands considerably exceeds that due to the fundamental band of \( \text{C}_2^1\text{O}_2^{16} \). Furthermore, the isotopic-band contribution varies with the isotopic source functions, hence significantly with variation of V-V rates. The hot-band emission also depends on V-V rates but variation with these rates is dominated by changes in the amount of absorbed solar radiation reradiated to space.

From this study, we draw the following inferences as regards the possibilities of remote sensing of temperature in the Venusian thermosphere. First, a technique would be preferred that filters out the hot band and isotopic radiances and looks only at \( \text{C}_2^1\text{O}_2^{16}, \nu_2 = 1 \) emission. Such an approach would minimize the effects of unknown physics on NLTE radiances and restrict the levels of significant NLTE effects to as low a pressure as possible. This filtering out the hot- and isotopic-band contributions would require some kind of \( \text{CO}_2 \) cell in front of the sensing instrument, and would have to be done with care in view of the large energy in the bands to be filtered.

Assuming the \( \text{C}_2^1\text{O}_2^{16} \) fundamental-band radiances can be separately measured, we infer from this study the following limitations as to pressure levels at which a temperature might be derived. First, in comparing Figs. 3 and 13a, we see that for \( p < 0.01 \mu \text{b} \) (\( z > -0.7 \)) the thermal excitation is less by a factor of 2 than the other contributions to the source functions. Since the accuracy by which the latter can be estimated is limited, this smallness of thermal excitation probably effectively precludes obtaining temperatures at such low pressures. Second, by comparing the same figures, we see that for \( p > 1.0 \mu \text{b} \) (\( z < -5.3 \)), the emission is effectively LTE so that nonthermal excitation can be neglected. Finally, it may be possible to derive temperatures for pressures between 1 and 0.01 \( \mu \text{b} \) but only if corrections are applied to account for the nonthermal excitation processes discussed in this paper. The most significant such term appears to be the excitation by solar absorption. This term will necessarily be dependent on solar zenith and for overhead sun will be more than double the values derived here.

Measurement of the emission of particular hot bands or isotopic bands at pressures near 0.1 \( \mu \text{b} \) would provide valuable information as to solar-heating processes and V-V exchange rates provided the temperature could first be obtained as outlined above.

REFERENCES


