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# EQUILIBRIUM TEMPERATURE STRUCTURE IN THE MESOSPHERE AND LOWER THERMOSPHERE

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## Abstract

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Calculations have been made of the radiative equilibrium temperature structure of the Earth's mesosphere and lower thermosphere, taking into account solar ultraviolet heating, and cooling by $CO_2$ and $O_3$.

For the evaluation of the absorption of solar energy, an equilibrium distribution of $O_3$ consistent with the temperature structure was calculated from the basic photochemical equations.

A "statistical" band model which takes into account both Lorentz and Doppler broadening of the spectral lines was employed in the determination of the atmospheric transmissions for both $15\mu$ $CO_2$ and $9.6\mu$ $O_3$ bands.

The departure from conditions of local thermodynamic equilibrium in the $15\mu$ $CO_2$ band due to vibrational relaxation was taken into account and the source function in this band was calculated over a range of relaxation times from $10^{-6}$ sec to $1.5 \times 10^{-5}$ sec.

The radiative equilibrium temperature calculations result in a pronounced temperature minimum in the vicinity of 80 km, corresponding to the Earth's mesopause.


Author

## 1. Introduction

The temperature structure of the Earth's atmosphere below about 55 km is well understood. The theoretical calculations of radiative equilibrium temperatures by Gowan (1947) have substantially explained the temperature features of this region. These investigations have shown that the observed temperature maximum or "mesopeak" in the vicinity of the 50 km level can be attributed to the absorption of solar ultraviolet energy by ozone.

Above the 55 km level, rocket observations indicate a decrease of temperature with height to a minimum of about 180°K near 85 km with an increase again at higher altitudes. Although the formation of this temperature minimum or "mesopause" should be explained in terms of the various physical and dynamic processes which occur at these levels, there has been no attempt to calculate theoretically the temperature structure of the higher atmosphere taking these processes into account.

Curtis and Goody (1956) have developed, in an elegant manner, the general equation of radiative transfer for a vibrationally relaxing gas and have used this formalism to calculate, for a known atmospheric structure, the cooling rates up to the level at which the mixing ratio of carbon dioxide is no longer constant. Young (1964) has adopted the basic transfer formalism of Curtis and Goody in his study of the influence of $CO_2$ on infrared transfer in the stratosphere and mesosphere.

In the present study, a comprehensive treatment of the

physical aspects of the problem of the mesopause formation is made by considering the radiative transfer under low pressures. In the highly attenuated regions of the atmosphere, "Lorentz" broadening of the spectral lines will not be significant compared with the "Doppler" broadening. Furthermore, in low pressure regions, molecular collisions become so infrequent that a Boltzmann distribution among the energy levels of the vibration-rotation transitions cannot exist. As a result, the atmosphere does not radiate as it would under conditions of local thermodynamic equilibrium (LTE), and its emission properties differ radically from the "Planck" type of emission. Therefore, both Lorentz and Doppler broadening, as well as departures from the conditions of LTE, must be taken into account in the treatment of the radiative transfer problem.

## 2. Radiative transfer in a vibrationally relaxing gas

The temperature of a gas is usually defined as the kinetic temperature or that associated with translational motions of the molecules. The velocity distribution of these kinetic motions is continuous and has a Maxwellian nature up to very great heights in the atmosphere (Spitzer, 1952). Thus the translational energies are unquantized.

Excitation to a vibrational or rotational state can occur as a result of either a molecular collision or absorption of a quantum of energy. Also, de-excitation may result from collisions or emission of a photon. When pressure is high and collisions are frequent, there is a rapid exchange of energy between the translation and vibration-rotation modes. Under these conditions, the energy levels of the vibrational and rotational states are populated in a Boltzmann distribution due to collisions. The gas then radiates according to Kirchhoff's

law and is said to be in local thermodynamic equilibrium. As pressure decreases, the collisions become less frequent and the transfer of energy between translations and vibration-rotations become less rapid. The population of the various energy levels is then determined by the radiative transitions rather than by collisional processes and so a Boltzmann dis tribution is not necessarily obtained. The gas no longer obeys Kirchhoff's law and a state of non-local thermodynamic equilibrium (non-LTE) exists.

Any excited state of a molecule has a natural lifetime for spontaneous de-excitation by a radiative transition. If a de-exciting collision does not occur during this lifetime, the energy involved in the de-excitation will be lost to the radiation field. At higher levels in the atmosphere the mean time between de-exciting collisions becomes longer than the spontaneous lifetime of the molecule. When this occurs, the gas is said to undergo "relaxation." Under these conditions, when a photon within the frequency range, $\Delta\nu$, of an absorption band is absorbed by a molecule, it will, on the average, be re-emitted without passing into the kinetic energy of the translation. The atmosphere is then said to be scattering. The scattered photon will not necessarily have the same frequency and direction as the incident photon, although its frequency must remain within the range $\Delta\nu$, since energy balance need not apply at each individual frequency, but only over the band as a whole.

The $15\mu$ $CO_2$ band is the most important band for the transfer of the infrared energy in the Earth's atmosphere. $CO_2$ is uniformly mixed up to altitudes of $\sim 100$ km, above which it is

significantly dissociated by solar ultraviolet radiation. "Vibrational" relaxation occurs in this band at altitudes where $CO_2$ remains undissociated. "Rotational" relaxation of $CO_2$ is of no importance since at the altitudes where such relaxation could occur, the gas is largely dissociated.

The 15μ band is actually composed of a fundamental ($\nu_2$ or "bending" mode of vibration) and several overtone and combination bands; in all, fourteen in number. The $\nu_2$ fundamental is by far the most intense band present, accounting for about 90 percent of the overall 15μ band intensity (Yamamoto and Sasamori, 1958; and Madden, 1961). Ultrasonic experiments which measure the relaxation time result in estimates of the order of $10^{-5}$ to $10^{-6}$ sec for the $\nu_2$ fundamental. The behavior of the various overtone and combination bands in the 15μ region, however, cannot be inferred from a knowledge of the characteristics of the fundamental alone.

In view of the fact that the band intensities of the other bands are much smaller, their radiative lifetimes must be proportionately larger than the lifetime of the fundamental. If it is assumed that their vibrational relaxation times are of an order comparable to that of the fundamental, then the other bands in the 15μ region will relax at much higher levels. One can then assume that these subsidiary bands follow Kirchhoff's law fairly well in the region of the atmosphere under consideration.

However, the contribution of the sub-bands to the radiated energy is proportional to their intensity and would be

quite small as compared with the contribution of the fundamental. Therefore, it is assumed in the present study that the subsidiary bands relax in the same manner as the fundamental.

Curtis and Goody (1956) have investigated the problem of radiative transfer in a vibrationally relaxing gas in detail and have obtained the emission of the gas, or "source function", under very low pressures. Their basic radiative transfer equation relates the net flux divergence to the difference between absorbed and emitted energies at any level:

$$\iint \frac{dI(\nu, \theta, z)}{ds} d\nu\, d\omega = - \int\int I(\nu, \theta, z)\, n(z) k(\nu, z)\, d\nu\, d\omega + \int\int J(\nu, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega \qquad (1)$$

where the symbols have the following meaning:

| | |
|---|---|
| $\nu$ | frequency of radiation |
| $\omega$ | solid angle |
| $\theta$ | zenith angle |
| s | geometric path length ($ds = \sec\theta\, dz$) |
| z | altitude |
| $n(z)$ | number density of absorbing molecules |
| $k(\nu, z)$ | absorption coefficient |
| $B(\nu, z)$ | Planck intensity |
| $J(\nu, z)$ | source function $[J(\nu, z) = B(\nu, z)\, E/\bar{E}]$ |
| E | total vibrational energy expressed in number of quanta per unit volume. ($E = \bar{E}$ under Boltzmann conditions) |
| $I(\nu, \theta, z)$ | intensity of radiation |

From the earlier discussion, $J(\nu, z)$ is given by the Planck intensity $B(\nu, z)$ in the dense regions of the atmosphere where collisions are numerous, while at higher levels, $J(\nu, z)$ must be calculated from

considerations of the molecular collisions and radiative transitions.

Equation (1) determines the rate at which energy is exchanged between the vibrational levels and the radiation field. If the vibrational levels are not populated according to Boltzmann's law, the rate of transfer between vibrational and transitional energy by collisions is given by:

$$\frac{dE}{dt} = \frac{\bar{E}}{\lambda} (1 - E/\bar{E}) \tag{2}$$

where $\lambda$ is the relaxation time for the entire 15 $\mu$ band which varies inversely with pressure. Under steady state conditions, the energy supplied to the vibrational levels by collisions must be equal to the energy lost to the radiation field:

$$\begin{aligned} \iint \frac{dI(\nu, \theta, z)}{ds} d\nu\, d\omega &= - \iint I(\nu, \theta, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega \\ &\quad + \iint J(\nu, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega \\ &= \frac{\bar{E}}{\lambda} (1 - E/\bar{E}) \end{aligned} \tag{3}$$

When one is dealing with the higher levels of the atmosphere, the magnitudes of the various terms involved in equation (3) warrant some consideration. From the radiative transfer we can see that the term $\iint I(\nu, \theta, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega$ depends strongly on the emission characteristic of the temperatures in the optically thick layers of the lower atmosphere, while the term $\iint J(\nu, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega$ depends on the local temperature. Only when the local temperature is much greater than the characteristic temperature of the incident radiation can the term $\iint I(\nu, \theta, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega$ be neglected in comparison with

$\iint J(\nu, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega$ . This is possible only when

$$\frac{1}{2} B_e << B(z) \frac{E}{\bar{E}}$$

or

$$\frac{E}{\bar{E}} >> \frac{B_e}{2B(z)} \tag{4}$$

where $B_e$ is the effective emission of the lower atmosphere, characteristic of a temperature of $\sim 250°K$. The factor 2 in the denominator on the right hand side of inequality (4) arises from the fact that the incident radiation originates almost entirely below the layer under consideration while the emission from the layer itself occurs in all directions.

Under these conditions, the radiative transfer of the atmosphere may be neglected and the flux divergence (cooling) is given by the emission of the gas. From equation (3) the cooling is also given by

$$\iint \frac{dI(\nu, \theta, z)}{ds}\, d\nu\, d\omega = \frac{\bar{E}}{\lambda} (1 - E/\bar{E}) \tag{5}$$

Furthermore, when we have

$$1 >> E/\bar{E} \tag{6}$$

the cooling may be expressed as $\bar{E}/\lambda$ .

In order for one to neglect radiative transfer and represent atmospheric cooling by the simple expression $\bar{E}/\lambda$ , inequalities (4) and (6) require that

$$1 >> \frac{E}{\bar{E}} >> \frac{B_e}{2B(z)}$$

or

$$2B(z) >> B_e \tag{7}$$

Inequality (7) can be fulfilled only when very hot regions of the atmosphere such as the thermosphere are considered. Thus, radiative transfer in the atmosphere in the 15μ band cannot be ignored until very hot levels are reached.

Curtis and Goody (1956) have shown that if $\Delta\nu$, the band width, is narrow, then $J(\nu, z)$ will have the same dependence on frequency as $B(\nu, z)$ and will be isotropic. From their equation (10) it follows that

$$J(\nu, z) = B(\nu, z) \left( 1 - \frac{\lambda}{\phi} \frac{\iint \frac{dI(\nu, \theta, z)}{ds} d\nu\, d\omega}{\iint B(\nu, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega} \right) \tag{8}$$

where $\phi$ is the radiative lifetime. This expression gives the nature of the source function for a vibrationally relaxing gas.

## 3. Radiative equilibrium under non-LTE conditions

When a source of heating outside the frequency range $\Delta\nu$ is present, the infrared flux divergence must be equal to the energy gain from this source in order for radiative equilibrium conditions to exist. In the Earth's atmosphere below 100 km, the principal heat source is the solar ultraviolet energy $Q(z)$ absorbed by oxygen and ozone. Then

$$\iint \frac{dI(\nu, \theta, z)}{ds} d\nu\, d\omega = Q(z) \tag{9}$$

The source function under these conditions is given by

$$J(\nu, z) = B(\nu, z) \left( 1 - \frac{\lambda}{\phi} \frac{Q(z)}{\iint B(\nu, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega} \right) \tag{10}$$

This equation suggests that the gas, when it is relaxing, does not

radiate with a Planck intensity in the band, but only as a fraction of $B(\nu, z)$, the fraction being given by the term in brackets. Thus the source function is directly related to the Planck function.

In order to obtain the radiative equilibrium temperature for a given layer, the absorbed solar energy plus the absorbed infrared energy must be balanced by the emission of the layer

$$Q(z) + \iint I(\nu, \theta, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega = \iint J(\nu, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega \tag{11}$$

Substituting for $J(\nu, z)$ from equation (10) and rearranging terms, we obtain

$$Q(z)\left(1 + \frac{\lambda}{\phi}\right) + \iint I(\nu, \theta, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega = \iint B(\nu, z)\, n(z)\, k(\nu, z)\, d\nu\, d\omega \tag{12}$$

It is clear from this equation that in the absence of solar heating (or any source of energy outside the range $\Delta\nu$) the atmosphere will eventually reach a state of LTE, regardless of the frequency of collisions.

Thus far no consideration has been given to the presence of any radiating gas other than $CO_2$ alone. In the Earth's atmosphere, both $O_3$ and water vapor are present as infrared transfer agents. $H_2O$, of course, is the main constituent responsible for the infrared transfer in the troposphere, but above $\sim 20$ km in the stratosphere and mesosphere, its concentration becomes so low that the role of $H_2O$ as a mechanism of energy transport can be neglected. In the stratosphere at about 30 km both $CO_2$ and $O_3$ are equally significant as transfer agents. Above 30 km the opacity of $O_3$ decreases more rapidly with height, so that in the upper atmosphere, radiative transfer is strongly controlled by $CO_2$.

The exact form which the equation of energy balance (equation (12)) would take if $O_3$ transfer were important is somewhat more complicated. However, it is possible to retain equation (12) and yet include the $O_3$ radiative transfer provided that the $O_3$ itself does not relax at levels where its contribution to the infrared transfer is significant. At lower levels in the atmosphere where the $O_3$ infrared energy transfer is large, the value of the parameter $\lambda/\phi$ is small and equation (12) has the character of LTE conditions. Inclusion of $O_3$ infrared transfer is permissible in this region. Above the level where the value of $\lambda/\phi$ becomes equal to $\sim 0.1$, the concentration of $O_3$ has so diminished that its energy contribution to the infrared transfer is less than about 5 percent of the $CO_2$ contribution and so it can be included in solving equation (12) with good accuracy.

## 4. Transmission by a Lorentz and Doppler broadened line

The width and shape of an absorption line is influenced by collisional or "Lorentz" broadening and by "Doppler" broadening arising from the motion of the molecules. "Natural" broadening, which occurs as a result of radiation damping, is comparatively small and can be neglected for studies of radiative transfer in planetary atmospheres.

The relative importance of Lorentz and Doppler broadening depends on the region of the atmosphere under consideration. In the optically thick layers of the lower atmosphere, where collisions are frequent, line broadening is predominantly Lorentz in

character. At very high levels, on the other hand, the Doppler broadening is important, while at intermediate heights, a combination of both Lorentz and Doppler effects is present. A general expression for the variation of the absorption coefficient over a spectral line which takes both phenomena into account is given by

$$k(\nu) = S \int_{-\infty}^{+\infty} \left(\frac{\nu_o}{\sqrt{\pi}\, c a_D}\right) \exp -\left(\frac{\nu_o U}{c a_D}\right)^2 \frac{a_L}{\pi} \frac{dU}{(\nu - \nu_o + U\nu_o/c)^2 + a_L^2} \tag{13}$$

Here, the symbols have the meaning:

| | |
|---|---|
| $S$ | total line intensity |
| $U$ | molecular velocity |
| $\nu_o$ | central frequency of line |
| $c$ | speed of light |
| $a_L$ | Lorentz half-width of line |
| $a_D$ | Doppler half-width of line . |

For small values of the parameter $a = a_L/a_D$ , Harris (1948) has expressed this integral as a power series in $a$, with coefficients $H_i$ which are tabulated as functions of the parameter $v = (\nu - \nu_o)/a_D$ :

$$k_v = \frac{S}{\sqrt{\pi}\, a_D}[H_o(v) + aH_1(v) + a^2 H_2(v) + \cdots] \tag{14}$$

This formulation was used to evaluate $k_v$ for $a < 0.5$ . Using this expression, the mean fractional absorption for a spectral interval is

$$\bar{A} = \frac{a_D}{d} \int_{-d/2a_D}^{+d/2a_D} [1 - \exp(-k_v u)]dv \tag{15}$$

where d is the mean line spacing and u is the optical path. Equation (15) can be solved numerically by substituting the tabulated functions $H_i$ in equation (14) for $k_v$.

Van der Held (1931) has shown that for values of $\alpha > 1$, the mean fractional absorption for a spectral interval is closely approximated by the Ladenburg-Reiche (1913) formula:

$$\bar{A} = 1 - \exp\left[-\beta x e^{-x}(I_o(x) + I_1(x))\right] \tag{16}$$

where

$$\beta = \frac{2\pi\alpha_L}{d}$$

$$x = \frac{Su}{2\pi\alpha_L}$$

and $I_o$ and $I_1$ are the Bessel functions of order zero and one and of imaginary argument.

The two equations (15) and (16) give the fractional absorption due to one spectral line. When wide enough spectral intervals consisting of a large number of lines are considered, the transmission and absorption of a gas can be represented by any one of several band models. Here we have adopted a "statistical" band model in which the mean line spacing is held constant throughout the band, while the line intensity is allowed to vary from interval to interval within the band. So, if the mean line spacing d for the whole band and mean line intensity S for each one of the spectral intervals within the band are known, the average transmission or absorption for each one of the spectral intervals can be calculated from equations (15) and (16).

## 5. Transmission functions for 15μ $CO_2$ and 9.6μ $O_3$ bands

The 15μ $CO_2$ band was divided into six wave number intervals of 50 $cm^{-1}$ width from 550 $cm^{-1}$ to 850 $cm^{-1}$. The Lorentz half-width $\alpha_L$ of the lines in this band is given as 0.064 $cm^{-1}$ by Kaplan and Eggers (1956) for a temperature of 298°K and a pressure of one atmosphere. Yamamoto and Sasamori (1958) have used a mean line spacing d of 1.55 $cm^{-1}$ in their calculation of the absorption of this band. Thus, a value of the parameter $\beta$ is determined as 0.24. With this knowledge of the magnitude of $\beta$, another parameter, $S/2\pi\alpha_L$, was deduced for the various wave number intervals from the transmission tables of Stull, Wyatt and Plass (1963). This parameter is tabulated in Table IA.

The 9.6μ $O_3$ band was treated as one wave number interval extending from 990 $cm^{-1}$ to 1090 $cm^{-1}$. Plass (1960) had made an analysis of the 9.6μ $O_3$ band area measurements by Walshaw (1957) and so had evaluated the parameters $\beta$ and $S/2\pi\alpha_L$ for this band. It was found that the values obtained by Plass can reproduce the band area as measured by Walshaw quite accurately and so they were adopted in our investigation. The Lorenz half-width of the spectral lines in the 9.6μ $O_3$ band is given by Goody (1964) as 0.076 $cm^{-1}$ at 293°K and 1000 mb. Using this value, the quantities S and d can be obtained (Table IB).

The value of the Doppler half width $\alpha_D$ at a temperature of 225°K was used in these calculations. At this temperature,

TABLE I

Band Parameters

A. 15μ $CO_2$ Band

| $\Delta\nu$ ($cm^{-1}$) | $\alpha_L$ ($cm^{-1}$) | d ($cm^{-1}$) | $S/2\pi\alpha_L$ ($atm^{-1}\ cm^{-1}$) | S ($atm^{-1}\ cm^{-2}$) | $\alpha_D$ ($cm^{-1}$) |
|---|---|---|---|---|---|
| 550-600 | | | $1.0 \times 10^{-2}$ | $4.0 \times 10^{-3}$ | |
| 600-650 | | | $2.5 \times 10^{0}$ | $1.0 \times 10^{0}$ | |
| 650-700 | $6.4 \times 10^{-2}$ | $1.6 \times 10^{0}$ | $4.5 \times 10^{1}$ | $1.8 \times 10^{1}$ | $6.5 \times 10^{-4}$ |
| 700-750 | | | $5.0 \times 10^{-1}$ | $2.0 \times 10^{-1}$ | |
| 750-800 | | | $2.0 \times 10^{-3}$ | $8.0 \times 10^{-4}$ | |
| 800-850 | | | $2.5 \times 10^{-5}$ | $1.0 \times 10^{-5}$ | |

B. 9.6μ $O_3$ Band

| | | | | | |
|---|---|---|---|---|---|
| 990-1090 | $7.6 \times 10^{-2}$ | $6.3 \times 10^{-2}$ | $5.3 \times 10^{-1}$ | $2.5 \times 10^{-1}$ | $9.5 \times 10^{-4}$ |

$\alpha_D$ for the 15μ $CO_2$ band is $6.5 \times 10^{-4}$ $cm^{-1}$ and for the 9.6μ $O_3$ band, $\alpha_D$ is $9.5 \times 10^{-4}$ $cm^{-1}$.

Using these values of the various band parameters the fractional absorption is calculated from equations (15) and (16) for different path lengths and pressures. The absorption thus obtained for the 15μ $CO_2$ and 9.6μ $O_3$ bands is plotted as a function of $2\pi\alpha x$ as shown in Figures 1 and 2. In these figures, lines of constant values of the parameter $\alpha$ are shown. Each of these lines corresponds to a line of constant pressure if the temperature remains unchanged. It is interesting to note that under low pressures (small $\alpha$) the absorption is mainly due to the Doppler broadening and, with the increase of path length, the absorption increases very slowly until the wings of the absorption lines gradually begin to absorb. Then the absorption increases in square root fashion with path length until the level of saturation is reached.

The numerical procedure involved in the calculation of the fractional absorption $\bar{A}$ outlined above is quite lengthy. Also, the evaluation of a radiative equilibrium temperature requires this procedure to be repeated innumerable times. In the interests of economy, an expedient method was developed for the evaluation of $\bar{A}$ for a given atmospheric path. From each of Figures 1 and 2, a table was constructed of the values of $\bar{A}$ as a function of $2\pi\alpha x$ and $\alpha$. These tables were used to obtain the value of $\bar{A}$ for any desired path in the atmosphere by a suitable interpolation scheme.

In the calculation of atmospheric transmissions over long path lengths, the variation of pressure and temperature along the

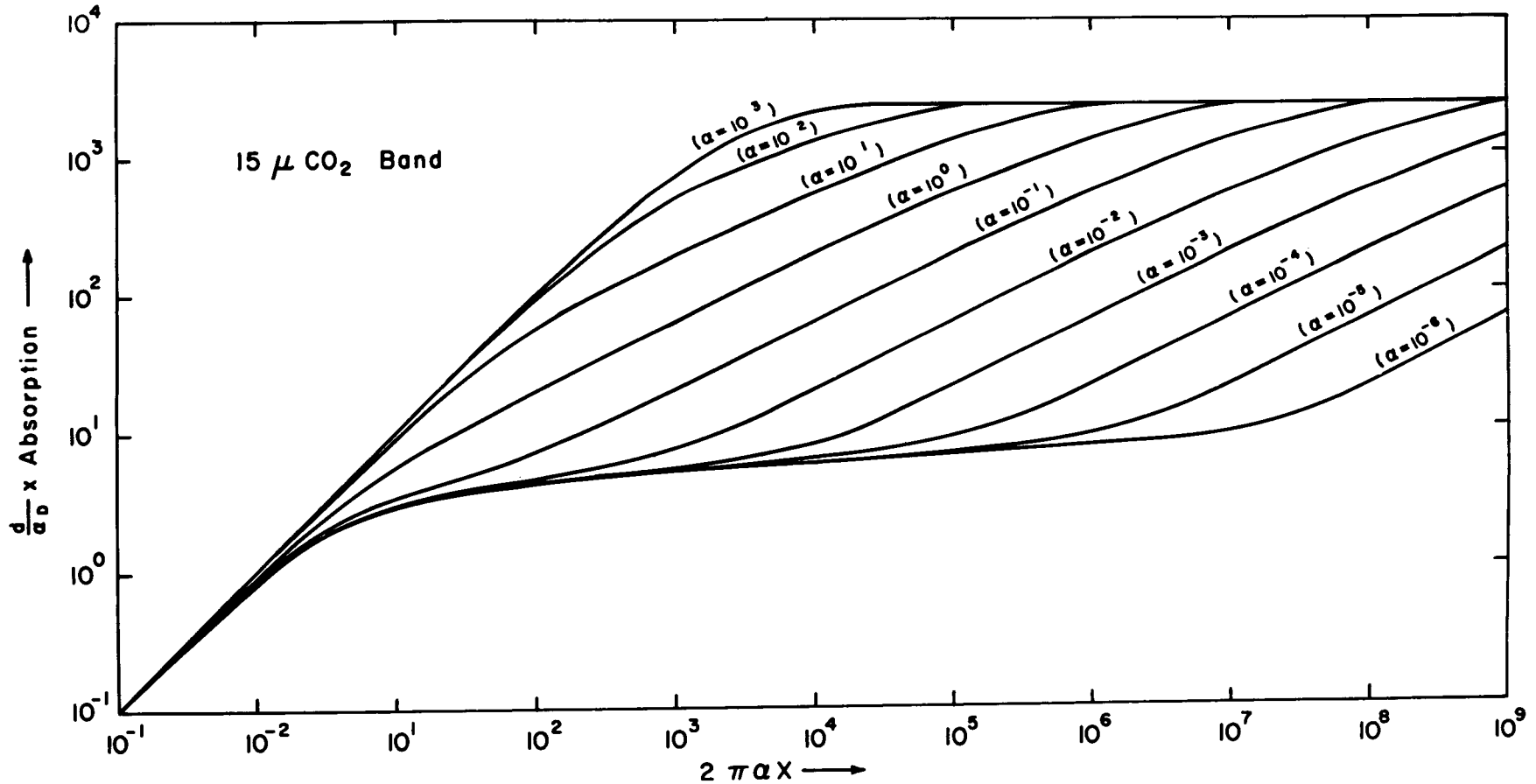


Figure 1. Absorption by mixed Doppler and Lorentz lines in the 15μ $CO_2$ band. The abscissa $2\pi\alpha x = Su \frac{d}{\alpha_D}$, and $\frac{d}{\alpha_D} = 2.46 \times 10^3$ .

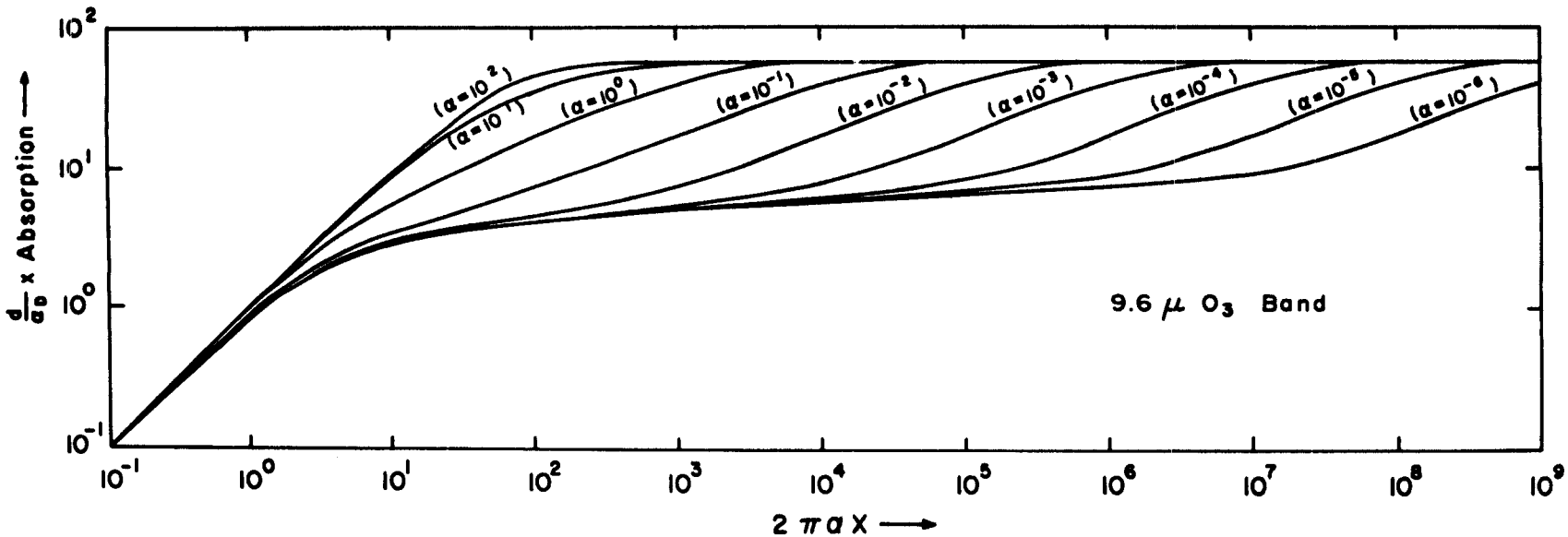


Figure 2. Absorption by mixed Doppler and Lorentz lines in 9.6μ $O_3$ band. The abscissa $2\pi a x = Su \frac{d}{a_D}$, and $\frac{d}{a_D} = 66.3$ .

path may be significant. Pressure may vary by several orders of magnitude, but the temperature changes will be much smaller. The temperature variation of the line intensity and Lorentz and Doppler line widths has not been included in this study, since in the regions of the atmosphere under consideration the range of temperature is not large.

The parameter $\alpha$ was calculated for any desired path length in the atmosphere using the weighting procedure developed by Curtis (1952) and Godson (1953).

## 6. Method of solution

With the boundary conditions of zero downward flux of infrared energy at the top of the atmosphere $z_H$, and a black body surface at the ground $z_o$, the basic equation of radiative transfer (equation (1)) can be solved to yield at any level $z_1$, the upward and downward intensities, $I\uparrow(\nu, \theta, z_1)$ and $I\downarrow(\nu, \theta, z_1)$ respectively:

$$I\uparrow(\nu,\theta,z_1) = B(\nu,z_o)\,\tau(\nu,\theta,z_1 - z_o) + \int_{z_o}^{z_1} J(\nu, z)\,\frac{\partial\tau(\nu, \theta, z_1 - z)}{\partial z}\,dz \tag{17}$$

$$I\downarrow(\nu, \theta, z_1) = \int_{z_1}^{z_H} J(\nu, z)\,\frac{\partial\tau(\nu, \theta, z - z_1)}{\partial z}\,dz \tag{18}$$

Here $\tau(\nu, \theta, |z_1 - z|)$ represents the transmission of the atmosphere at frequency $\nu$ and zenith angle $\theta$ between levels $z$ and $z_1$:

$$\tau(\nu, \theta, |z_1 - z|) = 1 - \bar{A}(\nu, \theta, |z_1 - z|) \tag{19}$$

Consider a thin slab of geometric thickness $\delta z$ centered at the level $z_1$ (Figure 3). The upward directed energy at the level

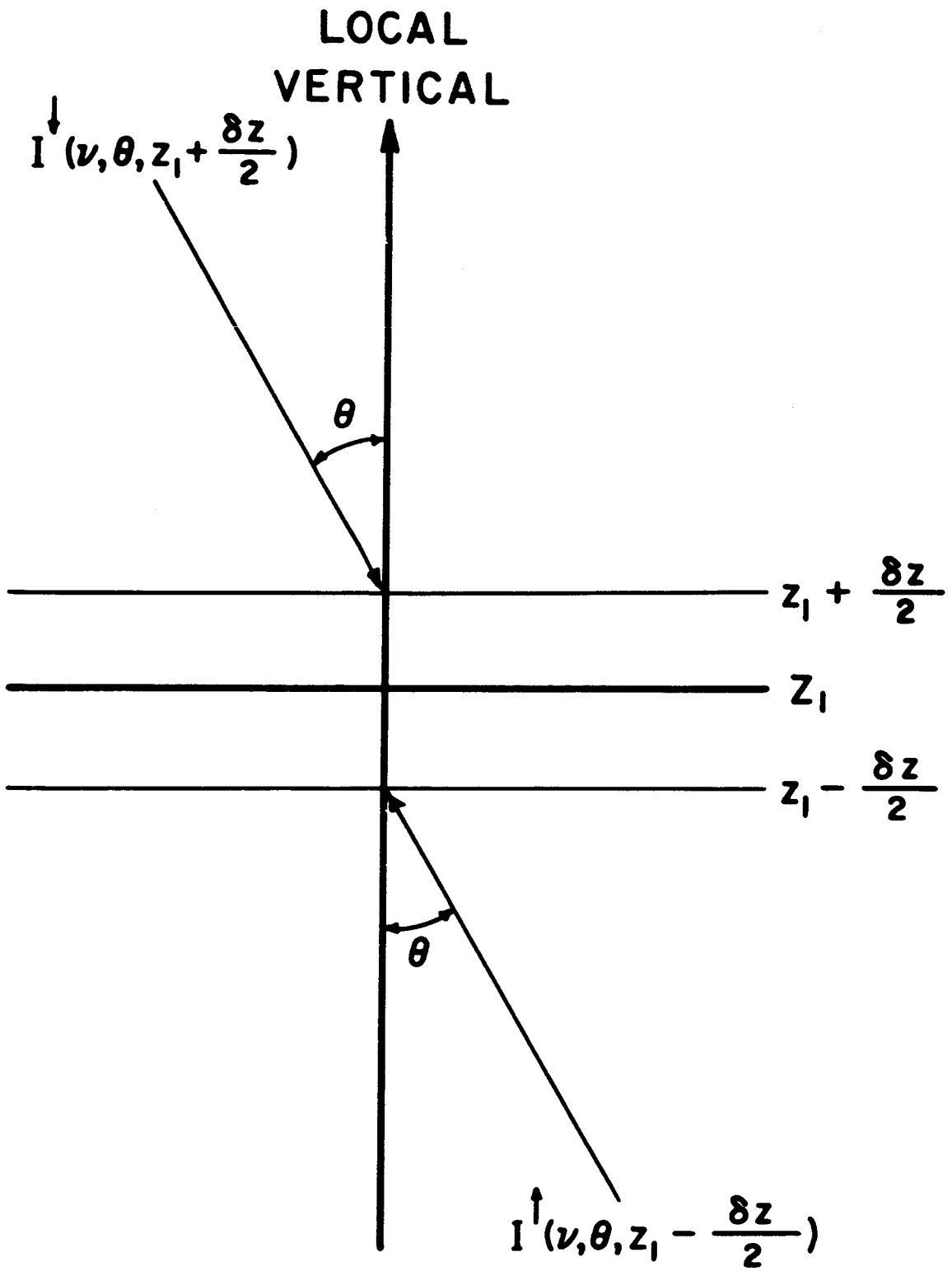


Figure 3. Schematic diagram of parameters.

$z_1 - (\delta z/2)$ which is absorbed by the slab, $A\uparrow(\delta z)$, is obtained by the expression

$$A\uparrow(\delta z) = \int_{\nu} \int_{o}^{2\pi} I\uparrow[\nu, \theta, z_1 - (\delta z/2)] \times \{1 - \tau(\nu, \theta, \delta z)\} d\omega d\nu \tag{20}$$

The integration with respect to frequency is made over the $15\mu$ $CO_2$ band and the $9.6\mu$ $O_3$ band.

Of the energy travelling in a downward direction, the amount absorbed by the slab is

$$A\downarrow(\delta z) = \int_{\nu} \int_{o}^{2\pi} I\downarrow[\nu, \theta, z_1 + (\delta z/2)] \times \{1 - \tau(\nu, \theta, \delta z)\} d\omega d\nu \tag{21}$$

The total flux of energy emitted by the slab in all directions under LTE condisions, $R(\delta z)$, depends on the mean temperature of the slab, here taken to be the temperature of the level $z_1$ :

$$R(\delta z) = \int_{\nu} \int_{o}^{4\pi} B(\nu, z_1) \{1 - \tau(\nu, \theta, \delta z)\} d\omega d\nu \tag{22}$$

The mean solar energy absorbed per unit area per unit time $Q(\delta z)$ in the ultraviolet and visible regions by oxygen and ozone is obtained from the same quantitative procedure used in an earlier work (Prabhakara and Hogan, 1965) with two exceptions. Here, a correction to the molecular oxygen concentration was included to account for the photodissociation which is significant at high altitudes in the Earth's atmosphere. Also the efficiency of the $O_2$ photodissociation process was considered using the quantum efficiency factors deduced by Leovy

(1964). It is assumed in this treatment that the sun is in the equatorial plane and that the mean solar energy absorbed is half of the solar energy absorbed during the sunlit part of the day.

For any given layer of the atmosphere, under radiative equilibrium conditions, the total absorbed energy in the infrared, visible and ultraviolet must be balanced by the total emitted energy.

Equations (10) and (12) were rewritten then as

$$J(\nu, z_1) = B(\nu, z_1) \left\{ 1 - \frac{\lambda(z_1)}{\phi} \frac{Q(\delta z)}{R(\delta z)} \right\} \tag{23}$$

$$Q(\delta z) \left( 1 + \frac{\lambda(z_1)}{\phi} \right) + A\uparrow(\delta z) + A\downarrow(\delta z) = R(\delta z) \tag{24}$$

The solution for an equilibrium temperature structure was obtained numerically from these equations by an iterative procedure as follows. The atmosphere below 100 km was divided into 50 layers of equal geometric thickness. An arbitrary initial atmospheric structure was specified and the atmosphere was assumed to be in LTE throughout. From this structure, $Q(\delta z)$, $\lambda(z_1)$, $A\uparrow(\delta z)$ and $A\downarrow(\delta z)$ were calculated and $R(\delta z)$ obtained directly from equation (24). The height distribution of $R(\delta z)$ determined a new distribution of temperature which was then used to evaluate the source function $J(\nu, z_1)$ from equation (23). The values of $J(\nu, z_1)$ so obtained were used to solve equation (24) for a new temperature structure. This procedure was repeated until an equilibrium temperature structure was obtained satisfying the convergence criterion that the temperature at any level vary no more than 0.1°K in two successive iterations.

Thus, a temperature, pressure and density stratification of the atmosphere consistent with the source functions and absorbed solar energy was obtained.

## 7. Results

Calculations of the temperature structure of the Earth's atmosphere have been made up to an altitude of 100 km assuming a constant mixing ratio for $CO_2$ ($3 \times 10^{-4}$ by volume). A vertical distribution of $O_3$ consistent with the temperature and density stratification was generated photochemically.

The temperature of the Earth's surface was assumed to be 285°K with atmospheric temperatures decreasing at a rate of 6.5°K $km^{-1}$ up to 10.5 km. Between 10.5 and 19 km the atmosphere was assumed to be isothermal at a temperature of 216.7°K.

It was necessary to fix the temperature structure of the lower atmosphere in this way since the presence of $H_2O$ was not explicitly taken into account in this calculation. Also, thermal convection controls the temperature structure of the troposphere, so that in order to incorporate the essential temperature features of this region, a standard atmosphere was adopted up to an altitude of 19 km. This procedure led to small discontinuities in temperature (~ 1°K to 2°K) immediately above 19 km. These discontinuities were smoothed out for presentation in the figures.

The effective emission leaving this fixed region of the atmosphere in the 9.6μ $O_3$ band, which lies in the $H_2O$ "window", was taken to be 75 percent of the emission of the surface in this spectral interval. With these constraints on the atmospheric

structure below 20 km, radiative equilibrium temperatures were calculated for the upper layers.

The vibrational relaxation lifetime at atmospheric pressure $\lambda_o$ was varied between $1.5 \times 10^{-5}$ sec and $10^{-6}$ sec. A value of $1.5 \times 10^{-5}$ sec was used by Curtis and Goody (1956). Several experimental determinations of the relaxation time (see, for example, Herzfeld and Litovitz, 1959; Lambert, 1962) give values between $\sim 10^{-5}$ and $\sim 10^{-6}$ sec. It appears that the presence of $H_2O$ in trace quantities is sufficient to decrease this time significantly due to a strong catalytic effect, so it is felt that representative values of this parameter are more likely to be $\sim 10^{-6}$ sec.

The temperature structures obtained as shown in Figures 4 through 6 are in good general agreement with the observed temperatures. A comparison is made in Figure 7 with observations made at Ft. Churchill and White Sands Missile Range (Groves, 1964). The best agreement is found for a value of $\lambda_o = 10^{-6}$ sec, which appears to be a good estimate for this parameter. The results show the usual temperature maximum appearing near the 50 km level due to strong solar heating by $O_3$. Above this altitude, the solar energy absorbed per unit volume decreases generally in proportion to the density (Figures 4 through 6). However, the opacity of $CO_2$ does not vary with the density in the same way. The Doppler broadening of the spectral lines becomes important in the low pressure regions and, as a consequence, the opacity of $CO_2$ (per 2 km layer) decreases more slowly with height than does the pressure or density, as can be inferred from

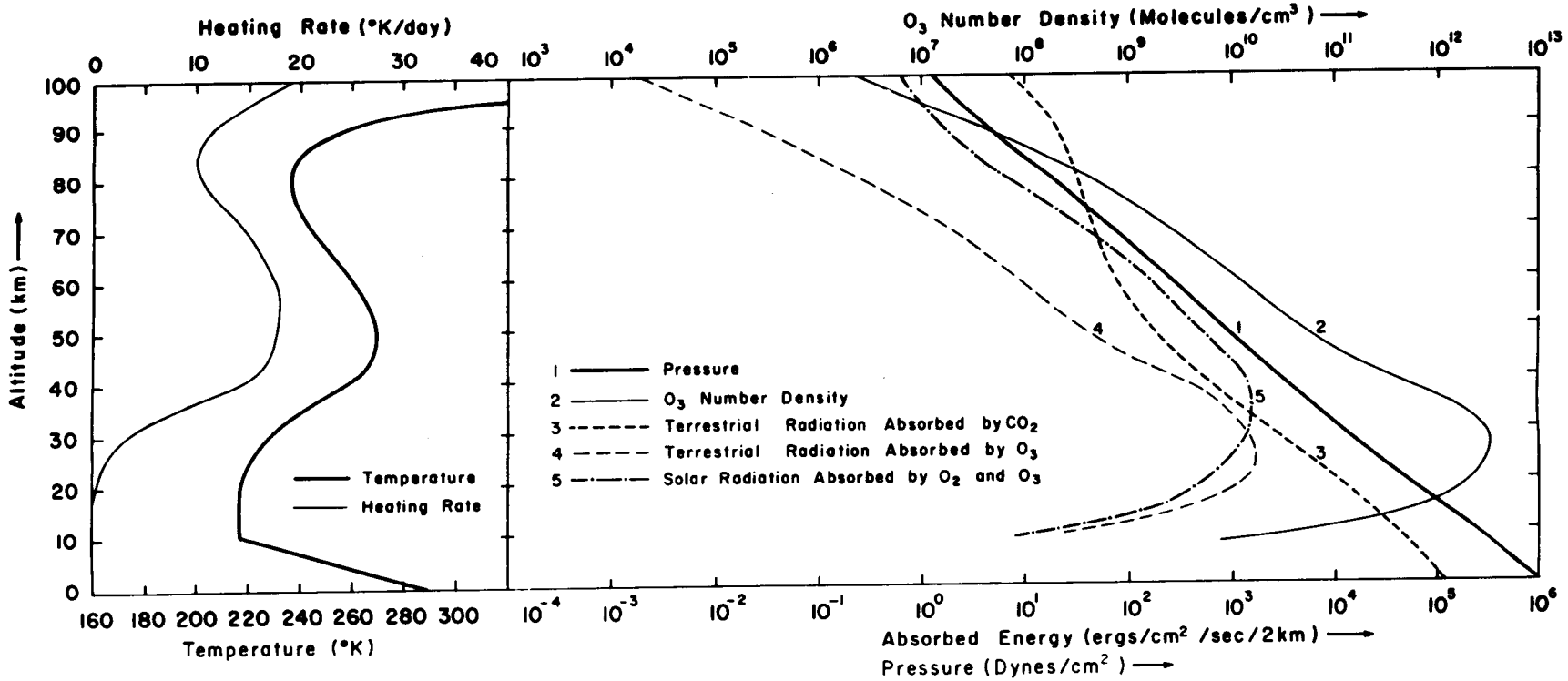


Figure 4. Radiative equilibrium structure of the atmosphere calculated for $\lambda_o = 1.5 \times 10^{-5}$ sec.

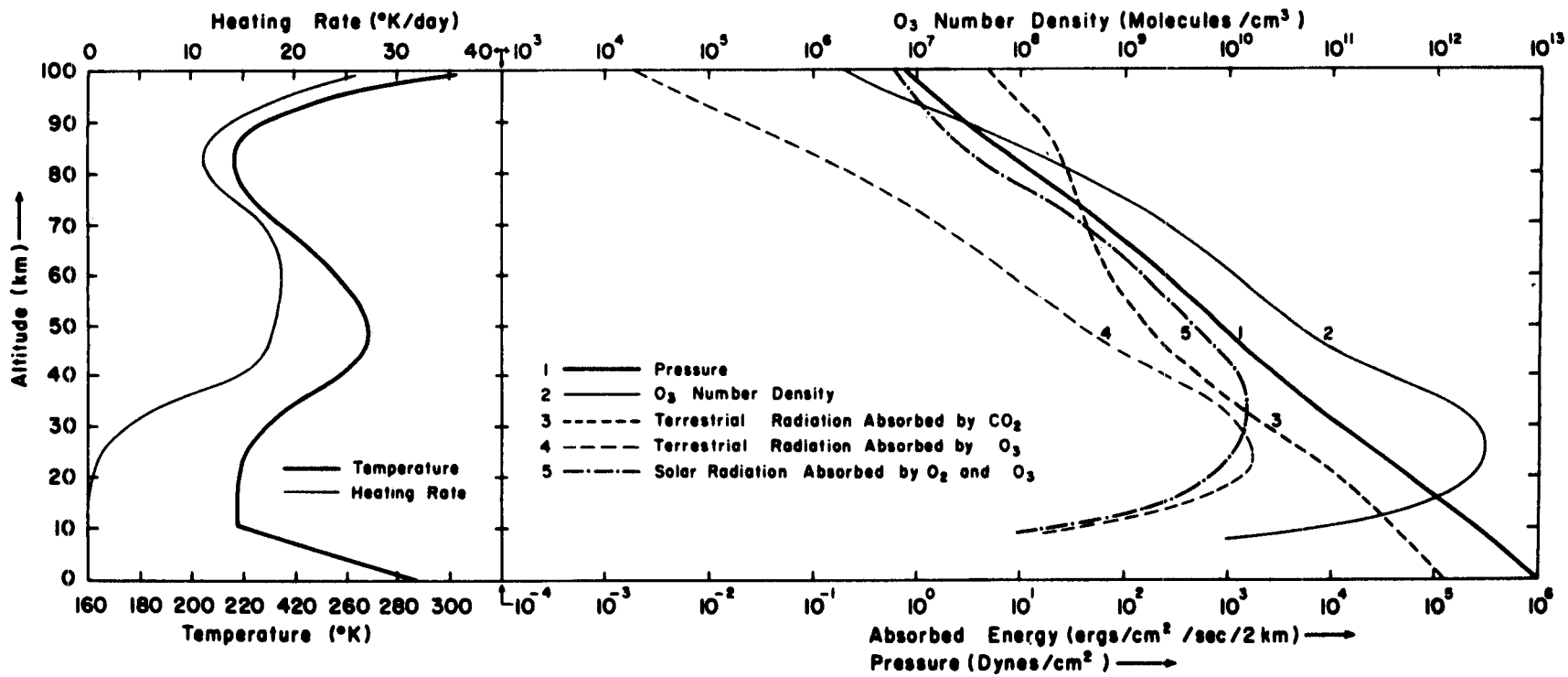


Figure 5. Radiative equilibrium structure of the atmosphere calculated for $\lambda_o = 5 \times 10^{-6}$ sec.

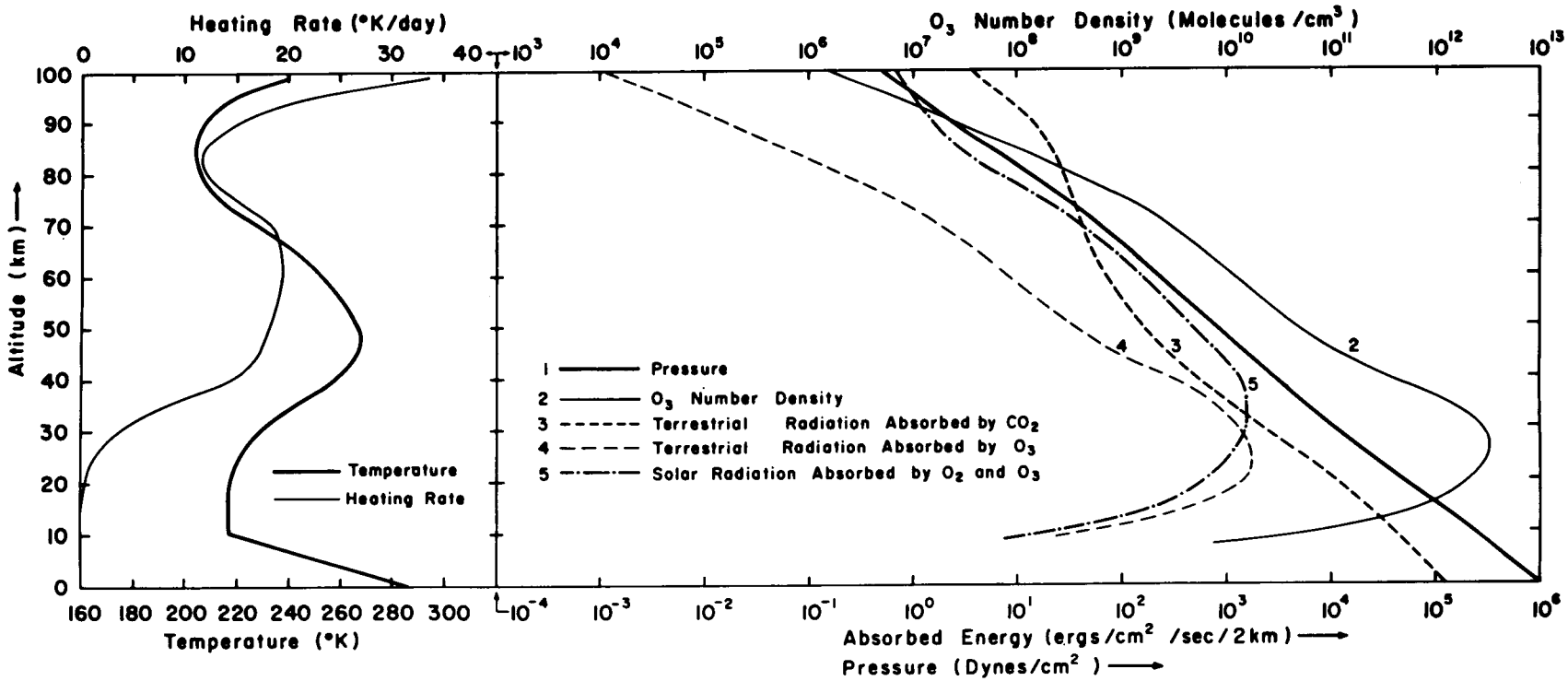


Figure 6. Radiative equilibrium structure of the atmosphere calculated for $\lambda_o = 10^{-6}$ sec.

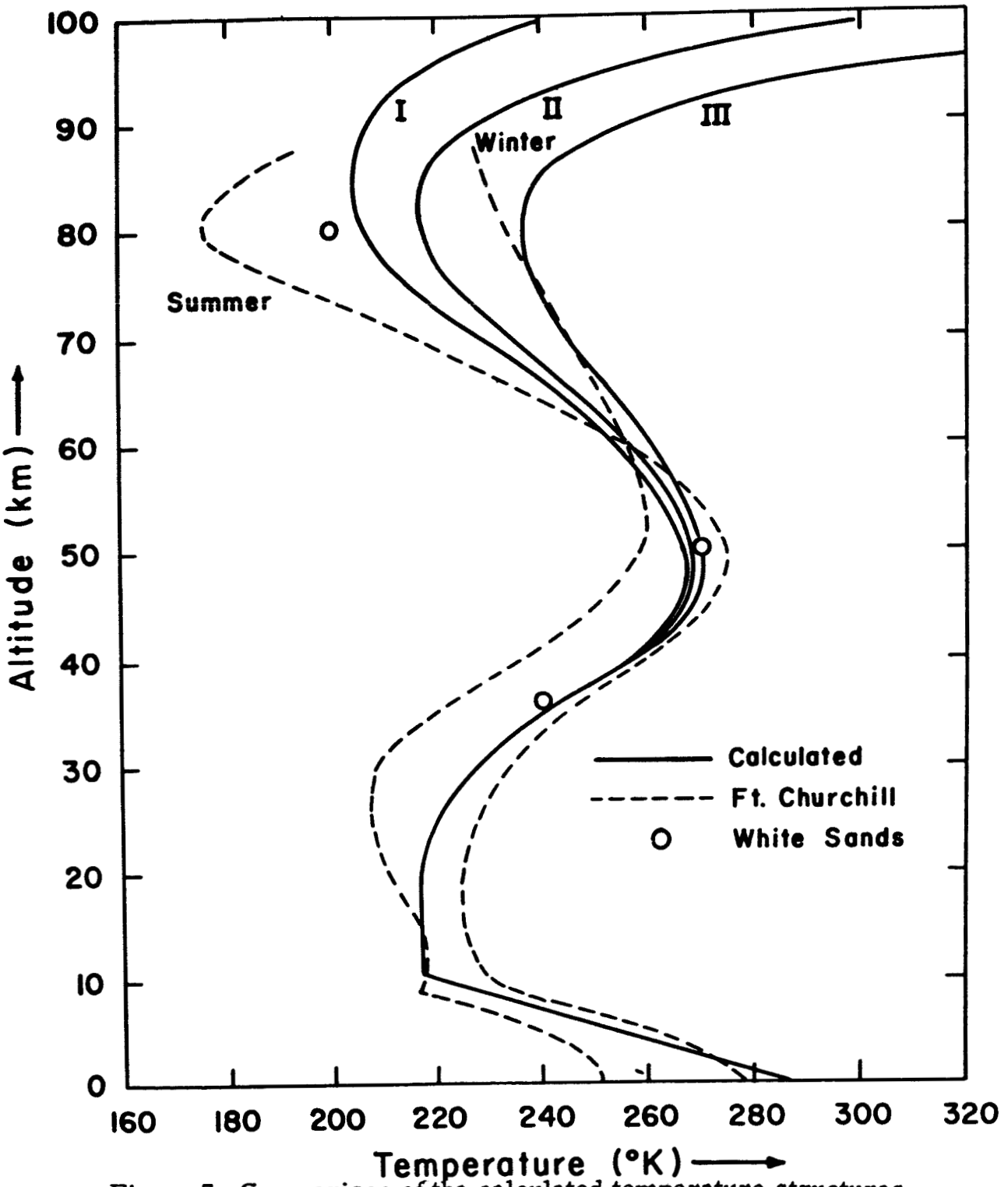


Figure 7. Comparison of the calculated temperature structures with the observations at Ft. Churchill and White Sands Missile Range. (I: $\lambda_o = 1.5 \times 10^{-5}$ sec; II: $\lambda_o = 5 \times 10^{-5}$ sec; III: $\lambda_o = 10^{-6}$ sec).

Figures 4 through 6. Thereby, the cooling influence of $CO_2$ decreases with altitude at a slower rate than the solar heating. The net result is a decrease of temperature with height up to the vicinity of the 80 km level. In this region, the collisional lifetime becomes longer than the radiative deactivation lifetime for $CO_2$, so that above this level, the efficiency of $CO_2$ to radiate is greatly diminished. The solar energy absorbed then regains control of the temperature structure, and temperatures increase again with altitude.

In Figures 4 through 6, the terrestrial radiation absorbed by $CO_2$ and $O_3$ in a 2 km layer is given along with the solar radiation absorbed by $O_2$ and $O_3$. The relative importance of $CO_2$ and $O_3$ as infrared transferring agents is revealed by comparison of the infrared energies absorbed by these constituents. It can be seen that $O_3$ and $CO_2$ are of comparable importance in the atmosphere near 30 km, but above and below this level $O_3$ infrared transfer can be neglected. Similarly, the region of temperature maximum in all three cases is seen to be at altitudes where the solar ultraviolet energy absorbed is larger than the infrared energy absorbed by $CO_2$. This pronounced maximum is due to the predominance of solar heating at these levels. Further, as indicated in the figures, the infrared energy absorbed by $CO_2$ is larger by nearly an order of magnitude than the solar energy absorbed near the top of the models. However, the solar energy goes ultimately into the kinetic energy of the molecules, while only a part of the infrared energy absorbed appears in the form

of kinetic energy, the rest being lost by radiative cascades. The probability of cascading increases with height, so that near the top of the atmosphere, the absorption of solar energy is the main source of the molecular kinetic energies and exerts a strong control on the temperature structure.

The variation of the ratio of the source function to the Planck function (J/B) with altitude for the three cases considered is shown in Table II. As one might anticipate, for large values of $\lambda_o$ the ratio J/B departs from unity at altitudes in the vicinity of 30 km, while for smaller $\lambda_o$, this departure occurs at higher levels. It is seen that a variation of $\lambda_o$ by a factor of 15 results in a change of the J/B ratio near the top of the atmosphere by a factor of only 2. This again demonstrates the importance of the infrared transfer emphasized in section 2.

The most significant feature of the temperature structure calculated is the temperature minimum appearing in the 80 to 85 km region. This minimum corresponds very well with that observed in the Earth's atmosphere with regard to its altitude and magnitude of temperature. It appears from these calculations that the general structure of the atmosphere in the stratosphere, mesosphere and lower thermosphere is basically governed by radiative transfer, with dynamic effects being of secondary importance, though not negligible.

TABLE II

VARIATION OF J/B WITH ALTITUDE

| z (km) | $\lambda_o = 1.5 \times 10^{-5}$ sec p (dynes $cm^{-2}$) | J/B | $\lambda_o = 5 \times 10^{-6}$ sec p (dynes $cm^{-2}$) | J/B | $\lambda_o = 10^{-6}$ sec p (dynes $cm^{-2}$) | J/B |
|---|---|---|---|---|---|---|
| 30 | $1.2 \times 10^4$ | 1.0 | $1.2 \times 10^4$ | 1.0 | $1.2 \times 10^4$ | 1.0 |
| 40 | $2.9 \times 10^3$ | .99 | $2.9 \times 10^3$ | 1.0 | $2.9 \times 10^3$ | 1.0 |
| 50 | $8.2 \times 10^2$ | .97 | $8.2 \times 10^2$ | .99 | $8.2 \times 10^3$ | 1.0 |
| 60 | $2.3 \times 10^2$ | .92 | $2.3 \times 10^2$ | .97 | $2.2 \times 10^2$ | .99 |
| 70 | $6.2 \times 10^1$ | .82 | $5.8 \times 10^1$ | .92 | $5.6 \times 10^1$ | .98 |
| 80 | $1.6 \times 10^1$ | .72 | $1.3 \times 10^1$ | .86 | $1.2 \times 10^1$ | .97 |
| 90 | $3.9 \times 10^0$ | .59 | $2.9 \times 10^0$ | .75 | $2.4 \times 10^0$ | .92 |
| 100 | $1.3 \times 10^0$ | .30 | $8.0 \times 10^{-1}$ | .42 | $5.2 \times 10^{-1}$ | .67 |

## 8. Limitations

Neither the conduction process nor the cooling by the magnetic dipole transitions between the components of the $^3P$ state of atomic oxygen (Bates, 1951) have been included in these calculations. Harris and Priester (1962) have made estimates of the conductive flux of energy at these levels. We find that such estimates of flux yield flux divergences of the order of $10^{-2}$ ergs per 2 km layer. The magnitude of the atomic oxygen cooling was found to be also about $10^{-2}$ erg per 2 km layer. Since both conduction and atomic oxygen cooling involve energies of the order of $10^{-2}$ erg per 2 km layer, while $O_2$ and $O_3$ heating in the solar ultraviolet involves energies 100 times larger, both of these processes were neglected as being unimportant mechanisms of energy transport in the layers of the atmosphere under consideration.

Atmospheric cooling by the OH airglow may be a somewhat more important phenomenon at these levels, the total energy radiated by a 20 km layer being $\sim 10$ ergs $cm^{-2}$ $sec^{-1}$ (Chamberlain, 1961). The distribution of OH molecules shows a peak in the vicinity of the mesopause (Packer, 1961; Wallace, 1962) and rapidly decreases above and below this level. The magnitude of the radiated energy at the maximum may be significant as compared with the absorbed solar energy at this level. Such radiative loss would lower the mesopause temperature from the values obtained here by $\sim 10°K$.

Also of importance may be the cooling effects of $O_3$ which

could increase markedly in concentration during the night at levels between 50 and 70 km (Leovy, 1964; Hunt, 1965). The scheme developed here (equation (12)) applies only when $CO_2$ is the dominant infrared transferring agent in the high regions of the atmosphere. If $O_3$ gains a comparable importance at these levels, the use of the basic equations employed cannot be justified. A crude estimate of the cooling effects of the nighttime increase in ozone by a factor of ~50 near 60 km indicates that the mean temperatures at this level would be lowered by ~20°K.

Needless to say, the dynamics of the atmosphere will exert a very large influence on the temperatures at these levels, enhancing cooling in the summer hemisphere and warming in the winter hemisphere (Murgatroyd and Singleton, 1961).

Despite these limitations, however, these calculations are sufficiently realistic to demonstrate that the mesopause appears due to the radiative transfer process.

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