

Direct Absorption of Solar Radiation by Atmospheric Water Vapor, Carbon Dioxide and Molecular Oxygen¹

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ABSTRACT

Based mainly on Howard, Burch and Williams' laboratory absorption data for the near infrared H₂O and CO₂ bands, and on the solar absorption data for the red and near infrared O₂ bands, the direct absorption of solar radiation in near infrared atmospheric bands has been estimated. The estimated absorptivities of the H₂O bands in the interval from 0.7 to 2.1 μ are in fair agreement with McDonald's estimates which are based on Fowle's absorption data. However the absorptivities of the H₂O bands from 0.7 to 6.3 μ are larger than McDonald's values. CO₂ and O₂ absorptions become increasingly important in the upper troposphere and in the stratosphere. Average heating (deg C day⁻¹) was also estimated for London's model atmospheres for clear sky conditions, and compared with the similar estimate made by Roach. For the atmosphere above 300 mb the heating estimated in this paper exceeds that estimated by Roach. Conceivable causes of this discrepancy are pointed out.

1. Introduction

According to Houghton in 1954, the most uncertain item entering into the estimation of radiation balance in the atmosphere is the absorption of solar radiation. This statement is still true. Recently, McDonald (1960) calculated the absorption of solar radiation by atmospheric water vapor using Fowle's absorption data (1912, 1915) and found that the insolation absorptivities calculated by him are about thirty per cent lower than those estimated by Houghton (1954). The latter are based on a set of water-vapor absorption values deduced from an analysis of the solar constant work of the Smithsonian Astrophysical Observatory, of which Fowle was a member. McDonald could not decide which estimate, his or Houghton's, was more reasonable. There is also a recent estimate by Möller (1957) using the laboratory absorption data of Howard, Burch and Williams (1955) which was not referred to by McDonald and which differs from both McDonald's and Houghton's estimates.

In this study the writer has also used Howard, Burch and Williams' data, so far as they were available. However, the methods of pressure scaling and extrapolation of the data were different from those involved in their empirical formulae. The absorption due to the red and near infrared O₂ bands was also considered.

After the present calculations had been finished, the author found that similar calculations were carried out by Roach (1961) based on the empirical formulae proposed by Howard, Burch and Williams. Therefore, comparison between his results and the present ones enables us to estimate the difference due to the improved

pressure scaling and extrapolation of the data adopted in this study.

2. Fractional absorption of near infrared bands

In their empirical formulae for the fractional absorption of the H₂O bands, Howard, Burch and Williams tried to incorporate the difference in collision cross sections between N₂-N₂ collision and N₂-H₂O collision. However, their estimate on this point differs from Benedict's (1956), which has a theoretical basis. Therefore, based upon Benedict's investigation, the pressure factor, $P+5.3p$, was used for the H₂O bands, where P is the total pressure, and p the partial pressure of water vapor. Benedict proposed to use one parameter, $w(P+5.3p)$, w being the optical thickness, in expressing the fractional absorption. In this work, however, two parameters were used; w and $(P+5.3p)/P_0$, where P_0 is the standard pressure. The merit of this method was shown elsewhere (Yamamoto and Sasamori, 1961).

Extrapolation of the fractional absorption for smaller values of w might be made most reasonably by fitting continuously to the observed data the Goody (1952) random model values for suitably chosen line intensity and spacing. However, for smaller values of w the absorption of the Elsasser band approaches that of the Goody model within small errors, and because of the availability of the numerical table for the Elsasser absorption (Wark and Wolk, 1960), this was used as the basis of extrapolation to smaller values of w .

Extrapolation of the absorption to larger values of w for $(P+5.3p)/P_0=1$ was made following the method of Howard, Burch and Williams. For other values of the pressure parameter, extrapolation was made so as to make the pressure effect proportional to pressure asymptotically with increasing w .

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Howard, Burch and Williams did not measure the absorption of the 0.72- and 0.8- μ bands, which are very weak. Their contribution to the absorption of solar radiation, however, cannot be neglected, as shown by McDonald, because of the large solar energy in this region. The fractional absorption of these bands was estimated from Fowle's data, which correspond to $w=0.5$ to 2 cm of precipitable water, assuming them to be obtained at the condition of $(P+5.3p)/P_0=0.8$. Fowle's data corresponding to $w=2$ to 8 cm *pr* water were discarded, because of the unreasonably large slope of the absorption curve. For other values of both w and $(P+5.3p)/P_0$ the values of the fractional absorption were inferred by analogy with those of the adjacent 1.1- μ bands.

As a result the fractional absorptions of the following spectral intervals were considered: 0.72 μ (13,514–14,286 cm^{-1}), 0.81 μ (11,905–12,658 cm^{-1}), 0.94 μ (9700–11,500 cm^{-1}), 1.1 μ (8200–9700 cm^{-1}), 1.38 μ (6200–8200 cm^{-1}), 1.87 μ (4800–6200 cm^{-1}), 2.7 μ +3.2 μ (2800–4400 cm^{-1}), and 6.3 μ (1015–2160 cm^{-1}).

Among many CO_2 bands, the absorptions of the following four band intervals were considered: 4.3 μ (2160–2500 cm^{-1}), 2.7 μ (3480–3800 cm^{-1}), 2.0 μ (4750–5050 cm^{-1}), [here the (20°1–00°0) band was neglected], 1.6 μ (6000–6550 cm^{-1}). Again Howard, Burch and Williams' data were used. In addition, R. H. Moore of the U. S. Weather Bureau provided the author with some unpublished data for the 4.3- μ band, which were also taken into account. Again the fractional absorption was expressed in terms of the optical thickness and the pressure parameter. Because the self-broadened half-width of CO_2 is only thirty per cent greater than for nitrogen broadening, P/P_0 was taken as the pressure parameter in the case of CO_2 .

As to the O_2 bands, the absorptions of the 0.69- μ (14,300–14,560 cm^{-1}), 0.76- μ (12,984–13,236 cm^{-1}) and 1.25- μ (7782–8085 cm^{-1}) bands were considered. From the measurements made by Fowle (1917), the fractional absorption of the 0.69- μ O_2 band was estimated to be 0.078 under the condition in which m (the air mass) = 1.1 and P_e (the pressure parameter) = $\int P dm / P_0 m = 0.5$. Under the same condition the fractional absorption of the 0.76- μ O_2 band was estimated to be 0.318 from Langley and Abbot's measurements (1900) and that of the 1.25- μ O_2 band to be 0.078 from those of Langley and Abbot (1900) and Gates (1960). The values of the fractional absorption at different values of m and P_e were assumed by analogy to the CO_2 bands, e.g., the 2.7- μ band.

3. Absorptivity of vertical air column for normal incidence

In this study we adopted the water-vapor distributions of London (1957) for the troposphere and extrapolated them to the stratosphere by assuming an asymptotic mixing ratio of 0.003 g kg^{-1} . For the CO_2

distribution, a constant mixing ratio 0.031 per cent by volume was assumed. We used two sets of values for the incoming solar energy outside the atmosphere. The first were taken from the Smithsonian Meteorological Tables (List, 1958) and used to compare the absorptivities of the present study with those of other workers. In this case the solar constant was assumed to be 1.94 ly min^{-1} . The second set of values was taken from the *Handbook of Geophysics* (compiled by Gast, 1957) and used in calculating absorption in section 4.

An effective pressure parameter similar to the Curtis-Godson (1952, 1955) approximation was used in applying the laboratory data to atmospheric cases. It is given by

$$P_e = \frac{1}{P_0 w} \int_0^w (P+5.3p) dw, \quad (1)$$

for water vapor and similarly for CO_2 and O_2 .

The definition of absorptivity is given by the ratio to the solar constant of the energy absorbed by the entire vertical air column for normal incidence. Calculated absorptivities are shown in Fig. 1. Curve 1 shows the absorptivities corresponding to the 0.72-, 0.81-, 0.94-, 1.1-, 1.38- and 1.87- μ bands. As can be seen from Fig. 1, McDonald's data, which are shown by the symbol (X) and which correspond to the same H_2O bands, are in fair agreement with curve 1. Since the two curves are based on different absorption data, this agreement suggests not only the soundness of Fowle's data, which was recorded about 50 yr ago, but also the soundness of McDonald's interpretation of them, and also the soundness of the Howard, Burch and Williams data. It should be noted, however, that there exist minor differences between McDonald and the present calculations for each band, with respect to not only band limits but also the absorbed energy.

To compare the present result with Möller's for the 0.94-, 1.1-, 1.38-, 1.87-, 2.7-, 3.2- and 6.3- μ bands (Δ , in Fig. 1), the absorptivity for the same band interval is shown by curve 2. The agreement of Möller's absorptivity and curve 2, both of which are based on Howard, Burch and Williams' data, is natural, particularly because the values of absorptivity shown in Fig. 1 correspond closely to the observed data.

Curve 3 in Fig. 1 shows the absorptivity due to all H_2O bands from 0.72 to 6.3 μ . This is greater than either McDonald's or Möller's absorptivities. Houghton's absorptivity shown by curve 4 does not coincide with any curve of ours. It is not yet clear whether the discrepancy is to be attributed to the observed absorption values in Abbot's solar constant data or to Houghton's method of deriving absorptivity from them.

In Fig. 1 the absorptivity due to the sum of the H_2O and CO_2 bands is shown by curve 5 and that due to the sum of the H_2O , CO_2 and O_2 bands by curve 6. In this estimation the contribution of the 2.7- μ CO_2 band was neglected because of overlapping by the strong 2.7- μ

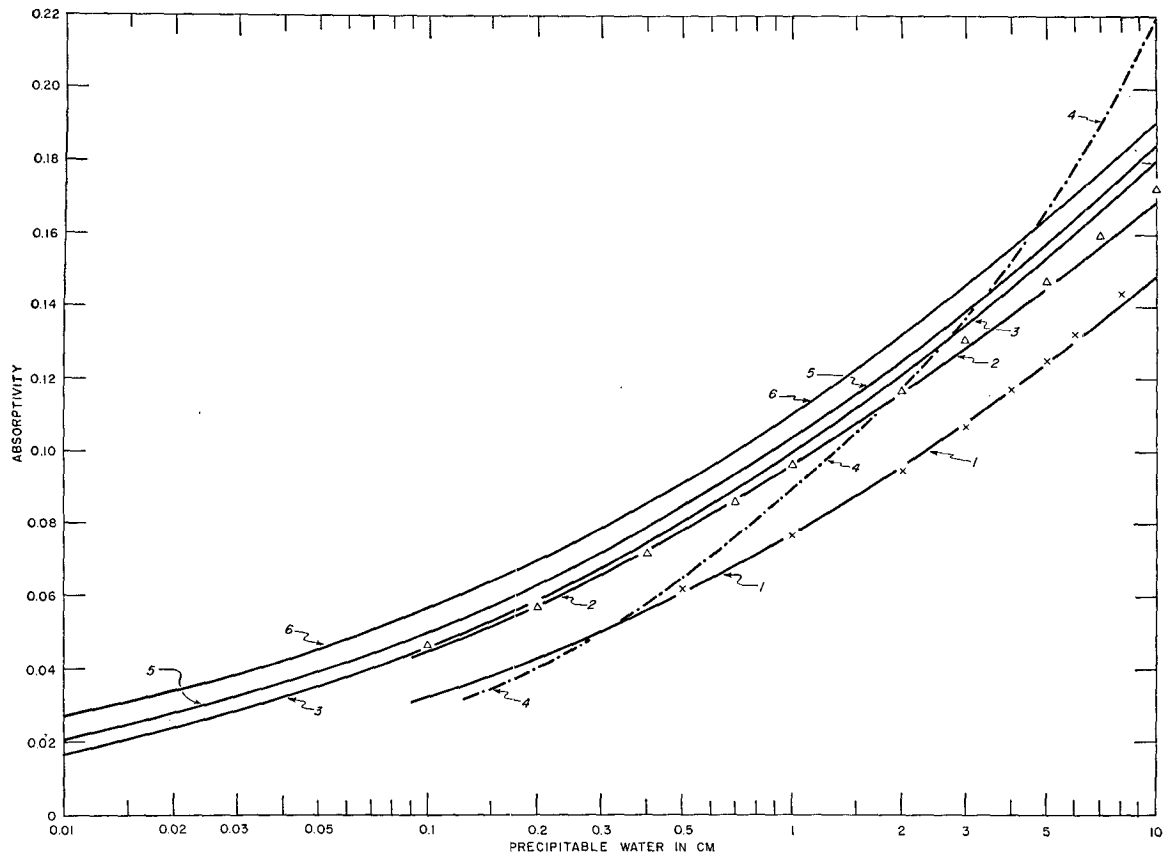


FIG. 1. Absorptivities of the near infrared bands. Curve 1=Absorptivities summed over the 0.72-, 0.8-, 0.94-, 1.1-, 1.38-, 1.87- μ H₂O bands. (X = Absorptivities estimated by McDonald over the same bands.) Curve 2=Absorptivities over the 0.94-, 1.1-, 1.38-, 1.87-, 2.7-, 3.2- and 6.3- μ H₂O bands. (Δ = Absorptivities estimated by Möller over the same bands.) Curve 3=Absorptivities over all the H₂O bands considered. Curve 4=Absorptivities estimated by Houghton. Curve 5=Absorptivities over the H₂O and CO₂ bands. Curve 6=Absorptivities over the H₂O, CO₂ and O₂ bands.

H₂O band and the assumed large amounts of water vapor in the lower atmosphere. It will be seen from Fig. 1 that although the absorptivity due to the CO₂ and O₂ bands is far smaller than that due to the H₂O bands, it is of some importance at high latitudes, where the amount of water vapor is small. Fig. 1 also shows that the contribution due to the CO₂ bands for the whole vertical air column is even smaller than that due to the O₂ bands.

4. Vertical distribution of solar heating due to the near infrared absorption

London (1952, 1957) has made an extensive study of heating due to water vapor absorption based on Mügge and Möller's (1932) absorption formula. Because of our improvement of the basic absorption data of H₂O and the inclusion of the CO₂ and O₂ data, it seems interesting to recalculate the rate of heating. In this calculation the effect of overlapping of the 2.7- μ H₂O and CO₂ bands was taken into account. The calculation was made by the following procedure: for the non-overlapped i -th band the absorbed energy

during the day time from the top of the atmosphere to a given level, \bar{A}_i , is given by

$$\bar{A}_i = 2 \int_0^{h_0} I_{0i} A_i (w \sec \zeta, P_e) \cos \zeta dh, \quad (2)$$

where A_i is the instantaneous value of the absorption of the i -th band, w the optical thickness and P_e the effective pressure, I_{0i} the solar energy outside the atmosphere in the i -th band, ζ the solar zenith angle, h the hour angle, and h_0 the hour angle at sunrise or sunset (these are assumed to be equal). For the overlapped band interval (3480–3800 cm⁻¹), the absorption due to water vapor is calculated by (2) for the 2800–4400 cm⁻¹ interval and a correction for the 3480–3800 cm⁻¹ interval due to the CO₂ absorption, A_{cor} , is added. This is given by

$$A_{cor} = 2 \int_0^{h_0} I_{0(3480-3800 \text{ cm}^{-1})} \tau_{\text{H}_2\text{O}} (1 - \tau_{\text{CO}_2}) \cos \zeta dh, \quad (3)$$

where $\tau_{\text{H}_2\text{O}}$ and τ_{CO_2} are the transmission values of

H₂O and CO₂ respectively for the 3480–3800 cm⁻¹ interval at a given height and time. Let the sum of the energy absorbed during the daytime by all bands from the top of the atmosphere to a given level with pressure *P* be $\overline{A}(P)$, then the vertical rate of heating, $\Delta T/\Delta t$, is

$$\frac{\Delta T}{\Delta t} = 16.33 \frac{\Delta \overline{A}(P)}{\Delta P} \quad (\text{deg C day}^{-1}), \quad (4)$$

where *P* is in mb. In actual calculations the values of the air mass given by Table 137 of the Smithsonian Meteorological Tables (List, 1958) were used instead of sec ζ , and the values of *h*₀ were estimated from the American Ephemeris and Nautical Almanac (1961).

Calculations were carried out for the model atmospheres mentioned in section 3. Taking the July 10–20N atmosphere as an example, the energies absorbed by the H₂O, CO₂ and O₂ bands separately and by the sum of these bands are shown in Fig. 2, in which the ordinate is the absorption, for the whole air column above a given pressure level and the abscissa the pressure in mb. Here the CO₂ absorption means the excess absorption by CO₂ over the H₂O absorption, and the minimum of the CO₂ absorption at about 400–500 mb is due to the overlapping of CO₂ and H₂O bands at 2.7 μ .

It will be seen from the figure that, while the absorption by H₂O bands is predominant in the lower

troposphere, that of the CO₂ bands is most important in the stratosphere. In the July 10–20N atmosphere the absorption by the CO₂+O₂ bands becomes equal to that by the H₂O bands at about the 210-mb level, which is considerably below the tropopause.

The distribution of heating with season, latitude and height is shown in Fig. 3. After the author had finished this work, he found that a similar estimate was made by Roach (1961). This was based on the empirical formulae for the fractional absorptions of the H₂O and CO₂ bands proposed by Howard, Burch and Williams, but he neglected absorption by the O₂ bands. Comparison of his results with the present ones averaged over seasons and latitudes, as a function of pressure is shown in Table 1. It will be seen from the table that the heating estimated by Yamamoto is larger than that estimated by Roach above 300 mb, while below this level the trend is reversed. The difference at low levels may be due to the use of different models of the water vapor distribution. The larger heating rates in the troposphere found by Roach would indicate that he assumed larger amounts of water vapor than in the present study. Therefore, a direct comparison of the tropospheric heating is difficult. In the stratosphere, particularly above 100 mb, heating is mainly due to CO₂ absorption, and in all probability both authors used the same CO₂ distributions. The difference of

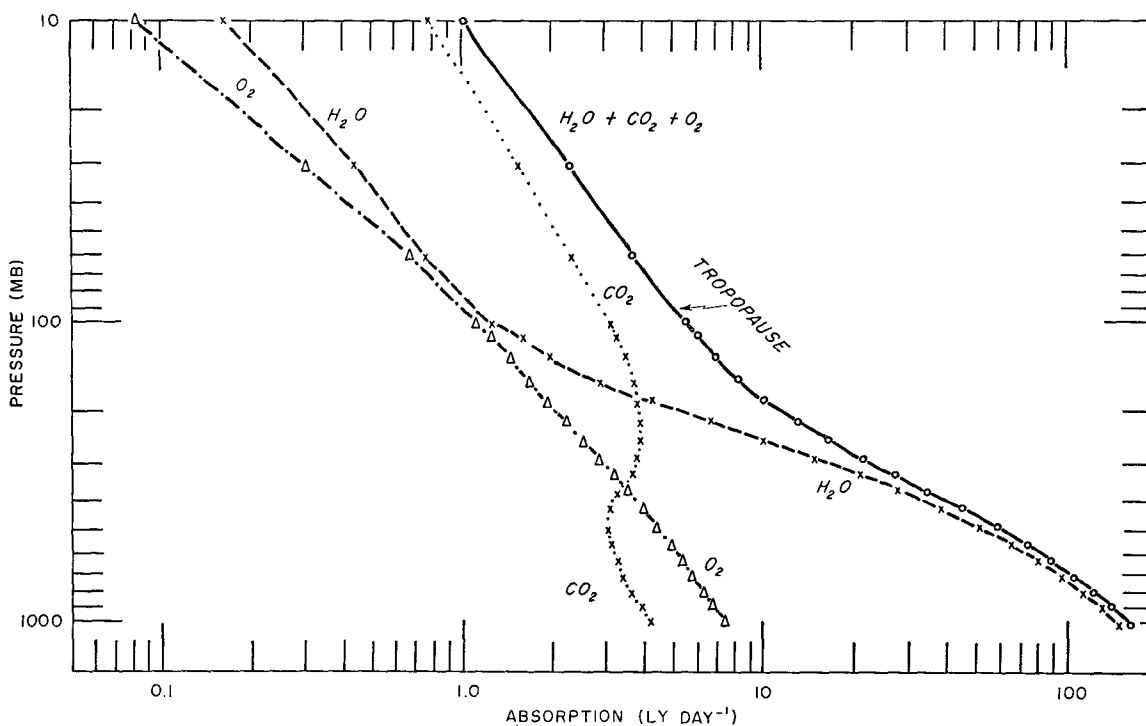


FIG. 2. The energies (1y day⁻¹) absorbed by H₂O, CO₂ and O₂ separately and the sum of them for one of London's model atmospheres, July, 10–20N. The CO₂ absorption means the excess absorption contributed by CO₂ over the absorption by H₂O alone when the band overlaps.

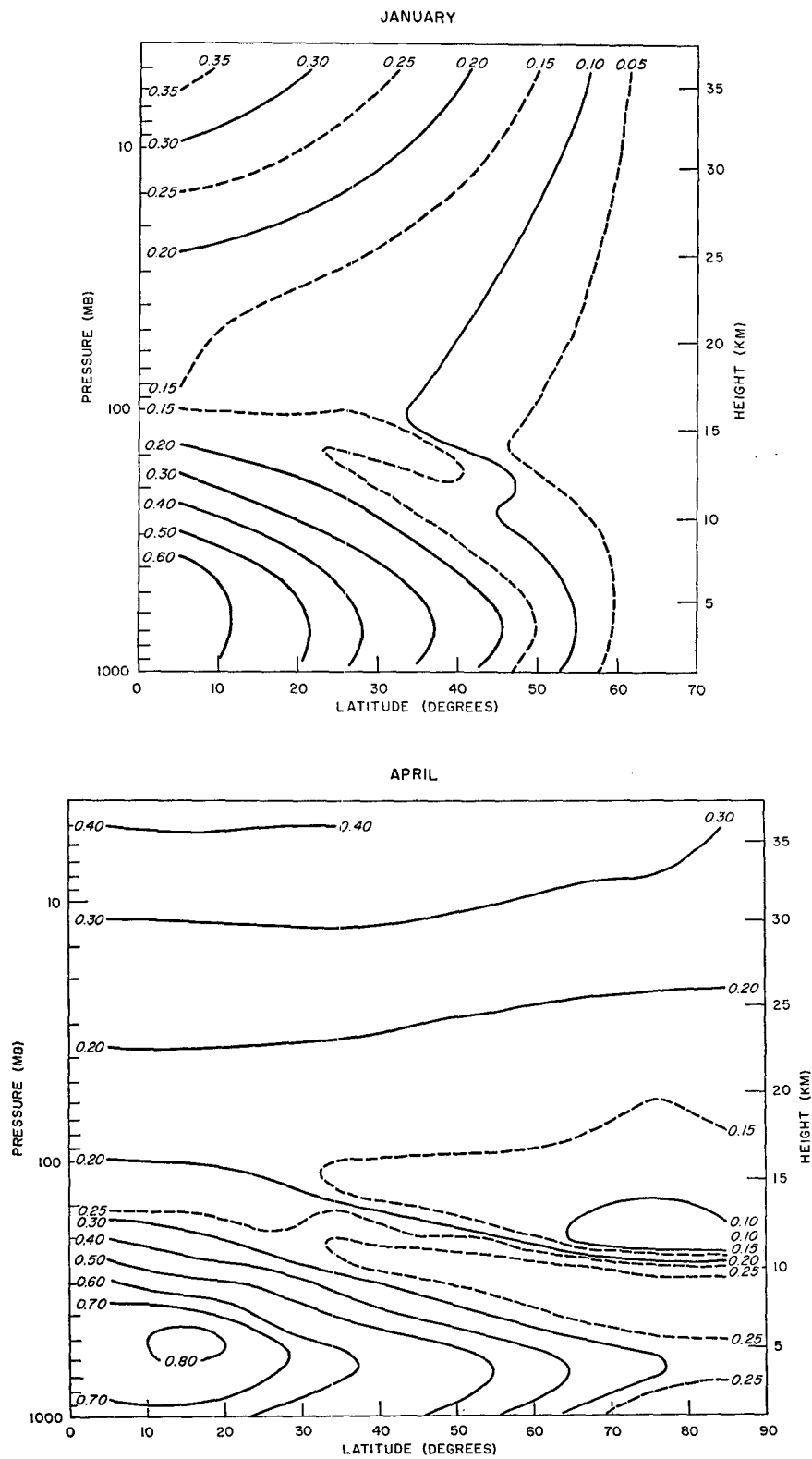


FIG. 3. Distribution of heating (deg C day^{-1}) with latitude and height. January (above) and April (below).

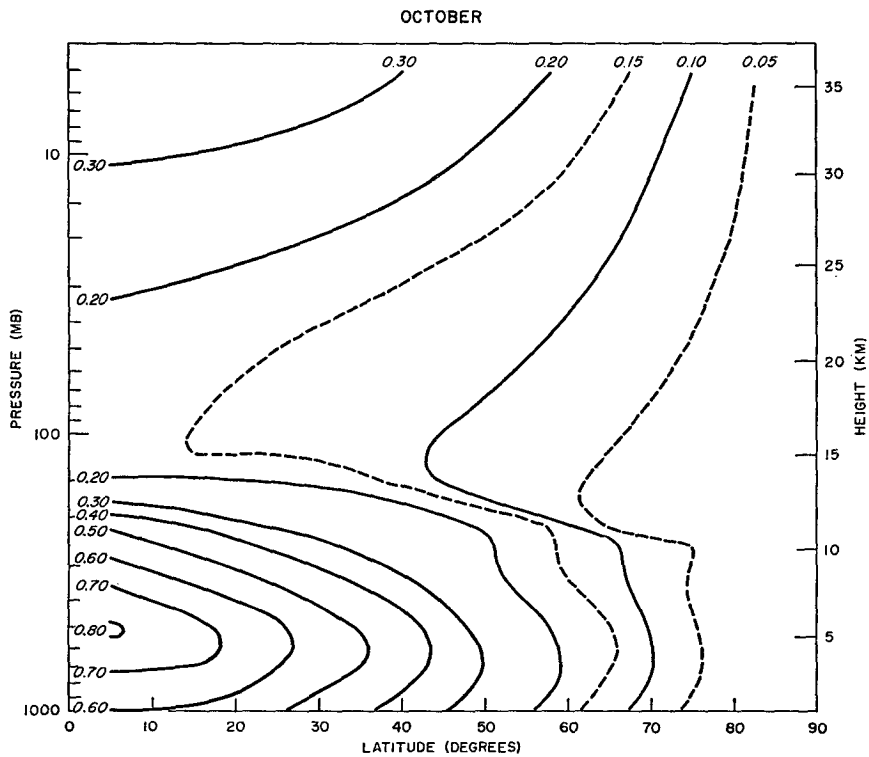
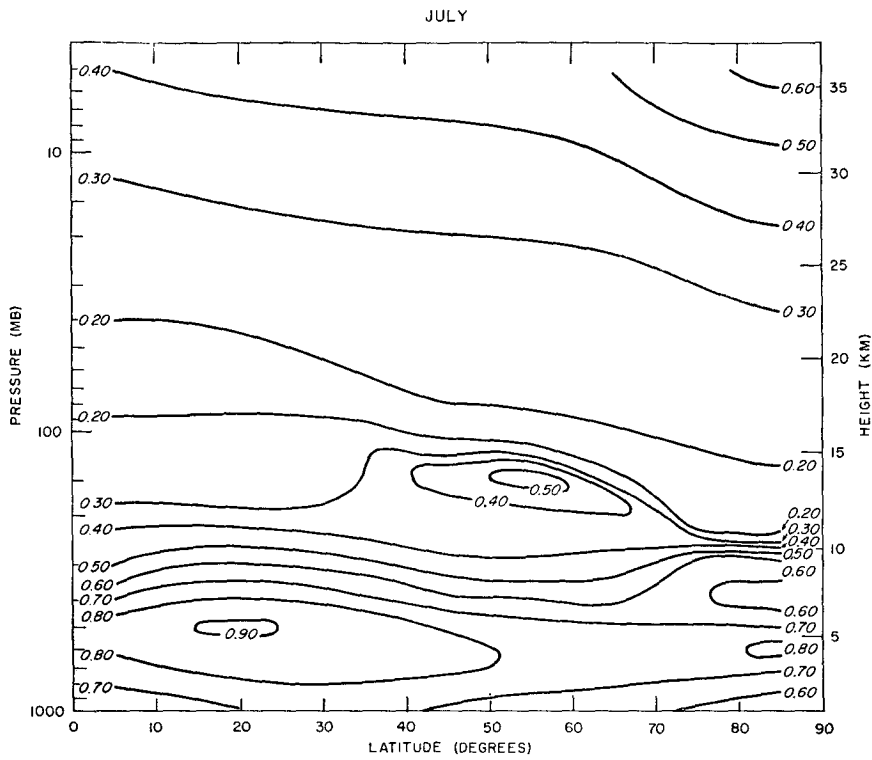


FIG. 3. Continued. July (above) and October (below).

heating above 100 mb, which amounts to 25–31 per cent (see Table 1) can be attributed to the following causes: First, absorption by the O₂ bands neglected by Roach, can be responsible for 10 per cent of the heating due to CO₂ (see Fig. 2). Second, the rest of the discrepancy may be attributed to the different methods used for pressure scaling, particularly at low pressure conditions, and also to the different methods of treating the absorption of the overlapping bands (at 2.7 μ).

TABLE 1. Comparison of heating ($C \text{ day}^{-1}$) averaged over seasons and latitudes estimated by Roach and Yamamoto.

| Pressure (mb) | 10 | 30 | 60 | 100 | 300 | 600 | 1000 |
|---------------------|----|----|----|-----|-----|-----|------|
| $\frac{Y-R}{Y}$ (%) | 25 | 27 | 29 | 31 | 10 | -3 | -7 |

The empirical formulae of Howard, Burch and Williams, which were used by Roach, have been criticized (see, for example, Yamamoto and Sasamori, 1961). At very low pressures the pressure dependence of the absorption should gradually decrease to zero owing to the increasing importance of weak line absorption. Although this effect was incorporated to some extent in the empirical formulae used by Roach, it was not taken into account to a sufficient degree. It may thus be expected that Roach's calculation will lead to an underestimate of the heating at low pressures, as in the stratosphere. Roach's treatment of the absorption of overlapping bands is based on an empirical formula which lacks theoretical justification. The extrapolation of this to low pressures also results in an under-estimate of stratospheric heating rates.

Although the present calculation did not extend to a sufficient height, it is expected that heating due to the CO₂+O₂ absorption will increase continuously for higher levels. Of course, the ozone absorption of ultraviolet solar radiation will be overwhelmingly predominant between the altitudes of, say, 25–60 km. However, above 60 km, where the ozone concentration decreases rapidly, it is expected that the near infrared CO₂+O₂ absorption will again be important for the heat balance of the transition layers between the ozonosphere and the ionosphere, say 60–80 km, provided that the mixing ratio of CO₂ does not change appreciably from its surface value. Doppler broadening, which prevents the decrease of the line half-width at high altitudes, favors this effect.

Heating in cloudy atmospheres was not estimated in this investigation, because the TIROS satellite series are now accumulating new information on clouds and the author hopes to use the satellite data for the calculation of heating in cloudy atmospheres.

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