

Methane and Nitrous Oxide: Their Effects on the Terrestrial Climate

L. DONNER¹ AND V. RAMANATHAN

National Center for Atmospheric Research², Boulder, CO 80307

(Manuscript received 29 May 1979, in final form 28 August 1979)

ABSTRACT

Simplified band models are developed for methane (CH₄) and nitrous oxide (N₂O) bands in the longwave radiation spectrum. The band models are then employed in a radiation model to calculate the seasonally and latitudinally varying contributions of CH₄ and N₂O to the radiative energy balance of the earth-troposphere system. From the energy balance calculations, it is concluded that the longwave opacity (i.e., the so-called "greenhouse effect") due to present-day observed concentrations of CH₄ and N₂O contribute nearly 2 K to hemispherical mean surface temperature with possible larger contributions to polar surface temperatures. The paper also discusses stratospheric effects of CH₄ and N₂O and examines the sensitivity of tropospheric radiation energy balance to large increases in CH₄ and N₂O.

1. Introduction

Methane and N₂O possess several strong absorption bands in the longwave radiation spectrum. The strength of these bands, when considered in conjunction with the observed present-day concentrations of CH₄ and N₂O, suggest that these species may exert a non-negligible influence on the present-day climate. The purpose of the present paper is to examine in detail the effects of these species on the zonal and seasonal radiative energy budget. This problem has not been considered before. However, Ellingson and Gille (1978) have included CH₄ and N₂O in their radiation model and Wang *et al.* (1976) have estimated with a radiative-convective model the sensitivity of global mean surface temperature to large increases in CH₄ and N₂O concentrations.

First, we present computationally efficient but accurate band models for longwave bands of CH₄ and N₂O. Next these band models are employed in a radiation model to estimate the following: effects on the seasonal and latitudinal radiation energy balance of the earth-troposphere system; effects on stratospheric temperatures; and sensitivity of earth-troposphere radiation energy balance to large increases in CH₄ and N₂O.

2. Model details

a. Band models

We adopt the band model proposed originally by Cess and Ramanathan (1972) and subsequently

modified slightly by Ramanathan (1976). The model describes the total band absorbance A as

$$A(U, \beta) = 2A_0 \ln \left\{ 1 + \frac{U}{[4 + U(1 + 1/\beta)]^{1/2}} \right\}, \quad (1)$$

where

$$U = SW/A_0, \quad (2)$$

$$\beta = \beta_0(P/P_0). \quad (3)$$

In Eq. (1), U is the dimensionless optical depth parameter, β the dimensionless line shape parameter with β_0 the value of β at a reference pressure of $P_0 = 1$ atm where P is the broadening pressure, and A_0 (cm⁻¹) is the bandwidth parameter. The quantities S and W are, respectively, the band intensity [cm⁻¹(cm atm)⁻¹] and the absorber amount (cm atm).

The present analysis includes the 1306 cm⁻¹ band of CH₄ and the 589 and 1285 cm⁻¹ bands of N₂O. Both these species have several other bands between 2000 and 6000 cm⁻¹ (Cess and Chen, 1975; Kunitomo *et al.*, 1977) whose contributions to terrestrial climate are negligible. For N₂O absorption in the 1285 cm⁻¹ spectral region, the analysis includes the fundamental and the first hot band and, furthermore, accounts for contribution from four isotopes. These N₂O bands overlap each other and the extension of (1) to overlapping bands is straightforward, as shown in Ramanathan (1976). The band intensity for the 1306 cm⁻¹ methane band is taken from Cess and Chen, while the N₂O band intensities are obtained from McClatchey *et al.* (1973). The band parameters A_0 and β_0 are obtained as follows. For CH₄, A_0 and β_0 were obtained by fitting A predicted by (1) to laboratory measurements of A by

¹ Present affiliation: Department of Geophysical Sciences, The University of Chicago.

² The National Center for Atmospheric Research is sponsored by the National Science Foundation.

TABLE 1. Methane and nitrous oxide band model parameters.

Parameter	CH ₄ (1306 cm ⁻¹)	N ₂ O (1285 cm ⁻¹)	N ₂ O (589 cm ⁻¹)
A ₀ (cm ⁻¹)	52 (T/300) ^{1/2}	20.4 (T/300) ^{1/2}	23 (T/300) ^{1/2}
β ₀	0.17 (300/T) ^{1/2}	1.12 (300/T) ^{1/2}	1.08 (300/T) ^{1/2}

Burch and Williams (1962a). For the N₂O band in the 1285 cm⁻¹ region, A was calculated from spectral line parameters measured by Kunitomo *et al.* (1977). These line parameters were employed in a statistical spectral band model (Malkmus, 1967) to obtain A for various values of W and P. The computed values of A were employed in (1) to obtain A₀ and β₀. For the 589 cm⁻¹ N₂O band, A₀ and β₀ were taken from Kunitomo *et al.* The computed A₀ and β₀ values for the various bands are shown in Table 1.

Fig. 1 compares the CH₄ band absorptance computed by (1) with Burch and Williams (1962a) data. We also computed A by employing the spectral parameters given by Green *et al.* (1964) in the statistical band model. The band was divided into six spectral intervals. The results obtained from these detailed calculations are also shown in Fig. 1. In addition, Table 2 compares values of A obtained from (1) with those measured by Gryvna *et al.* (1976). Generally, the agreement between (1) and measured absorptance is as good as the agreement between Green *et al.*'s detailed spectral model results and measurements. Furthermore, Green *et al.*'s model applies only in the strong line limit which is generally not valid for W < 0.1 cm atm. This limitation of Green *et al.*'s model is the source

for the large discrepancy between Eq. (1) and Green *et al.*'s model at small values of W (see Fig. 1, P = 0.5 atm).

Fig. 2 compares the N₂O band absorptance for the 1285 cm⁻¹ band as computed by (1) with the detailed band absorption calculations mentioned earlier and with laboratory data of Burch *et al.* (1960). Agreements similar to those shown in Fig. 2 are obtained when comparing (1) with absorptances measured by Burch and Williams (1962b) and by Burch *et al.* (1971).

b. Radiation model

The radiative energy budget calculations were performed with the radiation model of Ramanathan and Dickinson (1979), modified to include CH₄ and N₂O. The vertical, latitudinal and seasonal distribution of observed pressure, temperature, humidity, ozone and cloud cover as described in Ramanathan and Dickinson are combined with the CH₄ distribution of the U.S. Standard Atmosphere (1976) and the N₂O distribution of Crutzen *et al.* (1978) to define an unperturbed or base state atmosphere (surface concentration of CH₄ is 1.5 ppmv; surface concentration of N₂O is 0.30 ppmv). These observed distributions correspond to the Northern Hemisphere and, hence, our energy budget calculations apply to the Northern Hemisphere. Possible latitudinal variations in the vertical profiles of CH₄ and N₂O are not considered. The overlap of water vapor bands in the 1306 and 1285 cm⁻¹ regions with the corresponding CH₄ and N₂O bands is accounted for by multiplying the band absorptances of CH₄ and N₂O with the mean transmissivity of water vapor in the region of overlap. Similar

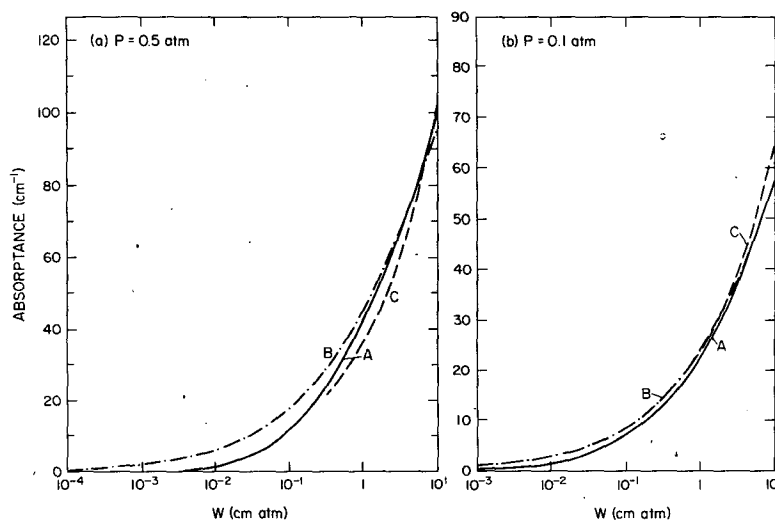


FIG. 1. Comparison of CH₄ 1306 cm⁻¹ band absorptance. A, Eq. (1) in text; B, Green *et al.*'s (1964) model; C, Burch and Williams' (1962a) data. W is the CH₄ amount (cm atm) and P is total pressure.

TABLE 2. Comparison of CH₄ 1306 cm⁻¹ band absorbance.

Total pressure (atm)	Absorber amount STP (atm cm)	Absorbance (cm ⁻¹)		
		(1)*	(2)*	Eq. (1)
1.0	0.916	50.1	54.0	51.6
1.0	0.505	35.2	47.8	41.6
1.0	0.458	34.0	41.6	36.5
1.0	0.231	22.8	31.8	24.4
0.3	0.275	18.6	20.9	19.1
0.3	0.137	12.3	15.4	12.8
0.3	0.069	7.2	11.3	8.2
0.1	0.092	7.4	7.9	6.9
0.1	0.046	3.6	5.6	4.5
0.1	0.023	2.5	4.0	2.8
0.03	0.028	2.3	2.4	2.1

* (1): Gryvnak *et al.*'s (1976) data; (2): calculated from Green *et al.*'s (1964) band model.

treatments were used to take into account overlap of CH₄ and N₂O bands in the 1285 cm⁻¹ region and the overlap by N₂O 589 cm⁻¹ band with water vapor and carbon dioxide bands. Transmissivities for water vapor were calculated using the formulations of Rodgers and Walshaw (1966), excepting the H₂O 8–12 μm continuum transmissivity, which was calculated using the method of Roberts *et al.* (1976). Green *et al.*'s (1964) model was used to calculate CH₄ transmissivity in the CH₄-N₂O overlap region. The CO₂ transmissivity in the CO₂-N₂O overlap region centered at 589 cm⁻¹ is calculated following the procedure described in Ramanathan (1976, Appendix A).

Various perturbations (adding or removing CH₄ or N₂O) were introduced after radiative flux calculations were performed for the base state. The tropospheric temperature profile was held fixed. The departure of stratospheric temperatures from the base state profiles were then calculated using the no-dynamic feedback assumption of Ramanathan and Dickinson (1979), in which the stratospheric temperatures are adjusted until the perturbation radiative heating within the stratosphere vanishes.

3. Results

The effect of removing CH₄ on the seasonal radiative energy input to the earth-troposphere system (ΔI^T) is shown in Fig. 3a and the annual mean values are shown in the lower half of Fig. 3b. Fig. 3 indicates that removing CH₄ cools the earth-troposphere system by 1–2 W m⁻², with the strongest effect at low latitudes, and the most pronounced latitudinal variation is during the winter. These latitudinal and seasonal variations are directly caused by corresponding variations in tropospheric temperature profiles. Values of annual mean ΔI^T for doubling and quadrupling CH₄ are shown in the upper half of Fig. 3b. The magnitude of ΔI^T is less for doubling CH₄ than for removing CH₄ entirely, a consequence of increasing saturation of the line centers as the concentration of CH₄ increases. The effects of perturbing N₂O concentration are shown in Fig. 4. The magnitude and latitudinal and seasonal variations of ΔI^T are quite similar to those for CH₄.

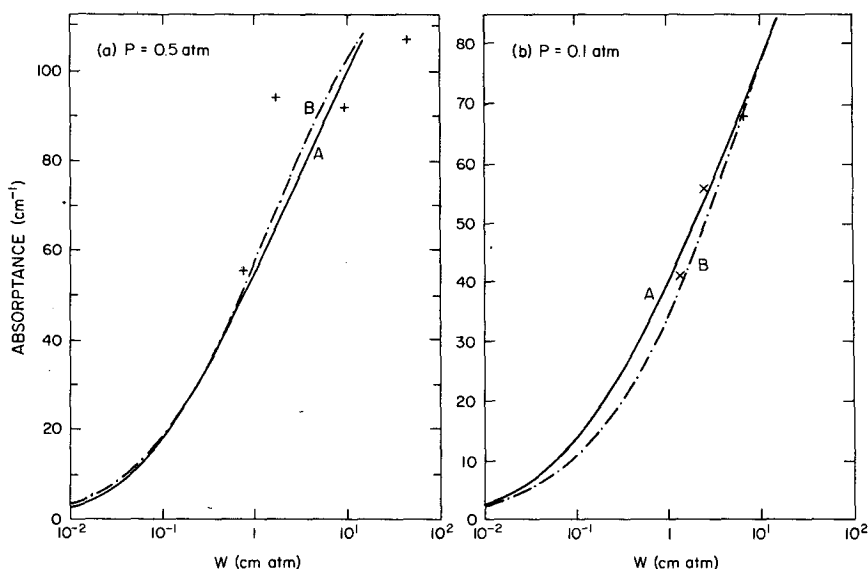


FIG. 2. As in Figure 1 except for 1285 cm⁻¹ N₂O bands. A, Eq. 1; B, statistical band model calculations from Kunitomo *et al.*'s (1977) line parameters. Laboratory data from Burch *et al.* (1960) is also shown by +’s and x’s, the former denoting P 10–15% greater than that shown in the figure and the latter P within ±5% of the value shown.

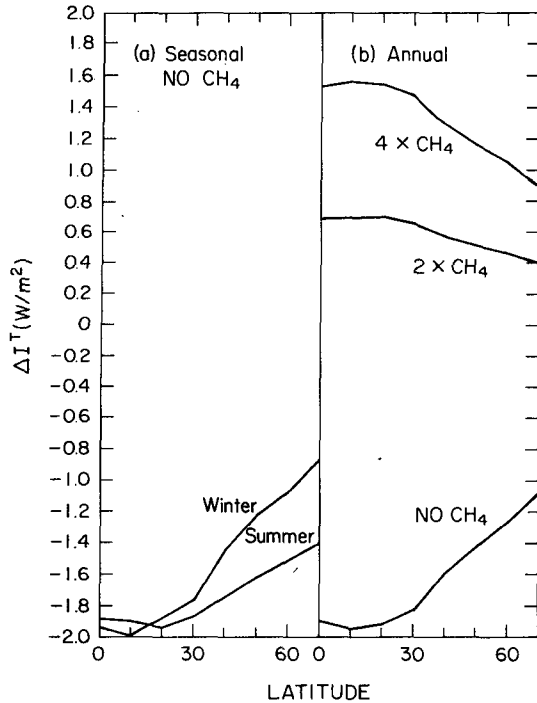


FIG. 3. Effect of CH_4 on the earth-troposphere radiative energy input. ΔI^T is the change in the energy input. (a) Seasonal values for removal of CH_4 ; (b) annual mean values for removal of CH_4 (the NO CH_4 curve), for doubling and quadrupling of CH_4 .

The effect of removing CH_4 or N_2O on the zonally and annually averaged stratospheric temperature profile at 40°N is illustrated in Fig. 5. Again, the no-dynamic feedback scheme of Ramanathan and Dickinson (1979) has been employed. Cooling in the lower stratosphere and heating further aloft is shown in Fig. 5. The temperature change profile has latitudinal variations, with the greatest temperature changes occurring at low latitudes (not shown in the figure). The cooling resulting from combined removal of CH_4 and N_2O is ~ 0.8 K in winter at the equator in the lower stratosphere. The role of CH_4 and N_2O in the hemispherical annual mean energy balance of the stratosphere is given in Table 3. These estimates were made by adding CH_4 and N_2O effects in the model, but holding the stratospheric temperatures fixed at the observed values.

The hemispherical annual mean contributions to the earth-troposphere radiative heating from CH_4 and N_2O are 1.7 and 1.4 W m^{-2} respectively, (obtained from Figs. 3b and 4b, respectively). We can relate the change in hemispherical annual mean earth-troposphere radiative heating $\langle \Delta I^T \rangle$ to a corresponding change in surface temperature $\langle \Delta T_s \rangle$ by

$$\langle \Delta T_s \rangle \approx 0.8 \langle \Delta I^T \rangle, \quad (4)$$

where the coefficient 0.8 $\text{W m}^{-2} \text{K}^{-1}$ has been obtained from Wetherald and Manabe's (1975) GCM

experiments which evaluated the sensitivity of the GCM climate to a change in solar constant. The procedure for obtaining this coefficient from the GCM experiments is described in Ramanathan (1977). The $\langle \Delta I^T \rangle$ value for CH_4 and N_2O is 3.1 W m^{-2} and from (4) it is seen that these two species may contribute about 2 K warming to the hemispherical mean surface temperature with significantly larger (by a factor of 2–3) contributions to polar regions due to ice-albedo feedback (cf., Wetherald and Manabe, 1975).

Wang *et al.* (1976) provide radiative-convective model estimates for the change in surface temperature due to a doubling of CH_4 and N_2O . A direct comparison between Wang *et al.*'s results and the present results is precluded because Wang *et al.* do not give results for ΔI^T . Furthermore, Wang *et al.* perform one-dimensional model calculations, whereas the present analysis performs latitudinal and seasonal calculations to obtain hemispherical mean ΔI^T . In spite of these differences, we provide below an approximate estimate of the differences between the two model results. As discussed in Ramanathan and Coakley (1978), the relation between $\langle \Delta I^T \rangle$ and $\langle \Delta T_s \rangle$ for a radiative-convective model with fixed relative humidity and fixed cloud altitude is given by

$$\langle \Delta T_s \rangle \approx 0.5 \langle \Delta I^T \rangle. \quad (5)$$

The coefficient 0.5 in (5) is smaller than the 0.8 value shown in (4) which applies to GCM results.

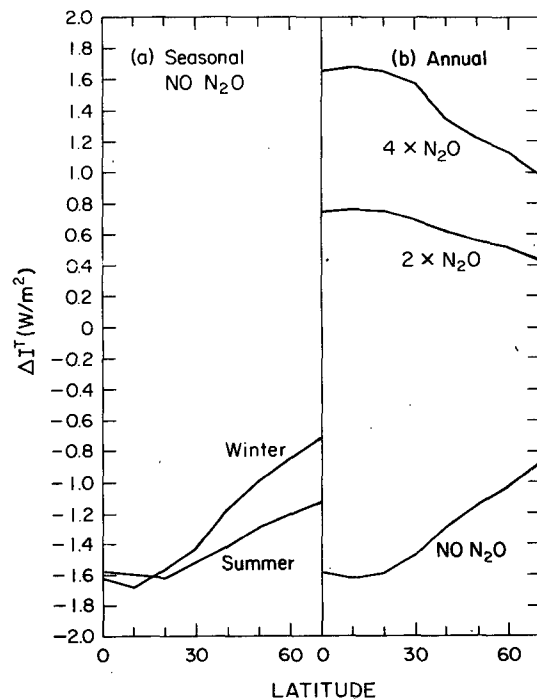


FIG. 4. As in Fig. 3 except for N_2O .

The GCM value is larger mostly due to the inclusion of ice-albedo feedback which is neglected in the radiative-convective model. From Figs. 3b and 4b, the hemispherical mean ΔI^T for doubled CH_4 is 0.61 W m^{-2} and that for N_2O is 0.65 W m^{-2} . From (5), $\langle \Delta T_s \rangle \approx 0.3 \text{ K}$ for both doubled CH_4 and for doubled N_2O . Wang *et al.* (1976) estimate 0.2 K and 0.44 K, respectively, for doubled CH_4 and doubled N_2O .

The present estimate of $\langle \Delta T_s \rangle$ for CH_4 doubling is somewhat larger than that of Wang *et al.* However, Wang *et al.* obtained $\langle \Delta T_s \rangle \approx 0.4 \text{ K}$ for CH_4 doubling by using a different set of absorption data. The value of $\langle \Delta T_s \rangle$ estimated in the present analysis lies between the low and high values computed by Wang *et al.* The present estimate of $\langle \Delta T_s \rangle$ for doubling N_2O is smaller than that of Wang *et al.* by about 30%. Wang *et al.* include the N_2O band centered at 2224 cm^{-1} . This band is neglected in the present analysis since its contribution to $\langle \Delta T_s \rangle$ is negligible. The 30% difference in the $\langle \Delta T_s \rangle$ computed by the two models (for doubling of N_2O) is perhaps due to the following modeling differences: (i) Wang *et al.*'s is a one-dimensional model calculation as opposed to the hemispherical averaging procedure employed in the present model; and (ii) the two models treat CO_2 overlap effects differ-

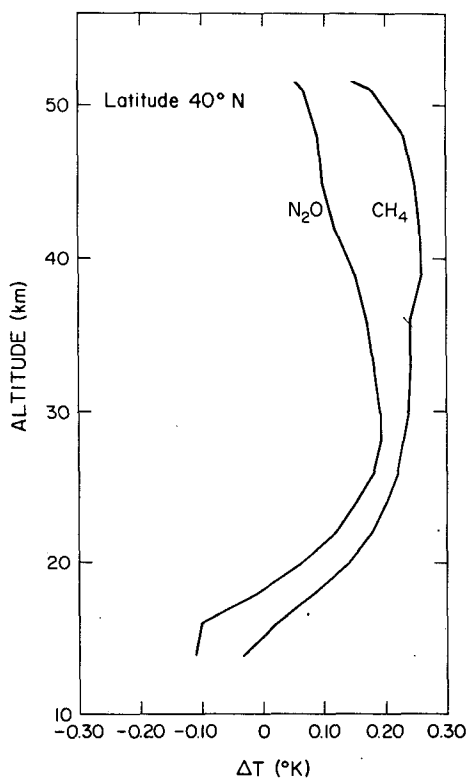


FIG. 5. Annual mean effect of removing CH_4 and N_2O at 40°N on stratospheric temperatures. ΔT is the change in stratospheric temperature from the observed values.

TABLE 3. Contribution of CH_4 and N_2O to the annual mean radiative energy balance of the Northern Hemisphere stratosphere. All units W m^{-2} . NET = absorption - emission.

	CH_4	N_2O
Emission	0.30	0.41
Absorption	0.27	0.45
NET	-0.03	0.04

ently in the 589 cm^{-1} region. The transmissivity of CO_2 in this region is a rapidly varying function of wavenumber, which makes it difficult to define a mean CO_2 transmissivity for the entire N_2O band. Consequently there could be considerable differences between the two models in the computed mean CO_2 transmissivity. This possible difference may contribute appreciably to the difference in $\langle \Delta T_s \rangle$ between the two models, particularly in view of the fact that ΔI^T due to N_2O is strongly dependent on CO_2 overlap effects (e.g., for N_2O doubling, ΔI^T without CO_2 overlap is about 60% larger than that with CO_2 overlap).

5. Summary

The latitudinally and seasonally varying contributions of CH_4 and N_2O (in their present-day concentrations) to the radiative energy budget of the surface-troposphere system are large enough to contribute approximately 2 K to the hemispherical mean surface temperature with possibly larger contributions to polar temperatures. The present results indicate the necessity for including the radiative effects of CH_4 and N_2O in climate models, at least in those climate models which explicitly allow for the radiative effects of various optically active atmospheric constituents.

Acknowledgments. Most of the work performed by one of the authors (LJD) was undertaken while a UCAR Graduate Fellow from the University of Michigan during the summer of 1978, supported by the NCAR Advanced Studies Program. Concluding work undertaken at the University of Chicago was made possible with assistance and advice of H. L. Kuo.

REFERENCES

- Burch, D. E., and D. Williams, 1962a: Total absorptance of carbon monoxide and methane in the infrared. *Appl. Opt.*, **1**, 587-594.
- , and —, 1962b: Total absorptance by nitrous oxide bands in the infrared. *Appl. Opt.*, **1**, 473-482.
- , E. B. Singleton, W. L. France and D. Williams, 1960: Infrared absorption by minor atmospheric constituents. Air Force Cambridge Research Laboratories [NTIS AD 256-952].
- , D. A. Gryvnak and J. D. Penbrook, 1971: Investigation

- of the adsorption of infrared radiation by nitrous oxide from 760 to 2380 cm^{-1} . Air Force Cambridge Research Laboratories, AFCRL No. 71-0620 [NTIS AD 739-839].
- Cess, R. D., and V. Ramanathan, 1972: Radiative transfer in the atmospheres of Mars and that of Venus above cloud deck. *J. Quant. Spectrosc. Radiat. Transfer*, **12**, 933-945.
- , and S. C. Chen, 1975: The influence of ethane and acetylene upon the thermal structure of the Jovian atmosphere. *Icarus*, **26**, 444-450.
- Crutzen, P. J., I. S. A. Isaksen and J. R. McAfee, 1978: The impact of the chlorocarbon industry on the ozone layer. *J. Geophys. Res.*, **83**, 345-363.
- Ellingson, R. G., and J. G. Gille, 1978: An infrared radiative transfer model. Part 1: Model description and comparison of observations with calculations. *J. Atmos. Sci.*, **35**, 523-545.
- Green, A. E. S., C. S. Lindenmeyer and M. Griggs, 1964: Molecular absorption in planetary atmospheres. *J. Geophys. Res.*, **69**, 493-504.
- Grzywnak, D. A., D. E. Burch, R. L. Alt and D. K. Zgonc, 1976: Infrared absorption by CH_4 , H_2O and CO_2 . Air Force Geophysics Laboratories, AFGL-TR-76-0246 [NTIS AD A039 380/161].
- Kunitomo, T., S. Ueoka, H. Masuzaki and K. Utsonomiya, 1977: Emissivity and band model parameters for infrared bands of nitrous oxide. *J. Quant. Spectrosc. Radiat. Transfer*, **18**, 405-417.
- Malkmus, W., 1967: Random Lorentz band model with exponential-tailed S^{-1} line-intensity distribution function. *J. Opt. Soc. Amer.*, **57**, 323-329.
- McClatchey, R. A., W. S. Benedict, S. A. Clough, D. E. Burch, R. F. Calfee, K. Fox, L. S. Rothman and J. S. Goring, 1973: AFCRL atmospheric absorption line parameters compilation. Air Force Cambridge Research Laboratories, AFCRL-TR-73-0096 [NTIS AD 762 904].
- Ramanathan, V., 1976: Radiative transfer within the earth's troposphere and stratosphere: A simplified radiative-convective model. *J. Atmos. Sci.*, **33**, 1330-1346.
- , 1977: Interactions between ice-albedo, lapse rate and cloud top feedbacks: Analysis of the nonlinear response of a GCM climate model. *J. Atmos. Sci.*, **34**, 1885-1897.
- , and J. A. Coakley, 1978: Climate modeling through radiative-convective models. *Rev. Geophys. Space Phys.*, **16**, 465-489.
- , and R. E. Dickinson, 1979: The role of stratospheric ozone in the zonal and seasonal radiative energy balance of the earth-troposphere system. *J. Atmos. Sci.*, **36**, 1084-1104.
- Roberts, R. E., J. E. A. Selby and L. M. Biberman, 1976: Infrared continuum absorption by atmospheric water vapor in the 8-12 μm window. *Appl. Opt.*, **15**, 2085-2090.
- Rodgers, C. D., and C. D. Walshaw, 1966: The computation of infrared cooling rate in planetary atmospheres. *Quart. J. Roy. Meteor. Soc.*, **92**, 67-92.
- U.S. Standard Atmosphere, 1976: *U.S. Standard Atmosphere, 1976*. NOAA-S/T 76-1562, U.S. Government Printing Office, 227 pp.
- Wang, W. C., Y. L. Yung, A. A. Lacis, T. Mo and J. E. Hansen, 1976: Greenhouse effects due to man-made perturbations of trace gases. *Science*, **194**, 685-690.
- Wetherald, R. T., and S. Manabe, 1975: The effects of changing the solar constant on the climate of a general circulation model. *J. Atmos. Sci.*, **32**, 2044-2059.