

A Study of the Radiative Effects of the 9.4- and 10.4-Micron Bands of Carbon Dioxide

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The potential radiative impact of the relatively weak 9.4- and 10.4- μm bands of CO_2 is investigated. Line-by-line calculations are employed as a standard against which to compare the accuracy of laboratory data, narrow-band models, and broadband models. A comparison of the line-by-line calculations to laboratory data demonstrates that the line-by-line procedure and laboratory data typically yield comparable results; however, there are cases of substantial disagreement between the line-by-line results and the laboratory data. It is observed that the Goody narrow-band model yields band absorptances in good agreement with the reference line-by-line calculations. For application to climate models, new broadband parameterizations, which are consistent with the band intensities found on the 1986 Air Force Geophysics Laboratory HITRAN data base, are presented for the 9.4- and 10.4- μm bands of CO_2 . Clear-sky flux calculations demonstrate that for projected increases of CO_2 the impact of the 9.4- and 10.4- μm bands is comparable to that attributed to projected increases of tropospheric ozone.

1. INTRODUCTION

Carbon dioxide exerts a significant radiative influence on the thermal structure of the atmospheres of Venus, Earth, and Mars. Many studies have focused on the radiative effects of the relatively strong absorption in the infrared due to the 15- μm band system and in the near infrared due to bands located between 1.5 and 4.5 μm . Carbon dioxide also possesses "weaker" absorption bands located at 9.4 and 10.4 μm . Most climate studies have neglected the importance of these bands. As concern grows over the radiative importance of various trace gases, however, it is important to consider the relative role of these weak bands of CO_2 with respect to the radiative role of various trace gases. Furthermore, Kiehl and Dickinson [1987], hereafter referred to as KD, have shown that these bands of CO_2 can exert a substantial climate effect for paleoclimate conditions. Indeed, projected enhancements of the CO_2 abundance for the paleoclimate of the Earth indicate that the atmospheric window region would be effectively closed by the presence of the 9.4- and 10.4- μm bands of CO_2 (e.g., see Figure 5 of KD).

The purpose of this work is to discuss the climatic impact and parameterization of the 9.4- and 10.4- μm bands of CO_2 . Section 2 begins with the presentation of the reference line-by-line procedure. The Goody narrow-band model is then demonstrated to yield band absorptances for the 9.4- and 10.4- μm bands of CO_2 which are in good agreement to those of the line-by-line calculations. Next for the sake of completeness, the broadband model described by Kiehl and Ramanathan [1983] is used to parameterize the homogeneous band absorptances of the reference line-by-line calculations for the 9.4- and 10.4- μm bands of CO_2 . Thus a

hierarchy of models is obtained which yield very similar homogeneous band absorptances.

The narrow-band model is employed in section 3 to calculate the radiative impact of the 9.4- and 10.4- μm bands of CO_2 for a clear-sky atmosphere containing not only CO_2 , but also O_3 and H_2O . The climatic effect of the 9.4- and 10.4- μm bands for enhanced CO_2 abundances are compared with results for the potential increases in various trace gases. Finally, the narrow-band and broadband models are compared to the line-by-line model for assumed paleoclimatic CO_2 amounts.

2. RADIATION MODELS

Line-by-Line Model

The line-by-line procedure is currently the most detailed approach for calculating molecular line absorption. For present purposes, both Voigt and Lorentz line shapes are employed with a wave number cutoff of 5 cm^{-1} ; i.e., the spectral absorption coefficient includes the effects of all rotational lines within a 10 cm^{-1} range centered at the wave number of the absorption coefficient. Such a cutoff is not only incorporated for computational efficiency, but is also an effective parameterization of the sub-Lorentzian nature of the far wings of the CO_2 lines [Fels and Schwarzkopf, 1981]. Furthermore, sensitivity studies indicate that larger wave number cutoffs add little to the band absorptance for atmospheric conditions (in agreement with Crisp *et al.* [1986] and Chou and Kouvaris [1986]). Sensitivity studies have also revealed that a wave number integration interval of 0.005 cm^{-1} is suitable for the 9.4- and 10.4- μm bands of CO_2 .

The line locations, intensities, air-broadened half widths, and lower state energies were taken from the 1986 version of the Air Force Geophysics Laboratory (AFGL) HITRAN data base [Rothman *et al.*, 1987], incorporating the lines for the 9.4- and 10.4- μm bands from the band systems given in

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TABLE 1. Band Parameters for the 9.4- μm and 10.4- μm Bands of CO₂

Band	ν_0 , cm ⁻¹	$S_0^0 (\times 10^{-22})$ at $T_0 = 296$ K, cm ⁻¹ (molecule cm ⁻²)	E''_{j-1} , cm ⁻¹	d_{j-1} , cm ⁻¹
9.4- μm Band				
1	1063.734	9.6863	1285.409	1.56
2	1071.540	0.7626	1933.352	0.78
3	1074.239	0.0304	2587.374	0.78
10.4- μm Band				
1	960.959	6.8008	1388.185	1.56
2	941.696	0.0136	2671.143	1.56
3	927.157	0.4144	2077.636	0.78

Table 1. The wave number regions involved in the line-by-line calculations span the range from 981 to 1114 cm⁻¹ for the 9.4- μm band and 863 to 1007 cm⁻¹ for the 10.4- μm band. The temperature dependence of the line intensities, $S(T)$, is given by

$$S(T) = S_0 \frac{Z_v(T_0)}{Z_v(T)} \left(\frac{T_0}{T} \right) \exp \left[\frac{hc}{k} E'' \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (1)$$

where h is Planck's constant, c is the speed of light, k is Boltzmann's constant, E'' is the energy of the lower state, Z_v is the vibrational partition function, $T_0 = 296$ K, S_0 is the line intensity at T_0 , and the exponent for the temperature dependence of the line intensity is taken to be 1.0 because CO₂ is a linear molecule. The air-broadened Lorentz half width was taken to be

$$\gamma = \gamma_i^0 \left(\frac{P_e}{P_0} \right) \left(\frac{T_0}{T} \right)^{0.5} \quad (2)$$

for each line, where γ_i^0 is the half width of the i th line, $P_0 = 1$ atm, and P_e is the effective pressure given by

$$P_e = P[1 + 0.3\mu\text{CO}_2] \quad (3)$$

where μCO_2 is the CO₂ volumetric mixing ratio. Note that the use of a constant average half width in place of the variable half widths, employed in this set of calculations, leads to approximately a 1% change in the flux calculations. The exponent of the temperature dependence of the air-broadened half width was taken from the kinetic theory of gases and thus is $\frac{1}{2}$. If the exponent of the temperature dependence were taken to be $\frac{2}{3}$, as is suggested from spectroscopic data of Yamamoto *et al.* [1969] for the 15- μm band of CO₂, less than a 0.5% difference is realized in the flux calculations.

Total band absorptances as calculated by the line-by-line procedure have been compared to the laboratory data of Burch *et al.* [1962] and Edwards [1960]. The Burch *et al.* data comprise 42 experimental points, and the Edwards data comprise 13 experimental points for band absorptances due to both the 9.4- and 10.4- μm bands. It is observed that the mean of the differences, normalized to the line-by-line calculations, between the line-by-line calculations and the Burch *et al.* data are $-4.5 \pm 4.7\%$ for the 9.4- μm band and $-0.4 \pm 6.7\%$ for the 10.4- μm band.

The comparison of the results of the line-by-line calculations to the Edwards [1960] data is similar to the comparison

of the broadband parameterization to the Edwards data found in Table A2 of KD. In both comparisons, the Edwards data demonstrate a disturbing tendency to deviate substantially from the theoretical calculations. Furthermore, while the present line-by-line calculations and the broadband calculations of KD are self-consistent, the Edwards data are not. This leads to significant doubt to the accuracy of the Edwards data.

It should be noted that the information contained in both of these laboratory data sets is for temperatures greater than or equal to 294 K and, in general, for pressures in excess of 1 atm, conditions not typical of the present climate. New laboratory band absorptance data for the 9.4- and 10.4- μm bands of CO₂, especially at lower temperatures and pressures, would therefore prove beneficial in determining the accuracy of the theoretical procedures presented here.

Narrow-Band Model

The two most commonly used narrow-band (or random-band) models are those of Goody [1952] and Malkmus [1967]. Letting $T_{\Delta\omega}$ denote the transmittance for a given spectral interval $\Delta\omega$, the Goody [1952] model is given by

$$T_{\Delta\omega} = \exp \left[-\frac{S_{\Delta\omega} m}{\Delta\omega} \left[1 + \left(\frac{S_{\Delta\omega} m}{\pi \bar{\gamma}} \right)^2 \right]^{-1/2} \right] \quad (4)$$

where $S_{\Delta\omega}$ is the sum of the line intensities within the interval $\Delta\omega$, m is the absorber amount, and $\bar{\gamma}$ is defined by the relation

$$\bar{\gamma} = \frac{4}{\pi} \frac{\left[\sum (S_i \gamma_i)^{1/2} \right]^2}{\sum S_i} \quad (5)$$

where S_i and γ_i denote the individual line intensities and line half widths, respectively, and the summation is over all lines within $\Delta\omega$. The Malkmus [1967] model is given by

$$T_{\Delta\omega} = \exp \left\{ -\frac{\pi \bar{\gamma}}{2\Delta\omega} \left[\left(1 + \frac{4S_{\Delta\omega} m}{\pi \bar{\gamma}} \right)^{1/2} - 1 \right] \right\} \quad (6)$$

As discussed by Kiehl and Ramanathan [1983], the Malkmus model yields much better agreement than the Goody model to the measured absorptances of Gryvnak *et al.* [1976] for the 560–780 cm⁻¹ region of the 15- μm band of CO₂. As noted by Kratz [1987], however, it is judicious to investigate the behavior of each band to discover which narrow-band model produces the best agreement with reference values. As will be demonstrated, for the 9.4- and 10.4- μm bands of CO₂, the Goody model yields the best results.

The spectroscopic data employed for the narrow-band models is identical to those used by the line-by-line procedure. For present purposes, the narrow-band model computations were performed with $\Delta\omega = 5$ cm⁻¹. As discussed by Kiehl and Ramanathan [1983] with respect to the 15- μm band of CO₂, significant errors can occur if an overly large spectral interval is employed. This is due to the statistics of the band structure, as manifested by the averaging procedure of (5), being variable throughout the band. The use of narrow intervals will of course minimize this effect; however, if the intervals are too narrow, it will not contain a sufficient number of lines to yield meaningful statistics.

Both the Goody and Malkmus narrow-band models have been compared to line-by-line calculations utilizing a temperature of 260 K and pressures of 1.0 and 0.1 atm, conditions typical for the present atmosphere. For these conditions there is very little to no distinction between the use of either the Voigt or Lorentz line shape within the line-by-line calculations, thus assuring consistency with the narrow-band models which incorporate Lorentz line shapes. An examination of the line strength distributions of the 9.4- and 10.4- μm bands of CO₂ suggests that the Goody narrow-band model should prove superior to the Malkmus narrow-band model for these bands, since the Goody probability distribution function is more representative of the line strength distributions of the 9.4- and 10.4- μm bands of CO₂. Indeed, the comparisons of the narrow-band models to the line-by-line calculations clearly reveal that the Goody narrow-band model produces the best results. Specifically, for a range of CO₂ abundances of 10^{-4} to 10 g/cm², the Goody model tends to remain within $\pm 6\%$ of the line-by-line calculations, while the Malkmus model varies between a 6% overestimate to a 16% underestimate. For this reason, the Goody model is adopted for subsequent calculations. Figures 1 and 2 illustrate comparisons of the Goody narrow-band model and line-by-line calculations for the 9.4- and 10.4- μm bands for a temperature of 260 K and pressures of 1.0 and 0.1 atm, respectively.

Broadband Model

The band intensities found on the 1986 AFGL HITRAN data base [Rothman *et al.*, 1987] for the 9.4- and 10.4- μm bands of CO₂ are substantially stronger than those listed by KD. With this in mind, the broadband procedure described by Kiehl and Ramanathan [1983] was employed to produce new parameterizations for the absorptance due to the 9.4- and 10.4- μm band systems. Recall that each of these systems is comprised of a number of individual bands. As with KD, the three strongest bands in each system were chosen. For each of these bands, the locations, intensities, lower state energies, and mean line spacing are given in Table 1. The units employed for the band intensities in Table 1 were chosen to be consistent with the units employed by the AFGL HITRAN data base [Rothman *et al.*, 1987]. Multiplying the band intensities by 2.446×10^{19} will facilitate a comparison with the band intensities presented by KD in their Table A1.

Following the discussion in the appendix of KD and employing as a reference the line-by-line results for the total band absorptance at a temperature of 260 K and pressures of 1.0 and 0.1 atm, the effective bandwidth parameter $A_0(T)$ is found to be for the 9.4- μm band

$$A_0(T) = 32.32(T/296.0)^{1/2} \quad (7)$$

and for the 10.4- μm band

$$A_0(T) = 33.07(T/296.0)^{1/2} \quad (8)$$

The much smaller values for the $A_0(T)$, as compared to KD, are a direct consequence of the enhanced band intensities contained on the 1986 AFGL HITRAN data base. Furthermore, the new values of $A_0(T)$ are significantly closer to values anticipated by analogy with the 15- μm band of CO₂.

The results from the calculated band absorptances for the

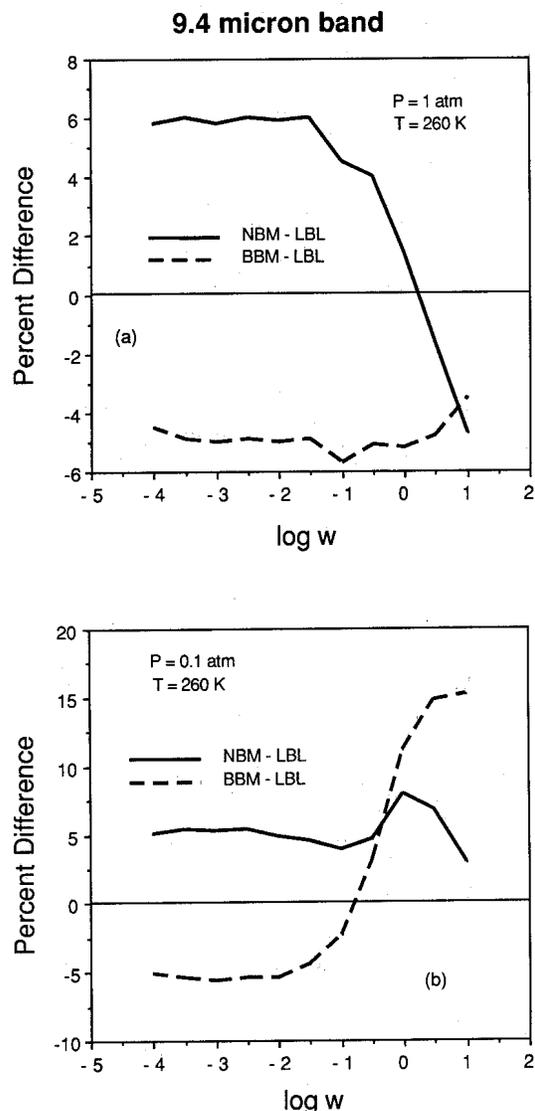


Fig. 1. Comparisons of narrow-band and broadband calculations to those of the line-by-line procedure for the total band absorptance of the 9.4- μm band of CO₂ for a temperature of 260 K and pressures of (a) 1.0 atm and (b) 0.1 atm.

broadband models are compared to the line-by-line results in Figures 1 and 2. The accuracy of the new broadband parameterizations are comparable to those of KD. The new values for $A_0(T)$, however, are consistent with the 1986 AFGL HITRAN data base, whereas the old values for $A_0(T)$ are not. It should be noted that, for consistency with other broadband models for CO₂, the mean half width employed for the broadband calculations was that of Kiehl and Ramanathan [1983]. As noted in the discussion of the line-by-line calculations, the use of a mean half width does not lead to a significant degradation of the model calculations.

3. ATMOSPHERIC FLUX CALCULATIONS

The relative importance of the radiative effects of the 9.4- and 10.4- μm bands of CO₂ can be understood by considering the effects of these bands upon the net infrared flux at the top of the atmosphere (50 km), the tropopause (13 km), and the surface. To be compatible with the Intercomparison of

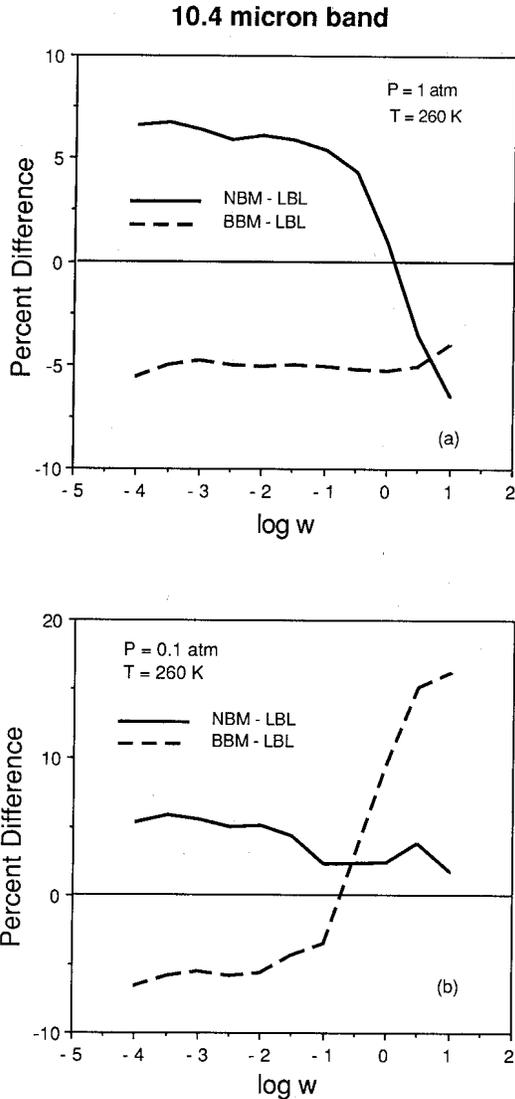


Fig. 2. Comparisons of narrow-band and broadband calculations to those of the line-by-line procedure for the total band absorptance of the 10.4- μm band of CO₂ for a temperature of 260 K and pressures of (a) 1.0 atm and (b) 0.1 atm.

Radiation Codes Used in Climate Models (ICRCCM) [Luther and Fouquart, 1984], the mid-latitude summer atmosphere of McClatchey *et al.* [1972] is adopted. Moreover, since the focus of the present work is on the radiative effects of 9.4- and 10.4- μm bands of CO₂ for the clear-sky case, overlap with clouds will not be considered. Fluxes are evaluated following the procedure described by Cess *et al.* [1986].

To better understand the potential impact of the 9.4- and 10.4- μm bands of CO₂, narrow-band model calculations have been performed which take into consideration the overlap of these bands with H₂O and O₃. To account for the overlap of the different gases, the transmissivity multiplication property [e.g., Goody, 1964] was employed. It has been demonstrated [Kratz, 1987] that the transmissivity multiplication property when utilized by a random-line narrow-band model is a valid technique to account for the overlap of the absorption bands of different gases. To determine the absorption of the 9.4- and 10.4- μm bands of CO₂, the Goody narrow-band model was employed. For the 9.6- μm band of

TABLE 2. Comparison of Model Calculations for the Reduction in the Infrared Flux due the Presence of the 9.4- μm and 10.4- μm Bands of CO₂, for a CO₂ Mixing Ratio of 3.0×10^{-4}

Model	Flux Reduction, W m ⁻²		
	Top (50)	Tropopause (13)	Surface
<i>9.4-μm Band</i>			
Line-by-line	0.355	0.336	0.882
Goody narrow band	0.358	0.334	0.854
Malkmus narrow band	0.329	0.309	0.787
Broadband	0.362	0.337	0.865
<i>10.4-μm Band</i>			
Line-by-line	0.278	0.265	0.790
Goody narrow band	0.275	0.259	0.751
Malkmus narrow band	0.255	0.241	0.696
Broadband	0.280	0.262	0.764

O₃ the Malkmus narrow-band model was employed, as recommended by Kratz and Cess [1988], while for the line absorption due to H₂O the Goody model was employed, as suggested by Kratz [1987]. For the water vapor continuum the method of Roberts *et al.* [1976] was utilized.

Reductions in the net upward flux due to the presence of the 9.4- and 10.4- μm bands of CO₂ are presented in Table 2 for a CO₂ mixing ratio of 3.0×10^{-4} , a value consistent with the ICRCCM (Luther and Fouquart). As demonstrated by Table 2, the Goody narrow-band model is quite adequate at reproducing the results of the line-by-line procedure. As with the band absorptance results, it is observed that for these bands the Malkmus model is somewhat inferior to the Goody model. Differences between the narrow-band models and the reference line-by-line calculations tend to be consistent with the band absorptance results. For completeness, the results of the flux calculations employing the presently derived broadband parameterizations are also presented in Table 2. It is observed that the broadband flux calculations compare favorably with the flux calculations of the line-by-line procedure.

Comparisons of the flux reductions due to the 9.4- and 10.4- μm bands of CO₂ are presented in Table 3 for the clear-sky mid-latitude summer cases of no overlap, overlap by O₃, overlap by H₂O, and overlap by O₃ and H₂O. There

TABLE 3. Comparison of Goody Narrow-Band Model Calculations for the Reduction in the Infrared Flux due to the Presence of the 9.4- μm and 10.4- μm Bands of CO₂, for a CO₂ Mixing Ratio of 3.0×10^{-4} , for the Clear-Sky Cases of No Overlap, Overlap by O₃, Overlap by H₂O, and Overlap by O₃ and H₂O

Overlap Gases	Flux Reduction, W m ⁻²		
	Top (50)	Tropopause (13)	Surface
<i>9.4-μm Band</i>			
	0.358	0.334	0.854
O ₃	0.203	0.255	0.665
H ₂ O	0.272	0.252	0.350
O ₃ and H ₂ O	0.161	0.200	0.291
<i>10.4-μm Band</i>			
	0.275	0.259	0.751
O ₃	0.272	0.258	0.746
H ₂ O	0.200	0.186	0.261
O ₃ and H ₂ O	0.198	0.186	0.260

TABLE 4. Comparison of Goody Narrow-Band Model Calculations for the Change in the Reduction in the Infrared Flux due to the Presence of the 9.4- μm and 10.4- μm Bands of CO₂, for an Increase in the CO₂ Mixing Ratio From 3.0×10^{-4} to 6.0×10^{-4} , for the Clear-Sky Cases of No Overlap, Overlap by O₃, Overlap by H₂O, and Overlap by O₃ and H₂O

Overlap Gases	Flux Reduction, W m ⁻²		
	Top (50)	Tropopause (13)	Surface
<i>9.4-μm Band</i>			
	0.265	0.254	0.620
O ₃	0.153	0.197	0.495
H ₂ O	0.211	0.201	0.286
O ₃ and H ₂ O	0.125	0.161	0.232
<i>10.4-μm Band</i>			
	0.214	0.206	0.572
O ₃	0.212	0.205	0.569
H ₂ O	0.163	0.156	0.215
O ₃ and H ₂ O	0.162	0.155	0.215

are several notable aspects of the results of Table 3. First, there exists a substantial impact by overlapping H₂O on both CO₂ bands. Second, the impact of overlapping the 9.6- μm band of O₃ with the 9.4- μm band of CO₂ is comparable to the overlapping H₂O with this band. It should be noted, however, that the effects of O₃ are concentrated in the stratosphere while those of H₂O are concentrated in the troposphere. Third, there is a virtual absence of overlap of the 9.6- μm band of O₃ with the 10.4- μm band of CO₂. This is as anticipated from an examination of the spectral data. Finally, the net flux reductions of both CO₂ bands are nearly equal.

Table 4 yields a comparison similar to Table 3 except that here the impact of doubling the CO₂ mixing ratio from 3.0×10^{-4} to 6.0×10^{-4} is examined. From Table 4, it can be seen that the combined change in the flux reduction at the tropopause for both bands for a doubling of CO₂ is 0.316 W m^{-2} . This value is nearly 10% of that attributed to a doubling of CO₂ due to the 15- μm band system alone.

Calculations have also been carried out for an increase in CO₂ from 339 to 450 ppmv to compare the forcing of the 9.4- and 10.4- μm bands with the trace gas forcing calculated by Ramanathan *et al.* [1985]. The forcing at the tropopause due to the CO₂ bands is 0.12 W m^{-2} for clear-sky conditions. Ramanathan *et al.* employed a model that included clouds. The presence of clouds, in general, reduces the climate forcing by $\sim 20\%$; thus the forcing due to the 9.4- and 10.4- μm bands is $\sim 0.1 \text{ W m}^{-2}$. This is to be compared with a forcing of 0.7 W m^{-2} from CFC11 (CFC1₃) and CFC12 (CF₂C1₂), and a forcing of 0.1 W m^{-2} from an increase in tropospheric O₃. The 9.4- and 10.4- μm band forcing is smaller than the forcing due to CFC11 and CFC12 due to the more rapid growth rate of the CFCs. For present amounts of these gases the forcings are approximately the same. Thus the 9.4- and 10.4- μm bands contribute as much or more greenhouse warming than that due to projected increases in tropospheric ozone and a few of the chlorocarbons (e.g. CH₃CCl₃).

To further determine the potential impact of these bands of CO₂, calculations have been performed to find the change in the mid-latitude summer heating rates due to a doubling of CO₂ from a mixing ratio of 3.0×10^{-4} to 6.0×10^{-4} . The heating rate calculations were performed not only for the

9.4- and 10.4- μm bands, but also the 15- μm band. In this manner the relative effects of the various bands could be compared. For the 9.4- and 10.4- μm bands the Goody narrow-band model was employed, while for the 15 μm band the Malkmus narrow-band model was employed as suggested by Kiehl and Ramanathan [1983]. The combined effect of the 9.4- and 10.4- μm bands, which present nearly identical heating rate profiles, is to enhance by nearly a factor of three the cooling in the lower troposphere. Elsewhere in the atmosphere the effect of the 15- μm band dominates.

In order to gauge the potential impact of these bands of CO₂ on the paleoclimate as well as on the present climate, flux reduction calculations were performed not only for the nominal abundance of CO₂, assumed to have a mixing ratio of 3.0×10^{-4} , but also for $2\times$, $4\times$, $8\times$, $12\times$, $25\times$, $100\times$, and $1000\times$ this abundance. Percentage differences of the narrow-band and broadband model surface-troposphere forcing from the line-by-line results for the two bands are shown in Figure 3. With the exception of extremely large enhancements of CO₂ the Goody model tends to yield results within 2% of the line-by-line procedure for the 9.4- μm band and within 4% of the line-by-line procedure for the 10.4- μm band. For enhancements of CO₂ by $100\times$ and $1000\times$ the Goody model underestimates the results of the line-by-line procedure by 6–8% for both bands. The broadband model is accurate to within 7% for both bands for CO₂ amounts below $100\times$ present levels. Large errors, however, occur for CO₂ amounts that are $1000\times$ present amounts. Recent calculations by KD indicate that amounts of approximately $200\times$ the present CO₂ could have offset the reduced solar luminosity in the early Archean. Thus the broadband models would still be sufficiently accurate to model these conditions, but would severely overestimate the radiative forcing for Venuslike conditions.

4. CONCLUDING REMARKS

Clear-sky flux calculations, which specifically account for the overlap of the 9.4- and 10.4- μm bands of CO₂ with the 9.6- μm band of O₃ and with H₂O, have demonstrated that the impact at the tropopause of the 9.4- and 10.4- μm bands of CO₂ for a doubling of CO₂ is nearly 10% of that attributed to the 15- μm band system for a doubling of CO₂. Comparisons of the forcing from these bands to the trace gas forcing obtained by Ramanathan *et al.* [1985] indicate that they contribute as much or more greenhouse warming as the projected increases in tropospheric O₃ or some of the chlorocarbons.

The present study has also demonstrated that the narrow-band model of Goody [1952] produces total band absorptances for the 9.4- and 10.4- μm of CO₂, which are in very good agreement with reference line-by-line calculations. For completeness and for consistency, new broadband parameterizations have been presented. It is found that the effective bandwidth parameters are significantly smaller than those presented by Kiehl and Dickinson [1987]. This has been attributed to the substantial increase in the band intensities from the data set employed by Kiehl and Dickinson [1987] to the 1986 version of the AFGL HITRAN data base employed in the present work.

Finally, comparisons of line-by-line calculations to laboratory data of Burch *et al.* [1962] and Edwards [1960] have

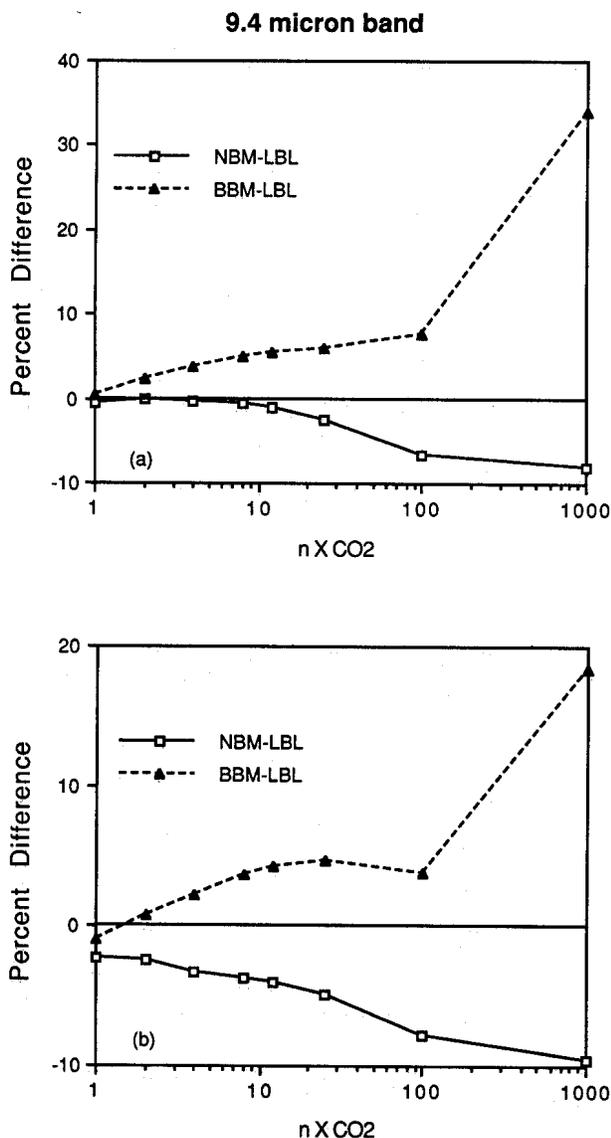


Fig. 3. Percentage differences of the Goody narrow-band model and the broadband model to the line-by-line procedure for the flux reductions at the tropopause for (a) the 9.4- and (b) the 10.4- μm bands of CO₂ for a range of CO₂ enhancements from 1 to 1000 times the current abundance.

demonstrated that, in general, the line-by-line calculations agree fairly well with the laboratory data. There is, however, a tendency for the line-by-line calculations to underestimate the Burch *et al.* [1962] data by 0–5%, and there are cases where the line-by-line calculations disagree significantly with the Edwards [1960] data. Moreover, both of the laboratory data sets are for temperatures and pressures which are not typical for the conditions of the present climate. This emphasizes the need for improved laboratory band absorbance measurements. In particular, such issues as possible departures from the Lorentzian line shape and the temperature dependence of the band intensity of these upper state bands can not be addressed without the availability of accurate laboratory measurements.

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REFERENCES

- Burch, D. E., D. Gryvnak, E. B. Singleton, W. L. France, and D. Williams, Infrared absorption by carbon dioxide, water vapor, and minor atmospheric constituents, *Rep. AFCRL-62-698*, 316 pp., Air Force Cambridge Res. Lab., Bedford, Mass., 1962.
- Cess, R. D., D. P. Kratz, S. J. Kim, and J. Caldwell, Infrared radiation models for atmospheric methane, *J. Geophys. Res.*, **91**, 9857–9864, 1986.
- Chou, M. -D., and L. Kouvaris, Monochromatic calculations of atmospheric radiative transfer due to molecular line absorption, *J. Geophys. Res.*, **91**, 4047–4055, 1986.
- Crisp, A., S. B. Fels, and M. D. Schwarzkopf, Approximate methods for finding CO₂ 15-micron band transmission functions in the atmospheres of Venus, Earth, and Mars, *J. Geophys. Res.*, **91**, 11,851–11,866, 1986.
- Edwards, D. K., Absorption by infrared bands of carbon dioxide gas at elevated pressures and temperatures, *J. Opt. Soc. Am.*, **50**, 617–626, 1960.
- Fels, S. B., and M. D. Schwarzkopf, An efficient, accurate algorithm for calculating CO₂ 15- μm band cooling rates, *J. Geophys. Res.*, **86**, 1205–1232, 1981.
- Goody, R. M., A statistical model for water vapor absorption, *Q. J. R. Meteorol. Soc.*, **78**, 165–169, 1952.
- Goody, R. M., *Atmospheric Radiation*, 436 pp., Oxford University Press, New York, 1964.
- Gryvnak, D. A., D. E. Burch, R. L. Alt, and D. K. Zgonc, Infrared absorption by CH₄, H₂O and CO₂, *Rep. AFGL-TR-76-0246*, 84 pp., Air Force Geophys. Lab., Bedford, Mass., 1976.
- Kiehl, J. T., and R. E. Dickinson, A study of the radiative effects of enhanced atmospheric CO₂ and CH₄ on early Earth surface temperatures, *J. Geophys. Res.*, **92**, 2991–2998, 1987.
- Kiehl, J. T., and V. Ramanathan, CO₂ radiative parameterizations used in climate models: Comparisons with narrow-band models and with laboratory data, *J. Geophys. Res.*, **88**, 7537–7545, 1983.
- Kratz, D. P., The effects of minor trace gases on the transfer of thermal infrared radiation through the Earth's atmosphere, Ph.D. thesis, 210 pp., State Univ. of N. Y. at Stony Brook, 1987.
- Kratz, D. P., and R. D. Cess, Infrared radiation models for atmospheric ozone, *J. Geophys. Res.*, **93**, 7047–7054, 1988.
- Luther, F. M., and Y. Fouquart, the intercomparison of radiation codes in climate models (ICRCCM), *Rep. WCP-93*, 37 pp., World Meteorol. Organ., Geneva, 1984.
- Malkmus, W., Random Lorentz band model with exponential-tailed S^{-1} line-intensity distribution function, *J. Opt. Soc. Am.*, **57**, 323–329, 1967.
- McClatchey, R. A., R. W. Fenn, J. E. Selby, F. E. Volz, and J. S. Garing, Optical properties of the atmosphere, 3rd ed., *Environ. Res. Pap. 411*, 108 pp., Air Force Cambridge Res. Lab., Bedford, Mass., 1972.
- Ramanathan, V., R. J. Cicerone, H. B. Singh, and J. T. Kiehl, Trace gas trends and their potential role in climate change, *J. Geophys. Res.*, **90**, 5547–5566, 1985.
- Roberts, R. E., J. E. A. Selby, and L. M. Biberman, Infrared continuum absorption by atmospheric water vapor in the 8–12 μm window, *Appl. Opt.*, **15**, 2085–2090, 1976.
- Rothman, L. S., et al., The HITRAN database, 1986 edition, *Appl. Opt.*, **26**, 4058–4097, 1987.
- Yamamoto, G., M. Tanaka, and T. Aoki, Estimation of rotational line widths of carbon dioxide bands., *J. Quant. Spectrosc. Radiat. Transfer*, **9**, 371–382, 1969.
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