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Overlap Emissivity of CO_2 and H_2O in the 15-μm Spectral Region

Abstract: Radiative transfer in model atmospheres including CO_2, water vapor, ozone, and clouds can be explored by computer simulation for the purpose of predicting the mean temperature at the surface of the earth. Where two or more gases have overlapping absorption lines, the overlap emissivity determined from the band-averaged expressions is a possible source of uncertainty. This method has been tested in a 250-cm^{-1} region around 15 μm where the CO_2 absorption overlaps the tail of the water vapor rotation band. Published high resolution spectra of these gases enable the overlap effects to be calculated for small spectral intervals and summed over the band. This calculation was made and compared with the value given by the approximate treatment for the same gas concentrations, pressure, and temperature. Agreement was within 10 percent, indicating that the more detailed spectral calculation is unnecessary.

Introduction

The possibility of man's inadvertent modification of climate by addition of carbon dioxide to the atmosphere from the burning of fossil fuels was discussed by Callendar[1] some thirty years ago and has recently attracted widespread attention[2–5]. Carbon dioxide is a minor constituent of the earth's atmosphere (0.03 percent by volume) but it has a profound effect on optical properties of the atmosphere, which to a large extent are responsible for the surface temperature of the earth and the thermal structure of the atmosphere.

The absorption bands of CO_2 are such that this gas is essentially transparent to the incoming solar flux but is opaque to the long wavelength black body radiation from the surface and the atmosphere. The absorbing gas reradiates black body radiation characteristic of its atmospheric temperature, thus increasing the total flux at the surface and raising the surface temperature above that which would exist in the absence of this gaseous blanket. In the actual atmosphere the radiative transfer characteristics are affected by the presence of water vapor and ozone, which also have important absorption bands in the solar and black body spectral regions. The existence of clouds further complicates matters. Add to that the vertical transfer of heat by turbulence and convection in the troposphere, the lower 12 km or so of the atmosphere, and one can appreciate that it is a formidable problem to model the atmosphere in a realistic way and to assess the effect of changing the concentration of CO_2 on the surface temperature of the earth.

Nevertheless, calculations of increasing sophistication have been made by Plass[6], Kaplan[7], Möller[8], and Manabe et al.[9–11] in which the equation of radiative transfer is solved in a plane parallel layered atmosphere subject to the boundary condition that the total upward flux at the top of the atmosphere is equal to the downward solar flux. The concentrations of gases and clouds are specified as functions of altitude, and the result is a temperature profile including a value for the temperature at the surface. The convective effects of the troposphere are accounted for by constraining the lapse rate (the rate of change of temperature with altitude) in that region to be −6°C/km, as is normally observed in the real atmosphere[10]. The complexity of the calculation arises because of the fine structure of the absorption lines of the gases, the variation of their line shapes with pressure and temperature, and the broad spectral range covered (0.3 to 18 μm). To make the problem tractable even on the highest speed computers available, certain simplifications and approximations have been made, such as the use of spectrally averaged values for the transmission of a gas and the treatment of clouds as black or partially black bodies, the influence of which on the final results has not been evaluated in detail.

The approximation that we examine in this paper involves the treatment of radiation through a layer containing two gases with overlapping absorption lines, examples being the overlap of the intense 15-μm band of CO_2 with the tail of the water vapor rotation band, and that of the 9.6-μm band of ozone with the water vapor band. Using published high resolution data on the 15-μm CO_2 and water vapor absorption lines, we have computed suitable band averages for each gas separately and have obtained the overlap properties by means of the approximation used in the latest of the above models[10, 11]. These results are compared with the overlap properties calculated over small spectral intervals using these high resolution spectra and summed over the same spectral region, thus allowing a test of the adequacy of the approximate formulation as compared to the more detailed but time consuming high resolution calculation.

Calculation and results

The flux transmission through the model atmosphere is determined from the solution of the equation of radiative transfer[12]. For a stratified atmosphere, the total flux is resolved into an upward component and a downward component, the integration over azimuth and zenith angles being accomplished by introducing a slab transmissivity $\tau_{\mathrm{f}}(u)$ related to the column transmissivity $\tau(u)$ of a gas (defined for a parallel beam) by the relation

$$\tau_{\mathrm{f}}(u,T) = 1.66\tau(u,T), \qquad (1)$$

where u is the optical mass in the path and T is the temperature[13]. This discussion is applicable to the infrared band from 550 to 800 cm^{-1} (12.5 to 18.2 μm), which includes the 00_00-01_10 transition of CO_2 centered at 667 cm^{-1}

For a single gas a typical equation, in this example for the downward flux at altitude z in the absence of clouds in the band interval $\Delta\nu$, is given by[10]

$$F_z\downarrow = \pi b_\infty \varepsilon_{\mathrm{f}}(y_\infty,T_\infty) - \int_{b_z}^{b_\infty} \tilde{\varepsilon}_{\mathrm{f}}(y,T)\pi\, db, \qquad (2)$$

where T_∞ is the temperature at the top of the atmosphere;

$$\begin{aligned} y[B(T)] &= |u_{\mathrm{r}}(T) - u_{\mathrm{r}}(T_z)|; \\ y_\infty &= |u_{\mathrm{r}}(T_\infty) - u_{\mathrm{r}}(T_z)|; \\ b(T) &= \int_{\Delta\nu} B_\nu(T)d\nu; \\ b_\infty &= b(T_\infty); \end{aligned}$$

B_ν is the black body intensity at wave number ν; $u_{\mathrm{r}}(T)$ is the effective optical mass of the gas between the surface and the layer at temperature T; ε_{f} is the mean slab emissivity defined by

$$\varepsilon_{\mathrm{f}}(u,T) = \int_{\Delta\nu} B_\nu(T)\ [1 - \tau_{\mathrm{f}}(k_\nu u)]d\nu \Big/ \int_{\Delta\nu} B_\nu(T)d\nu, \qquad (3)$$

where k_ν is the absorption coefficient; and $\tilde{\varepsilon}_{\mathrm{f}}$ is the mean slab "absorbtivity" defined by

$$\tilde{\varepsilon}_{\mathrm{f}}(u,T) = \int_{\Delta\nu} \frac{dB_\nu(T)}{dT}\ [1 - \tau_{\mathrm{f}}(k_\nu u)]d\nu \Big/ \int_{\Delta\nu} \frac{dB_\nu(T)}{dT}\, d\nu. \qquad (4)$$

The first term in Eq. (2) represents the downward flux emitted at the top layer of the atmosphere and attenuated by the mass of gas between that layer and level z. The second term represents the sum of the emission of each infinitesimal layer between level z and the top of the atmosphere attenuated by the optical mass in the intervening layers. Because of the narrow spectral region we are considering,

$$\tilde{\varepsilon}_{\mathrm{f}}(u,T) \approx \varepsilon_{\mathrm{f}}(u,T). \qquad (5)$$

We can define an emissivity and an absorptivity from Eqs. (3) and (4) separately for CO_2, which we label $\varepsilon_{\mathrm{f}}^{\mathrm{c}}$ and $\tilde{\varepsilon}_{\mathrm{f}}^{\mathrm{c}}$, and for water vapor, which we label $\varepsilon_{\mathrm{f}}^{\mathrm{w}}$ and $\tilde{\varepsilon}_{\mathrm{f}}^{\mathrm{w}}$. When both gases are present, the approximation used by Manabe et al.[10,11], apparently first introduced by Yamamoto[14], is

$$\begin{aligned} \varepsilon_{\mathrm{overlap}}\ (u^{\mathrm{c}},u^{\mathrm{w}},T) &= \varepsilon^{\mathrm{c}}(u^{\mathrm{c}},T) + \varepsilon^{\mathrm{w}}(u^{\mathrm{w}},T) \\ &\quad - \varepsilon^{\mathrm{c}}(u^{\mathrm{c}},T)\varepsilon^{\mathrm{w}}(u^{\mathrm{w}},T), \qquad (6) \end{aligned}$$

which gives the band-averaged overlap properties in terms of the band-averaged emissivities of each gas.

For gases with overlapping spectra, the transmissivity of the mixture is the product of the individual transmissivities if the two spectra are uncorrelated[15]. This overlap emissivity, for instance, is given by

$$\varepsilon'_{\mathrm{overlap}}\ (u^{\mathrm{c}},u^{\mathrm{w}},T) = \int_{\Delta\nu} B_\nu(T)[1 - \tau^{\mathrm{c}}(k_\nu{}^{\mathrm{c}}u^{\mathrm{c}})\tau^{\mathrm{w}}(k_\nu{}^{\mathrm{w}}u^{\mathrm{w}})]d\nu \Big/ \int_{\Delta\nu} B_\nu d\nu. \qquad (7)$$

With the availability of high resolution spectra of the two gases, it is possible to calculate the overlap emissivity by the two methods, Eqs. (6) and (7), and thus appraise the validity of the approximation.

The radiative transfer in this spectral range was also computed independently in the program of determining atmospheric temperature profiles from multichannel radiometer data collected by earth orbiting satellites. Smith[16] has published data on these spectra with a resolution of 5 cm^{-1}, which were used to compute transmissivities in the spectral ranges of the radiometers. These data were presented in the form of an eight-term polynomial expansion in the variables u, T, and P/P_0, the latter being pressure normalized to surface pressure (10^3 mbar); this is a convenient form for the band summations required in the present work. Transmissivities determined from the polynomial representation have an rms error of about one percent and agree within experimental error with transmissivities determined from balloon soundings.

We used this polynomial representation to compute the slab emissivities for CO_2 and water vapor from Eq. (3). These values are shown in Figs. 1 and 2 as a function of scaled optical thickness $[u(P/P_0)^k]$ with $k = 0.67$ for CO_2 and $k = 0.7$ for water. Comparison with Figs. 29 and 26(f) of Ref. 11, based on different data,

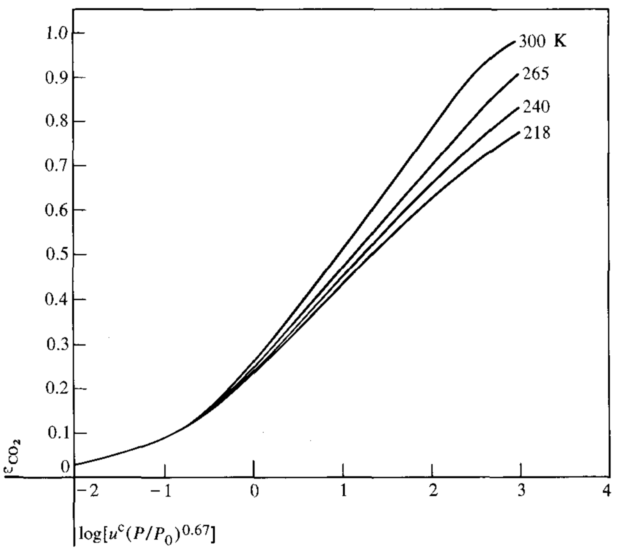

Figure 1 Slab emissivity of carbon dioxide for the spectral band 550 to 800 cm^{-1} as a function of effective optical thickness (cm STP, determined from the data of Ref. 16).

Figure 2 Slab emissivity of water vapor for the spectral band 550 to 800 cm^{-1} as a function of effective optical thickness ($g\text{-}cm^{-2}$, determined from the data of Ref. 16).

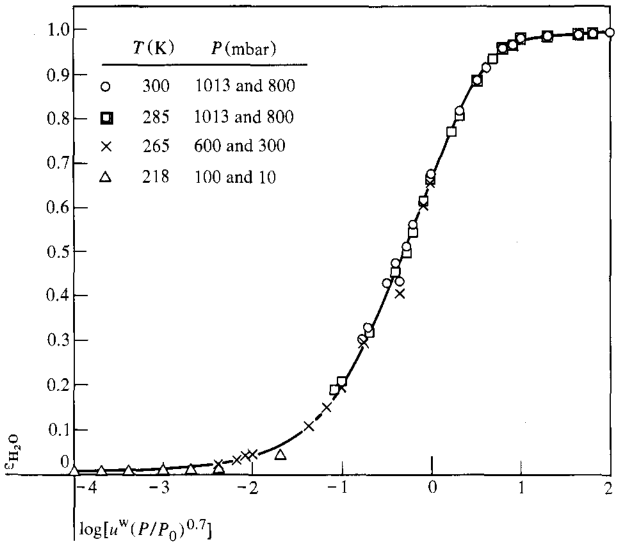

Table 1 Overlap emissivities calculated by the averaging approximation (ε) and by detailed spectral treatment (ε′).[a]

log u^w	*log* u^c	ε	ε'	
1	2	0.997	0.994	$T = 300$ K $P = 1013$ mbar
	1	0.995	0.990	
	0	0.992	0.988	
0	2	0.927	0.908	
	1	0.838	0.830	
	0	0.757	0.756	
−1	2	0.801	0.802	
	1	0.614	0.618	
	0	0.422	0.427	
0	2	0.889	0.884	$T = 265$ K $P = 1013$ mbar
	1	0.816	0.813	
	0	0.738	0.739	
−1	2	0.742	0.738	
	1	0.572	0.572	
	0	0.389	0.393	
0	2	0.639	0.637	$T = 265$ K $P = 101$ mbar
	1	0.465	0.468	
	0	0.318	0.320	
−1	2	0.568	0.561	
	1	0.361	0.358	
	0	0.184	0.184	
−1	2	0.533	0.516	$T = 218$ K $P = 101$ mbar
	1	0.338	0.329	
	0	0.179	0.167	
−2	2	0.508	0.497	
	1	0.303	0.303	
	0	0.135	0.136	
−3	2	0.505	0.492	
	1	0.298	0.296	
	0	0.130	0.128	
−2	1	0.170	0.155	$T = 218$ K $P = 10.2$ mbar
	0	0.069	0.061	
	−1	0.034	0.031	

[a] Common units used for the optical mass of CO_2, u^c, are cm STP and for water vapor, u^w, $g\text{-}cm^{-2}$.

shows reasonable agreement except for large values of the scaled optical mass for CO_2, which would be significant only for layers close to the surface or for a very coarse stratification of the model atmosphere. The temperature independence of water vapor emissivity in the range 218 K $< T <$ 300 K was confirmed.

Overlap emissivities were calculated using Eq. (6) and emissivities taken from Figs. 1 and 2 for a range of values of u^c, u^w, P, and T encountered in a realistic atmosphere. The overlap emissivity for the same values was calculated using Eq. (7). Some of these results are presented in Table 1 and show quite satisfactory agreement between the procedures, the difference not exceeding 10 percent for the parameter ranges spanned.

Summary

Since it is very difficult to explore the effects of inadvertent modification of climate by man except by computer simulation, it is important to develop a high level of confidence in our atmospheric models if we are to make use of the results obtained from them. We have investigated an approximation used in one of the most sophisticated models available today, which could be a source of uncertainty in the model predictions, and have shown that the approximation is sufficiently accurate, when compared to a detailed computation, that it will not be a significant source of error in calculating infrared fluxes in the earth's atmosphere.

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