

Full spectrum k -distribution correlations for CO₂ from the CDS-1000 spectroscopic databank

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Introduction

Radiative heat transfer through molecular gases is a very important mode of energy transfer when dealing with combustion systems or modelling atmospheric processes. The most accurate radiative transfer results are obtained through line-by-line (LBL) calculations, which require, however, a prohibitively large computational effort. Consequently a number of global and band models have been proposed. Presently, the most accurate global models are the Full-Spectrum k -distributions (FSK) by Modest and coworkers [1, 2]. Earlier, somewhat less refined, related methods include the Spectral-Line-Based Weighted-Sum-of-Gray-Gases [3–5] or SLW and Absorption-Distribution-Function(ADF) [6, 7] models. All of these methods are orders-of-magnitude more efficient than LBL calculations, and they all use full-spectrum k -distributions, which, in general, need to be calculated from high-resolution databases, such as HITRAN [8], HITEMP [9] or —for CO₂— the new CDS-1000 [10, 11]. Both the SLW and ADF methods use simplified k -distributions reducing them to step-functions (gray gases), whereas the full-spectrum k -distribution method uses Gaussian quadrature to integrate over g -space resulting in better accuracy. Assembling such k -distributions is a rather tedious task and, therefore, to make simple engineering calculations feasible, Denison and Webb [12, 13] have proposed several simple full-spectrum k -distribution correlations for CO₂ and H₂O, based on the outdated HITRAN92 [8] database, combined with some extrapolations of their own for high temperatures. Recently, Zhang and Modest [14] provided an updated correlation for CO₂ based on the newer HITEMP database which is purported to be accurate to at least 1000K. Unfortunately, it appears that the HITEMP database shows some erroneous behavior for temperatures beyond 1200K, as seen by comparison with experimental data [10, 15]. The new CDS-1000 databank [10, 11], on the other hand, follows experimental data much more closely. Thus, it is the purpose of this note to provide a simple engineering correlation for full-spectrum k -distributions evaluated from the CDS-1000 databank.

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Mathematical Formulation

The k -distributions are obtained by reordering the spectrally varying absorption coefficient into a monotonically increasing function with, in the case of full-spectrum k -distributions, the blackbody intensity (Planck function) as a weight factor. This has been described in detail in the original paper by Modest and Zhang [16].

The full-spectrum k -distribution is defined as

$$f(T_p, T_g, p, x, k) = \frac{1}{I_b} \int_0^\infty I_{b\eta}(T_p) \delta(k - \kappa_\eta) d\eta, \quad (1)$$

which is a function of temperature T_p through the black body intensity and of the state of the gas through the absorption coefficient $\kappa_\eta(T_g, p, x; \eta)$ where T_g is the gas temperature, p is the absolute pressure, x is the concentration and η is the wave number.

For RTE solution methods, the cumulative full-spectrum k -distribution is used, defined by

$$g(T_p, T_g, p, x; k) = \int_0^k f(T_p, T_g, p, x; k) dk = \frac{1}{I_b} \int_0^\infty I_{b\eta}(T_p) H(k - \kappa_\eta) d\eta, \quad (2)$$

where $H(k - \kappa_\eta)$ is the Heaviside unit step-function. Physically, g is the Planck-function-weighted fraction of the spectrum over which the absorption coefficient $\kappa_\eta < k$.

The cumulative full-spectrum k -distribution $g(T_p, T_g, p, x; k)$, or rather its inverse $k(T_p, T_g, p, x; g)$ is used by today's sophisticated spectral solution methods, i.e. SLW [3, 4, 12, 13, 17], ADF [6, 7, 18], and FSK [1, 2]. Determination of such cumulative k -distributions from high-resolution databases is a rather tedious and lengthy process and is, thus, not suitable for simple engineering calculations. With a small loss of accuracy, simple correlations may be employed instead, as first suggested by Denison and Webb using the outdated HITRAN92 [8] database. It is our aim here to present a similar but updated correlation for CO₂, employing the new CDSD-1000 databank [10, 11]. Following Denison and Webb, we have,

$$g(T_p, T_g, p, x; k) = \frac{1}{2} \tanh[P(T_p, T_g; k)] + \frac{1}{2} \quad (3)$$

where

$$P(T_g, T_p, k) = \sum_{l=0}^3 \sum_{m=0}^3 \sum_{n=0}^3 d_{lmn} \left(\frac{T_g}{1000} \right)^n \left(\frac{T_p}{1000} \right)^m (\log_{10} k)^l \quad (4)$$

where $P(T_p, T_g; k) = P(T_p, T_g, p = 1\text{bar}, x = 0; k)$ with k in $(\text{cm}\cdot\text{bar})^{-1}$, i.e., the correlation given here is valid only for the most common total pressure of $p \simeq 1\text{bar}$, and, since CO₂ does not show strong self-broadening effects, the correlation is essentially independent of the CO₂ mole-fraction, which has thus been neglected. The errors that are introduced due to this approximation are small compared to errors of the correlated fit.

The correlation coefficients d_{lmn} listed in Table 1 were found by a least squares fit for full-spectrum k -distributions for CO₂ evaluated at 23 gas temperatures and 23 Planck function temperatures between

300K and 2500K, with 10 orders of magnitude variation in k (cm-bar)⁻¹ from $k = 10^{-8}$ (cm-bar)⁻¹ to $k = 200$ (cm-bar)⁻¹. Some representative k -distributions built from this correlation are plotted against the actual ones in Figs. 1 and 2. Unlike k -distributions calculated from HITRAN and HITEMP, those from CDS-1000 show magnified undulations at higher temperatures which are difficult to fit with a given number of coefficients. This is due to much more well defined rovibrational bands for CO₂ when modelled with CDS-1000, in regions where HITEMP shows suspicious behavior from extrapolated lines in the band wings. However, as shown in sample heat transfer calculations below, the smoothening effect of the polynomial fit does not appear to seriously affect the accuracy of radiative calculations.

As a first check of the accuracy of the correlation, cumulative k -distributions are used to calculate the total emissivity of isothermal CO₂-N₂ mixtures. Fig. 3 shows total emissivities obtained directly from the CDS and HITEMP databases (using LBL or, equivalently, FSK calculations), from the present correlation and, Denison and Webb correlation [12], and finally, from Leckner's correlation [19], which is based on fairly dated experimental data. As already noted by Zhang and Modest [14], HITEMP overpredicts emissivities at elevated temperatures, as compared with Leckner's model. Modest and Bharadwaj [15] have reported spurious absorption predicted by HITEMP at elevated temperatures in the band wings of the important 4.3 μm and 2.7 μm bands of carbon dioxide. Emissivities from the CDS-1000 databank and the present correlation are in better agreement with experimental data than HITEMP. Emissivities predicted by CDS-1000 are generally lower than those measured by Leckner. This is an expected result since CDS-1000 does not include all high-temperature lines. On the other hand, HITEMP emissivities become much too large at high temperatures due to the spurious lines, as discussed by Modest and Bharadwaj [15] and Tashkun et al. [10, 11]. The old correlation by Denison and Webb [3, 4] does reasonably well, but underpredicts emissivities at high temperatures, due to missing hot lines. The disagreement at high pressure path lengths is assumed to be due to inaccuracy of the measured data. A similar trend, as shown in Fig. 4, is seen for the Planck-mean absorption coefficient obtained as outlined in [14], with HITEMP predicting much higher absorption at high temperatures than CDS. The correlation does a reasonably good job approximating the Planck-mean absorption coefficient with a maximum error of about 10% at low temperatures.

Radiative heat loss from simple one-dimensional layer between two parallel, cold, black walls is presented to further test the accuracy of the correlation, and is compared with "exact" (LBL or FSK) results obtained from the HITEMP and CDS databanks. The medium is a N₂-CO₂ mixture at 1 bar total pressure and a CO₂ mole fraction of 10%, and the mixture temperature is varied from 300K to 2500K. The flux exiting the walls is plotted in Fig. 5, showing a maximum error between the correlation and LBL calculations for CDS of about 10%. As expected, at higher temperatures the heat-flux predicted by CDS is less than that predicted by HITEMP, due to absence of the spurious lines that appear in the HITEMP spectrum at higher temperatures.

Finally, heat loss from a similar setup with one hot wall and one cold wall are predicted to test the accuracy of the correlation for transmission calculations. The mixture is kept at 1000K with a 10% CO₂

mole fraction and hot wall temperature varying from 300K to 2500K. Shown in Fig. 6 are the fluxes leaving the cold end. The error between LBL results obtained from the CDSD databank and from the present correlation are always less than 10%.

Conclusion

A simple correlation for full-spectrum k -distributions of N_2 - CO_2 mixtures was developed, based on the new spectroscopic databank CDSD-1000. The correlation was tested through typical one-dimensional problems and found to achieve reasonable accuracy as compared to full-spectrum k -distributions obtained directly from the database. Thus the correlation allows simple, yet accurate determination of radiative fluxes in CO_2 mixtures, without need of tedious calculations employing a high-resolution databank.

Acknowledgment

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Table 1:

Coefficients for the full-spectrum k -distribution of carbon-dioxide for CDSD-1000

	l	$m \setminus n$	0	1	2	3
d_{lmn}	0	0	1.85071	0.33373	0.62660	-0.12890
		1	-0.20643	-2.57690	0.30090	-0.14090
		2	0.27664	1.81420	-0.24728	0.10052
		3	-0.37435E-01	-0.37762	0.53014E-01	-0.20836E-01
	1	0	0.67523	1.25760	0.67523E-01	-0.39669E-01
		1	-0.70897	-3.07080	1.71150	-0.57694
		2	0.48493	2.04603	-1.20220	0.40510
		3	-0.98138E-01	-0.41928	0.24956	-0.84109E-01
	2	0	0.20690	0.28500	-0.48324E-01	0.15174E-01
		1	-0.39473	-0.42333	0.54095	-0.23469
		2	0.29020	0.21882	-0.34748	0.15857
		3	-0.61998E-01	-0.38629E-01	0.68728E-01	-0.32314E-01
3	0	0.38488E-01	0.18292E-01	-0.18958E-01	0.61307E-02	
	1	-0.41013E-01	-0.59115E-02	0.47118E-01	-0.23229E-01	
	2	0.37740E-01	-0.30114E-01	-0.11303E-01	0.12140E-01	
	3	-0.87906E-02	0.98357E-02	-0.53884E-04	-0.20604E-02	

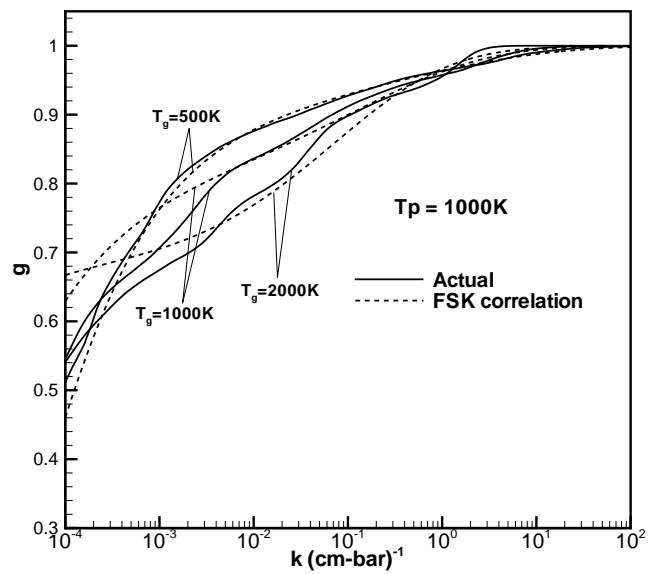


Figure 1: Actual and approximate full-spectrum k -distribution functions for CO_2 , calculated at a fixed Planck function temperature of 1000K, with absorption coefficient taken at various temperatures

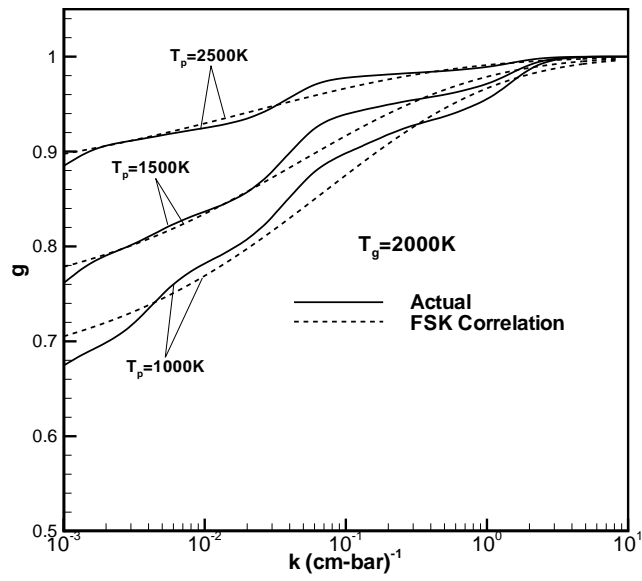


Figure 2: Actual and approximate full-spectrum k -distribution functions for CO_2 , calculated at a fixed gas temperature of 2000K , for different Planck function temperatures

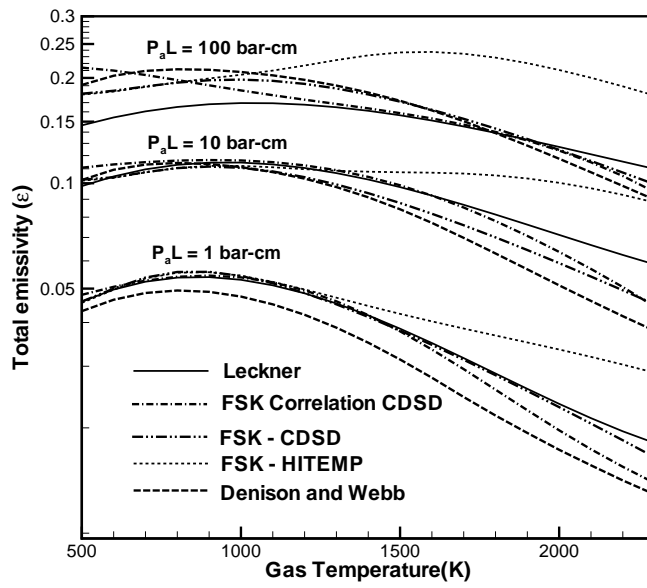


Figure 3: Total emissivities for different pressure path lengths from Leckner’s correlation, direct calculations from HITEMP and CDS-1000 databanks, and from the present correlation for CDS.

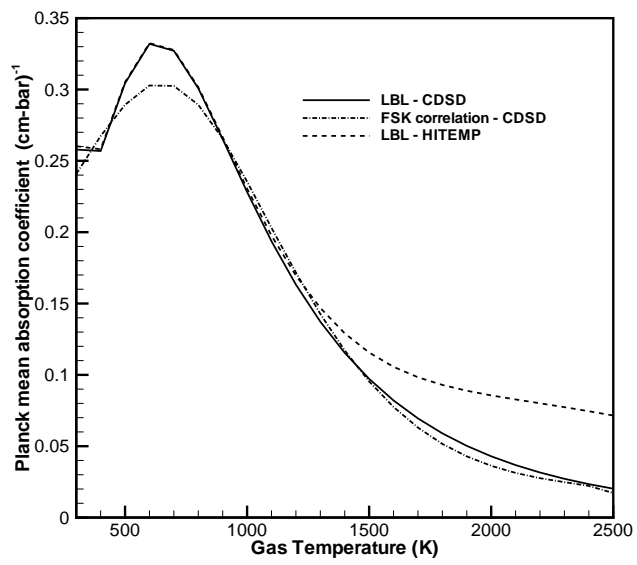


Figure 4: Pressure based Planck-mean absorption coefficient of CO₂ at different gas temperatures

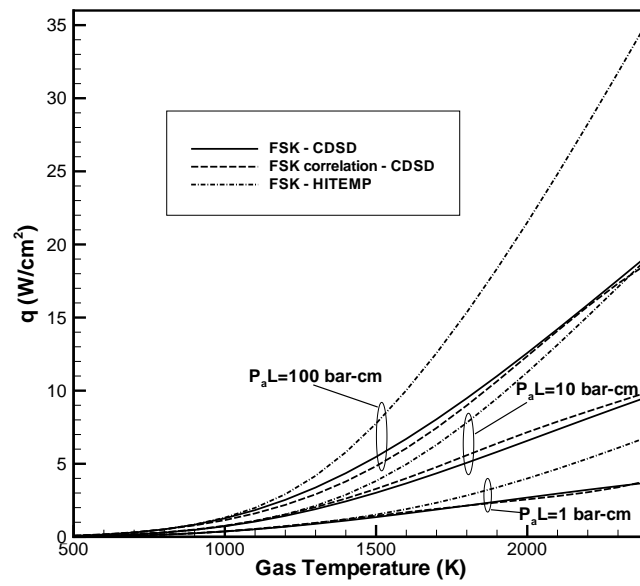


Figure 5: Radiative flux leaving a hot isothermal 90% N₂-10% CO₂ mixture bounded by cold walls for varying gas temperatures.

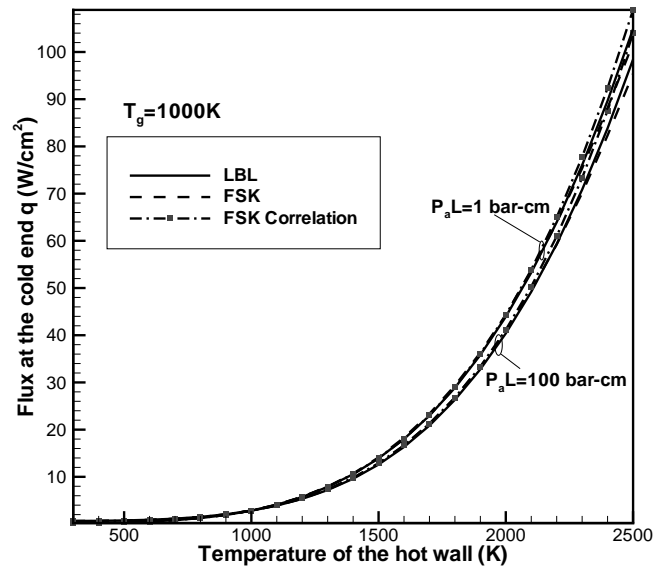


Figure 6: Radiative flux leaving from cold end of an isothermal 90% N₂-10% CO₂ mixture at 1000K between a hot and a cold, black wall for varying hot, black wall temperatures.