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On the accuracy of HITEMP-2010 calculated emissivities of Water Vapor and Carbon Dioxide

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Abstract. Line-by-line (LbL) calculations using either HITRAN or HITEMP spectral data bases are often used for predicting gas radiation properties like absorption coefficients or emissivities. Due to the large size of these data bases, calculations are computationally too expensive to be used in regular CFD-simulations and are rather used for benchmark calculations to validate less complex models. In order to determine the accuracy of these simplified models, the accuracy of HITRAN/ HITEMP data bases must be known. We summarize important high temperature measurements and compare them with line-by-line calculations. Furthermore, we point out the difficulties that arise when the line-by-line method is used at high pressures.

Keywords: Line-by-Line, HITEMP-2010, High Temperature, High Pressure, Lorentz line shape

1 Introduction

Thermal gas radiation has long been recognized to be the most important heat transfer mechanism in furnaces, boilers and gasifiers. Many models are available for predicting gas radiation properties, in particular for H2O-CO2-N2 mixtures. The models differ in complexity, accuracy as well as their constraints. The most accurate one is the line-by-line (LbL) model which theoretically is not subjected to any restrictions. Line-by-line calculations are computationally too expensive to be used in CFD simulations, so they are rather used as benchmark calculations for development of faster and/or approximate models. In such calculations, large data bases consisting of several millions or so individual spectral lines are required. HITEMP-2010 [1] is by far the most complete and accurate data base for temperatures beyond 1000 K. However, many of the spectral lines stem from theoretical calculations and experimental validation is essential. Measurements of spectral properties that span the whole spectral range are hardly available in the literature and, therefore, it is difficult to determine the accuracy of HITEMP-2010 calculated properties. The goal of this publication is to summarize important measurements available in the literature for H2O-CO2-N2 mixtures and to estimate the accuracy of HITEMP-2010 data base when used in high temperature and/or high pressure applications.

The mathematical procedure of calculating spectral as well as spectrally averaged (total) emissivities from spectral data bases is comprehensively summarized in Sec. 2 In Sec. 3 we present important measurements available in literature which we use here to estimate the accuracy of HITEMP-2010 calculated emissivities. In Sec. 4, calculated spectral and total emissivities are compared with measurements.

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2 Line-By-Line Calculations

2.1 Methodology of obtaining emissivity values

For the sake of arguments, we begin with the differential form of the radiative transfer equation (RTE) where in- and out-scattering has been omitted. At local thermal equilibrium, the change of spectral intensity $i'_\eta$ inside a radiatively participating medium alters with path length $s$ through [2]

$$\frac{d i'_\eta}{d (a_\eta s)} = -i'_\eta(\eta, s) + i'_{\eta,b}(\eta, T)$$

(2.1)

where $i'_\eta$ is given in units of W cm sr$^{-1}$ cm$^{-2}$, $i'_{\eta,b}$ is the spectral directional (blackbody) intensity, $a_\eta$ is the linear absorption coefficient in units of reciprocal length (cm$^{-1}$), $s$ is the path length in cm. The wavenumber $\eta$ is then in units of cm$^{-1}$. Eq (2.1) is valid for one wavenumber and one direction only. In case of a homogeneous medium, i.e. $a_\eta = \text{const.}$, the solution can be written as

$$i'_\eta(\eta, s) = \exp(-a_\eta \cdot s) \cdot i'_\eta(\eta, 0) + (1 - \exp(-a_\eta \cdot s)) \cdot i'_{\eta,b}(\eta, T)$$

(2.2)

Introducing the spectral transmissivity $\tau_\eta$ and the spectral emissivity $\varepsilon_\eta$, Eq (2.2) can be re-written as

$$i'_\eta(\eta, s) = \tau_\eta \cdot i'_\eta(\eta, 0) + \varepsilon_\eta \cdot i'_{\eta,b}(\eta, T)$$

(2.3)

The linear absorption coefficient $a_\eta$, and therefore, spectral transmissivity as well as emissivity, varies rapidly with wavenumber, so that it is common to calculate spectrally averaged values. For example, the emissivity averaged between two wavenumbers $\eta_1$ and $\eta_2$ can be defined as

$$\varepsilon_{\Delta \eta} = \frac{\int_{\eta_1}^{\eta_2} \varepsilon_\eta \cdot i'_{\eta,b}(\eta, T) \cdot d\eta}{\int_{\eta_1}^{\eta_2} i'_{\eta,b}(\eta, T) \cdot d\eta}$$

(2.4)

$\hat{e}_{\eta,b}$ is given by Planck’s function. If the integration is carried out over the whole spectral range, i.e. $\eta_1 \rightarrow 0$ and $\eta_2 \rightarrow \infty$, it is called total emissivity $\varepsilon_{\text{tot}}$ and the denominator is given by the Stefan-Boltzmann-Law. When the absorption/ emissivity spectrum is known, integration in Eq. (2.4) can easily be carried out numerically.

The absorption spectrum, i.e. $a_\eta$ versus $\eta$, is calculated with the help of spectral data bases. The procedure for evaluating such spectra is known [3]. Such data bases list certain parameters describing each individual absorption line. Each parameter is given at standard pressure $p_0$ and at standard temperature $T_0$. The most relevant parameter are the line position ($\eta_j$ in cm$^{-1}$), the integrated line intensity ($S_{\eta,j}^0$ in cm$^{-1}$ molecule$^{-1}$ cm$^{-2}$), the ground level of the transition energy ($E_j$ in cm$^{-1}$ atom$^{-1}$), the half-width of the line for self-broadening ($\Delta_{\text{self}}^0$ in cm$^{-1}$ atom$^{-1}$), the half-width for the foreign $N_2$ / Air broadening ($\Delta_{\text{foreign}}^0$ in cm$^{-1}$ atom$^{-1}$), the pressure-shift parameter ($\delta$ in cm$^{-1}$), and the temperature-dependence exponent ($n$, dimensionless) [3]. An appropriate line shape function $g(\eta - \eta_j)$ has to be chosen to perform the line-by-line calculation. Typical line shapes are Doppler (low pressure, high temperature), Lorentz (high pressure, low temperature), and Voigt (convolution of both). Then, the monochromatic linear absorption coefficient $K_{a,\eta}$ in units of cm$^{-1}$ for a single line of gas $j$ is calculated using

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*[4] See the descriptions in Refs. [14, 9, 6]*
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\[ K_{a\eta}(\eta, T, P, x_j, L) = S_{H}(T) \cdot N(p_j, T) \cdot g(\eta - \eta_i) \]  

(2.5)

\( S_{H}(T) \) stands for the temperature-scaled line intensity given through

\[ S_{H}(T) = \frac{Q(T_0)}{Q(T)} \cdot \frac{\exp\left(-\frac{C_2 \cdot E_{\eta}}{T}\right)}{1 - \exp\left(-\frac{C_2 \cdot E_{\eta}}{T_0}\right)} \cdot \frac{1 - \exp\left(-\frac{C_2 \cdot \eta_i}{T}\right)}{1 - \exp\left(-\frac{C_2 \cdot \eta_i}{T_0}\right)} \]  

(2.6)

where \( Q \) is the total internal partition function accounting for the distribution of energy states of molecules in thermodynamic equilibrium. One can use either closely spaced tabulated values of \( Q \) for each molecule/isotopologue at different temperatures or the FORTRAN code TIPS [4] which uses tabulated values and Lagrangian interpolation. The line position \( \eta_i \) varies with total pressure

\[ \eta_i = \eta_i^0 + \delta \cdot P_t \]  

(2.7)

and \( N(p_j, T) \), the number of molecules of species \( j \) per \( \text{cm}^3 \), can be calculated using an equation of state, e.g. using the ideal gas law. If collisions are the main broadening mechanism, the Lorentz line shape is applicable, which is

\[ g(\eta - \eta_i) = \frac{1}{\pi} \cdot \frac{\Delta}{\Delta^2 + (\eta - \eta_i)^2} \]  

(2.8)

For pressures not too far from atmospheric, this line shape function can be used up to 2500 K [5], see also Ref. [6]. The half-width at half-maximum for a binary mixture of gas species \( j \) and air is calculable using

\[ \Delta(p_t, x_j, T) = P_t \cdot [x_j \cdot \Delta_0^\text{self} + (1 - x_j) \cdot \Delta_0^\text{foreign}] \cdot \left(\frac{T_0}{T}\right)^n \]  

(2.9)

Summation over all spectral lines results in the final absorption spectrum, i.e.

\[ a_{\eta} = \sum_{\text{all lines}} K_{a\eta} \]  

(2.10)

If more than one radiatively active gas component is present, Eq. (2.9) is used, assuming that foreign broadening is sufficiently described by \( N_2/\text{Air} \) broadening. For a \( H_2O-CO_2-N_2 \) mixture, this simplification is applicable without a substantial loss of accuracy at atmospheric pressures, see Ref. [6]. At high densities, i.e. low temperatures and/or high pressures, the Lorentz line shape overestimates the absorption in the line wings [7]. To remedy this imperfection, one can make use of so-called \( \chi \)-functions which are multiplied with the line shape function. \( \chi \)-functions are typically one near the line center (core) and smaller than one a few \( \text{cm}^{-1} \) away from the center (wing). Most of the available data sets\(^5\) are based on measurements for a certain wavenumber range, temperature, pressure, and data base only. Therefore, care should be taken when using \( \chi \)-functions at other conditions or data bases. In case of \( CO_2 \), one model exist which accounts for the so-called line-mixing effect [8]. The model is applicable for temperature up to 400 K. However, perhaps the simplest way to remedy the overestimation of absorption coefficients in the line wings, is to cut each line at a certain distance away from the center, see Ref [9]. At high densities and very large distances \( s \), this cutting procedure leads to total emissivities that could be a bit underestimated. However, in engineering applications, path lengths are typically small at high pressures [9].

\(^5\) An overview of available \( \chi \)-functions is given in Ref. [7]
2.2 Spectral data bases
Several spectroscopic data bases exist like HITRAN [10], CDSD [11], and GEISA [12]. HITEMP-2010 [1] is the extension of HITRAN-2008 [13] by the inclusion of the hot lines, those which become active at high temperatures. HITEMP-2010 includes parameter for five molecules: H$_2$O, CO$_2$, CO, OH, and NO. Since the last update in 2010, many of the lines in case of carbon dioxide where taken from the Russian CDSD data base and it has been shown that both data bases lead to nearly the same results [14]. Therefore, we focus on the high-temperature spectroscopic data base HITEMP-2010.

2.3 Software
The software described in Refs. [9, 6] is used to perform the mathematical procedure described in the sections above. A C-Language version of the TIPS [4] is used to calculate the total internal partition sums at a certain temperature. The software is compatible to most of the HITRAN / HITEMP / CDSD versions and, additionally, different $\chi$-functions have been implemented. In this work however, we focus on the most up-to-date $\chi$-factors of Tran et.al. [23] because they are applicable for the most important spectral region (750 to 8500 cm$^{-1}$) and do not cover a small part of the spectrum only.

3 Measurements
A large number of spectral absorption and transmissivity measurements exist but there are hardly any measurements covering the whole spectral range that is of importance for technical applications. Measurements are typically available either at high resolution and small spectral range (e.g. see Refs. [15, 16]) or at relatively low resolution and a larger spectral range (e.g. see Ref. [17]). It is not possible to calculate the total emissivity from these measurements in order to compare the results with the HITEMP-2010 calculated total emissivities. Becher et.al. [17] compared spectral transmissivity measurements of a few H$_2$O/ CO$_2$ absorption bands with calculated transmissivities using different HITRAN / HITEMP versions. Alberti et.al. [14] used data of Bharadwaj and Modest et.al. [18, 19] to compare measured and calculated band emissivities of nearly all important spectral absorption of H$_2$O and CO$_2$ at temperatures between 1000 K and 1550 K and 1 atm pressure. Although many measurements of the important bands existed, it was not possible to calculate directly total emissivity values since the conditions like molar fractions or path lengths were different. Recently, Alberti et.al. [6] presented full spectrum (450 to 7600 cm$^{-1}$) measurements with an excellent signal-to-noise ratio for different H$_2$O-CO$_2$N$_2$ mixtures and temperatures up to 1770 K. The total emissivities calculated from the high resolution data serve here as the main benchmark data for the high temperature cases. In case of high pressures, there are hardly any measurements available for such a large spectral range, so that comparison between calculated and measured total emissivities is not possible. However, there exist a small number of high pressure measurements which were performed for at least one whole absorption bands. In this work, we restrict to measurements of CO$_2$ from Fukabori et.al. [20] and use the high accurate full line mixing software of Lamouroux [8] as a benchmark.

4 Results
Fig. 1 shows an example calculation of the pure CO$_2$ and the pure H$_2$O spectrum, each calculated at 50 cm path length and atmospheric pressure. The main absorption bands are marked within the figures. A few comments can be made. First, the CO$_2$ spectrum is smoother if compared to H$_2$O Second; both molecules have absorption bands that overlap if mixtures of both are concerned. Third, at 1800 K temperature, the Planck function has its maximum at a wavenumber of approximately 3400 cm$^{-1}$. When the temperature increases, this position is shifted to higher wavenumbers while the maximum emissive power increases. When the temperature decreases, the opposite is true; the position of the maximum is shifted to lower wavenumbers while the maximum emissive power
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decreases. Therefore, due to the shift of Planck’s function\(^6\), the amount of contribution of individual absorption bands to the total (integrated) emissivity varies with temperature. Eq. (2.4) indicates that the gas emissivity is given as the ratio of the area under the emissive power and the blackbody (maximum) emissive power. The maximum of the Lorentzian line shape, see Eq. (2.8), decreases with increasing temperature for strong lines in the vicinity of the band center while for other (weak) lines, the maximum generally increases so that these lines contributes to the total emissivity at elevated temperatures (hot lines). The maximum of the individual Lorentzian line shapes (in case of linear absorption coefficients) is basically unaltered with pressure while the width of each line increases with increasing total pressure and, therefore, the spectrum becomes smoother.

![Fig. 1 Calculated spectrum of pure CO\(_2\) / H\(_2\)O at 1800 K temperature](image)

**4.1 High temperature\(^7\)**

We start with the determination of the accuracy of HITEMP-2010 calculated total emissivities of CO\(_2\) and H\(_2\)O at high temperatures up to nearly 1800 K. Recently, Alberti et al. [6] published high resolution spectral measurements of different H\(_2\)O-CO\(_2\)-N\(_2\) mixtures at atmospheric pressure. The total emissivities have been calculated using Eq. (2.4) setting \(\eta_1 = 450 \text{ cm}^{-1}\) and \(\eta_2 = 7600 \text{ cm}^{-1}\) so that nearly the whole spectrum is taken into account. At 500 K temperature, around 93% of the whole blackbody emissive power is covered by this spectral range, at 1300 K a value of 96% is applicable while at 1770 K 87% of the blackbody power is covered. Therefore, the actual total emissivity is slightly different if compared to the emissivities calculated in Ref. [6]. Assuming that the (small) missing spectral regions are accurately calculated, the relative error is the same regardless whether the emissivities calculated in Ref. [6] or the actual total emissivities are concerned.

In order to visualize the differences between the calculations and measurements, we have produced emissivity charts showing the change of total emissivity with temperature using HITEMP-2010. Each curve is calculated at a constant pressure path length \((p_j \cdot L)\) value, where \(p_j\) is the sum of the partial pressures of all radiatively active species. We use the relative errors given in Ref. [6]\(^6\) at the corresponding \((p_j \cdot L)\) and \(T\) values to estimate what should be measured. These points are named as Alberti (2014). Fig. 2 shows the emissivity chart for carbon dioxide. It can be seen that marginal differences occur in case of HITEMP-2010 calculated emissivities which, at 1770 K mainly stems from the spectral differences in the lower wavenumber wing of the 4.3\(\mu\)m-band [6].

Fig. 3 shows the emissivity chart for water vapor at atmospheric pressure. If compared to CO\(_2\), larger differences between calculated and “measured” emissivities occur. These differences tend to become

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\(^6\) For the temperature scaling of individual absorption lines, see Sec. 2.

\(^7\) Most of the results are taken from Ref. [6]  

\(^6\) The relative error for carbon dioxide at 1550 K is taken from Alberti et al. [14]
larger with increasing temperature but hardly changes with the pressure path length $p_{H2O}L$ and stem from the generally underestimation of spectral transmissivities at higher temperatures [6].

![Emissivity chart for carbon dioxide at atmospheric pressure](image1)

**Fig. 2** Emissivity chart for carbon dioxide at atmospheric pressure, calculated using $x_{CO2} = 0.5$ and 2000 Lorentz half-widths for each absorption line.

![Emissivity chart for water vapor at atmospheric pressure](image2)

**Fig. 3** Emissivity chart for water vapor at atmospheric pressure, calculated using $x_{H2O} = 0.5$ and 2000 Lorentz half-widths for each absorption line.

Finally, Fig. 4 shows the emissivity chart for different CO$_2$ / H$_2$O mixtures at constant pressure path length $(p_{H2O} + p_{CO2})L = 47$ bar cm. Due to the good agreement between the calculated and measured transmissivities / emissivities, the HITEMP-2010 calculated total emissivities differ marginally only from the “measured” ones. However, with increasing amount of water vapor, i.e. increasing ratio $p_{H2O}/p_{CO2}$, and increasing temperature, larger differences occur and a maximum relative difference of 7.3% is obtained at $p_{H2O}/p_{CO2} = 4$ and $T = 1770$ K.

In summary, line-by-line calculations using HITEMP-2010 in case of H$_2$O-CO$_2$-N$_2$ mixtures at atmospheric pressures lead to total emissivities that differ by not more than 8% from emissivities calculated using the measured transmissivity spectra. Differences between the measured and calculated spectral transmissivities in case of water vapor tend to become larger with increasing
temperature so that the calculated total emissivities for $\text{H}_2\text{O}-\text{N}_2$ mixtures differ by more than 8% if the temperature exceeds 1800 K.

![Emissivity chart for gas mixtures of carbon dioxide and water vapor at atmospheric pressure, using 2000 Lorentz half-widths for each absorption line.](image)

**Fig. 4** Emissivity chart for a gas mixture of carbon dioxide and water vapor at atmospheric pressure, using 2000 Lorentz half-widths for each absorption line.

### 4.2 High Pressure

As already stated in Sec. 2, care must be taken with the Lorentzian line shape at elevated densities since it overestimates spectral absorption coefficients in the line wings. Fig. 5 shows CO$_2$ spectral emissivity measurements of Fukabori [20] at 11 bar pressure. Three different line shape adjustments were applied:

- **“No limit”**: Each spectral line is completely calculated.
- **“Limited”**: Each spectral line is cutted after a certain number $n$ of Lorentz half-width, calculated using the relationship [9]:
  \[ n(T, P) = 4 \cdot (T/P)^{0.822} \]
- **χ- Tran (2011)**: The absorption coefficients of each spectral Lorentz line are multiplied with the χ-factors given in Tran et al. [23].

Additionally, the emissivity spectrum calculated using the full-line-mixing software (labeled as “FLM”) of Lamouroux [8] is shown. This software should predict the most accurate spectrum but can be used for temperatures below 400 K only. At 300 K, 90% of the blackbody radiation is emitted in the 0 to 1500 cm$^{-1}$ range. Therefore, the 15 µm is the most important spectral band in this case.

As can be seen from Fig. 5, the standard Lorentz approach (“No limit”) substantially overestimates the emissivity values in the 4.3 µm-band which also influences the spectral emissivities of the neighboring bands, namely the 15 µm and the 2.7 µm-band. Cutting each line at a certain distance away from the line center results in a considerably more accurate spectrum and the total (integrated) emissivity decreases from $\varepsilon_{\text{tot, No limit}} = 0.287$ to $\varepsilon_{\text{tot, Limited}} = 0.182$. The emissivities of the line-by-line calculation including the χ-factors of Tran [23] are accurate if compared to both, measurements and the FLM software. The total emissivities are very similar to the one calculated using the “Limited”-approach: $\varepsilon_{\text{tot, Tran}} = 0.175$, $\varepsilon_{\text{tot, FLM}} = 0.177$. Similar comparisons can be found in Alberti et.al. [9]. It is important to note that this overestimation of the spectral line wings is also visible at 500 K temperature and 1 bar pressure, see Ref. [6].

In order to visualize the difference of the methods concerning the line shape function, we have produced Fig. 6. To the best of our knowledge, no reliable measurements for the whole spectral range at such conditions are available in the literature. Therefore, the full-line-mixing software of Lamouroux [8] is assumed to provide the most accurate results. Fig. 6 shows an emissivity chart for a
fixed molar composition $x_{CO_2} = x_{N_2} = 0.5$ and the temperature is 300 K. Using the standard Lorentzian lineshape without further line shape treatment results in emissivities at $p_{CO_2} \cdot L = 80$ bar cm that are more than twice as large if compared to the emissivities calculated using the cut-off criterion or the $\chi$-factors. At a pressure path length of $p_{CO_2} \cdot L = 500$ bar cm, the emissivities differ by as much as 230%. In case of the method “Limited”, the maximum difference to the “FLM” calculations occur at $p_{CO_2} \cdot L = 5$ bar cm and a total pressure of 30 bar where the line-by-line (“Limited”) calculated total emissivity is 16% larger if compared to the FLM one. Generally, the relative difference is in the 1% to 16% range and an average value of 6% is applicable. In case of the $\chi$-factor approach with parameters of Tran [23] the emissivities differ by -1% to 3% (1% on average) from the FLM-calculated values. The higher the gas density and the larger the path length, the more important is the appropriate line shape treatment, e.g. at 1500 K temperature and a pressure path length of $p_{CO_2} \cdot L = 500$ bar cm, the total emissivities using the method “No Limit” would be 32% larger if compared to the $\chi$-Tran (2011) method.

Fig. 5 Comparison of different line shape adjustments at elevated densities, see also Ref. [9].

Fig. 6 Emissivity chart for carbon dioxide at 300 K, scaled with total pressure, calculated using $x_{CO_2} = x_{N_2} = 0.5$
5 Conclusion

The accuracy of scaling the emissivity with temperature depends mainly on the parameters of the spectral data base while at high density also the lineshape function essentially contributes to the accuracy.

If compared to the total emissivities calculated using high resolution transmissivity measurements for temperatures up to 1770 K and atmospheric pressure, the HITEMP-2010 line-by-line calculated emissivities differ by around -2% in case of CO\textsubscript{2} while in case of H\textsubscript{2}O a value of 9% is applicable, see Ref. [6]. When gas mixtures of both molecules are concerned, the difference between HITEMP-2010 and measured total emissivities is, therefore, just between -2% and 9%, depending on the mixing ratio. In the measurements of Ref [6], a maximum difference of +7% was reported for a ratio of \( p_{H_2O}/p_{CO2} = 4 \) and 1770 K temperature. At high densities, a proper treatment of the line wings is essential, otherwise errors beyond 200% occur. If compared to full-line-mixing calculations in case of CO\textsubscript{2} which show excellent agreement to spectral transmissivity measurements, cutting off the spectral lines at a certain number \( n \) of Lorentz half-widths as reported in Ref. [9], results in maximum difference of +16%. A somewhat better agreement can be achieved using \( \chi \)-factors of Ref. [23], where a maximum value of 3% is applicable. However, with increasing temperature so that the density decreases, differences between the cut-off criterion and the \( \chi \)-factors becomes smaller.

We want to finish this paper with a remark. There seems to be no need for further measurements of CO\textsubscript{2} and/or H\textsubscript{2}O at high temperatures because the work of Bharadwaj and Modest [19, 18] and Becher et.al. [17] have been completed with the work of Alberti et.al. [6]. But there is still a need for full spectrum high pressure measurements of H\textsubscript{2}O-CO\textsubscript{2}-N\textsubscript{2}. These measurements should also be performed at elevated temperatures and maybe CO should be included so that the line-by-line method can be validated for gasification applications.

References


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