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Comparison of models for predicting band emissivity of carbon dioxide and water vapour at high temperatures

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ABSTRACT

A comparison of different models for predicting band emissivity of CO_2 and H_2O at temperatures up to 1550 K is presented. The calculations do not contain line-by-line databases only; a narrow-band as well as a wide-band model are also included. The main objective of this work is in comparing the spectral transmissivity and band emissivity values obtained from line-by-line calculations using the most recent HITEMP-2010 as well as CDSD-1000 spectral database with measured data. Differences between the previous HITEMP-2004 and the HITEMP-2010 spectral databases are depicted. The measurements are also compared with a narrow-band model as well as a wide-band model because both have frequently been used in heat transfer calculations. It is demonstrated that line-by-line calculations show high accuracy when computing CO_2 transmissivities but inaccuracies still remain in case of H_2O at temperatures above 1000 K. The narrow-band model as well as the wide-band model show larger discrepancies if compared to the line-by-line predictions.

1. Introduction and objectives

Radiative heat transfer is due to the emission and absorption of photons and its energy flux is maximum in vacuum. If a medium is present, it may or may not participate in the radiative energy exchange. Generally, molecules with a defined dipole moment take part in radiative heat transfer only. Carbon dioxide, water vapour, and carbon monoxide are relevant in combustion. Molecules can absorb and emit photons in certain wavenumber intervals only and in order to predict radiative fluxes knowledge of radiative properties is required. It is known from quantum mechanics that energy – that is mainly the sum of electronic, rotational, and vibrational energies – of atoms and molecules is quantized. If an atom or molecule absorbs or emits a photon, its energy is either increased or decreased by the amount of the photon's energy. Due to the fact that the energy states are quantized, only photons with a certain energy and, therefore, wavenumber can be absorbed or emitted. There are numerous possible transitions leading to several thousand individual absorption lines over an entire absorption band, which makes the calculation of radiative heat transfer in case of participating media cumbersome [1–6].

Considering spectral intensity i'_η incident on an elemental gas volume leads to the radiative transfer equation (RTE). If both in- and out-scattering can be omitted, the radiative transfer equation at local thermal equilibrium reads [3–6]

$$\frac{\mathrm{d}\, i'_\eta(\eta,s)}{a_\eta \cdot \mathrm{d}\, s} = -i'_\eta(\eta,s) + i_{\eta,b}(\eta,T) \tag{1}$$

In the above equation a_η is the linear absorption coefficient in units of reciprocal length (cm^{-1}), s is the pathlength, and $i'_{\eta(,b)}$ is the spectral directional (blackbody) intensity in units of $\mathrm{W\,cm\,sr^{-1}\,m^{-2}}$ while η stands for wavenumber expressed typically in cm^{-1}. The linear absorption coefficient can be seen as the reciprocal mean free path that a photon can travel through a column of gas before being absorbed. Eq. (1) is valid for one direction and one wavenumber only and if the medium is homogeneous, a_η = const., its solution is

$$i'_\eta(\eta,s) = i'_\eta(\eta,0)\cdot\exp(-a_\eta\cdot s) + i_{\eta,b}(\eta,T)\cdot[1-\exp(-a_\eta\cdot s)] \tag{2}$$

Then, the spectral directional transmissivity can be defined as

$$\tau_\eta = \exp(-a_\eta\cdot s) \tag{3}$$

and the spectral absorptivity as

$$\alpha_\eta = 1-\exp(-a_\eta\cdot s) \tag{4}$$

which equals the spectral emissivity (ϵ_η) in the case of thermal equilibrium [3–6]. Now, the RTE can be written in terms of spectral transmissivity as well as spectral emissivity

$$i'_\eta(\eta,s) = \tau_\eta\cdot i'_\eta(\eta,0) + \epsilon_\eta\cdot i_{\eta,b}(\eta,T) \tag{5}$$

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The first term in the above equation accounts for the extinction of incoming radiation intensity due to absorption whereas the second term accounts for the increase of intensity due to spontaneous emissions of the radiatively participating species. Because the absorption coefficient and, therefore, spectral transmissivity varies rapidly with wavenumber, it is common to use spectrally averaged – so-called – total values. For example, total emissivity, that is the emissive power divided by the blackbody emissive power is calculated as follows

$$\epsilon(s) = \frac{\int_0^\infty \epsilon_\eta \cdot i_{\eta,b}(\eta, T) \cdot \mathrm{d}\ \eta}{\int_0^\infty i_{\eta,b}(\eta, T) \cdot \mathrm{d}\ \eta} \tag{6}$$

The spectral intensity can be replaced by spectral emissive power divided by π number, (the factor π is due to the conversion of projected area to real area, see e.g. [4,5]) so that

$$\epsilon(s) = \frac{\pi \cdot \int_0^\infty \epsilon_\eta \cdot \dot{e}_{\eta,b}(\eta, T) \cdot \mathrm{d}\ \eta}{\pi \cdot \int_0^\infty \dot{e}_{\eta,b}(\eta, T) \cdot \mathrm{d}\ \eta} \tag{7}$$

Introducting Planck's Radiation Law as well as Stefan–Boltzmann-Law, the total emissivity finally becomes

$$\epsilon(s) = \frac{1}{\sigma \cdot T^4} \cdot \int_0^\infty \epsilon_\eta \cdot \frac{C_1 \cdot \eta^3}{\exp\left(\frac{C_2 \cdot \eta}{T}\right) - 1} \cdot \mathrm{d}\ \eta \tag{8}$$

where σ is the Stefan–Boltzmann constant, C_1 and C_2 are Planck's First and Second constants. With properly averaged values of transmissivity and emissivity, it is possible to solve the RTE without considering the rapidly varying absorption coefficient. If the integration in Eq. (7) is performed over a spectral interval instead of the whole spectrum, the value is called band emissivity [3–6].

Radiative transfer equation is important not only because it provides the basis for spectroscopic measurements of monochromatic transmissivity but it is also the starting point in the development of methods for calculating radiative transfer in absorbing-emitting media. In the latter case methods of averaging over both the wavenumber and direction are needed. Averaging over wavenumber results in a spectral model for calculating either the absorption coefficient or transmissivity (or both) in a certain wavenumber band. Averaging over wavenumber can be carried out either experimentally or theoretically. In the past, the measurements of band transmissivity, carried our for several temperatures and pressures of the absorbing gas, provided the basis for the development of narrow-band-models (NBM) and wide-band-models (WBM). More recently, line-by-line data are used for the development of narrow-band-models or emissivity correlations for specific spectral bands. Obviously, such developed NBMs or correlations are as good as the database which was used for their development. Recently, HITEMP-2010 [7] database has been released as an update to its previous version called here as HITEMP-2004, which is just HITRAN-2004 extended by the hot lines listed in Refs. [8,9]. The main difference between HITEMP-2010 and HITEMP-2004 is in the inclusion of a number of CO_2 lines of the Russian CDSD-1000 [10] database (for details see Ref. [7]). Furthermore, in case of H_2O the number of lines has been increased roughly by a factor of ten.

The main objective of our work is in comparing the emissivity/transmissivity values obtained by performing line-by-line calculations using HITEMP-2010 with the measured transmissivity data of Bharadwaj et al. [11–14] (see below). As a matter of fact, publications of Bharadwaj et al. [11–13] contain not only the measured transmissivity but also HITEMP-2004 based line-by-line calculations. One may argue, that their work has identified the shortcomings of the HITEMP-2004 and has perhaps prompted the update. Since the release of HITEMP-2010, a number of projects have been initiated to asses its value for combustion applications. Recently, Becher et al. [15] have validated HITEMP-2010 (CO_2 and H_2O molecules) in the temperatures up to 1773 K using the transmissivity data measured by Fateev and Clausen [16,17]. It will be demonstrated later that the findings of our work are in agreement with those of Becher et al. [15].

Over the last two decades or so, RADCAL narrow band model [18] has been used not only in numerous heat transfer calculations but also in interpreting in-flame data after performing a narrow-angle radiometry across flames, as exemplified by Refs. [19,20]. Since the model became widely used, we also include this model in our work to demonstrate the departure from HITEMP-2010. Similarly, the Exponential Wide Band Model of Edwards and Balakrishnan [21,22] has been included since it has been used in many works concerning combustion [23–25].

2. Measured data [11–14]

Medium resolution transmission measurements (resolution of approximately 4 cm^{-1}) for the most important bands of both CO_2 and H_2O at ambient pressure, temperatures up to 1550 K, and pathlengths up to 50 cm were recently published in [11–14]. In the case of CO_2, the following bands were measured: 2.0, 2.7, 4.3, and 15.0 μm, and for H_2O: 1.8, 2.7, and 6.3 μm bands. Fig. 1 shows the location of the bands together with Planck's function for three different temperatures. As expected, the importance of lower wavelengths bands increases at elevated temperatures, as shown in Fig. 1.

The measurements that have been performed by Bharadwaj and Modest [11–14] are used in this paper as a basis for the comparison between the two spectral databases CDSD-1000 [10] and HITEMP-2010 [7] as well as NBM and EWBM. It will be shown in Section 5 that the current HITEMP-2010 update brought the most improvements to the carbon dioxide database. Therefore, the focus in this paper is on CO_2 and fewer calculations are presented for H_2O.

3. Spectral models used

A software written in FORTRAN named ABS-EMI [26] is used to carry out line-by-line (LBL) calculations, see also Ref. [27]. This software uses purely Lorentzian line shapes to account for line broadening. A short discussion whether the Lorentzian line shape is appropriate is presented below. A spectral averaging of 4 cm^{-1} is chosen for the spectra of Section 4. It should be noted that the CDSD-1000 version used in this paper includes pure $^{12}C^{16}O_2$ only and no isotoplogues are enclosed while HITEMP-2010 includes seven isotopologues weighted by their standard atmospherical abundances. Therefore, the HITEMP-2010 database used in this paper contains approximately five times more lines than CDSD-1000. Nevertheless, it will be shown in Section 4 that there are no substantial differences between transmissivities calculated using the two databases.

Generally, absorption lines in spectral databases are mainly characterised by line position and intensity. Broadening mechanisms are accounted for by multiplying the intensity with a normalised lineshape. Each shape has its own maximum and half-width at half maximum. The most important broadening mechanisms are due to molecular collisions and due to the Doppler Effect; the correspponding lineshapes are named Lorentzian or Doppler. When both mechanisms are important it is convient to calculate the convolution of both shapes resulting in the Voigt lineshape. A measure of whether the Voigt function has a similar distribution to Lorentz or Doppler is given by the ratio of Lorentz to Doppler half-width at half maximum. If the ratio is large, there are small differences between Voigt and Lorentz; if the ratio is small, the Voigt function approaches the Doppler lineshape. It