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Validation of HITEMP-2010 for carbon dioxide and water vapour at high temperatures and atmospheric pressures in 450–7600 cm^{-1} spectral range

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ABSTRACT

The objective of the work is validation of HITEMP-2010 at atmospheric pressures and temperatures reaching 1770 K. To this end, spectral transmissivities at 1 cm^{-1} resolution and excellent signal-to-noise-ratio have been measured for 22 $CO_2/H_2O/N_2$ mixtures. In this paper we consider the 450 cm^{-1}–7600 cm^{-1} spectral range. The LbL calculations and their comparison with the measured spectra have clearly shown that HITEMP-2010 is an excellent database (superior to previous versions) for calculating emissivities and absorption coefficients for CO_2 and H_2O molecules in the 500–1770 K range. Several absorption lines listed in HITEMP-2010 have not been observed in the measured spectra and/or are wrongly scaled with temperature. The complete (there are no missing bands) spectra spanning the 450–7600 cm^{-1} range are appended as Supplementary Material.

1. Introduction and objectives

It has long been known that absorption and emission of gaseous species play an important role in thermal radiation calculations. Numerous models for predicting emissivity or transmissivity do exist which can generally be classified into spectral and total models. The latter models predict total emissivity, i.e. emissivity that is spectrally averaged over the whole spectrum and an integration is needed to calculate a total emissivity. Total models can be based on measured data or on spectral models. Nowadays, spectral line-by-line calculations are believed to yield the most accurate results and HITRAN, HITEMP, and CDSD databases are often used. Thus, it is essential that such databases, in particular HITEMP and CDSD, are validated. Modest and Bharadwaj [1–3] used a FTIR spectrometer to measure spectral transmissivity of the important bands of CO_2 (2.0, 2.7, 4.3, 15 μm) and H_2O (1.8, 2.7, 6.3 μm) at different path lengths, concentrations and temperatures. The path length was varied between 20 and 50 cm, mole fraction between 0.01 and 1.0, and the temperature between 600 K and 1550 K. The spectral resolution was 4 cm^{-1}. They compared their measurements with (among other models) line-by-line calculations using CDSD [4] and HITEMP-1995 [5] databases. Alberti et al. [6] used these data to validate the line-by-line calculations using the most recent HITEMP-2010 [7] database. Becher et al. [8] used measurements of Evseev et al. [9], who used a ceramic high temperature flow gas cell up to 1773 K temperature, to validate line-by-line predictions concerning CO_2 (2.7, 4.3 μm, 1, 10, and 100%) at 1000–1773 K temperature and H_2O (1.87, 2.7, 6.3 μm, 10

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and 35 vol%) at 1000–1773 K temperature using HITRAN-2004 [10], HITRAN-2008 [11], HITEMP-1995 [5], and HITEMP-2010 [7] databases. Evseev et al. [9] have already shown that their experimental setup yields results comparable to those of Modest and Bharadwaj [1–3]. All of the comparisons showed good validity of HITEMP-2010 and CDSD-1000 database in case of carbon dioxide. However, in case of water vapour at temperatures higher than 1000 K and higher volumetric fractions, differences appear, especially in the band wings. All the above considered measurements were taken at certain wavenumber intervals only and, to the best of our knowledge, spectral measurements spanning the whole spectrum are not available. Therefore, when such measurements are used to calculate total emissivities, the missing bands must be modelled.

The objective of our work is to validate the HITEMP-2010 database for CO_2/N_2 and H_2O/N_2 gas mixtures as well as for $CO_2/H_2O/N_2$ mixtures. To this end, we carry out new high temperature spectral measurements using the hot ceramic gas cell of Evseev et al. [9] and show differences between the measured and the calculated transmissivities using the most recent HITEMP-2010 database. The measurements are performed at temperatures up to 1770 K and a high nominal resolution of 1 cm^{-1} is used in order to obtain a higher signal-to-noise ratio. Furthermore, the whole spectrum from 400 to 8000 cm^{-1} is recorded in order to allow for calculation of band as well as total emissivities.

2. Measurements

2.1. Experimental setup

Measurements have been performed using a high temperature ceramic flow gas cell, shown in Fig. 1, that was also used by Becher et al. [8] and Evseev et al. [9]. The gas cell consists of three parts: the 53.3 cm long main part containing the hot sample gas and two N_2-purged gas-zones (buffer zones) on both sides of the hot gas cell. The aperture of the main part is 1.5 cm. The variation in length of the inner (main) part due to thermal expansion (ϑ in °C) is accounted for through [8]

$$L(T) = 53.3\ \text{cm} \cdot (1.0 + 7.25 \times 10^{-6} \cdot \vartheta + 1.047 \times 10^{-9} \cdot \vartheta^2) \quad (1)$$

The gas mixture, consisting of radiating species and nitrogen, is preheated and flows concentrically between the outer and the inner ceramic tubes and finally enters the main part in the middle of the cell. The gas stream is divided into two streams flowing to both ends where they mix with the purge dry air gas flow and build up a laminar flow window [12]. Dry air taken from a purge generator has been used as purge gas in the buffer zones of the gas cell. Flow rates of both the gas sample under investigation and the purge flow are kept constant at 2 L/min in order to prevent window collapse. The principle of the cell design can be traced back to Hottel and Mangelsdorf [13].

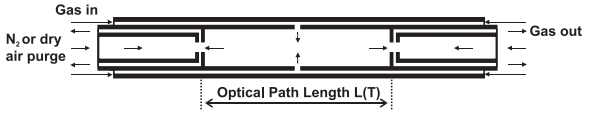

Fig. 1. High temperature flow gas cell (HGC) used in experiments. Flow direction is shown by arrows, see Refs. [12,14].

Fig. 2 shows the optical setup for the transmission measurements. The gas cell is designed as a three-zone furnace so as to obtain uniform temperature along the length of the inner part of the cell. To this end the heat losses at the cell-ends are minimized. KBr windows are placed on both ends of the buffer parts. Either a hot dry air-purged blackbody at 1773 K or a water-cooled cold blackbody at around 300 K is interchangeably used due to a flipping mirror made out of metal substrate coated by gold. A FTIR spectrometer (Nicolet 5700) has been used with an external emission port and a DTGS detector, see Ref. [9]. From the recorded interferograms the single beam spectra have been calculated using OMNIC software (ThermoFischer). The software performs the Fast Fourier Transformation and triangular apodization function as well as Mertz phase correction is applied. Nominal resolution of the measurements is 1 cm^{-1}. High purity nitrogen (purity better than 99.9999%) has been used as a reference and dilution gas; carbon dioxide's purity is 99.998%. Demineralized water is evaporated inside of an evaporation system (Bronkhorst evaporator) in case of H_2O measurements. A small amount of nitrogen is needed to transport the vapour from the evaporator to the gas cell so it was possible to perform measurements with a maximum of 98.11% water vapour. The pressure has been measured at the cell outlet and all total pressures given in this paper are values averaged over six to twelve readings.

The whole spectral range from 400 $cm^{-1}$to 8000 cm^{-1} has been recorded so that all absorption bands are included which makes it possible to calculate not only emissivities of specific bands but also total emissivity without resorting to modeling of any missing bands. In short, the measured spectra are complete in the 400–8000 cm^{-1} range. Furthermore, the high nominal resolution of 1 cm^{-1} makes the spectral integration, necessary for the evaluation of band as well as total emissivities, very accurate. Additionally, such a resolution allows for identification of wrongly scaled individual absorption lines. Although the spectral range from 400 cm^{-1} to 8000 cm^{-1} has been recorded, the 450–7600 cm^{-1} range has been only considered (see below).

Four measurements are needed to calculate spectral transmissivities at one condition [12,14,8]:

- reference gas spectra using hot blackbody and N_2-filled cell: $I_{N_2}^{hot}$,
- reference gas spectra using cold blackbody and N_2-filled cell: $I_{N_2}^{cold}$,
- gas of interest spectra using hot blackbody and gas-filled cell: I_{gas}^{hot},
- gas of interest spectra using cold blackbody and gas-filled cell: I_{gas}^{cold},

Then, the spectral transmissivities can be calculated as [12]

$$\tau_\eta(\eta) = \frac{I_{gas}^{hot} - I_{gas}^{cold}}{I_{N_2}^{hot} - I_{N_2}^{cold}} \quad (2)$$