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Medium resolution transmission measurements of CO_2 at high temperature

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Abstract

Medium resolution transmissivities of CO_2 were measured at temperatures between 300 and 1550 K for the 4.3, 2.7 and 2.0 μm bands. Measurements were made with a new drop tube design, which guarantees a truly isothermal high-temperature gas column. Data were collected with an FTIR-spectrometer, allowing for much better spectral resolution than most previous high-temperature measurements. The measured data were compared with two line-by-line and two narrow band databases. The data show some discrepancies with high-resolution databases at higher temperatures, indicating missing and/or incorrectly extrapolated spectral lines.

Keywords: Radiative properties; Transmissivity; Narrow band; Carbon dioxide; High temperature

1. Introduction

Knowledge of radiative properties of combustion gases is required to accurately predict radiative fluxes in a number of physical systems like fires and combustion systems. Unfortunately, absorption coefficients of absorbing gases are not known with sufficient accuracy to make reliable heat transfer calculations, especially at high temperatures. Gas spectra broadened by N_2, air and other buffer gases have been studied by a number of investigators, some in the atmosphere and others in a laboratory setting. Atmospheric measurements are done using the absorbing gas that is present in the atmosphere. For example, Rinsland et al. [1] describe atmospheric measurements of water vapor properties using an FTIR spectrometer and a telescope. Atmospheric ozone measurements have been made by Bouazza et al. [2] and Flaud et al. [3]. Both these measurements were done with FTIR spectrometers. Farrenq et al. [4] have made atmospheric measurements of solar CO lines, also with an FTIR spectrometer. Atmospheric measurements have the advantage of long optical paths. However,

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isothermality and homogenity of the optical path are not ensured. Also, it is not possible to make high-temperature atmospheric measurements.

There have been basically three types of laboratory experiments: window cell (uncooled [5–8], or water-cooled [9–11]), nozzle seal cell [12–15] and free jet devices [16,17]. The hot-window cell uses an isothermal gas within a container that is closed off at both ends by windows that are kept at the same temperature as the gas. While this setup is the most ideal situation for measurements, it is generally very difficult to find window material that (i) can withstand the high temperatures at which gas properties need to be measured, (ii) are transparent in the spectral regions where measurements are desired (usually near-infrared to infrared) and do not experience "thermal runaway" (strong increase in absorptivity at a certain temperature level), and (iii) do not succumb to chemical attack from the test gas and other gases. Therefore, hot-window cell measurements have been limited to 800 K and below. The cold-window cell lets the probing beam enter and exit the test cell through water-cooled windows. Tien and Giedt [9] designed a high-temperature furnace consisting of a zirconia tube, surrounded by a graphite heater, that allowed temperatures up to 2000 K, and that was fitted with water-cooled, movable zinc selenide windows. While allowing high temperatures, it is impossible to obtain truly isothermal gas columns with such a device. For example, for a nominal cell at 1750 K of 30 cm length, they found that the temperature gradually varied by a rather substantial 350 K over the central $\frac{2}{3}$ of the cell, and then rapidly dropped to 330 K over the outer $\frac{1}{3}$. Nozzle seal cells are open flow cells in which the absorbing gas is contained within the cell by layers of inert gases on each end, such as argon or nitrogen. These systems eliminate some of the problems with windows, but may also cause density and temperature gradients near the seal; in addition, some scattering may be introduced by the turbulent eddies of the mixing flows [18]. Using a burner and jet for gas radiation measurements eliminates the window problems, and is in many ways similar to the nozzle seal cell. Free jet devices can be used for extremely high temperatures, but they also introduce considerable uncertainty with respect to gas temperature and density distribution and to path length.

Rosenmann et al. [19] have made diode laser measurements of CO_2 line intensities at temperatures up to 800 K using a grating monochromator and an absorption cell. A monochromator can only measure a small spectral region at a time. Thus, it takes a long time to make measurements across the spectrum. Some researchers have used FTIR spectrometers, which can measure the whole spectrum in a short time. For example, Devi et al. [20] have made measurements of pressure broadening and shifting by nitrogen in the 4.3 μm band of CO_2 using an absorption cell and an FTIR spectrometer. Johns [21] described absolute intensity and broadening measurements of CO_2 using a spectrophotometer with an InSb photovoltaic detector and a brass absorption cell with CaF_2 windows. Phillips [22] has made CO_2 measurements in the 4.3 μm region at temperatures up to 1000 K using a stainless steel absorption cell. His measurements were made at a moderate resolution of 0.06 cm^{-1} using an FTIR spectrometer.

Radiative properties for gases other than CO_2 have been measured by other investigators. For example, Goldman et al. [23] have made high resolution studies of NO_x using an FTIR spectrometer. Their studies use an absorption cell and also include some atmospheric measurements. Absorption cell measurements have been made for water vapor by Esplin et al. [24] using an FTIR spectrometer. Varberg and Evenson [25] have made far IR measurements of CO using a tunable far IR spectrometer. Their absorption cell consisted of a 4 m long 12 mm diameter copper tube with 75 μm thick polyproplyene windows. Their measurements were made at pressures between 0.03 and 1 Torr.

Tarrago et al. [26] describe absolute absorption measurements of the methane isotope CH_3D, using a stainless steel cell with KBr windows. Their measurements were made with a dual beam TDLS for pressures of 0.15–2 Torr.

In the present work, measurements are made with a drop tube mechanism, which is basically a variable length absorption cell, with a FTIR spectrometer. The length of the absorption cell is controlled by moving a drop tube with a window at the end within the cell. Since the drop tube is only kept within the high-temperature region of the cell for a short time while the measurements are being made, isothermality of the absorbing path is ensured. Also, the window may be rated to withstand a much lower temperature than the measurement temperature.

A number of gas property databases have been assembled for gas heat transfer calculations. Some of them, like HITRAN [27,28] and HITEMP [29] are high-resolution line-by-line databases, while others like EM2C [30] and Radcal [31] are based on narrow band data. HITRAN contains line strengths, line widths and other parameters for many gases. Most of these data have been obtained from experimental measurements, although a number of "hot lines" have been artificially calculated, to extend the databases' validity to higher temperatures. HITRAN is assumed valid for temperatures up to 600 K. HITEMP gives the same information as HITRAN, but contains data for many more hot lines, which become active at high temperatures, which have all been generated artificially and have not yet been validated by experiment. Our data will show that HITEMP can be used for temperatures up to about 1000 K. EM2C is a narrow band database, which has been generated from the HITRAN database together with some proprietary high-temperature extensions. A FORTRAN code provided with the database allows calculation of the spectral transmissivity of gas mixtures containing various fractions of N_2, CO_2, CO, H_2O, CH_4 and soot. Radcal is a low resolution (around 25 cm^{-1}) narrow band database, which is based on experimental data. Like EM2C, the spectral transmissivity of gas mixtures can be calculated using a FORTRAN routine.

2. Experimental details

Measurements of CO_2 transmissivity were made at temperatures up to 1550 K with a resolution of 4 cm^{-1} using an FTIR spectrometer and a drop tube mechanism. A schematic of the experimental apparatus is shown in Fig. 1. The setup consists of a light source and optical path, a drop tube with a CaF_2 window at the bottom, a gas delivery system, furnace and FTIR spectrometer. The entire optical path was purged with dry N_2 to avoid absorption by atmospheric CO_2 and H_2O. The optical path consists of a system of mirrors that send the light beam into the test cell inside the furnace. A platinum mirror inside the furnace reflects the beam back to the detector in the FTIR. An iris placed just before the FTIR is used to allow only light reflected or emitted from the platinum mirror to enter the spectrometer. The drop tube consists of a stainless steel tube, which can be moved up and down within the furnace to vary the optical path length. The motion of the drop tube is controlled by a lead screw and a high-speed stepper motor with a positional accuracy of 1 μm. The absorbing gas column is inside the furnace and is defined by the platinum mirror at the bottom, and the CaF_2 window at the top (at the bottom of the drop tube). The length of the gas column for transmissivity measurements is twice the distance between the platinum mirror and the window, as can be seen from the figure. The partial pressure of the CO_2 that flows through the furnace is controlled by a gas delivery system. Data were collected using a narrow band MCT detector with a

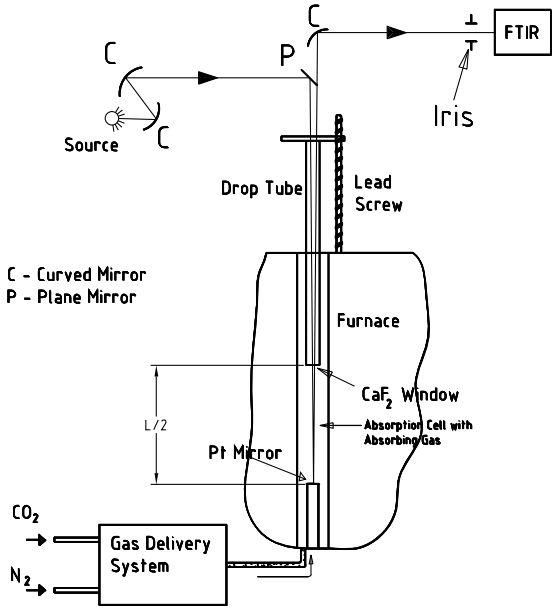

Fig. 1. The Experimental setup.

KBr beamsplitter and an IR source for the 4.3 and 2.7 μm bands of CO_2, and an InGaAs detector with a quartz beamsplitter and tungsten-halogen source for the 2.0 μm band. At room temperature, the transmissivity of CO_2 was obtained by ratioing two signals; one obtained with a certain fraction of CO_2 and a particular path length, and the other with no CO_2 at the same path length. At higher temperatures, it was necessary to account for emission from the hot platinum mirror and the gas itself. The signal reaching the detector, with the light source switched on, is the sum of the reflected signal from the source and emission from the mirror. The pure emission signal, obtained when the light source is blocked, was subtracted from the total signal to obtain the reflected signal, and this was used to obtain the spectral transmissivity.

The measured data at each temperature are compared with results from HITRAN, HITEMP, EM2C and Radcal. Areas of differences and agreement with the different databases are identified. The line-by-line data from HITRAN and HITEMP are used to calculate narrow band transmissivities at the measured resolution, accounting for instrument broadening by the FTIR. EM2C and Radcal each provide a FORTRAN routine for the calculation of narrow band transmissivity.

3. Results and discussion

The room temperature transmissivity of CO_2 was measured initially to validate the setup. Fig. 2 shows the room temperature transmissivity of CO_2 for the 2.7 μm band. The measured data are seen to agree well with all the databases at room temperature. The uncertainty bars in the figure include the experimental standard deviations as well as the uncertainty in CO_2 partial pressure in the gas mixture and the uncertainty in the length of the optical path. Some differences are seen at the band

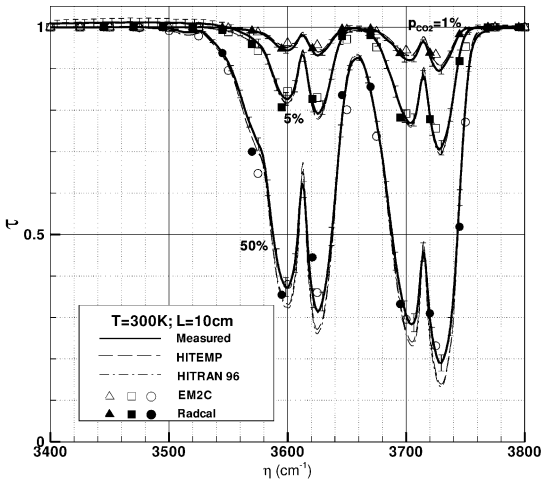

Fig. 2. Room temperature transmissivity of CO_2 for the 2.7 μm band.

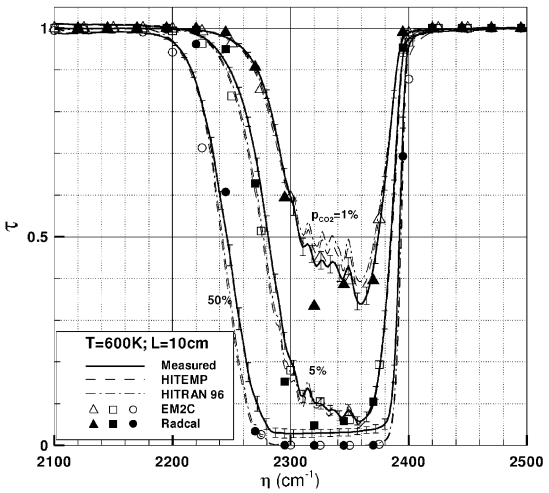

Fig. 3. Transmissivity of CO_2 for the 4.3 μm band at 600 K.

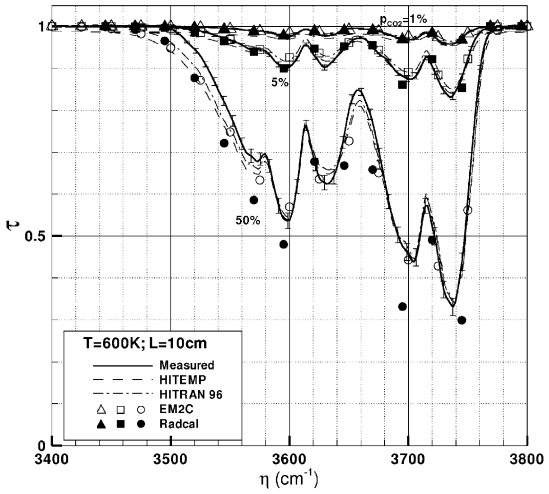

Fig. 4. Transmissivity of CO_2 for the 2.7 μm band at 600 K.

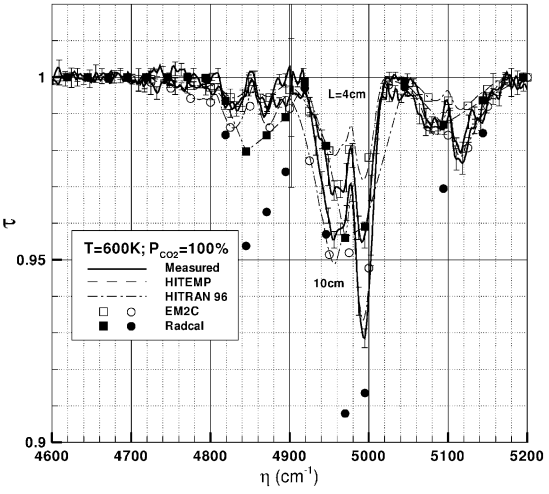

Fig. 5. Transmissivity of CO_2 for the 2.0 μm band at 600 K.

centers, where the measured data show less sharp absorption peaks and valleys. This may be an indication that the instrument broadening of the FTIR spectrometer was somewhat different from the manufacturer's specifications.

Figs. 3–5 show the transmissivity of CO_2 at 600 K compared with the databases. It can be seen from the figures that Radcal starts showing differences at the band centers of the 4.3 and 2.7 μm bands, while the other databases are accurate for these bands. For the 2.0 μm band, all databases

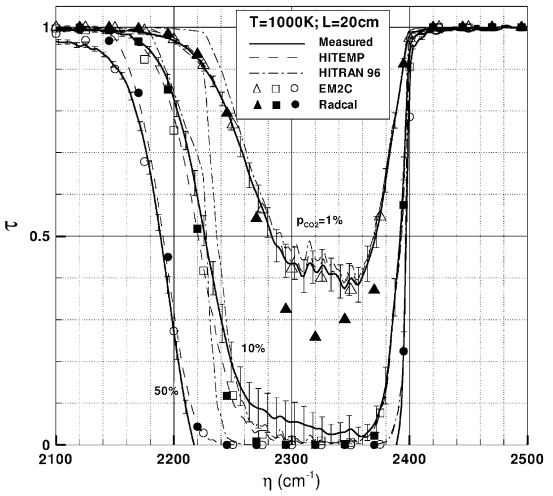

Fig. 6. Transmissivity of CO_2 for the 4.3 μm band at 1000 K.

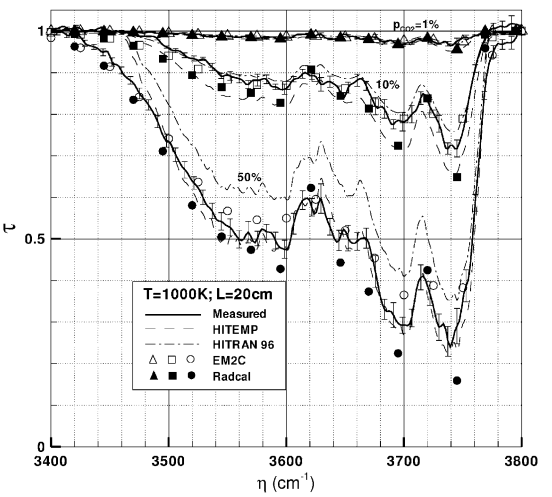

Fig. 7. Transmissivity of CO_2 for the 2.7 μm band at 1000 K.

deviate somewhat from the measured data. It can be seen from Fig. 3 that the measured data do not go to zero at the optically thick regions at the band center of the 4.3 μm band.

As explained earlier, the emission signal from the hot gas was subtracted from the total signal to obtain the reflection signal. At 600 K, the emission signal was a small part of the total. The subtracted signal shows a non-zero contribution at the band center. This is most probably due to detector non-linearity. When the signal is very small, the detector output does not vary linearly with incident energy. At higher temperatures, the emission signal is of the same order as the total signal, and is within the linear range of the detector. Thus, the subtracted signal goes to zero in the optically thick regions at higher temperatures.

Figs. 6–8 show some transmissivities of CO_2 at 1000 K for the three bands. Radcal is again seen to overestimate absorption near the centers of the 4.3 and 2.7 μm bands. HITRAN is seen to underestimate absorption across the wings of these bands, while HITEMP and EM2C are still in good agreement with measured data. HITRAN is expected to deviate from measured data at this temperature, since it does not contain information for high-temperature lines. The uncertainty bars are seen to be much higher than at 600 K. This could be because a large part of the total signal was contributed by emission from the platinum mirror and the hot gas. Thus the subtracted signal has a greater uncertainty.

Sample transmissivities of CO_2 at 1300 K are shown in Figs. 9–11. HITRAN is seen to severely underpredict absorption for all bands. EM2C and Radcal are in good agreement with measured data, while HITEMP starts to overestimate absorption for the wings of the 4.3 and 2.7 μm bands. This appears to indicate that some of the generated line data for the wings of the 4.3 and 2.7 μm bands are incorrect in HITEMP (in contrast to the HITELOR database [32] used in EM2C). All databases are seriously off for the 2.0 μm band. However, the 2.0 μm band is a relatively weak band, and in a part of the spectrum which becomes important only at very high temperatures. Thus its contribution is not significant in practical radiative heat transfer applications.

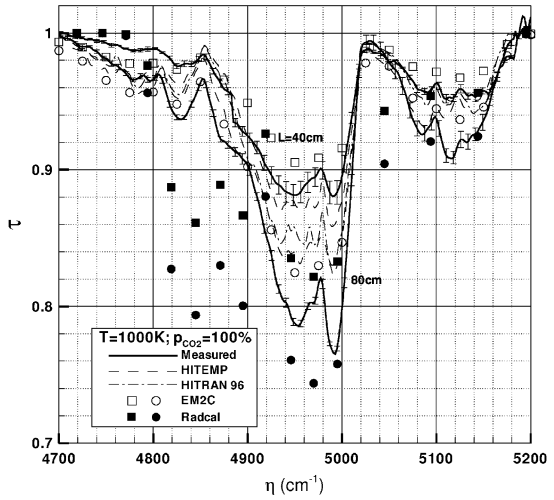

Fig. 8. Transmissivity of CO_2 for the 2.0 μm band at 1000 K.

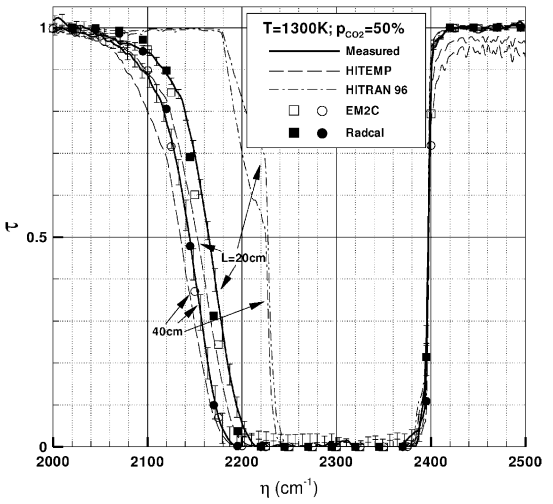

Fig. 9. Transmissivity of CO_2 for the 4.3 μm band at 1300 K.

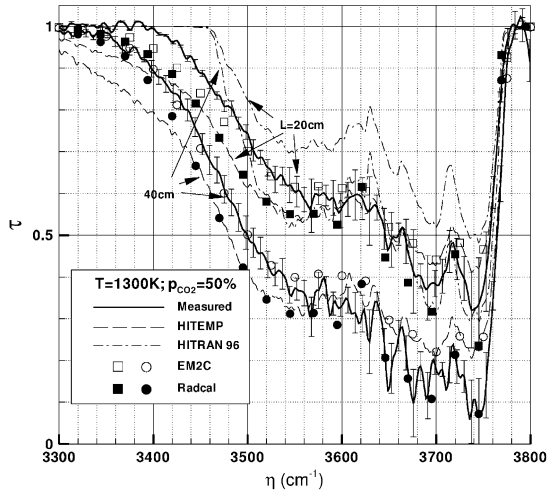

Fig. 10. Transmissivity of CO_2 for the 2.7 μm band at 1300 K.

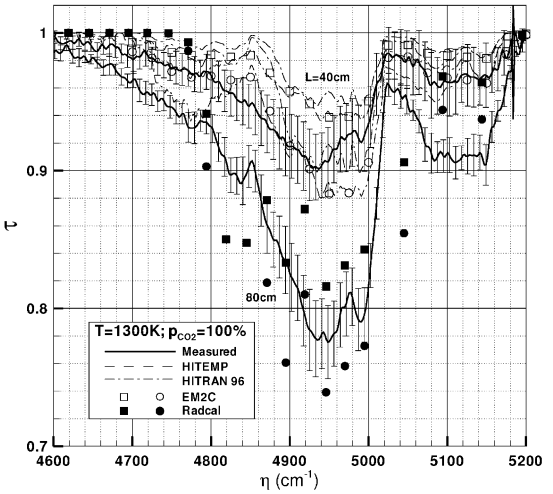

Fig. 11. Transmissivity of CO_2 for the 2.0 μm band at 1300 K.

Figs. 12–14 show the transmissivity of CO_2 at 1550 K. HITRAN is seen to underestimate absorption of the wings of the 4.3 μm band and everywhere across the 2.7 μm band. HITEMP, however, overestimates absorption at the bandwings of the 4.3 and 2.7 μm bands. EM2C remains accurate for the 2.7 μm band, and is in good agreement with the measured data for the 4.3 μm band. This appears to indicate that the proprietary high-temperature extrapolations for EM2C have been somewhat more successful than HITEMP's. Radcal is in surprisingly good agreement with the measured data for the 4.3 and 2.7 μm bands.

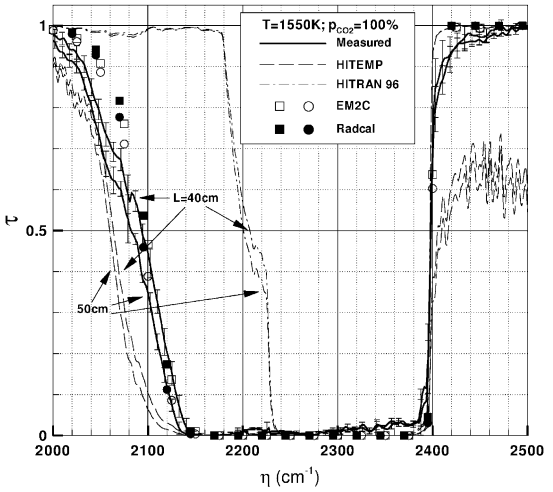

Fig. 12. Transmissivity of CO_2 for the 4.3 μm band at 1550 K.

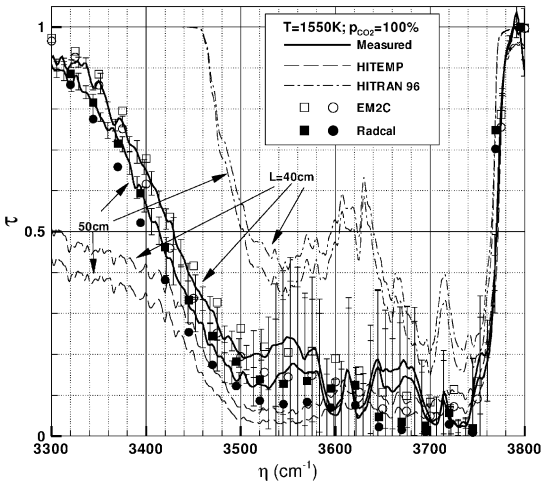

Fig. 13. Transmissivity of CO_2 for the 2.7 μm band at 1550 K.

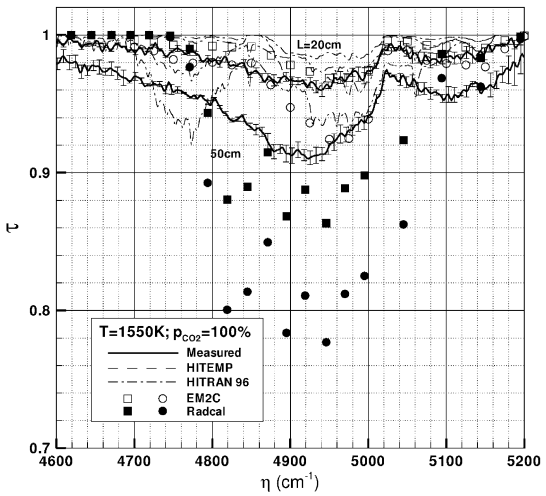

Fig. 14. Transmissivity of CO_2 for the 2.0 μm band at 1550 K.

4. Conclusions

The spectral transmissivity of the 4.3, 2.7 and 2.0 μm bands of CO_2 was measured with a drop tube absorption cell apparatus at five temperatures between 300 and 1550 K. The measured transmissivity at each temperature was compared with two line-by-line and two narrow band databases. Areas of agreement and disagreement with the databases were identified. HITEMP was found to agree better with measured data than HITRAN, as expected, but large differences at the band wings remain at higher temperatures. Radcal was found to deviate from measured data near the band centers, for

optically intermediate conditions, but was otherwise in good agreement with measured data. EM2C was found to be very accurate compared to measured data up to 1300 K, but also to miss lines for higher temperatures, as shown by comparison with measured data at 1550 K.

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