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Medium resolution transmission measurements of CO_2 at high temperature—an update

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Abstract

The current work presents updated measurements of narrow-band transmission for the 2.0, 2.7 and 4.3 μm bands of CO_2 at temperatures of up to 1550 K. In addition, measurements for the 15 μm band of CO_2 are also presented for the first time. Data were collected with an improved drop tube design (as compared to the earlier measurements) and an FTIR-spectrometer. The measured data were compared with the CDSD and HITEMP databases, as well as with previous data obtained from the old drop tube apparatus. The new data have less uncertainties at extreme temperatures than the old data and eliminate some of the problems associated with subtraction of the emission signal with the old apparatus. The data show minor discrepancies with the high-resolution databases, particularly with HITEMP at higher temperatures, but in general agreement is good.

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

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1. Introduction

Radiative properties of combustion gases are required to accurately predict radiative fluxes in a number of physical systems like fires and combustion systems. Narrow-band transmission measurements for the 4.3, 2.7 and 2.0 μm bands of CO_2 have earlier been made by the authors [1] at temperatures up to 1550 K. These measurements showed good agreement with the HITRAN [2] and HITEMP [3] databases for low to moderate temperatures, but some serious deviations from HITEMP at temperatures above 1000 K. However, the measurements also displayed large uncertainties above 1000 K. A more extensive discussion of gas property measurements, and CO_2 measurements in particular, can also be found in Modest and Bharadwaj [1].

In the current work, new narrow-band transmission measurements have been made for the 15, 4.3, 2.7 and 2.0 μm bands of CO_2 at temperatures up to 1550 K. These measurements are compared with the HITEMP and CDSD [4] databases, as well as with our previous data (except for the 15 μm band).

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2. Experimental details

Narrow-band CO_2 transmission measurements were made at temperatures of up to 1550 K with a resolution of $4\,cm^{-1}$ using an improved drop tube mechanism and FTIR spectrometer. A diagram of the new setup is shown in Fig. 1.

As in the previous CO_2 measurements, a gas delivery system was used to obtain the required mole fraction of CO_2 in the test cell. A KCl window at the bottom of the drop tube prevented the absorbing mixture from entering the rest of the optical path, which was purged with dry N_2 to eliminate atmospheric CO_2 and H_2O. Further details of the setup and the experimental procedure followed may be found in Bharadwaj et al. [1,5].

The earlier setup was modified to increase the signal strength, to eliminate reflection from the KCl window and to prevent modulated furnace emission from reaching the detector. The optical path was opened up using larger mirrors/irises to improve the signal-to-noise ratio. The mirror sizes and focal lengths required to maximize the energy throughput through the optical path were obtained from a custom-written ray-tracing code. Window reflection was eliminated by increasing the tilt of the window from 1° to 4.5°. Also, the corner-cube mirror design of our FTIR (Mattson infinity HR series) allowed us to eliminate modulated furnace emission (i.e., furnace emission entering the FTIR, and exiting again in modulated fashion) from reaching the now external detector. The mirror holder was also redesigned to make it easier to align the platinum mirror. Further details of these modifications may be found in Bharadwaj et al. [6,7].

Since the modulated emission from the furnace was eliminated, it was no longer necessary to subtract the emission signal from the total of emission and reflection as described in Modest and Bharadwaj [1]. A wide-band MCT detector with a KBr beamsplitter and an IR source was used to collect data for the 15, 4.3 and 2.7 μm bands of CO_2, and an InGaAs detector with a quartz beamsplitter and tungsten–halogen source were used for the 2.0 μm band.

3. Data analysis

The measured data at each temperature are compared with results from the HITEMP and CDSD databases, as well as with data obtained with the old apparatus. Only data for temperatures beyond 1000 K are presented, since the older data showed little uncertainty at and below that temperature. Areas of differences and agreement with the databases are identified. Line data from the HITEMP database were used to calculate narrow band transmissivities at the measured resolution, taking into account instrument broadening by the FTIR spectrometer. The measurements were made over a period of 8–12 h for each

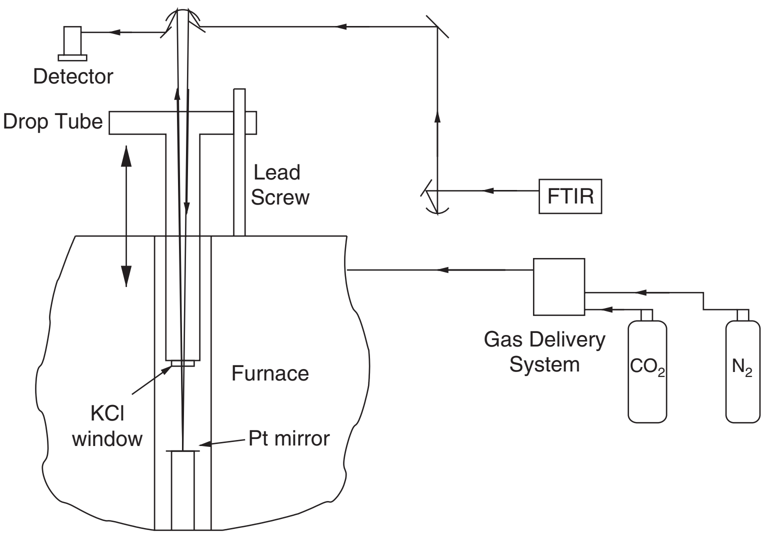

Fig. 1. The experimental setup.

temperature, which made it necessary to correct for the drift in the strength of the signal at the detector. This drift could be due to temperature fluctuations of the optical components (mirrors and beamsplitters) or varying detectivity of the cryogenic MCT detector. Since the transmissivity was obtained as the ratio of two signals, a varying signal strength manifests itself as a transmissivity (henceforth called the 'baseline transmissivity') which is different from 100% in the regions of the spectrum over which the gas is transparent. Thus, an estimate of the factor by which the signal has changed at each spectral location within the bands may be obtained by interpolating the baseline transmissivity in the band regions. The experimental transmissivity in the bands is then divided by the interpolated transmissivity to correct for the drift.

4. Results and discussion

Fig. 2 compares the experimental data for the 2.0 μm band of CO_2 at 1000 K with the HITEMP and CDSD databases, as well as with data obtained with the old setup. As the figure shows, the experimental uncertainties (represented by the error bars on the plot) for the new data are of the same order as the old uncertainties. The new data agree with the old data over most of the band, but show somewhat less absorption than either of the databases at the low wavenumber end of the band (below about 4850 cm^{-1}).

Experimental data for the same band at 1300 and 1550 K are compared with the databases and with the old data in Figs. 3 and 4. As Fig. 3 shows, the new data have smaller uncertainties than the old data, but show about the same absorption throughout the band. The experimental data agree with CDSD, while HITEMP predicts more absorption below about 4850 cm^{-1}. At 1550 K, the new data are again seen to be in agreement with CDSD and with the old data, while HITEMP predicts drastically more absorption throughout the band. This might indicate superfluous/incorrectly extrapolated lines in the HITEMP database.

Fig. 5 compares the measured data for the 2.7 μm band of CO_2 at 1000 K with the databases and the previous data. The old measurements have much larger uncertainties and show less absorption than the current measurements. The new measurements are in close agreement with the CDSD database, while showing somewhat more transmission than HITEMP below about 3500 cm^{-1}. The old data again have large

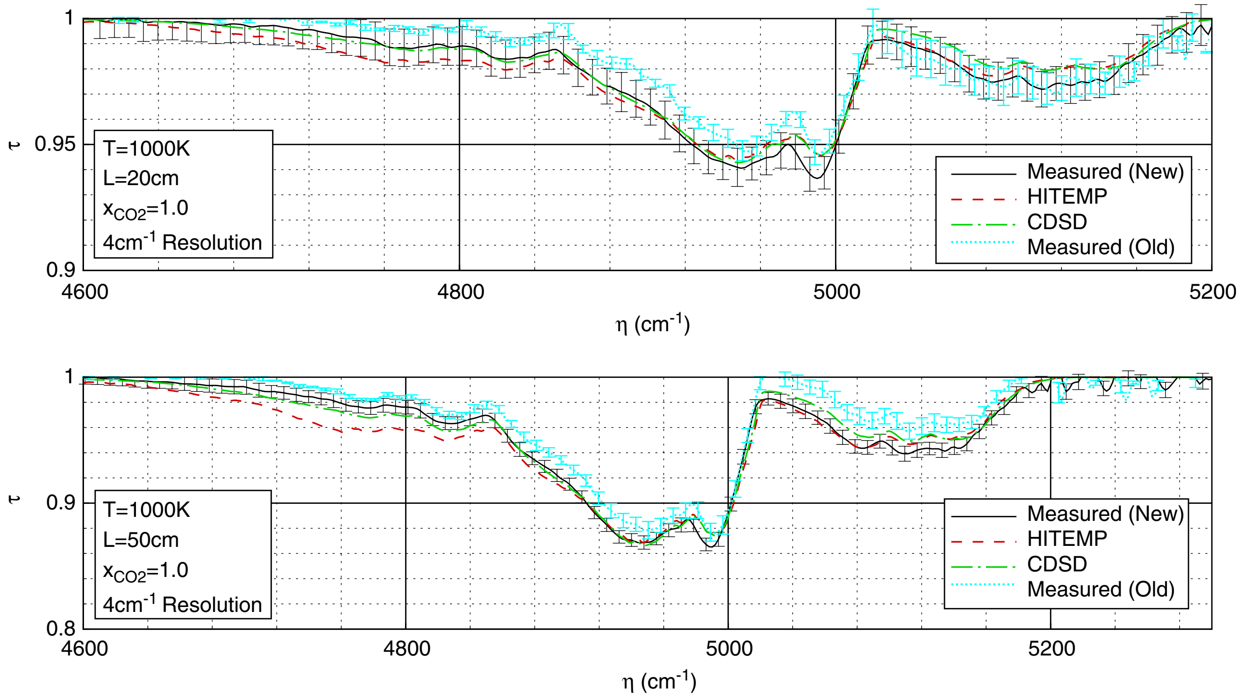

Fig. 2. Comparison of experimental data with HITEMP and CDSD (1000 K, 2.0 μm band of CO_2).

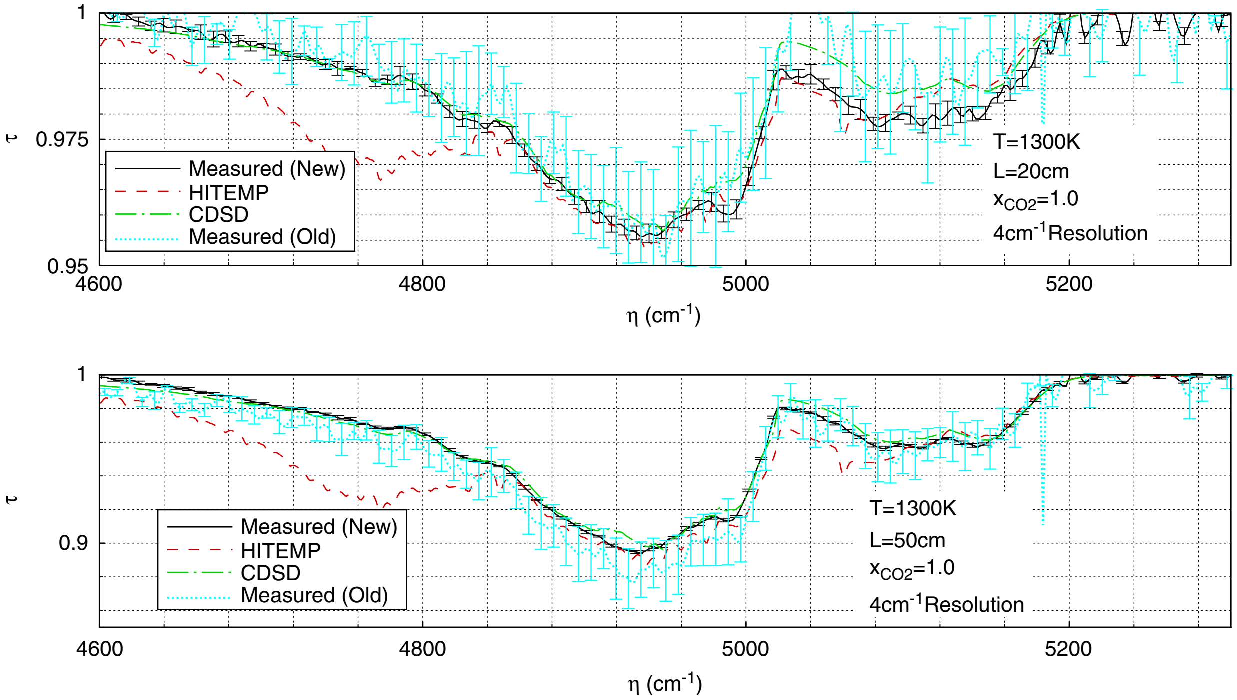

Fig. 3. Comparison of experimental data with HITEMP and CDSD (1300 K, 2.0 μm band of CO_2).

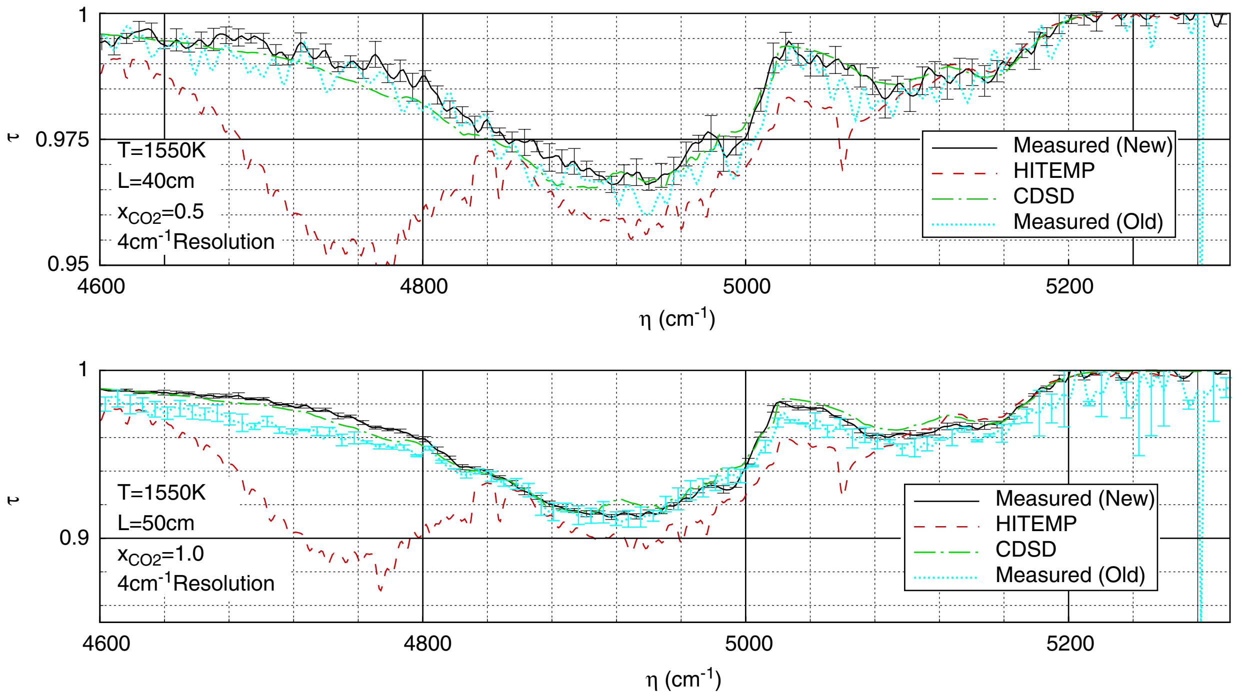

Fig. 4. Comparison of experimental data with HITEMP and CDSD (1550 K, 2.0 μm band of CO_2).

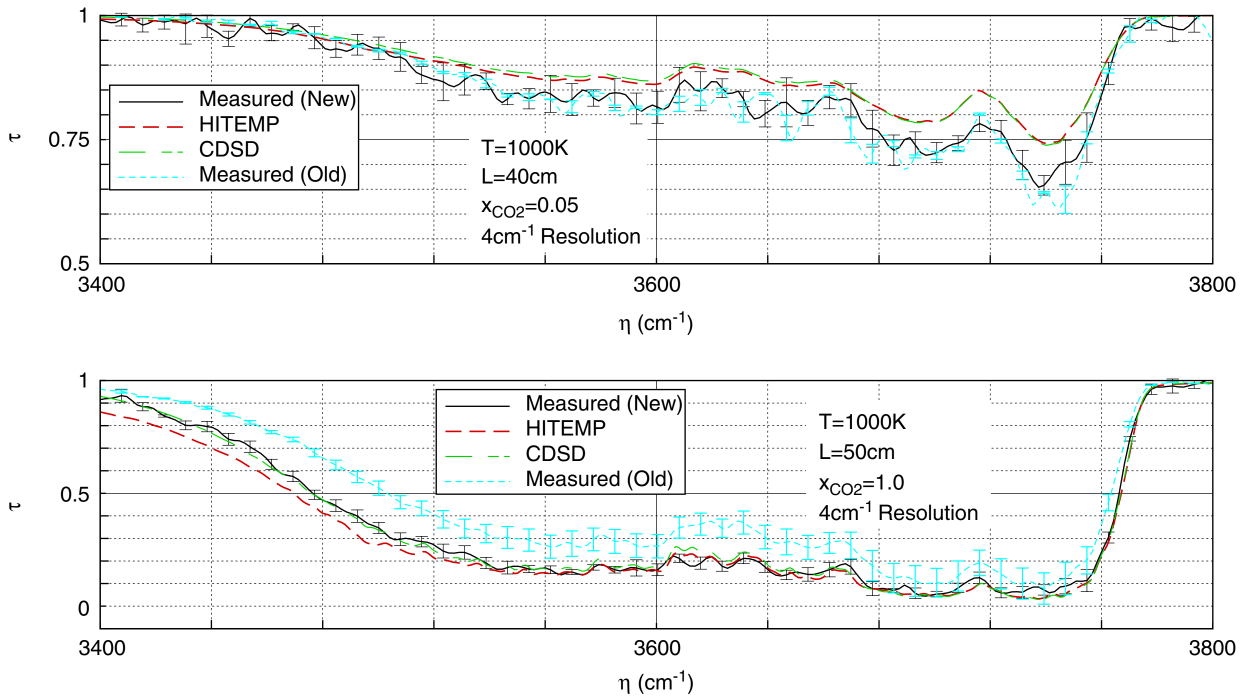

Fig. 5. Comparison of experimental data with HITEMP and CDSD (1000 K, 2.7 μm band of CO_2).

uncertainties at 1300 and 1550 K (Figs. 6 and 7). The current data are in very good agreement with CDSD, while HITEMP shows significantly more absorption below 3600 cm^{-1} at both temperatures. Again, this might indicate the presence of spurious or incorrectly extrapolated high-temperature lines in the HITEMP database.

The older data show somewhat less absorption than HITEMP in the wings of the 4.3 μm band of CO_2 at 1000 K (Fig. 8). The uncertainties are also large, and the data show negative transmission at the center of the band, due to errors resulting from subtraction of the large emission component of the signal. The new measurements are seen to be in very good agreement with both the HITEMP and CDSD databases at this temperature.

The HITEMP database is seen to show more absorption than CDSD and the new measurements in the wings of the 4.3 μm band at 1300 K, and significantly more absorption throughout the band at 1550 K (Figs. 9 and 10). The old data are in close agreement with the new data at 1300 K, but were unreliable for 1550 K, as the large uncertainties at the band center show. The new data, on the other hand, have negligible uncertainties. The CDSD database is seen to be in close agreement with the new measurements at both temperatures, perhaps indicating that this database, unlike HITEMP, does not suffer from the problem of incorrectly extrapolated high-temperature lines.

Experimental data for the 15 μm band of CO_2 at 1000 K are compared with the HITEMP and CDSD databases in Fig. 11. Since the older setup used a CaF_2 window, which is opaque above 10 μm, data for the 15 μm band were not collected previously. As the figure shows, the measured data agree well with both the databases over the band. The measurements show large standard deviations below 600 cm^{-1}, because the globar source has little strength below 600 cm^{-1} and because the wide band MCT detector used for these measurements has an effective range of 600–3500 cm^{-1}.

Fig. 12 shows the same band at 1300 K. Again, the measurements are in good agreement with both databases. At 1550 K, CDSD is seen to show a little less absorption than measurement above around 800 cm^{-1}, while HITEMP predicts less absorption than experiment above around 900 cm^{-1} (Fig. 13).

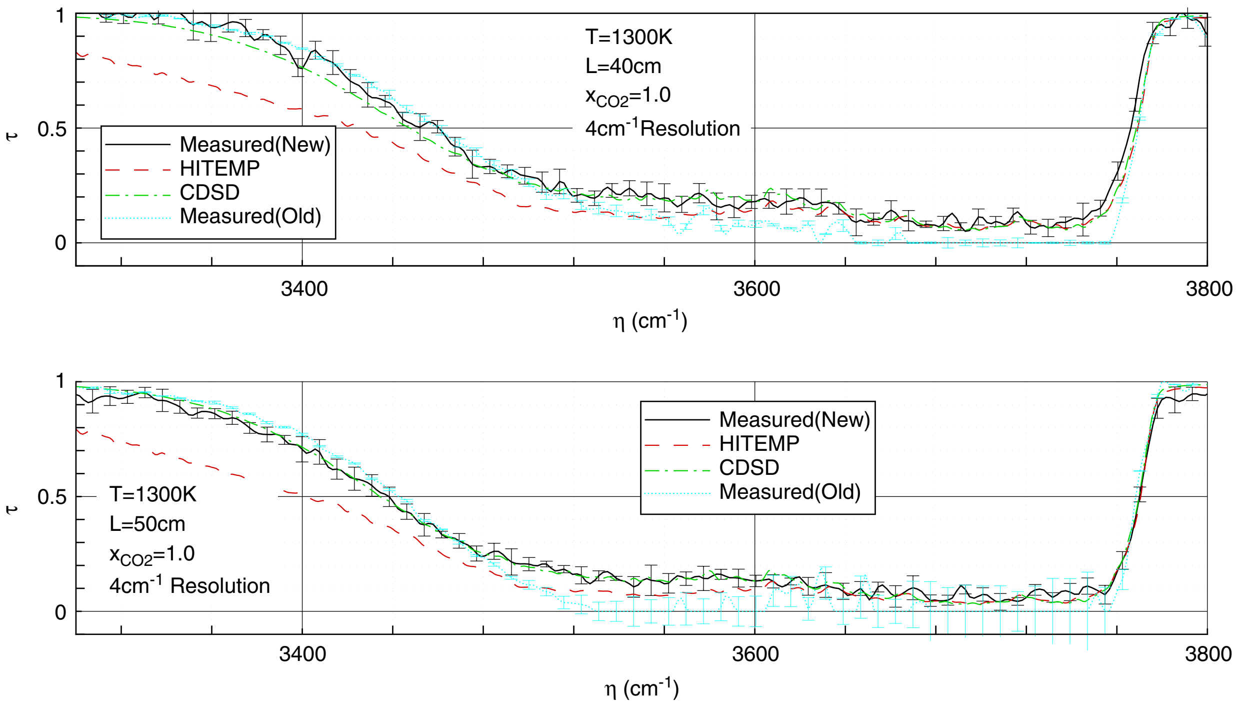

Fig. 6. Comparison of experimental data with HITEMP and CDSD (1300 K, 2.7 μm band of CO_2).

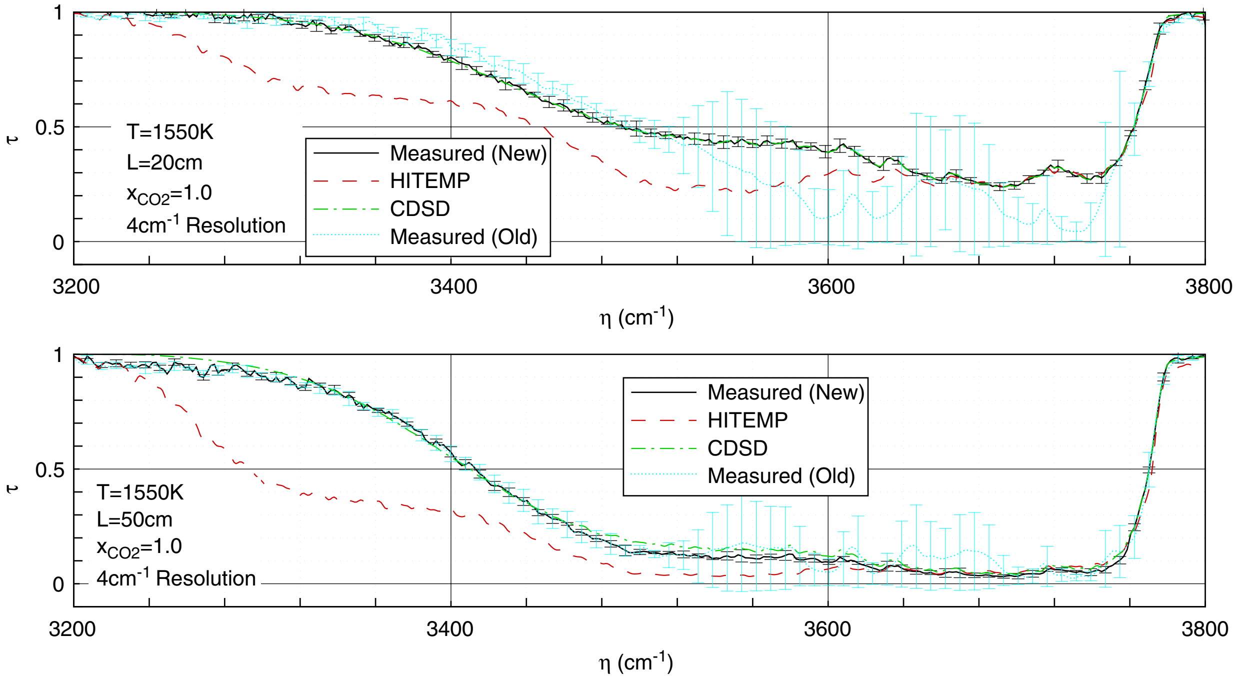

Fig. 7. Comparison of experimental data with HITEMP and CDSD (1550 K, 2.7 μm band of CO_2).

5. Conclusions

A new set of improved narrow-band transmission measurements was made for the 2.0, 2.7, 4.3 and 15 μm bands of CO_2 at temperatures ranging from 300 to 1550 K. These measurements were compared with

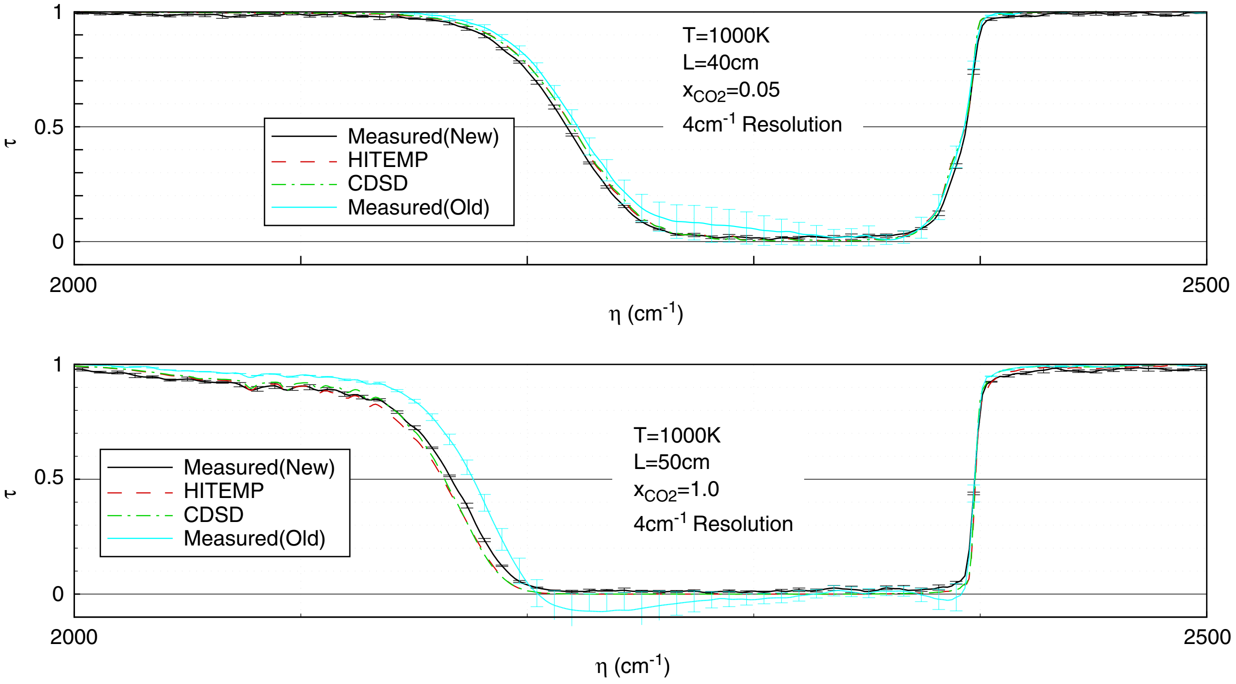

Fig. 8. Comparison of experimental data with HITEMP and CDSD (1000 K, 4.3 μm band of CO_2).

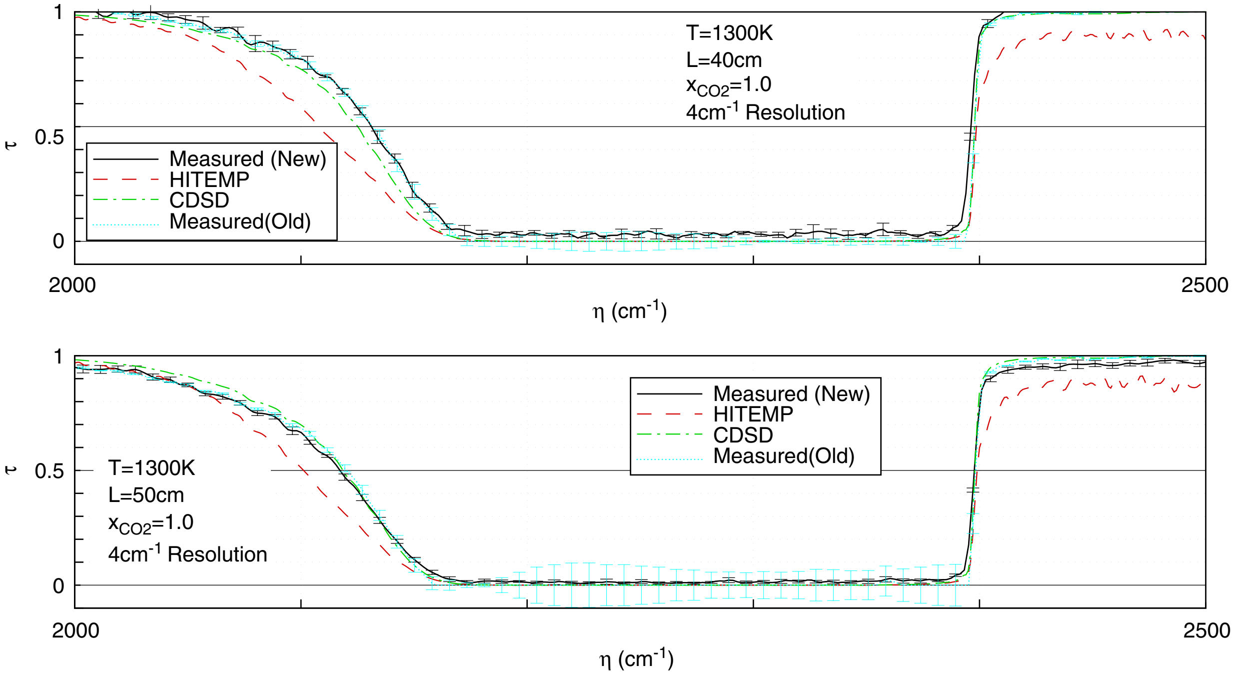

Fig. 9. Comparison of experimental data with HITEMP and CDSD (1300 K, 4.3 μm band of CO_2).

transmission data obtained from the HITEMP and CDSD databases, as well as with earlier data. Areas of similarity and differences between the experimental and database spectra were identified. The older measurements were seen to be accurate at lower temperatures, but to show large uncertainties at and beyond

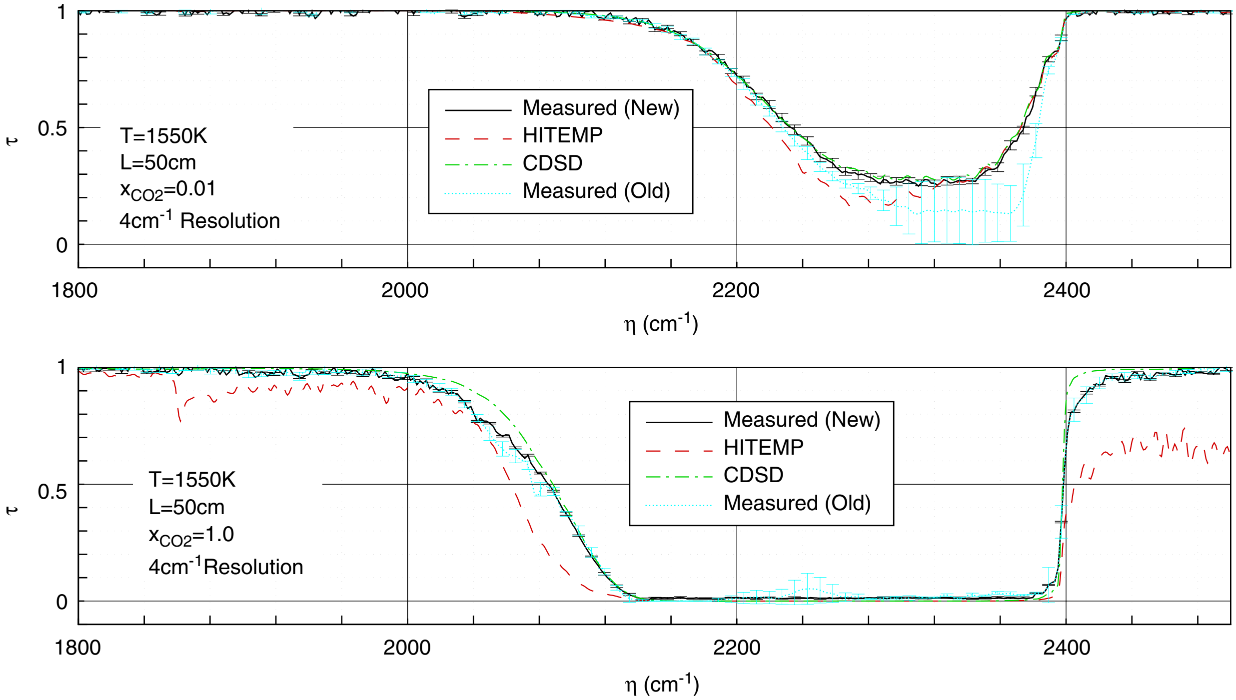

Fig. 10. Comparison of experimental data with HITEMP and CDSD (1550 K, 4.3 μm band of CO_2).

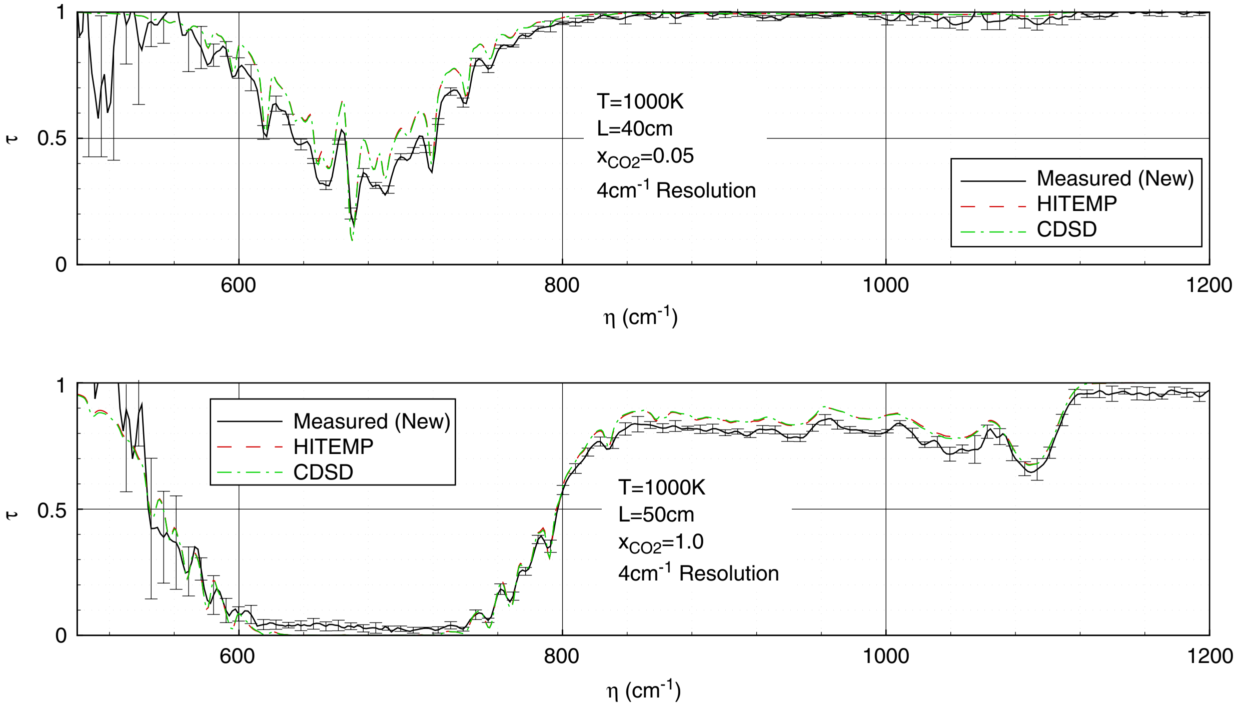

Fig. 11. Comparison of experimental data with HITEMP and CDSD (1000 K, 15.0 μm band of CO_2).

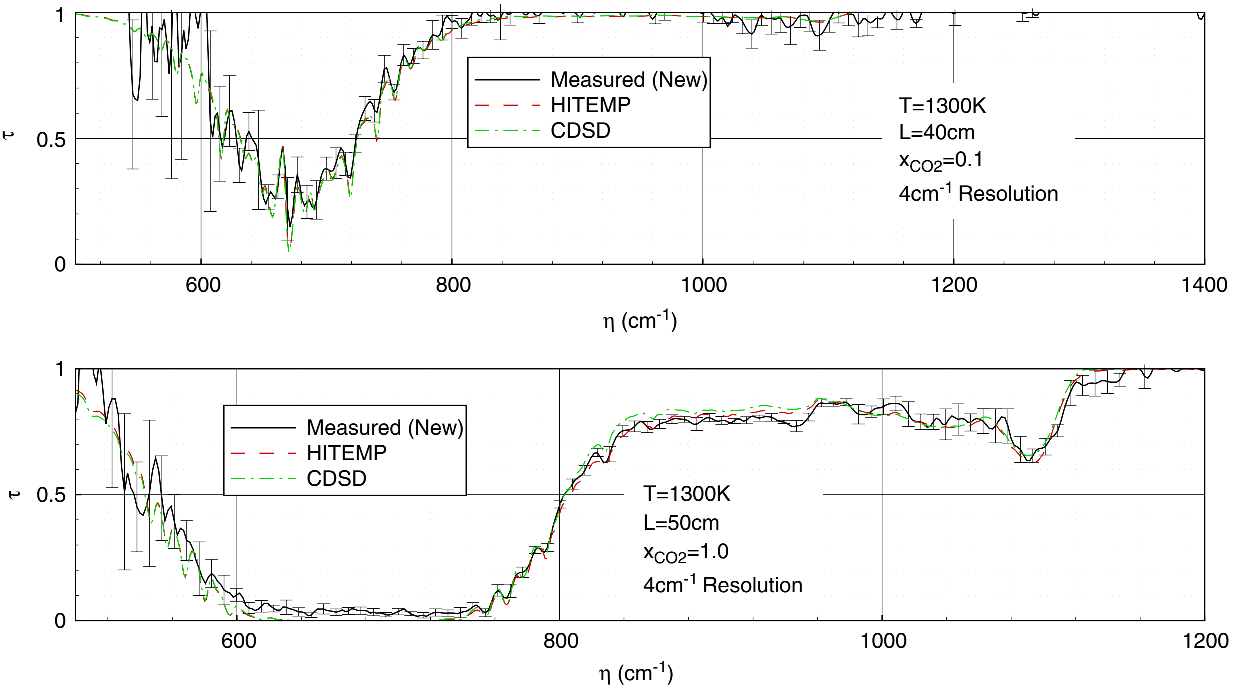

Fig. 12. Comparison of experimental data with HITEMP and CDSD (1300 K, 15.0 μm band of CO_2).

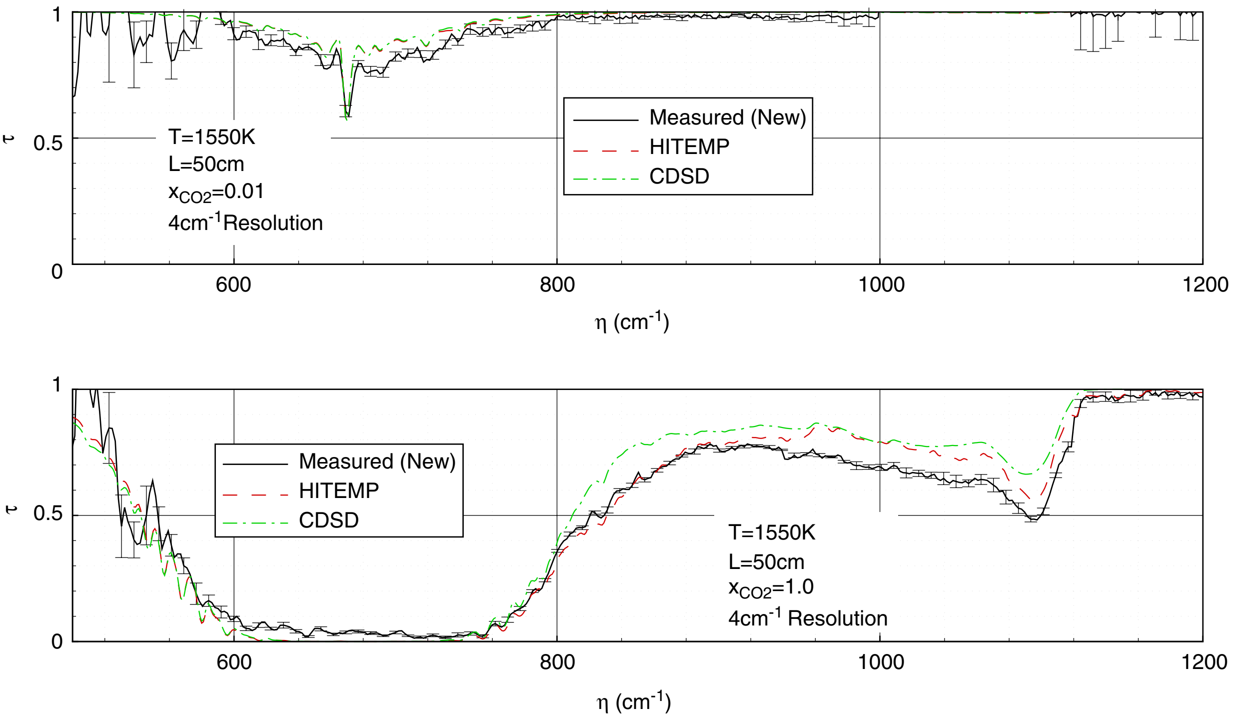

Fig. 13. Comparison of experimental data with HITEMP and CDSD (1550 K, 15.0 μm band of CO_2).

1300 K. HITEMP was seen to show more absorption than experiment over most bands beyond 1300 K, indicating that the database may have spurious or incorrectly extrapolated lines. In contrast, CDSD was seen to be in close agreement with the current measurements for all bands at all temperatures considered. This may indicate that the CDSD database does not suffer from the problems associated with HITEMP, and allows confident use of this database for temperatures up to 1600 K.

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