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High temperature comparison of the HITRAN2012 and HITEMP2010 water vapor absorption databases to frequency comb measurements

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ABSTRACT

The HITEMP2010 and HITRAN2012 databases are important tools for predicting molecular absorption under various environmental conditions. At room temperature, the databases can be quite accurate, owing to their development using room temperature absorption data. However, at elevated temperatures common to combustion and planetary research, their broadband accuracy is largely unexplored. We utilize a dual frequency comb spectrometer and a high temperature optical cell to assess the capability of these databases to accurately predict water vapor absorption for over 600 transitions at conditions up to 1300 K from 6800 cm^{-1} to 7200 cm^{-1}. We demonstrate that at 1300 K, HITEMP2010 and HITRAN2012 accurately predict the existence and position (within 0.033 cm^{-1}) of >99% of transitions with an intensity greater than 1E−28 (cm^{-1}/molecule cm^{-2}), which is the approximate minimum detectable intensity for our absorption spectra. Of the slightly less than 1% of transitions that are misreported, all have linestrengths below 1E−23 (cm^{-1}/molecule cm^{-2}). HITEMP more often predicts transitions that are not observed in the absorption spectra, while HITRAN more often fails to predict an observed line. Updated temperature-scaling coefficients for air-broadening and updated line assignments improve the high temperature performance of HITRAN compared to HITEMP for lineshapes and positions. Our analysis also shows that adding simple temperature-scaling relationships for air-pressure shift and self-broadening half width increase the predictive accuracy of simulations using both databases, and should be employed whenever transition-specific information is unavailable.

1. Introduction

High temperature water vapor absorption measurements are critical to several areas of research. Design and optimization of gas turbines, rocket engines, coal gasifiers, and other combustion devices benefit from high-speed, in-situ optical diagnostics of temperature, pressure, and species concentration [1]. Many of these diagnostics are based on water vapor absorption because water vapor is both present in ambient air and is a key product of combustion. Understanding high temperature water vapor absorption is also critical for the study of exoplanets that are close to their parent star [2,3]. The absorption spectrum of starlight that has passed through the exoplanet atmosphere is used to remotely study its environmental composition.

Temperature, pressure, and species concentrations are typically extracted from measured absorption spectra through comparison with an absorption model. The model is generated by combining a lineshape function (e.g. Voigt, Lorentzian, etc.) with database values of the intensity, position, and broadening parameters for each transition. Water vapor absorption transition information repositories relevant to high temperatures are HITRAN2012 [4], HITEMP2010 [5], HITRAN2008 [6] and BT2 [7], which are composed of both measured and computed transition parameters spanning from 0 to 25,000 cm^{-1}. We focus in this paper on HITRAN2012 (HITRAN) and HITEMP2010 (HITEMP) because they combine BT2 and older versions of HITRAN and HITEMP with newer data and calculations. Additionally, these databases are carefully vetted and widely used by researchers from various fields.

A majority of the experimental data incorporated in HITRAN and HITEMP are collected with high resolution Fourier-transform infrared (FTIR) spectrometers in well-controlled optical cells at temperatures below 400 K [8–15]. Experimental investigations of the databases at higher temperature are crucial because many lineshape temperature-scaling effects – particularly line shift and broadening – cannot be easily computed nor accurately extrapolated from room temperature measurements. The lineshape pa-

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rameters for a small number of water vapor transitions have been measured at up to 2500 K in shock tubes with narrow bandwidth diode laser sources, [16] or up to 3000 K in flames with lower resolution spectrometers, [17]. Liu et al. [18] studied a similar temperature and pressure range as this work but examined fewer transitions at a lower frequency accuracy. They extracted lineshape parameters from fits to 47 transitions and compared their results to HITRAN2004 [19], HITRAN2000 [20], and Toth [21]. Their fit intensities and air-broadening coefficients were typically within approximately 20% and 50% of the published data, respectively. They showed that the parameters could widely vary between databases and do not always extrapolate well above room temperature.

The databases have evolved significantly since the Liu et al. work (see Section 2.6). In this paper, we examine the ability of simulations using the HITRAN2012 and HITEMP2010 databases to accurately predict the absorption of more than 600 transitions measured with a broadband, high resolution dual frequency comb spectrometer at up to 1300 K. Our measured spectra span from 6780 cm^{-1} (1475 nm) to 7217 cm^{-1} (1385 nm) with a point spacing of 0.0033 cm^{-1} (0.68 pm at 1429 nm). The data were collected under carefully controlled conditions in a quartz optical cell contained within a high-uniformity furnace. To our knowledge, this is the broadest high resolution/accuracy test of high temperature absorption under carefully controlled conditions in an optical cell.

We demonstrate that at 1300 K, HITEMP and HITRAN accurately predict the existence and position (within 0.033 cm^{-1}) of >99% of transitions with intensity > 1E−28 (cm^{-1}/molecule cm^{-2}) in the measured spectral region, despite having been developed without broadband high temperature experimental data. Further results of this paper include:

(1) HITEMP more often predicts transitions that are not observed in the absorption spectra, while HITRAN more often fails to predict an observed line. Combined, both of these error types account for less than 1% of the more than 600 transitions examined in this work and fall between a maximum intensity of 1e−23 (cm^{-1}/molecule cm^{-2}) and our approximate minimum detectable intensity of 1e−28 (cm^{-1}/molecule cm^{-2}).
(2) The MARVEL line position updates [22] from HITEMP to HITRAN significantly improve the predicted line positions of weak transitions in HITRAN.
(3) HITRAN more accurately predicts the air-broadened width of water vapor absorption features at high temperature thanks to improved power-law temperature-scaling coefficients for air-broadening [15].
(4) Both databases do not contain temperature-scaling of the air-pressure shift parameters and self-broadening parameters. This leads to consistent, significant error in the lineshape prediction at high temperature. The inclusion of a simple temperature-scaling relationship for these parameters significantly improves simulations using both databases.

The results contained in this paper are valid up to 1300 K. Measurements in much higher temperature flames suggest that HITRAN and HITEMP still require further refinement to predict spectra at those conditions [23].

2. Methods

We collect high resolution absorption spectra for pure water vapor and air-water vapor mixtures at five temperatures using dual frequency comb spectroscopy. This section describes the dual-comb spectrometer, the high temperature optical facility, and the data collection and analysis methods.

2.1. Dual frequency comb spectroscopy (DCS)

The dual frequency comb spectrometer is composed of two ring-cavity, Er-doped fiber frequency comb lasers with 100 MHz pulse repetition rates. The spectrometer was adapted from that described in [24]. In the frequency domain, each comb produces hundreds of thousands of narrow-linewidth modes (hereafter referred to as comb teeth) spaced precisely by the pulse repetition rate. Each comb spectrum is separately amplified with an Er-doped fiber amplifier, pulse-compressed in large mode area fiber, and spectrally broadened in highly nonlinear fiber to generate spectra spanning from ∼5800 cm^{-1} to ∼8300 cm^{-1}. We optically filter the broadened spectrum to cover the water absorption region of interest (6780.3 cm^{-1} to 7217.7 cm^{-1}) with a grating-based filter [25,26]. This range encompasses 131,073 comb teeth spaced at 0.0033 cm^{-1} (100 MHz), and was chosen because it contains transitions that have been previously validated at high temperature and because the transitions in this region have highly variable lower state energy values (which is desirable for temperature sensing).

We use dual-comb spectroscopy to detect the absorption on each comb tooth across the spectrum after transmission through the high temperature cell. Dual-comb spectroscopy is a form of multiheterodyne spectroscopy that uses two frequency combs [27,28]. In this approach, the two combs are stabilized with slightly different pulse repetition rates, yielding slightly different comb tooth spacing. The small difference in comb tooth spacing creates a unique frequency difference between each corresponding pair of teeth. When the two combs are combined on a single detector, this frequency difference gives rise to a unique radio frequency (RF) beat note at an integer multiple of the difference in repetition rates, Δf_{rep}, as shown in Fig. 1. If absorption by a molecule in the sample region attenuates a comb tooth pair, the corresponding RF beat note is attenuated. Dual-comb spectroscopy can also be considered in the time-domain where the interference signal manifests as an interferogram similar to those created by FTIR spectrometers. Interferograms repeat at $1/\Delta f_{rep}$ and are coherently averaged to increase the SNR of the measured spectrum. In this work, interferograms are averaged for approximately 90 min for each measured spectrum to obtain absorbance SNR values of approximately 2000:1 across the 101,372 comb teeth spanning the central 400 cm^{-1} of the spectrum.

2.2. Remote DCS

The experimental setup is detailed in Fig. 2. At the time this data was taken, mobile dual-comb spectrometers were not yet available [29,30]. The fixed dual-comb spectrometer used here is located at NIST Boulder and the spectroscopic cell and high temperature furnace are located at the University of Colorado Boulder (CU). The dual-comb spectrometer and spectroscopic cell are connected via two telecommunications optical fibers in the Boulder Research and Administration Network (BRAN) fiber bundle that join the separate labs over a distance of ∼3 km [31]. As shown in Fig. 2d–e, the light from the two frequency comb lasers is passed through these fibers to the CU laboratory. To avoid cross phase modulation, one fiber was used for each comb. Thermal gradients, nonequivalent strains, and mechanical vibrations induce a varying optical path difference between these fibers, resulting in differential phase noise between the two combs upon arrival at CU. To combat this, a portion of the cavity-stabilized 1535 nm reference laser light is co-propagated in each BRAN fiber. After passing over the link, the 1535 nm light in each fiber is separated from the frequency comb light with dense wavelength division multiplexers and interfered to create an error signal that represents the phase difference between the two fiber links. A servo loop and piezoelectric fiber stretcher (General Photonics FST-002) are used to