H$_2$O absorption thermometry accuracy in the 7321–7598 cm^{-1} range studied in a heated static cell at temperatures up to 1723 K

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ABSTRACT

Gas temperature may be inferred by comparing smoothed measurements of absorption spectra spanning >100 cm^{-1} to smoothed simulations of the same. Using this thermometry approach in a heated static cell at temperatures up to 1723 K, we studied H$_2$O vapor absorption near 7450 cm^{-1}, dominated by features in the R-branch of the v$_1$ + v$_3$ absorption band. In a first experiment, the cell was operated at 1200–1723 K and 0.0235 bar, while a commercial external cavity diode laser scanned the 7321–7598 cm^{-1} range. Temperatures inferred from the measured spectra using BT2 simulations were, on average, within 2 K of the actual cell temperature and fell within the limits of error ($\pm$0.5% of reading) for the thermocouple used to monitor gas cell temperature. Temperatures inferred using HITEMP2010 simulations were, on average, 38 K lower than actual cell temperatures. In a second experiment, the cell was operated at 296–1723 K and 1 bar while a swept-wavelength laser monitored the 7347–7536 cm^{-1} range at 10 kHz repetition rate. Temperatures inferred using BT2 simulations were within 3 K of the actual cell temperatures, within the limits of error for the gas cell thermocouple measurements.

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1. Introduction

Laser-absorption spectroscopy (LAS) is a well-developed diagnostic capable of providing quantitative measurements of properties such as gas temperature, species concentration, and velocity in a variety of practical applications. LAS is well suited for measurements in harsh environments. Accurate temperature measurements are critically important in the development of advanced combustion systems due to the governing role temperature plays in chemical kinetics. Hence, numerous LAS sensors have been developed for diagnostics and characterization of combustion systems [1–3]. A typical sensor monitors 2–8 discrete wavelengths; at least 2 of these wavelengths are chosen such that the ratio of their absorbances for the target species is temperature sensitive [4–6]. By comparing the measured absorbances with simulations, the concentration of the absorber in the optical path, and its temperature, can be inferred. Alternatively, gas properties may be inferred by monitoring a broad spectral band (typically 100 cm^{-1} or more). Measuring a broad spectrum ensures a diversity of lower state energies are sampled, generally providing adequate temper-

ature sensitivity regardless of the gas properties. The gas properties are again obtained by comparison of the broadband spectrum to simulation. In this paper, we call this broad band measurement technique *band shape thermometry*. For both the discrete and band shape thermometry techniques, the accuracies of the inferred gas properties depend on the accuracy with which the molecular spectra can be simulated. Spectroscopic parameters for these simulations are generally obtained from databases such as BT2 [7] and HITEMP2010 [8], or from empirically derived databases [9,10]. In this work, we examine the band shape temperature calculation accuracy of broadband sensors using an adaptation of the least-squares technique demonstrated by Kranendonk et al. [11].

The least-squares fitting technique is a robust method for inferring gas properties from measured broadband spectra. This technique had been demonstrated in a variety of practical test articles including aeropropulsion [12,13] and piston [14–16] engines. Sensors using the band shape technique have been demonstrated in a shock tube to have accuracy within 2% at 1000 K using the database parameters available in BT2 [15]. However, for applications at temperatures above 1000 K, band shape thermometry accuracy has not been validated. At temperatures up to 1300 K, many high-resolution reference spectra have been collected covering narrow spectral regions for validation of specific applications [17–19]. Alternatively, recent measurements with broad spectral

coverage have been performed with low spectral resolution ≥ 1 cm^{-1} [20] for validation of heat transfer coefficients such as emissivity. However, high-resolution broadband reference spectra at temperatures >1300 K which are required to validate the band shape fitting technique are sparse in the literature. This is due largely to the experimental difficulties in gaining optical access to a uniform stable gas sample at these conditions.

In this paper, we present two band shape thermometry accuracy studies using BT2 and HITEMP2010 parameters for spectral simulations. These studies were performed on broadband H_2O absorption spectra measured in a static gas cell in the 7321 -7598 cm^{-1} range. Section 2 presents a high-resolution database accuracy study using measured spectra at P < 0.03 bar and temperatures up to 1723 K. These low pressure, high signal-to-noise ratio (SNR) spectra reveal thousands of transitions. Comparison of these high-resolution spectra to database simulations provides a fundamental temperature accuracy limit for broadband sensors operating in this wavelength range. In Section 3, we describe measurements of H_2O absorption spectra in the heated static gas cell spanning 7347–7536 cm^{-1} at 10 kHz using a micro-electro-mechanical-system vertical-cavity surface-emitting laser (MEMS-VCSEL) spectrometer at P = 1 bar and temperatures up to 1723 K. The accuracy of temperatures inferred using this spectrometer with the least-squares technique is then evaluated to demonstrate the capabilities of this system as a gas thermometer.

2. High-resolution accuracy study of database parameters

Recently, Melin and Sanders [21] demonstrated a novel gas cell based on optically contacted sapphire for collection of reference spectra at combustion-relevant temperatures. Using this setup, high-resolution reference H_2O absorption spectra were collected from 1200–1723 K at P < 0.03 bar. Absorption spectra for neat H_2O vapor were obtained with cell pressure monitored using a pressure gauge (Granville Phillips Convectron, 105,353). The measured spectra cover a wavelength range of 7321–7598 cm^{-1} with a spectral resolution of 0.0001 cm^{-1}, standard deviation absorbance noise level of 4.2×10^{-5}, and SNR of 1750 for the strongest absorption features at 1723 K. The spectral resolution presented was based on the point spacing acquired by the spectrometer and was based on the scan rate of the ECDL source. The line width of the laser was sufficient measurement of sub-Doppler broadened spectra, however, the resolution limit based on the laser linewidth has not yet been assessed. Absorption measurements were performed using a fiber-coupled tuneable-wavelength external cavity diode laser spectrometer (New Focus, TLB – 6600). The experimental setup and procedure for obtaining these measured spectra are discussed in detail in [21]. Using these reference spectra, the accuracy of the HITEMP2010 and BT2 database parameters were assessed with respect to band shape thermometry. Compared to practical measurement devices where the high repetition rate sources like the MEMS-VCSEL have been used [14,22], the reference spectra feature relatively low instrumental broadening, baseline artifacts, and noise. This study places a lower bound on the temperature calculation accuracy which may be obtained via this technique based on the spectral database parameters; in practice accuracies could be worse due to instrumental broadening, baseline artifacts, and noise associated with harsh measurement environments.

2.1. Band shape temperature fitting procedure

The first step in the spectral fitting technique was to generate a library of simulated spectra at spanning the range of expected measurement temperatures. Individual measured absorption spectra were then compared with the library to identify a best match. The spectral library simulations were created assuming a test gas

of pure H_2O, pressure of 0.0235 bar, a path length of 16 cm, and a temperature range spanning ±40 K from the furnace set point in temperature intervals of 3 K. The simulations spanned a spectral range of 7315–7630 cm^{-1} with resolution of 0.001 cm^{-1}.

Two simulation libraries were compiled, one using spectral parameters from the BT2 database and the other from HITEMP2010. Spectra simulated using the HITEMP2010 database parameters were modeled using the same techniques and underlying assumptions as in SpectraPlot [23]. In brief, line centers were shifted using only the air-pressure-induced line shift parameters from the HITEMP database. Self-broadening coefficients were scaled as 296/T and the temperature-dependence coefficient. For this work, an intensity cutoff of 1E-40 (cm^{-1}/molecule cm^{-2}) was used at a reference temperature of 1500 K. Additional details for modeling of these molecular spectra have been previously described in the literature [24].

BT2 spectra were simulated using the Tennyson Vidler H_2O calculated internal partition function [25] evaluated from 10 K to 6000 K, while simulations using the HITEMP2010 parameters made use of the HITRAN partition sums evaluated from 70 K to 3000 K. In both simulations, a numerically approximated Voigt lineshape [26] was used. The Voigt lineshape was chosen over more advanced lineshapes due to its simplicity. The band-shape temperature fitting routine is sensitive to absorption cross-sectional area and relies on an underlying assumption that absorption area is conserved. Based on the use of subsequent broadening of the spectra and the conservation of absorption cross-sectional area, the effect of advanced lineshapes on temperature accuracy of the band-shape technique is expected to be negligible. For HITEMP 2010 simulations, database parameters for each transition were used to model the Voigt lineshape.

The BT2 database does not contain broadening coefficients, hence, a best-fit uniform collisional (Lorentzian) width was assigned as follows. First, the FWHM of a relatively isolated feature from the high-wavenumber range of the experimental spectrum, and the FWHM of a relatively isolated feature from the low-wavenumber range of the experimental spectrum were measured. Then the average of these two measurements was computed and set as the target average FWHM for each simulated spectrum. Finally, for each simulated spectrum, the average FWHM was measured in the same way, and the single, uniform Lorentzian FWHM of the simulation was adjusted until the two averages matched. Due to the subsequent over-smoothing of the measured and simulated spectra, the band shape temperature fitting technique is forgiving with regard to imperfect match in the broadening between the measurement and the simulations. For example, the measured data has transition-dependent broadening that typically varies by a factor of 2 over our wavelength range, while the Lorentzian width applied in our simulations is uniform; because of the subsequent over-smoothing, these variations do not significantly affect end results (inferred gas temperatures).

Once the spectral simulation library was built, each spectrum was compared iteratively with a measured spectrum as follows. First, the simulated spectrum was interpolated to match the measured spectrum wavelength axis range and resolution. Second, the simulated and measured spectra were each artificially broadened using a Gaussian convolution filter with constant FWHM. This broadening was applied to reduce sensitivity to database errors in linecenter and/or collisional broadening coefficients, visible in Fig. 1. For this technique, the conservation of absorption area is critical. Broadening the spectra in this manner retains the relative location of absorption peaks and the total cross-sectional area, hence, relevant temperature fitting information. The broadened spectra allow the study of the combined effects of line-strength and lower-state energy with reduced sensitivity to linecenter and collisional broadening coefficients.