Experimental 1.5-1.6 µm Water Line List at 1950 K

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Abstract: We demonstrate a high-temperature water absorption spectrum measured in a flame using cavity-enhanced frequency comb-based Fourier transform spectroscopy. We retrieve transition intensities and frequencies and assign them using the POKAZATEL line list.
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1. Introduction

Understanding the spectrum of water at all wavelengths and temperatures is important for a whole range of terrestrial and astronomical applications. For remote sensing applications, the spectrum of hot water is of particular interest in regions where absorption by room temperature water is weak. We present an experimental high-temperature water line list [1] in one such region, namely 1.5-1.6 µm, which overlaps with the conventional telecom window as well as the astronomers' H-band. The observed lines are assigned to transitions involving high rotational levels and hot bands by comparing them to predictions of a new POKAZATEL variational line list [2].

2. Experimental line list

The high-temperature water spectrum was measured in a premixed methane/air flat flame at atmospheric pressure using a cavity-enhanced optical frequency comb Fourier transform spectrometer (FTS) [3]. An Er:fiber femtosecond laser was locked to an open-to-air cavity with a finesse of 150 using the two-point Pound-Drever-Hall method [4]. The burner was placed at the center of the cavity and operated at stoichiometric ratio with a flow rate of 10 L/min. The intracavity comb beam passed 2.5 mm above the burner, where the flame diameter is 3.8 cm, the temperature, T, is 1950$\pm$50 K and the water concentration is 17$\pm$1% [5]. The transmitted light was analyzed using a fast-scanning FTS that acquires a spectrum with nominal resolution of 0.033 cm^{-1} in 0.4 s. The optical path difference was calibrated using a stabilized HeNe laser co-propagating with the comb beam. The frequency axis was calibrated by comparing the positions of the OH lines present in the spectrum to the line positions from the HITRAN2012 database [6]. This yielded an accuracy of 0.01 cm^{-1}, limited by the lack of pressure shift parameters for OH lines in HITRAN. The flame transmission spectrum, normalized to a background spectrum measured when the flame is off, is shown in Fig. 1(a). It was converted to the absorption spectrum shown in Fig. 1(b) using an approximation of the cavity transmission model given in [4]. The center frequencies of the water lines were found from the zero-crossings of the first derivative of the absorption spectrum. The intensities were calculated as $S_{exp} = \alpha_{max}/(n_T\chi_{max})$, where α_{max} is the absorption coefficient at the center frequencies, as shown by the markers for a small spectral range in Fig. 1(c), n_T is the water density (6.4×10^{17} mol/cm^3 for a water concentration of 17% and T = 1950 K) and χ_{max} is the on-resonance value of the Voigt profile calculated assuming a homogenous width of 0.027 cm^{-1} for all lines. The absorption lines less than 0.02 cm^{-1} from OH lines, shown by vertical bars in Fig. 1(c), were removed from the list.

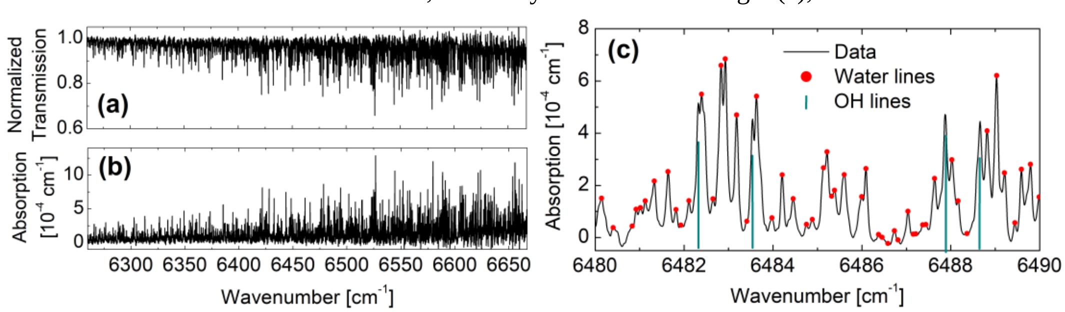

Fig. 1. (a) Normalized transmission spectrum in the flame (20 averages). (b) The corresponding absorption spectrum. (c) Enlargement of the absorption spectrum (black curve) with line positions and intensities (red markers). The positions of the OH lines, removed from the list, are indicated by vertical bars.

3. Line assignment

The spectral analysis of the experimental line list was performed using the high temperature POKAZATEL line list [2] computed with energies replaced by empirical levels coming from a recent study of water spectra [7], in which the MARVEL procedure [8] was used to invert measured line frequencies to energy levels. A portion of the measured spectrum (black) compared to simulations based on the experimental line list (red) and the POKAZATEL line list (blue), with Voigt profiles and homogenous broadening fixed to 0.027 cm^{-1}, are shown in Figs. 2(a) and 2(b), respectively. They demonstrate the good frequency agreement between the two line lists and the experimental data, which enables reliable line assignments. The intensity discrepancies visible in Fig. 2(b) may be partly attributed to the equal homogeneous width assumed for all lines, while variations are likely to occur. The computed line list was used to make a first assignment by identifying the experimental lines within 0.03 cm^{-1} from the computed lines, for which both the lower and upper states are already known. This enabled the assignment of 1900 experimental lines, with half of them assigned to more than one computed transitions, as visible in Fig. 2(c). A second analysis was performed using the method of branches, which allows tracking states with quantum numbers close to MARVEL levels [9]. This led to the assignment of 300 additional lines, involving 126 new energy levels. As a result, 2030 out of the 2417 experimental lines are assigned to 2937 computed transitions. The remaining unassigned lines cannot be unambiguously attributed to water or any other species expected in the flame (e.g. CO_2 or CO).

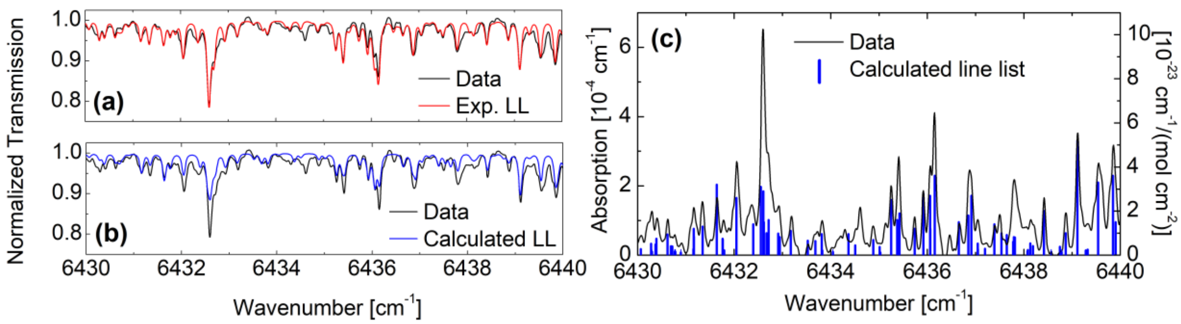

Fig. 2. (a) and (b) Measured spectrum (black) compared to the model calculated using the experimental line list [red, panel (a)] and the calculated POKAZATEL line list [blue, panel (b)]. (c) Enlargement of a portion of the absorption spectrum (black) with line assignments (blue vertical bars); multiple transitions are assigned to single observed absorption lines.

4. Conclusion and outlook

Water transitions from hot bands and high rotational energies were retrieved from a broadband near-infrared spectrum of water recorded in a flame using cavity-enhanced optical frequency comb-based Fourier transform spectroscopy. About 85% of the measured lines were assigned using previous information on empirical energy levels and by comparing them to a new variational line list. About half of the experimental lines were assigned to multiple transitions and the majority of the assigned lines were associated with hot bands. These new data will form part of the input for the update of MARVEL energy levels for water, which is currently under preparation.

5. References

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