Journal of Quantitative Spectroscopy & Radiative Transfer 205 (2018) 213–219

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

# An experimental water line list at 1950 K in the 6250–6670 cm$^{-1}$ region

Lucile Rutkowski[a], Aleksandra Foltynowicz[a], Florian M. Schmidt[b], Alexandra C. Johansson[a], Amir Khodabakhsh[a], Aleksandra A. Kyuberis[c], Nikolai F. Zobov[c], Oleg L. Polyansky[d], Sergei N. Yurchenko[d], Jonathan Tennyson[d,*]

[a] *Department of Physics, Umeå University, 901 87 Umeå, Sweden*
[b] *Thermochemical Energy Conversion Laboratory, Department of Applied Physics and Electronics, Umeå University, 901 87 Umeå, Sweden*
[c] *Institute of Applied Physics, Russian Academy of Sciences, Ulyanov Street 46, Nizhny Novgorod, Russia 603950, Russia*
[d] *Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK*

ARTICLE INFO

*Article history:*
Received 29 August 2017
Revised 25 October 2017
Accepted 25 October 2017
Available online 27 October 2017

*Keywords:*
Water
Absorption
Fourier transform spectroscopy
Optical cavity
Frequency comb
*ab initio* Calculations

## ABSTRACT

An absorption spectrum of $H_2{}^{16}O$ at 1950 K is recorded in a premixed methane/air flat flame using a cavity-enhanced optical frequency comb-based Fourier transform spectrometer. 2417 absorption lines are identified in the 6250–6670 cm$^{-1}$ region with an accuracy of about 0.01 cm$^{-1}$. Absolute line intensities are retrieved using temperature and concentration values obtained by tunable diode laser absorption spectroscopy. Line assignments are made using a combination of empirically known energy levels and predictions from the new POKAZATEL variational line list. 2030 of the observed lines are assigned to 2937 transitions, once blends are taken into account. 126 new energy levels of $H_2{}^{16}O$ are identified. The assigned transitions belong to 136 bands and span rotational states up to $J = 27$.

## 1. Introduction

Water is ubiquitous and its spectrum is important for a whole range of terrestrial and astronomical applications. Serious attempts have been made to characterize the spectrum of hot water both experimentally by observation of spectra [1–17] and theoretically by the computation of extensive line lists [18–24]. These line lists are used to inform databases concerned with models of hot bodies such as HITEMP [25] and ExoMol [26,27]. A comprehensive assessment of water spectroscopy was undertaken by an IUPAC task group [28,29] whose work is currently being updated [30].

The ubiquity of water means that understanding its spectrum at all wavelengths and temperatures is always important. The spectrum of hot water is of particular interest in regions were absorption by room temperature water is weak. The present work concentrates on one such region as it probes the spectrum of hot water in the conventional telecom window (1.53–1.565 µm) as well as the astronomers' H-band (1.5–1.8 µm). These regions are useful for remote sensing of hot water spectra due to the reduced atmospheric absorption. Previous high-temperature water spectra analyzed for this region [10,12,13,31–35] were recorded in emission in flames at atmospheric pressure at moderate spectral resolution; in addition, due to the lack of thermal stability, these spectra did not provide usable information on the line intensities.

This paper presents a high temperature water absorption spectrum measured at Umeå University. The spectrum is measured in a premixed methane/air flat flame at atmospheric pressure using a cavity-enhanced optical frequency comb-based Fourier transform spectrometer (FTS) [36]. The combination of an FTS with a frequency comb allows the measurement of broadband and high resolution molecular spectra in short acquisition times and without visible influence of the instrumental line shape [37,38], while the cavity provides high sensitivity to absorption [39]. The ability to measure the present spectrum simultaneously over a broad bandwidth reduces systematic errors and the influence of fluctuations of the environmental conditions. The spectrum is recorded at high resolution (0.033 cm$^{-1}$) in the near-infrared 6250–6670 cm$^{-1}$ region, and line positions are identified with an accuracy of 0.01 cm$^{-1}$. Knowledge of the temperature and water concentration, which have previously been measured for that specific burner by Qu et al. [40] using tunable diode laser absorption spectroscopy, as

---

[*] Corresponding author.
*E-mail address:* j.tennyson@ucl.ac.uk (J. Tennyson).

https://doi.org/10.1016/j.jqsrt.2017.10.016
0022-4073/

well as the thermally stable conditions, allow absolute line intensities to be determined.

The measured absorption spectrum is compared to the newly computed POKAZATEL hot line list [24] augmented by the inclusion of empirical energy levels [28]. This comparison allows us to assess both the contents of the measured spectrum and the reliability of the computed line list. The POKAZATEL line list is then used to make assignments to the spectrum resulting in a significant number of newly identified transitions and energy levels.

The following two sections of the paper describe the experimental set-up and results. Section 4 presents the experimental water line list. Comparisons with the computed line lists, particularly the most recent one [24], are given in Section 5, followed by conclusions in Section 6.

## 2. Experimental setup

The experimental setup is described in detail in references [36,41] and is therefore only briefly summarized here. The spectrometer consists of an Er:fiber femtosecond laser with a repetition rate of 250 MHz ($0.0083\,\mathrm{cm}^{-1}$), a 60 cm long enhancement cavity with a finesse of around 150, and a fast-scanning Fourier transform spectrometer (FTS). The comb is locked to the cavity using the two-point Pound–Drever–Hall method [39,42] with locking points at 6330 and $6450\,\mathrm{cm}^{-1}$. The cavity is open to air, and a flat flame burner [43] is placed in its center. The burner is operated on premixed methane/air at stoichiometric ratio with a total flow rate of 10 L/min. The comb beam probes the line of sight in the flame (flame diameter of 3.8 cm) at atmospheric pressure and at a height above the burner (HAB) of 2.5 mm. At this HAB the temperature and species are rather homogeneously distributed along the line of sight [40,43], the average flame temperature is $1950 \pm 50$ K, the average water concentration is $17 \pm 1\%$ (both characterized using tunable diode laser absorption spectroscopy [40]), and the average hydroxide (OH) concentration is 0.28% [41].

The light transmitted through the cavity is coupled into an optical fiber connected to the input of a fast-scanning FTS with an auto-balancing detector that acquires a spectrum with $0.033\,\mathrm{cm}^{-1}$ resolution in 0.4 s. The optical path difference is calibrated using a stabilized HeNe laser whose beam is co-propagating with the comb beam in the FTS. The wavelength of the HeNe laser is calibrated by comparing the positions of the OH lines in the spectrum to the line positions in the 2012 edition of the HITRAN database [44]. The standard deviation of the relative difference between the experimental and HITRAN OH line positions is $0.0076\,\mathrm{cm}^{-1}$. Since HITRAN does not contain data on the pressure shift of the OH lines, we estimate the shift to be 10% of the pressure broadening at atmospheric pressure, i.e. 0.007 $\mathrm{cm}^{-1}$. Thus we estimate that the frequency accuracy of the spectrum is $0.01\,\mathrm{cm}^{-1}$. The high-temperature spectrum is averaged 20 times and normalized to a background spectrum measured when the flame is off. The baseline is additionally corrected for slowly varying etalons fringes.

We note that the influence of broadband flame emission can be neglected since the probability of emission into the cavity mode is low and the cavity thus acts as an effective filter. Moreover, the collimator for coupling the cavity transmitted light into the fiber does not face the flame and is placed few tens of cm away from the flame, where the intensity of emission is already very low.

## 3. Cavity-enhanced absorption spectrum

The normalized transmission spectrum measured in the flame is shown in Fig. 1(a). To extract the absorption coefficient from this spectrum, we use the model for the normalized transmission, $I_T$, given by Foltynowicz et al. [42]

$$I_T(\nu) = \frac{(1-r)^2 \exp[-\alpha(\nu)L]}{1 + r^2 \exp[-2\alpha(\nu)L] - 2r \exp[-\alpha(\nu)L] \cos[2\phi(\nu)L + \varphi(\nu)]}, \tag{1}$$

where $L$ is the interaction length between the light and the sample (i.e. the flame diameter), $r$ is the frequency-dependent intensity reflection coefficient of the cavity mirrors, determined experimentally by cavity ringdown, $\alpha$ and $\phi$ are the molecular absorption and dispersion coefficients, respectively, and $\varphi$ is the round-trip phase shift in the cavity. The round-trip intracavity phase shift is equal to a multiple of $2\pi$ for comb lines locked to the centers of the corresponding cavity modes. Because of the intracavity dispersion, caused by the cavity mirror coatings as well as the gas sample inside the cavity, the cavity modes are not equally spaced and only the comb lines around the locking points are exactly on resonance with their corresponding cavity modes [42]. However, because of the low cavity finesse, the relative comb-cavity offset is small in the entire spectral range of the comb, and the intracavity phase shift can be set to $2\pi$, or zero. To extract the absorption coefficient from Eq. (1) we also neglect the molecular dispersion, since then the equation can be solved analytically. This approximation gives correct values for on-resonance absorption coefficients, since molecular dispersion is equal to zero at these frequencies.

The absorption spectrum obtained using the analytical solution to Eq. (1) with molecular and cavity dispersion put to zero is plotted in Fig. 1(b). The noise on the baseline is $5 \times 10^{-7}$ $\mathrm{cm}^{-1}$, which translates into a signal-to-noise ratio (SNR) of 2400 for the strongest lines. The negative absorption values and the slight line asymmetry at frequencies above $6550\,\mathrm{cm}^{-1}$ are caused by the neglected comb-cavity offset, which increases away from the locking points [42].

## 4. Experimental water line list

The center frequencies of absorption lines are found by taking the first derivative of the absorption spectrum [Fig. 1(b)] and finding the points where it crosses zero. Most of the absorption lines are water transitions but the spectrum contains also several OH transitions [41]. The OH transition frequencies, identified using the 2012 edition of the HITRAN database [44], as well as water lines less than 0.02 $\mathrm{cm}^{-1}$ away from an OH line, are removed from the list. The precision of the center frequencies is below 0.0005 $\mathrm{cm}^{-1}$ for most lines, limited by the line width of the molecular lines (0.7 $\mathrm{cm}^{-1}$) and the SNR of up to 2400. The accuracy is limited to 0.01 $\mathrm{cm}^{-1}$ by the HeNe wavelength calibration. It should be emphasized that positions of overlapping water lines, i.e. those separated by less than the line width, cannot be identified using this method. Note also that the transition frequencies are at atmospheric pressure.

The experimental line intensities, $S$, are calculated from the value of absorption $\alpha_{\max}$ corresponding to each center frequency, using

$$S = \frac{\alpha_{\max}}{n_T \chi_{\max}}, \tag{2}$$

where $\chi_{\max}$ is the peak (on-resonance) value of the Voigt profile (in cm), and $n_T$ is water density at the temperature $T$ (equal to $6.4 \times 10^{17}$ molecule/$\mathrm{cm}^3$ for $T = 1950$ K and [$H_2O$]=17%). Since no data exists for the pressure broadening parameter of water at these temperatures, we assume a Lorentzian half width of 0.027 $\mathrm{cm}^{-1}$ for all lines, as it matches relatively well to the data. The Doppler half width varies from 0.0237 to 0.0253 $\mathrm{cm}^{-1}$ across the spectrum. The experimental line list contains 2417 lines; it is plotted in Fig. 2 and given in the supplementary information. The lowest line intensity that can be identified is $10^{-25}$ cm/molecule, limited by the