Water line parameters for weak lines in the range 7400–9600 cm^{-1}

Roman N. Tolchenov, Jonathan Tennyson*

Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

Abstract

A long pathlength, Fourier transform spectrum of pure water vapour [J. Mol. Spectrosc. 211 (2002) 169] has been fitted and analysed. Line centres, intensities, and self-broadening parameters have been obtained for about 3900 lines with intensities less then 1×10^{-24} cm/molecule. Transitions to 240 newly observed energy levels of H_2O have been identified. 855 lines have been assigned to three other major isotopologues of water. It is pointed out that a new intensity measurements are needed for the stronger lines in this region.
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1. Introduction

Water is molecule number 1 in the HITRAN database because of it importance for the transmission of radiation through the earth's atmosphere, and elsewhere, at all wavelengths from the microwave to the near ultraviolet. The 2004 update of the HITRAN database [1] includes a comprehensive revision of the spectroscopic data for water vapor included in the data base. For example the mid infrared is completely updated using the recent work of Toth [2]. Specifically Toth's work spans the region from 500 to 8000 cm^{-1}. Similarly the whole visible region has similarly been updated using spectra recorded by the Brussels–Rheims collaboration [3–5]. The near infrared region between 9500 and 11 000 cm^{-1} was the subject of a particularly careful study by Brown et al. [6] which is also included in HITRAN-2004.

There is observational evidence that further weak water lines in both the mid infrared [8] and visible [9–11] need to be considered before the database is complete. However, it would appear that the gap in HITRAN updates between 8000 and 9500 cm^{-1} is probably a more serious problem. For this region HITRAN still relies on the measurements of Mandin et al. [12,13] which come from the same measurement campaigns as much of the data superceded at other frequencies.

In a much more recent campaign Schermaul et al. [9] recorded a series of long pathlength Fourier Transform spectra of pure water at room temperature which spanned wavelengths between 6000 and 14 500 cm^{-1}. While several of these spectra have already been analysed [9–11], the lowest frequency spectrum, which probed the region between 6500 and 11 000 cm^{-1}, has been ignored until now.

Fig. 1 compares two portions of the spectrum recorded by Schermaul et al. [9] with predictions made for the same experimental conditions using HITRAN-2004 [1]. The lower frequency range overlaps with that recently studied by Toth [2]. In this region HITRAN-2004 gives a reasonable representation of the spectrum, although it is clear that Schermaul et al.'s experiment detected weak lines which are not yet in the database. The higher frequency data corre-

* Corresponding author. Fax: +44 20 7679 7145.
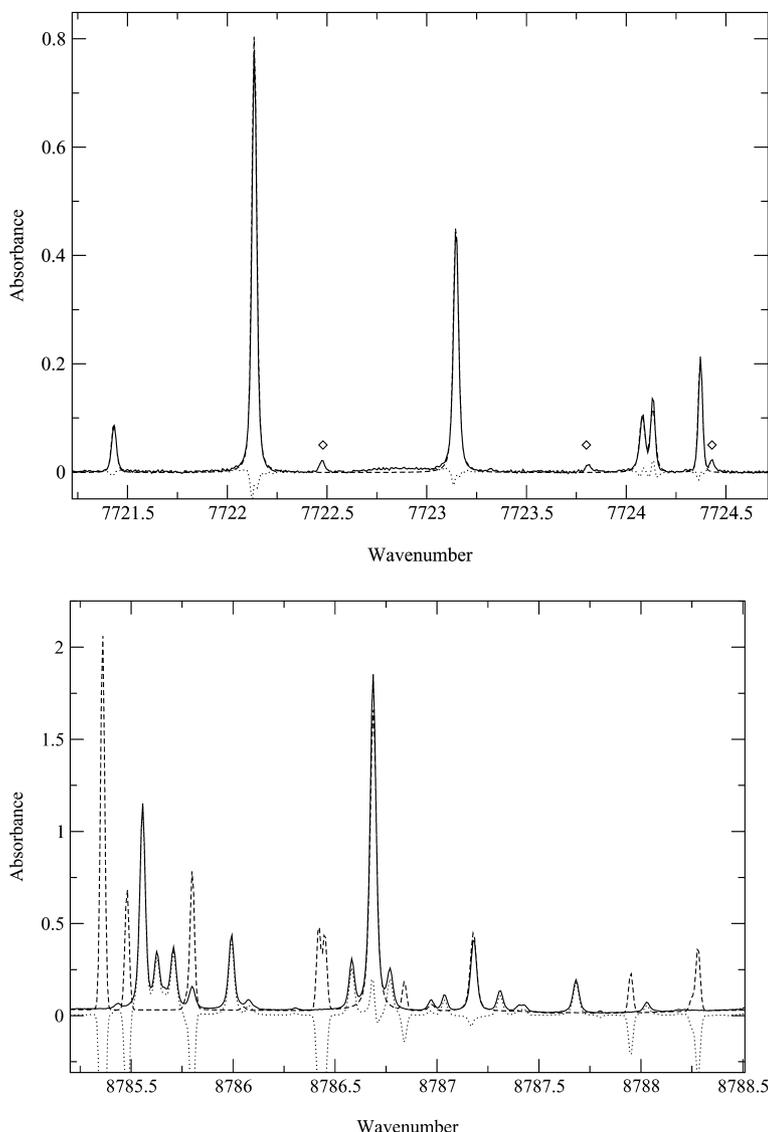*E-mail address:* j.tennyson@ucl.ac.uk (J. Tennyson).

Fig. 1. Comparison of the spectrum of Schermaul et al. [9] with that predicted by HITRAN-2004 [1] for the same conditions. Solid line, experiment; long dashed line, simulation; short dashed line, residual. Diamonds on the upper plot denote lines missing in HITRAN-2004.

sponds to that of Mandin et al. [12]. In this region HI-TRAN-2004 performs much more poorly with, in particular, spurious lines included in the database and problems with line intensities. In this work, we present new line parameters for weak water vapour transitions in the 7400–9000 cm^{-1} region which should provide significantly more comprehensive and reliable parameters for this region.

2. Retrieval of line parameters and assignment

Spectrum 1 of Schermaul et al. [9] was recorded at a temperature $T = 294.4 \pm 0.7$ K, pressure $p = 20.08 \pm 0.08$ hPa, and pathlength $l = 480.8 \pm 0.6$ m. The spectral resolution is 0.009 cm^{-1} and the signal-to-noise ratio is estimated to be about 500:1. This spectrum

spans the range 6500–11 000 cm^{-1}. For the spectrum, Schermaul et al. prepared water vapor samples from liquid water using a clean glass vacuum line, and purified to remove dissolved air using freeze–pump–thaw cycles. We found no spectral evidence of species other than water.

In this work, line parameters are retrieved for the frequency interval 7400–9500 cm^{-1}. The 6000–7400 cm^{-1} region has recently been studied by Toth [2] and Macko et al. [8]; this region is very saturated in Schermaul et al.'s spectrum and is unsuitable for fitting. Above 9500 cm^{-1}, the spectrum overlaps spectrum 2 of Schermaul et al. [9] and which has been previously analysed by Tolchenov et al. [11]. This region has also been well studied by Brown et al. [6].

In fitting the experimental spectrum, a Voigt profile was used to represent the line shape. The line centre, line

intensity and self-broadening coefficient were used as fitting parameters, while the Dopper contribution was fixed to its calculated thermal value. For the fitting purposes, the signal was expressed in terms of absorbance, by which we mean the negative logarithm of the transmittance.

Many of the stronger lines are saturated in Schermaul et al.'s spectrum meaning that their parameters could not be reliably determined from the fit. As the first step the parameters of these stronger lines were estimated using values from the HITRAN-2004 database. However, these parameters reproduced the spectrum with insufficient accuracy so additional adjustments were made to the line parameters of these stronger lines to improve the residual in the absorption wings below a certain acceptable value. A correct characterisation of the baseline is important for reliably determining the intensity of weak lines; the baseline of the spectrum is very complex due to both instrumental effects and the under-fitted wings of the strong lines. A cubic spline drawn through the points placed carefully to minimize the residual was used to simulate the baseline.

The spectrum was assigned using a linelist produced using variational nuclear motion calculations. In particular we constructed a natural isotopic abundance linelist using line parameters taken from the Tomsk web database [14] for four of the most abundant isotopologues of the water molecule: $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$, and HDO with intensities scaled to the natural abundances. These linelists were constructed following the work of Partridge and Schwenke [15,16]. The accuracy of this linelist for the mid-infrared made assignment a relatively straightforward matter. However, in a number of cases lines were found to be comprised of two or three components with almost the same frequency. For these lines the intensity of each component was ratioed according to the calculated intensities and the total constrained to sum to the original experimental value. Taking into account all components of the blended lines, parameters for 5126 lines have been obtained.

Because the baseline is unknown we think that the standard error analysis of the fitted parameters does not reflect the real accuracy of the fit. We estimated the errors in the line positions from an analysis of the combination differences formed by transitions to the same upper energy level. This gave us the error distribution with respect to the line intensity from which we estimated the 80% confidence interval as a function of the intensity. This function was used to calculate the errors for all lines except cases when combination differences give bigger errors. The minimum error was found to be $0.001 \, cm^{-1}$ and it increases inversely proportional to the line intensity. The errors in the line intensity and the self-broadening

parameter are assumed to be proportional to the frequency error.

Due to saturation effects, parameters for the lines with intensities greater then 1×10^{-24} cm/molecule are not reliable.

In total 5091 lines have been assigned of which 4236 lines belong to $H_2^{16}O$, 502 to $H_2^{18}O$, 183 to $H_2^{17}O$, and 170 to HDO. The assignment has allowed us to obtain new experimental values for 240 rovibrational levels of $H_2^{16}O$ in comparison with the work of Tennyson et al. [17]. A summary of these energy levels is given it Table 1 and a complete tabulation in the electronic archive. Some of these new energy levels were also determined by Macko et al. [8] who performed a high sensitivity, cavity ringdown study of the 6130–6748 cm^{-1} region. Our levels agree well with theirs.

There have been several studies of water vapor spectra in the 7400–9000 cm^{-1} region using isotopically enhanced sample [18–22]. However, it would appear that our assignments yield a number of isotopologue transitions and energy levels which have not been observed previously. A list of the new energy levels is given in the electronic archive.

Fig. 2 compares transition intensities from this work and HITRAN-2004 [1]. The points forming a straight line at unity are because many of the line intensities for stronger lines were fixed to the values from HITRAN during the fit. However, apart from these values, there is a significant scatter between the values given by HITRAN and ours. In particular our average weak line intensities are less by about 7% than those reported by Toth [2] (for the region below 8000 cm^{-1}) but higher by about 9% than those of Mandin et al. [13] (for the region above 8000 cm^{-1}). The latter observation is consistent with the results of several previous studies at shorter wavelength (Brown et al. [6], Mérienne et al. [4], and Belmiloud et al. [7]). The linelist with experimental line parameters and the list of newly derived energy levels can be found in the supplementary materials to this article (see Fig. 3).

Table 1
Summary of $H_2^{16}O$ newly derived rovibrational energy levels

Band	ω (cm^{-1})	New levels[a]
120	6775.093	2
101	7249.818	10
002	7445.045	13
050	7542.437	12
130	8273.976	39
031	8373.850	11
210	8761.582	70
111	8806.998	28
012	9000.136	34
140	9274.2	16
022	10521.7	5

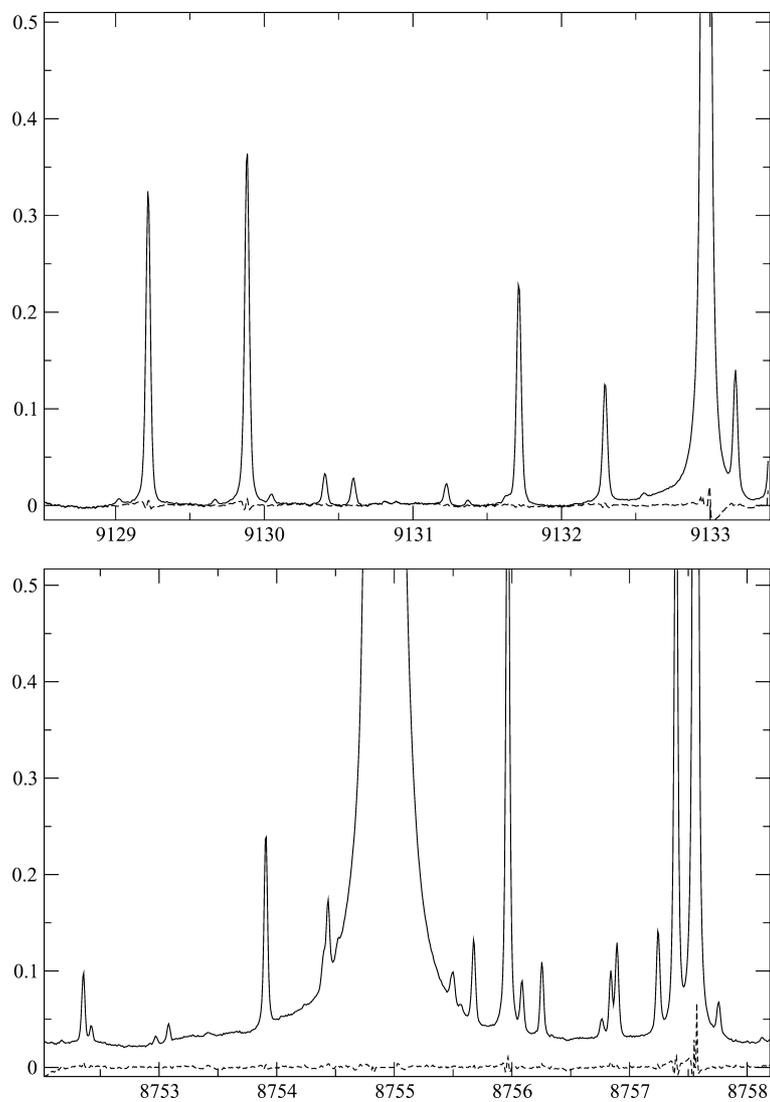[a] New levels in comparison with Tennyson et al. [17].

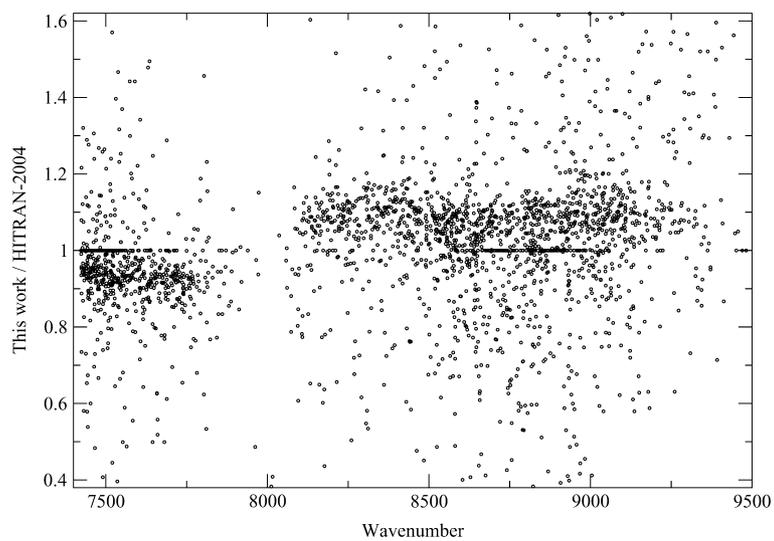Fig. 2. Two portions of the experimental spectrum. The dashed line is the residual in our fit.

Fig. 3. Comparison of the line intensities from this work with those from the HITRAN-2004 database.

3. Conclusion

We have analysed a mid-infrared, long pathlength Fourier Transform recorded by Schermaul et al. [9]. This spectrum is not well reproduced by the HITRAN-2004 database [1]. At the lower frequencies, 7400–8000 cm^{-1}, although the stronger transitions are well-modelled by HITRAN, many weak lines are absent from the database. At higher frequencies, 8000–9500 cm^{-1}, the data in HITRAN-2004 is older [12] and would appear to be significantly less reliable. This study should provide a suitable source of weak line parameters to update the database. However, the spectrum we analyse here was recorded at a single pathlength of 480.8 m. At this pathlength the stronger transitions, those with an intensity greater than 10^{-24} cm/molecule, show saturation effects. The line parameters for these lines determined here cannot be regarded as reliable, so that a complete data compilation for the 8000–9500 cm^{-1} can only be achieved with the aid of a new experiment designed to characterise the stronger transitions in this region.

Acknowledgments

Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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