Accurate line intensities for water transitions in the infrared: Comparison of theory and experiment

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ABSTRACT

Ab initio calculations of water intensities are becoming mature and are claimed to have 1% accuracy in many cases. Experimental intensities with 1% accuracy can be achieved with some care. An inter-comparison of *ab initio* against experimental water intensities is presented for a variety of infrared bands for $H_2^{16}O$ and some for $H_2^{18}O$ and $H_2^{17}O$. A new calculated $H_2^{16}O$ line list is presented for which un-certainties in the *ab initio* line intensities are evaluated. Much of the data show agreement within 2% between *ab initio* and experiment, however, for some bands, notably those involving excitation of some stretching modes, there are larger offsets of up to 8% attributed to *ab initio* calculation errors but still within the uncertainty of the *ab initio* calculation. In the ν_1 fundamental band differences of between +5% and −13% are found which show systematic dependence on wavenumber, ΔK_a, and ΔJ, again at-tributable to *ab initio* calculation errors. In the ν_2 band, intensity-dependent differences up to 2% ori-ginate from the analysis of the experimental data. At present experiments are important to validate *ab initio* calculations but *ab initio* predictions can be very useful in validating the experiment. As the two procedures display significantly different systematic errors, it is suggested that combining both gives the best results; this study will also facilitate further improvements of the theoretical methodology.

1. Introduction

Water is molecule number one in HITRAN [1], the major ab-sorber of incoming sunlight in Earth's atmosphere and its biggest greenhouse gas. Its spectrum is therefore very well studied, see Refs. [2–7] for systematic compilations of experimental spectra of the various water isotopologues. However the demands of atmo-spheric science in general and satellite instruments such as MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) on ENVISAT [8] mean that the laboratory data on water spectra must be of high quality. A particular issue is the reliability of the avail-able transition intensities.

There are two approaches to obtaining accurate intensities for individual transitions. Traditionally this is done experimentally and there are a number of studies [9–11] which have produced intensity measurements which are accurate to 1% or better. For these measurements an extensive error analysis of systematic and random errors was carried out. In case of the 1 μm region, two independent measurements, those of Hodges et al. [10] and the DLR (German Aerospace Center) results included in HITRAN2012 [1], show intensities in agreement to better than 1% and within their combined uncertainties. In some cases, such high-accuracy measurements comprise only a few selected lines and therefore serve as a benchmark rather than a dataset suitable for inclusion in standard databases. The intention of laboratory spectroscopy work at DLR is to provide spectroscopic data with small well-defined uncertainties. This is certainly true for H_2O spectroscopy, as well. Laboratory infrastructure such as absorption cells have been con-tinuously improved together with analysis software. Special focus was placed on validation of data product accuracy, *i.e.* proving the error budget by redundancy, χ test and so forth [12]. More details are given in Section 2 which details our experimental studies on water line intensities.

The second approach is to make use of the increasing accuracy of *ab initio* calculations. A number of studies have focussed on trying to determine the dipole moment surface (DMS) of the water molecule to high accuracy [13–16]. However, computed vibration-rotation transition intensities are also sensitive to the nuclear-motion wavefunctions of the initial and final state, and hence to the potential energy surface (PES). Lodi and Tennyson [17]

Table 1
Overview of H_2O intensity measurements performed at DLR. Experiment are numbered and referred to in the text as Expt. N.

N	Year	Spectral region (cm^{-1})	Refs.	Purpose	Profile[a]	Fit[b]	Funded by
1	2003–05	1250–1750	[20,12]	MIPAS/ENVISAT	Voigt	Single	HGF national
2	2006–07	10,000–11,000	[1]	WALES	SD-Voigt	Single	DLR project national
3	2016	1850–2280, 2390–4000	[21–23]	NDACC, TCCON	QSDHC+LM	Multi	DFG national
4	2016	4190–4340	[24,25]	TROPOMI/Sentinel 5-P	QSDHC+LM	Multi	ESA

[a] SD-Voigt: Speed-Dependent Voigt; QSDHC+LM: quadratic-Speed-Dependent Hard-Collision profile plus Rosenkranz line-mixing.
[b] Single spectrum or multi-spectral fits.

developed a procedure to test for sensitivity of the results to both the PES and DMS. The results of such a procedure are analyzed below. Lodi and Tennyson's computed intensities formed the major input into HITRAN2012 [18] for the water isotopologues $H_2^{18}O$ and $H_2^{17}O$. A subsequent experimental validation of HITRAN2012 yielded generally good agreement with these results in the 6450–9400 cm^{-1} region [18].

Clearly there is a case for considering a similar treatment for the main water isotopologue, $H_2^{16}O$, whose spectrum is crucial for atmospheric and many other applications. However, given the volume of experimental work on $H_2^{16}O$ spectra and that measurements for the main isotopologue can generally be made more accurately due to its high natural abundance, it is necessary to properly benchmark the *ab initio* intensities for this system. This is the purpose of the present paper which, indeed, demonstrates that while the *ab initio* predictions are excellent in many cases there are a number of bands which display systematic differences from observation which are too large for these data to be used in the present form.

The paper is organized as follows. The following section describes the experimental studies performed at DLR against which the *ab initio* intensities are benchmarked. Section 3 outlines our theoretical procedure and presents a new, high-accuracy line list for $H_2^{16}O$ which includes uncertainties for the line intensities. Section 4 presents a detailed band-by-band comparison between the two sets of line intensities. Finally we present our conclusions. All experimental intensities and the intercomparisons shown in the paper include HITRAN's isotopologue abundance – unless specified otherwise. The *ab initio* intensities in the Supplementary material are given for 100% abundance.

2. Experimental water line intensities

The hardware in the DLR spectroscopy laboratory was developed over 25 years with a focus on prevention of systematic errors. Absorption cells cover path lengths, L, from 20 cm to 200 m and a temperature range from 195 to 350 K. Special care has been taken to achieve high temperature homogeneity. The Fourier Transform (FT) spectrometer was originally a Bruker IFS 120HR, which was upgraded to a Bruker IFS 125HR in 2009. Due to the high spectral resolution, the influence of the instrumental line shape can be minimized, which helps avoiding systematic errors. As sample gas evaporated water vapor from a liquid tap water reservoir was used. The water was purified prior to usage by freezing it several times using liquid nitrogen and pumping off the gas phase. During the sample gas evaporation process only water contributed significantly to the vapor phase. Especially in case of water and water/air mixtures steady flows have been used to counter the effects of wall stickiness. Water/air mixtures are generated in an 800 l stainless steel vessel for high mixing ratio accuracy. High accuracy pressure and temperature sensors are employed. Spectral processing corrects for several systematic error sources such as detector non-linearity, sample and cell window thermal radiation, and standing waves in the optics. The

measurement plan includes sufficient redundancy, *e.g.* the same transition is measured with different optical depths. Redundancy helps to find unidentified systematic errors since the impact of error sources mostly changes with optical depth, sample and total pressure, mixing ratio, temperature and absorption path. Measurement conditions are selected to match the requirements from atmospheric spectra. Several methods were developed for validation of data product accuracy. For example, gas temperatures are fitted from relative line intensities and compared to sensor temperatures. Furthermore, residuals are investigated with respect to single measurements, called file cuts [19]. More details on methods for validation of data product accuracy can be found in [19].

A list of all DLR H_2O experiments contributing to this work, sorted by date, is given in Table 1. These experiments are detailed in turn below.

Expt. 1: The FT instrument was a Bruker IFS 120HR. The old multireflection cell setup with unoptimized temperature homogeneity and 100 m maximum absorption path was used. Nine pure H_2O ($L = 0.25 - 85$ m, $p_{H_2O} = 0.2 - 5$ mbar, ambient temperature, 0.6/MOPD = 0.0032 cm^{-1}) and 14 air-broadened measurements ($L = 21 - 85$ m, $p_{H_2O} = 0.2 - 5$ mbar, $p_{air} = 50 - 400$ mbar, ambient temperature, 0.6/MOPD = 0.0032 cm^{-1}, for relative line intensities only) were used for intensity analysis. Line parameters were retrieved with FitMAS [26] in single spectrum Voigt fits with $sinc \otimes box$ idealized instrumental lineshape and afterwards merged together. The number of lines with statistical uncertainty ≤1% was 579 for the main isotopologue in the line intensity range 2×10^{-23}–3×10^{-19} cm molecule^{-1}, and 276 for $H_2^{18}O$ (statistical uncertainty ≤5%) in the line intensity range 5×10^{-25}–7×10^{-22} cm molecule^{-1}, including lines of the ν_2 fundamental and its first hot band. Spectral lines for this region are given in Supplementary data as two files: one each for $H_2^{16}O$ and $H_2^{18}O$. This region has been the subject of a number of studies by Toth [27–29] which formed the basis of input to previous versions of HITRAN and Coudert et al. [30] which provided the input to the recent GEISA update [31].

Expt. 2: The FT instrument was a Bruker IFS 120HR. The old multireflection cell setup was used. Two pure H_2O ($L=85$ m, $p_{H_2O} = 1 - 5$ mbar, ambient temperature, 0.6/MOPD = 0.03 −0.013 cm^{-1}) and nine air-broadened measurements ($L=85$ m, $p_{H_2O} = 0.8 - 16.4$ mbar, $p_{air} = 200 - 1000$ mbar, ambient temperature, 0.6/MOPD = 0.06 − 0.03 cm^{-1}, for relative line intensities only) were used for intensity analysis. Line parameters were retrieved with an IDL single spectrum speed-dependent Voigt [32] fit with $sinc \otimes box$ idealized instrumental lineshape and afterwards merged together. The number of lines analyzed with statistical uncertainty ≤ 1% was 326 for the main isotopologue in the line intensity range 1×10^{-24}–6.5×10^{-22} cm molecule^{-1}, including lines of the bands from (0 0 0) to (1 2 1), (2 2 0), (3 0 0), (2 0 1), (0 0 3) and (1 0 2). Spectral lines for this region are given in Supplementary data. The 1% accuracy achieved represents a significant improvement on previous state-of-the-art studies of this region [33–35].

Expt. 3: The FT instrument was a Bruker IFS 125HR. A short absorption path cell ($L=24.9$ cm) and the refurbished