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An accurate and complete empirical line list for water vapor between 5850 and 7920 cm^{-1}

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ABSTRACT

An empirical line list has been constructed for "natural" water vapor at 296 K in the 5850–7920 cm^{-1} region. It was obtained by gathering separate line lists recently published on the basis of spectra recorded by high sensitivity Continuous Wave Cavity Ring Down Spectroscopy (CW-CRDS) of natural water, complemented with literature data for the strongest lines. The list includes 38,318 transitions of four major water isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{16}O$) with an intensity cut-off of 1×10^{-29} cm/molecule at 296 K. The list is made mostly complete over the whole spectral region by including a large number of weak lines with positions calculated using experimentally determined energy levels and intensities obtained from variational calculations. In addition, we provide $HD^{18}O$ and $HD^{17}O$ lists in the same region for transitions with intensities larger than 1×10^{-29} cm/molecule. The $HD^{18}O$ and $HD^{17}O$ lists (1972 lines in total) were obtained using empirical energy levels available in the literature and variational intensities.

The global list (40,290 transitions) for water including the contribution of the six major isotopologues will be adopted for the next edition of the GEISA database in the region.

The advantages and drawbacks of our list are discussed in comparison with the list provided for the same region in the 2012 edition of the HITRAN database. The direct comparison of the CRDS spectra to simulations based on the HITRAN list has revealed some insufficiencies which could easily be corrected: missing HDO lines, duplicated lines, inaccurate line positions or line intensities from variational calculations.

1. Introduction

A detailed knowledge of the spectral line parameters of water vapor is a prerequisite for many atmospheric and planetary applications including remote sensing (water being the target species or an interferent), atmospheric radiative transfer calculations, etc. In recent years, advances of theory and increased performances of experimental techniques have allowed important improvements in the determination of the spectroscopic parameters (center, line intensity and profile, temperature dependence, etc.).

Both theory and experiment approaches present specific advantages. In general, the water line lists constructed from variational calculations have the advantage of completeness (in particular for the minor isotopologues which are less documented) but are unable to achieve the experimental accuracy on the line positions. As a result, the "best" line lists are obtained by combining the advantages of the experimental and theoretical approaches. A suitable procedure consists in correcting variational line

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positions using empirical values of the energy levels derived from experiments. This approach is the one followed by an IUPAC task group (IUPAC-TG hereafter) under the project “A database of water transitions from experiment and theory”. This IUPAC task group has performed an exhaustive evaluation of rovibrational line positions, energy levels and assignments for all the main isotopologues of water: $H_2{}^{16}O$ [1], $H_2{}^{18}O$ and $H_2{}^{17}O$ [2,3], $HD^{16}O$, $HD^{18}O$ and $HD^{17}O$ [3]. By using the procedure and code Measured Active Rotational–Vibrational Energy Levels (MARVEL) [4,5], practically *all* the high quality experimental data available in the literature were reviewed to determine and validate the energy levels together with their self consistent uncertainties. As far as line intensities are concerned, the problem is more complex. It is well established that state of the art variational intensity values are *overall* in very good agreement with the best experimental determinations (within about 1%) but variational intensities show deficiencies for a number of bands in particular those involving a large bending excitation.

In this work, we focus on the 5850–7920 cm^{-1} region that we extensively investigated during the last years using high sensitivity Continuous Wave Cavity Ring Down Spectroscopy (CW-CRDS). The investigated region covers the entire H atmospheric transparency window and the lower energy part of the J window which are both of particular interest for trace gas monitoring. Water vapor being a spectroscopic interferent, its weak absorption spectrum must be accurately characterized in those near infrared windows. On the other hand, the lines near 1.38 μm which are about 10^5 stronger than those in the H and J windows are frequently used for the monitoring of water vapor in different environments.

The last edition of the HITRAN database [6] provided for water vapor line list is a composite of experimental and variational line parameters depending on the spectral range and on the isotopologue. Fig. 1 shows an overview of the HITRAN2012 list in our region of interest for the main isotopologue, $H_2{}^{16}O$. In this figure, the transitions with experimental line parameters are highlighted. These were mostly obtained by Toth from spectra recorded at Kitt Peak by Fourier Transform Spectroscopy (FTS) with a long optical path length (up to 432 m). This experimental dataset, corresponding roughly to lines with intensities larger than 3×10^{-26} cm/molecule, was complemented with lines with IUPAC-TG positions and variational intensities. The HITRAN intensity cut-off was fixed to 1×10^{-29} cm/molecule at 296 K.

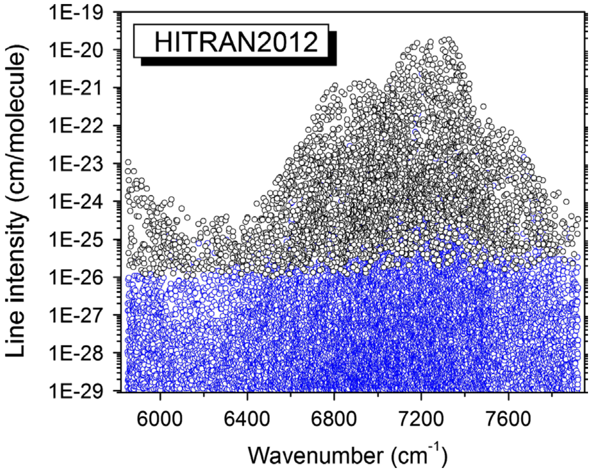

Fig. 1. Overview of the HITRAN2012 [6] water line list between 5850 and 7920 cm^{-1} for the main isotopologue, $H_2{}^{16}O$. The transitions with experimental line parameters from Toth [10] are marked with black circles.

In fact, in our CW-CRDS investigations of water vapor, we were able to measure many lines with intensities down to 5×10^{-30} cm/molecule i.e. four orders of magnitude below the smallest experimental intensities included in the HITRAN list [6]. The set of spectroscopic parameters relying on experimental values can then be significantly enlarged using the CW-CRDS line lists found in Refs. [7–9]. This is the aim of the present work which consists in gathering spectroscopic parameters from mainly three sources:

(i) FTS data of Ref. [10] for the strongest lines,
(ii) CRDS data of Refs. [7–9] for the weak and medium lines, and
(iii) transitions with positions calculated using known energy levels and intensities obtained from variational calculations for the unobserved lines.

We will show that this approach applied to the four major isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{16}O$) allows correcting a number of inaccuracies of the HITRAN line parameters both for positions and intensities. In addition, it allows completing importantly the line list of $HD^{16}O$ in particular in the transparency windows where the contribution of this minor isotopologue is very important.

The rest of the paper is organized as follows. After summarizing the CRDS results (Section 2), we will detail the construction of our list (Section 3) and then compare it to the HITRAN list in the Discussion (Section 4).

2. Summary of the CRDS studies

The CRDS data used for the construction of our list were obtained from three recent investigations of “natural” water at room temperature. The spectra were recorded at high sensitivity with typical noise equivalent absorption between $\alpha_{min} \sim 2 \times 10^{-11}$ and 2×10^{-10} cm^{-1}. The calibration of the frequency axis of the CRDS spectra relies on the values provided by a wavemeter. It was checked and sometimes refined using reference line positions of H_2O from the HITRAN2008 database [11]. We estimate to 1×10^{-3} cm^{-1} the maximum uncertainty on the line positions of isolated lines.

The line centers and intensities were determined using an interactive least squares multi-line fitting program assuming a Voigt profile, the HWHM of the Gaussian component being generally fixed to the theoretical value of the Doppler width of $H_2{}^{16}O$.

The vibration–rotation assignments were performed using, for each isotopologue, theoretical spectra [12] computed by Tashkun using the results of the variational calculations by