



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

High sensitivity CW-CRDS of ^{18}O enriched water near $1.6\ \mu\text{m}$

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ARTICLE INFO

Article history:

Received 6 March 2009

Received in revised form

17 April 2009

Accepted 20 April 2009

Keywords:

Cavity ring down spectroscopy

Water

 H_2^{18}O H_2^{17}O H_2O HD^{18}O

Rovibrational assignments

HITRAN

MARVEL

ABSTRACT

The absorption spectrum of ^{18}O enriched water has been recorded by continuous wave cavity ring down spectroscopy between 5905.7 and $6725.7\ \text{cm}^{-1}$ using a series of fibred DFB lasers. The investigated spectral region corresponds to the important $1.55\ \mu\text{m}$ transparency window of the atmosphere where water absorption is very weak. The typical CRDS sensitivity (noise equivalent absorption of $5 \times 10^{-10}\ \text{cm}^{-1}$) allowed for the detection of lines with intensity as low as $10^{-28}\ \text{cm}/\text{molecule}$ while the minimum intensity value provided by HITRAN in the considered spectral region is $1.7 \times 10^{-24}\ \text{cm}/\text{molecule}$. The line parameters were retrieved with the help of an interactive least squares multi-lines fitting program assuming a Voigt function as line profile. Overall, 4510 absorption lines belonging to the H_2^{18}O , H_2^{16}O , HD^{18}O , HD^{16}O and H_2^{17}O water isotopologues were measured. Their intensities range between 3×10^{-29} and $5 \times 10^{-23}\ \text{cm}/\text{molecule}$ at $296\ \text{K}$ and the typical accuracy on the line positions is $1 \times 10^{-3}\ \text{cm}^{-1}$. 2074 of the observed lines attributed to H_2^{18}O , HD^{18}O and H_2^{17}O are reported for the first time. The transitions were assigned on the basis of variational calculations resulting in 288, 135 and 38 newly determined rovibrational energy levels for the H_2^{18}O , HD^{18}O and H_2^{17}O isotopologues, respectively. The new data set includes the band origin of the $4\nu_2$ bending overtone of H_2^{18}O at $6110.4239\ \text{cm}^{-1}$ and rovibrational levels corresponding to J and K_a values up to 18 and 12, respectively, for the strongest bands of H_2^{18}O : $4\nu_2$, $\nu_1+2\nu_2$, $2\nu_2+\nu_3$, $2\nu_1$, $\nu_1+\nu_3$, and $\nu_2+\nu_3$. The obtained experimental results have been compared to the spectroscopic parameters provided by the HITRAN database and to the recent IUPAC critical review of the rovibrational spectrum of H_2^{18}O and H_2^{17}O as well as to variational calculations. Large discrepancies between the $4\nu_2$ variationally predicted and experimental intensities have been evidenced for the H_2^{18}O and H_2^{16}O molecules.

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1. Introduction

In spite of its low relative concentration compared to the main isotopologue (3.1×10^{-3}), H_2^{18}O is the fifth most important atmospheric absorber. Due to the vibrational isotopic shift, the relative contribution of the H_2^{18}O absorption may largely exceed its relative abundance in some spectral regions. Such situations may occur in the regions corresponding to very weak absorption as the presently studied $1.55\ \mu\text{m}$ transparency window. In the $6000\text{--}8000\ \text{cm}^{-1}$ range including our

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region of interest, the HITRAN database in its last versions [1,2] provides for H_2^{18}O the spectroscopic parameters obtained by Chevillard et al. [3] and Toth [4] by Fourier transform spectroscopy (FTS). These FTS spectra were recorded with ^{18}O enriched water in various experimental conditions. The maximum ^{18}O enrichment and pathlengths were (73%, 217.4 m) and (31.4%, 2.39 m) for the recordings of Refs. [3,4], respectively. The minimum intensity values provided in the HITRAN database in our region are on the order of 2×10^{-24} cm/molecule (for pure H_2^{18}O). Recently, the detection limit was lowered by nearly two orders of magnitude from FTS spectra recorded between 1000 and 8000 cm^{-1} at USTC (Hefei) with 95% ^{18}O enrichment and a 105 m absorption pathlength [5,6].

A still higher sensitivity can be achieved by continuous wave cavity ring down spectroscopy (CW-CRDS). Our preceding studies of water in natural isotopic abundance [7,8] have shown that transitions with intensity as low as 10^{-29} cm/molecule can be detected and measured.

The present work is devoted to a detailed analysis of the highly sensitive CW-CRDS ^{18}O enriched water spectrum between 1.69 and 1.49 μm (5905.7–6725.7 cm^{-1}).

After the description of the experimental set up and of the presentation of the retrieval of the spectroscopic parameters (Section 2), we will present the rovibrational analysis using the results of the variational calculations performed by Shirin et al. [9] and Schwenke and Partridge (SP) [10]. The SP line lists of the different water isotopologues can be downloaded from the <http://spectra.iao.ru> web site. The obtained results relative to the H_2^{18}O and H_2^{17}O isotopologues will be compared to the very recent exhaustive review of rovibrational line positions and levels of H_2^{17}O and H_2^{18}O [11] performed by an IUPAC sponsored task group (TG).

Under the project “A database of water transitions from experiment and theory”, this IUPAC task group aims at an exhaustive evaluation of rovibrational line positions, transition intensities, energy levels and assignments for all the main isotopologues of water. By using the procedure and code MARVEL (Measured Active Rotational–Vibrational Energy Levels) [12,13], all the high quality experimental data available in the literature have been reviewed to determine and validate the H_2^{18}O and H_2^{17}O energy levels together with their self consistent uncertainties. The experimental H_2^{18}O line positions used to derive the MARVEL energy levels in our region include studies based on spectra recorded with water in natural isotopic abundance—[14] (107 lines), [8] (61 lines) and [7] (386 lines)—or with ^{18}O enriched samples—[15] (35 lines), [16] (1 line), [3] (367 lines), [4] (60 lines), [5] (49 lines) and [6] (626 lines). It is worth noting that the high sensitivity achieved either by CW-CRDS [7,8] or by FTS with long absorption path lengths [14] allowed compensating the low H_2^{18}O concentration in natural isotopic abundance and provided a significant amount of observations. Up to the present work, the Hefei spectra [5,6] provided the highest detectivity of H_2^{18}O transitions in the region and then the largest amount of transitions used in the MARVEL procedure [11].

The H_2^{18}O and H_2^{17}O lines validated and recommended by the IUPAC TG have been deposited with their corresponding references as Supplementary Material of Ref. [11]. We will then refer to the 5905.7–6725.7 cm^{-1} section of these line lists for the comparison to our observations. Hereafter, we will call “IUPAC TG transitions and levels” the transitions and energy levels provided in Ref. [11].

The IUPAC TG transitions include a total of 1691 and 228 entries for the H_2^{18}O and H_2^{17}O species respectively. Taking into account that a given spectral line may have been measured in several experimental works, they correspond to 754 and 185 distinct transitions. As upper energy levels determined in the present study may have been accessed through transitions located in different spectral regions (this is in particular the case of the presently observed hot bands), we will also compare our energy levels values to the complete set of 4851 and 2687 energy levels validated by MARVEL code [11] for the H_2^{18}O and H_2^{17}O isotopologues, respectively.

2. Experiment and data reduction

2.1. The CW-CRDS spectrometer

We have developed a fibred CW-CRDS spectrometer using DFB diode lasers dedicated to the characterization of the important 1.5 μm atmospheric window of transparency. The typical achieved sensitivity of 2.5×10^{-10} cm^{-1} and the 4–5 decades dynamics on the intensity scale, have allowed to significantly improve the knowledge of the absorption spectrum of species of major atmospheric interest: H_2O [7,8], $^{12}\text{CO}_2$ [16,17], $^{13}\text{CO}_2$ [18], N_2O [19] and ozone [20]. This spectrometer was described in details in Refs. [7,21,22]. Briefly, 38 fibred DFB diode lasers were used to cover the 5905–6726 cm^{-1} region, each of them having a typical tuning range of 7 nm (~ 30 cm^{-1}) by temperature variation from -10 to 60 $^\circ\text{C}$ within about 70 min. The spectrum could be continuously covered except two gaps between 6122.3 and 6131.4 cm^{-1} and 6655.6 and 6667.1 cm^{-1} .

The ringdown cell temperature (typical value 299 K) and the gas pressure, measured by a capacitance gauge (MKS Baratron, 10 Torr range) were monitored during the spectrum acquisition. The spectrum in the 5905–6587 cm^{-1} region was recorded with 10 Torr. Lower pressures of about 0.1–1 Torr were used as lines with intensities as high as 10^{-23} cm/molecule are observed above 6587 cm^{-1} . An overview of the CW-CRDS spectrum is presented in Fig. 1. The small section presented in Fig. 2 illustrates the high signal to noise ratio of the spectra and that the noise equivalent absorption defined as the *rms* value of the noise level is about 5×10^{-10} cm^{-1} .

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