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Comb-Assisted Cavity Ring Down Spectroscopy of ^{17}O enriched water between 6667 and 7443 cm^{-1}

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ABSTRACT

The room temperature absorption spectrum of water vapour highly enriched in ^{17}O is studied by Comb Assisted-Cavity Ring Down Spectroscopy (CA-CRDS) near 1.4 µm. The investigated spectral region (6667–7443 cm^{-1}) is a strong absorbing region corresponding to the first hexade of interacting vibrational states. As a consequence of the high sensitivity of the recordings (Noise Equivalent Absorption, $\alpha_{min}\sim 10^{-10}$ cm^{-1}), a series of spectra could be recorded at very low pressure (less than 0.1 Torr) allowing for accurate determination of line centres and the spectral resolution of highly blended multiplets. For instance, 85 lines of the main isotopologue located near much stronger lines are measured for the first time.

The assignments were performed using known experimental energy levels as well as calculated line lists based on the results of Schwenke and Partridge. Overall, the experimental list includes 9144 water lines which were assigned to 9988 transitions of six isotopologues ($H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$ and $HD^{18}O$). Their intensities span six orders of magnitude from 10^{-27} to 10^{-21} cm/molecule at 296 K.

Most of the new results concern the $H_2{}^{17}O$ isotopologue: more than 2300 new lines were measured, 64 new levels were determined and seven levels were corrected. In the case of $HD^{17}O$, 152 new transitions were assigned and ten levels were newly determined. The center values of non-blended lines are reported with an accuracy better than 3 MHz (10^{-4} cm^{-1}) which represents an improvement compared to previous determinations. The comparison to the water vapor line list provided by the recently released 2016 version of the HITRAN database reveals a number of issues.

1. Introduction

The present work is devoted to a detailed analysis of the ^{17}O enriched water vapor spectrum between 6667 and 7443 cm^{-1} by highly sensitive Comb-Assisted Cavity Ring Down Spectroscopy (CA-CRDS). The investigated spectral interval is included in the overview spectrum presented in Fig. 1. It corresponds to the central part of the first hexade bands of $H_2{}^{17}O$ and fills the gap between our two previous studies in the 5850–6671 cm^{-1} [1] and 7443–7921 cm^{-1} [2] regions. The intensities of the strongest transitions reach values on the order of 10^{-20} cm/molecule which makes the detection easily feasible by Fourier Transform Spectroscopy (FTS) [3–5]. The most extensive previous FTS study is due to Toth who used a 2.39 m long cell and a ^{17}O enrichment of about 55% [3]. In spite of the very low abundance of $H_2{}^{17}O$ in natural water samples (≈3.7×10^{-4}), the sensitivity of the CRDS technique allowed for the detection of a significant number of additional lines in the spectra of natural water [6–11] (see Fig. 1).

Similarly to Ref. [2], a self-referenced frequency comb (SRFC) was used for the frequency calibration of the CRDS spectra. Our CA-CRDS approach [15,16] relies on the “on the fly” measurement of the beat note frequency between one of the longitudinal modes of the frequency comb and a small part of the light emitted by a Distributed Feedback (DFB) laser diode injected in the CRDS cell. As illustrated in Ref. [2], the CA-CRDS line centers have in routine an absolute accuracy at the 1×10^{-4} cm^{-1} level or better for unblended lines, providing a large set of accurate transition frequencies not only for the $H_2{}^{17}O$ isotopologue but also for the main $H_2{}^{16}O$ species. In addition, the very low pressure of the recordings

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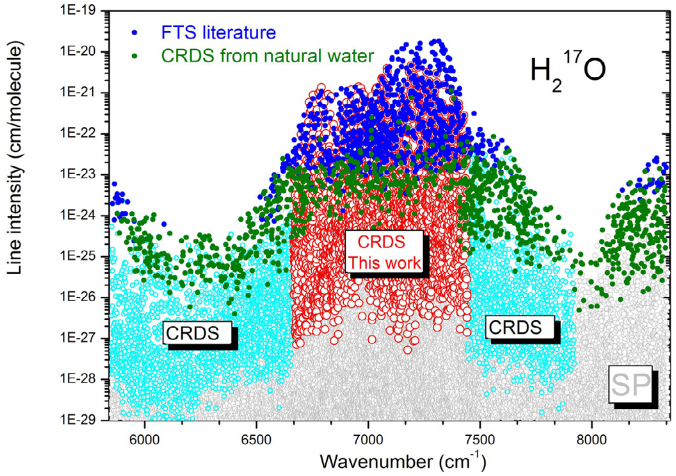

Fig. 1. Overview of the $H_2{}^{17}O$ spectrum between 5850 and 8340 cm^{-1} (line intensities are for pure $H_2{}^{17}O$ at 296 K). Experimental observations are superimposed to the calculated line list based on the results of Partridge and Schwenke [12–14] (grey circles). The present study (red open circles) fills the gap between our two previous CRDS studies of ^{17}O enriched water vapor in the 5850–6671 cm^{-1} [1] and 7443–7921 cm^{-1} [2] regions (cyan open circles). Previous observations by FTS with enriched ^{17}O [3] and natural water [4,5] (full blue circles) and CRDS in natural water [6–11] (full green circles) are also plotted for comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

helps to lower the uncertainty on the line center values close to zero pressure.

After the description of the experimental set up and the presentation of the retrieval of the spectroscopic parameters (Section 2), we will present the rovibrational analysis in Section 3. The obtained results will be compared to the energy levels available in the literature and recommended by an IUPAC task group (IUPAC-TG hereafter) [17–19]. The reported results will also be used for comparisons to the recently released HITRAN2016 water list [20].

2. Experimental set up

The description of the experimental set up and the coupling of the self-referenced frequency comb (SRFC) to the CRD spectrometer have been presented in Refs. [2,15,21]. Briefly, in the present work, twenty eight fibered Distributed Feedback (DFB) laser diodes were used to cover continuously the 6667–7443 cm^{-1} spectral interval. As detailed in Ref. [15], an accurate frequency determination requires *(i)* the frequency measurement of the beat note between a fraction of the DFB laser light and a tooth of the SRFC (Model FC 1500–250 WG from Menlo Systems) and *(ii)* the tooth number deduced from the frequency value provided by a commercial Fizeau type wavemeter (HighFinesse WSU7-IR, 5 MHz resolution, 20 MHz accuracy over 10 h). As a result, an accurate frequency is determined “on the fly” and attached to each ring down event.

The gas pressure was continuously measured by a capacitance gauge (MKS Baratron, 10 Torr, 0.25% accuracy of the reading). Several series of spectra recordings were performed at pressures less than 0.01 Torr, around 0.1 Torr and 1.0 Torr.

The cell was filled with high purity water highly enriched in ^{17}O (from Sigma Aldrich). According to the certificate of analysis obtained by mass spectrometry, the ^{17}O enriched water sample has the following stated relative abundance of the oxygen atoms: ^{16}O: 28%, ^{17}O: 70% and ^{18}O: 2%. In fact, the real ^{17}O enrichment of water vapor in the CRD cell is lower. The continuous exchange between water molecules in the gas phase and adsorbed on the walls of the cell or in the gas admission tubes leads to a depletion of the ^{17}O isotopic enrichment which is particularly pronounced at low pressure. In Ref. [2], for each recording corresponding to one DFB diode laser, the real isotopic abundances in $H_2{}^{16}O$ and $H_2{}^{17}O$ was estimated with an estimated error bar of 5%, using reference line intensities. In the present work, we did not attempt to apply a similar procedure because a large part of the spectra was recorded at very low pressure. In that situation, the isotopic changes are even more pronounced and difficult to correct. In the line list provided as Supplementary Material, the recording number is indicated for each measured line. While the relative intensities are believed to be reasonably accurate for a given spectrum, the consistency between recordings obtained at different pressures or with successive DFB laser diodes is expected to be poor (up to a factor of 2 in the worst cases). In addition, the absolute value of the total pressure was not accurately determined for the lowest pressure recordings ($<$0.01 Torr).

The line parameters were obtained by using a homemade interactive least squares multi-lines fitting written in LabVIEW. A Voigt profile with the width of the Gaussian component fixed to the calculated Doppler broadening was adopted for each line.

At the final stage of the analysis, a list of 9284 lines was obtained by gathering measurements performed at different pressures between 6667 and 7443 cm^{-1}. The experimental line list is provided as Supplementary Material. A tag is included for each line in order to indicate whether line parameters were obtained from spectra at 1.0 Torr or lower pressure (0.1 Torr or less). The high dynamic range offered by our instrument and the use of various pressure values allowed us for determining line parameters for transitions with intensities ranging over more than 6 orders of magnitude (10^{-27}–10^{-21} cm/molecule). Let us mention that about two hundred of the strongest lines are absent from our line list because they could not be retrieved by CRDS even from the low pressure recordings at disposal.

As an illustration of the quality of the spectrum and of the advantage of the very low pressure recordings, we present in Fig. 2 two examples of first observation of lines of $H_2{}^{16}O$ in the close vicinity of a much stronger line. The very small pressure broadening of the recordings makes mostly negligible the Lorentzian component of the strong line profile. The resulting nearly pure Gaussian profile allows for the new detection of very small absorption features located very close to the centre of the strong lines. The first example displayed on Fig. 2 shows the $2\nu_3$ $8\ _{1\,8}$ - $9\ _{4\,5}$ line at 6804.47289 cm^{-1} newly detected in a spectrum recorded at about 0.07 Torr (the standard $J\ K_a\ K_c$ notation is used for the rotational levels). This line has an intensity value on the order of 5.7×10^{-25} cm/molecule about 2000 times smaller than the nearby $2\nu_2+\nu_3$ $2\ _{0\,2}$ - $3\ _{0\,3}$ line at 6804.4011 cm^{-1}. The second example shows the line of the $\nu_1+2\nu_2$ $7\ _{7\,0}$ - $7\ _{6\,1}$ and $7\ _{7\,1}$ - $7\ _{6\,2}$ unresolved doublet at 7181.09681 cm^{-1} ($S\sim 9\times 10^{-23}$ cm/molecule), located near the $\nu_1+\nu_3$ $2\ _{0\,2}$ - $3\ _{0\,3}$ line at 7181.155 cm^{-1} ($S \sim 1.5\times 10^{-20}$ cm/molecule). The corresponding spectrum was recorded at a pressure of only about 0.004 Torr.

Fig. 3 illustrates the achieved sensitivity coming with a high dynamic range on the intensity scale. The noise equivalent absorption coefficient defined as the *rms* value of the noise level is about 10^{-10} cm^{-1}.

3. Rovibrational assignments

The rovibrational assignments were performed using known experimental energy levels, in particular those of an IUPAC task group [17–19]) as well as calculated line lists based on the results of Schwenke and Partridge [12–14]. Overall, 9144 lines were assigned to 9988 transitions of six water isotopologues ($H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, and $HD^{18}O$). In addition, ninety-six lines were assigned to three isotopologues of carbon dioxide ($^{12}C^{16}O_2$, $^{12}C^{17}O_2$ and $^{16}O^{12}C^{17}O$) leaving only fifty-five lines unas-