Cavity ring-down spectroscopy of $^{17}$O-enriched water vapor between 12,055 and 12,260 cm$^{-1}$

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ARTICLE INFO

Article history:
Received 23 April 2019
Revised 14 September 2019
Accepted 14 September 2019
Available online xxx

Keywords:
Cavity ring-down spectroscopy
Water molecule
Vibration-rotation assignments
H$_2^{17}$O

ABSTRACT

The absorption spectrum of oxygen-17-enriched water vapor in the 12,055–12,260 cm$^{-1}$ region was recorded with a continuous-wave cavity ring-down spectrometer (CW-CRDS) at room temperature. In total, 1342 lines were observed in this region, while more than 1400 absorption transitions were assigned based on previously published experimental energies and the variational calculations based on the results of Partridge and Schwenke. The typical frequency accuracy of 0.002 cm$^{-1}$ was achieved in this work. Three hundred and fifty-eight ro-vibrational energy levels of H$_2^{17}$O water isotopologue were retrieved, which belong to the $v_1 + 1/2v_2 + v_3=3.5$ and 4 polyads: (0 1 3), (0 3 2), (1 1 2), (1 3 1), (2 1 1), (2 2 1), (2 3 0), (3 0 1), and (3 1 0) states. One hundred and ten of them were reported for the first time. Comparisons of experimental line positions with those in the HITRAN database were given for H$_2^{16}$O and H$_2^{17}$O isotopologues. The obtained vibration-rotation energy levels were also compared with MARVEL values.

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1. Introduction

Following the previous work on the oxygen-17 enriched water vapor absorption spectrum studied in the 12,277–12,894 cm$^{-1}$ region [1], the present paper is devoted to a detailed analysis of the high resolution cavity ring-down spectrum of the water vapor between 12,055 and 12,260 cm$^{-1}$. An exhaustive review on nine isotopic species of the water molecule has been performed by the IUPAC task group (IUPAC-TG) [2–4] which gives a set of validated and recommend water vapor transitions as well as the empirical energy levels. These data sets were based on critical evaluation of the available experimental data before 2013 and have been used to update the water line list in HITRAN2016 [5]. Along with the advanced development of high-resolution spectroscopy techniques, especially the cavity-ring down spectroscopy (CRDS), it became increasingly realistic to detect experimental line positions for water vapor with high accuracy of a few MHz or even better up to a few kHz [1,6–9]. Since 2013, there have been many new studies of water vapor absorption spectra, in particular, using the optical-frequency-comb-based measurements to archive very accurate transition frequencies. A serial of work has been performed by Mondelain and Mikhailenko et al. using cavity ring-down spectroscopy (CRDS) to study the room temperature absorption spectrum of water vapor highly enriched in $^{17}$O in the region between 5850 and 7921 cm$^{-1}$ since 2015 [6–8]. More recently we have presented a study on $^{17}$O-enriched water vapor spectrum in the 12,277–12,894 cm$^{-1}$ region [1]. In comparison with other isotopic species of water, the data set for H$_2^{17}$O is less complete. Only a small amount of gas samples is needed in CRDS experiments compared to the requirement of filling large multi-pass sample cell in other measurements, therefore, there were only a few H$_2^{17}$O transitions reported before, including the intra-cavity laser absorption spectroscopy (ICLAS) study of $^{18}$O-enriched water vapor sample [10,11].

In the investigated spectral region, the HITRAN2016 database provides the line parameters for the transitions of H$_2^{16}$O and H$_2^{17}$O water isotopologues stronger than $1 \times 10^{-29}$ cm$^{-1}$(molecule$^{-1}$·cm$^{-2}$) with natural abundance as shown in Fig. 1. Our previous work with 7.5 Torr enriched $^{17}$O water vapor provided more than 2700 transitions of H$_2^{16}$O and H$_2^{17}$O isotopologues, including 762 new and 162 corrected transitions in the region of 12,277 – 12,894 cm$^{-1}$ in comparison with HITRAN2016 database. The present measurement was extended to 12,055 cm$^{-1}$ for these two water isotopic species in this work, mainly corresponding to the $v_1 + 1/2v_2 + v_3=3.5$ polyad. The absorption in the lower spectral region is mainly contributed from some transitions of H$_2^{16}$O with intensities in the order of $10^{-24}$–$10^{-23}$ cm$^{-1}$(molecule$^{-1}$·cm$^{-2}$), which would easily saturate the ring-down signal and blind some weaker transitions. Therefore,
lower pressures were chosen in addition to avoid the overlapping of strong lines. About 270 new transitions of H$_2^{17}$O isotopologue were reported for the first time by CRDS with $^{17}$O enriched water sample at room temperature.

In this paper, we describe the experimental procedure and the methodology of the line list preparation in brief. The next context is devoted to the vibration-rotation assignments of the recorded spectrum, and the construction of the line positions and the obtained ro-vibrational energy levels for four water isotopic species as well. Comparisons between this work and those from the literature will be discussed in Section 4. A conclusion will be given in the last section.

2. Experimental set up and Spectral analysis

The spectra of $^{17}$O-enriched water vapor sample were continuously recorded at room temperature (296 ± 1 K) in the 12,055–12,260 cm$^{-1}$ region by using a CW-CRDS spectrometer based on a Ti: Sapphire laser except in some strong saturated spectral sections: 12,144.5–12,147.9, 12,148.7–12,150.5, 12,151.4–12,152.0, 12,218.0–12,219.6, 12,225.8–12,227.0, and 12,247.8–12,249.6 cm$^{-1}$. The structure of the experimental set up is quite similar to that presented in Ref. [1,12,13]. A CW tunable Ti: sapphire laser (Coherent MBR 110) is used to produce the laser beam and the ring-down cavity is about 65.5 cm long-sealed with a couple of reflective mirrors (99.995% Layertec GmbH). The ring-down signal is then detected by a photo-diode and recorded by an analog-digital converter (ADLink PCI 9228) installed on a personal computer. The sample absorption coefficient $\alpha(\nu)$ was obtained by measuring the ring-down time $\tau(\nu)$ of the transmitted laser beam power:

$$\alpha(\nu) = \frac{1}{c} \left( \frac{1}{\tau(\nu)} - \frac{1}{\tau_0} \right)$$  \hspace{1cm} (1)

Where $c$ is the speed of light and $\tau_0$ is the ring-down time of the empty cavity. The noise-equivalent minimum detectable absorption coefficient $\alpha_{\text{min}}$ was about 2 × 10$^{-10}$ cm$^{-1}$ in the measurement.

The $^{17}$O-enriched water sample used in the measurements was purchased from ICON services. The stated isotopic concentration of the $^{17}$O atom in the sample is about 70%. A total sample pressure of 2.0–2.2 Torr measured with a capacitance gage (full range 100 kPa, 0.5% accuracy) was used in this work. Due to the continuous exchange between the molecules in the gas phase and those absorbed on the walls of the sample cell which is mainly contributed from the main isotopologue H$_2^{16}$O, the concentrations of the H$_2^{16}$O and H$_2^{17}$O isotopic species were changing along with the measurement. The isotopic abundance in the water vapor was increasing for H$_2^{16}$O species, while the H$_2^{17}$O abundance was decreasing. The relative concentrations of H$_2^{16}$O and H$_2^{17}$O water isotopologues were calculated through the intensity ratio of some relatively strong and isolated H$_2^{16}$O and H$_2^{17}$O transitions in the same spectral region by using the intensities in HITRAN2016 database as a reference. Therefore, the estimated water isotopic abundance was listed in Table 1 for the H$_2^{16}$O, H$_2^{17}$O, and H$_2^{18}$O species, together with the respective natural abundances of water isotopologues given in the HITRAN2016 database [5].

The frequency calibration of the CRDS spectra relies on the readings given by a calibrated lambda-meter (Burleigh WA-1500) with 60 MHz accuracy. The pressure-induced shift was calculated to be less than one MHz at the pressure of about 2.0 Torr, which is much smaller than the experimental uncertainty and considered negligible. The accuracy of the unblended and not very weak lines is estimated to be better than 0.002 cm$^{-1}$. An overview of the measured CRDS spectrum is given in Fig. 2(a). An example with the molecular species and rotation-vibration assignments illustrating the quality of the spectrum near 12,065 cm$^{-1}$ is presented in Fig. 2(b and c) as well.

3. Rotational assignments and line list construction

The least-squares multi-line fitting program called “intwin” was used to obtain the complete line list [14–16]. The line shape was modeled by a Voigt profile while the Gaussian line width was fixed at the Doppler line width. Line position, integrated line ab-

![Fig. 1. Overview of the recorded transitions in combination with previous CRDS study and HITRAN2016 between 12,055 and 12,900 cm$^{-1}$ for line intensities in the natural abundance at 296 K. The gray and orange squares are corresponding to the HITRAN2016 database from Ref. [5] while the violet stars and green triangles are from the previous CRDS study [1]. The magenta stars and blue triangles are corresponding to line positions observed in this work with intensities from the calculations by Partridge and Schwenke in the natural abundance [17,18].](image-url)
Table 1
Summary of the assignments of observed water lines.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Abundance (estimated)</th>
<th>Number of transitions</th>
<th>$J_{max}$</th>
<th>Range (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2^{16}$O</td>
<td>0.60–0.63</td>
<td>674</td>
<td>13</td>
<td>12,055.3444–12,260.4892</td>
</tr>
<tr>
<td>H$_2^{17}$O</td>
<td>0.39–0.37</td>
<td>508</td>
<td>12</td>
<td>12,056.6326–12,260.3562</td>
</tr>
<tr>
<td>H$_2^{18}$O</td>
<td>0.005</td>
<td>192</td>
<td>12</td>
<td>12,059.0578–12,260.1371</td>
</tr>
<tr>
<td>HD$^{16}$O</td>
<td></td>
<td>45</td>
<td>13</td>
<td>12,058.1131–12,233.1512</td>
</tr>
<tr>
<td>Unassigned</td>
<td></td>
<td>138 (lines)</td>
<td></td>
<td>12,057.1515–12,260.5331</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1557</td>
<td></td>
<td>12,055.0578–12,260.5331</td>
</tr>
</tbody>
</table>

Fig. 2. (a) An overview of the recorded spectrum between 12,055 and 12,260 cm$^{-1}$ in the upper panel; (b) and (c) an example of the quality and assignments of the observed spectrum around 12,066 cm$^{-1}$ as shown in the middle panel; (d) the residuals between the recorded spectra and the calculation in the range of 12,065–12,067 cm$^{-1}$. Note that H$_2^{16}$O, H$_2^{17}$O, H$_2^{18}$O and HD$^{16}$O are represented as 161, 171, 181 and 162 in the figure, respectively.
sorption, and Lorentzian width can be adjusted for each line during the fitting procedure. The typical sensitivity of $2 \times 10^{-10}$ cm$^{-1}$ allows the determination of more than 1300 lines stronger than $10^{-28}$ cm$^{-1}$(molecule cm$^{-2}$). An example of the residuals between the recorded spectra and simulated spectra around 12,065 cm$^{-1}$ was illustrated in Fig. 2(d). The complete line list of all 1342 lines determined in this work is given as Supplementary Material I to this paper. The list includes the observed positions, the observed intensities and calculated intensities scaled to the isotopic abundance together with the molecular species and vibration-rotation assignments.

The general information about all assigned transitions related to four water isotopologues ($H_2^{16}$O, $H_2^{17}$O, $H_2^{18}$O, and HD$^{18}$O) is given in Table 1. The variational line lists calculated by Tashkun (Tomsk, Russia) based on the results from Partridge and Schwenke [17,18] were used to assign the observed water lines. These water line lists could be retrieved online at the system “Spectroscopy of Atmospheric Gasses”, http://spectra.ioa.ru [19]. More than 60% observed lines were directly assigned through the line lists calculated using IUPAC-TG energy levels. The trend of the rovibrational energy difference between the determined levels from these directly assigned transitions and those in P&S variational calculation, and intensity comparison between the observation and the P&S calculation, led us to continue the assignments of the weaker transitions in the same vibrational band. In total, there are 1182 transitions assigned to $H_2^{16}$O and $H_2^{18}$O water isotopologues. About 192 and 45 transitions were also identified for $H_2^{18}$O and HD$^{18}$O water isotopologues, respectively, using the line lists from IUPAC-TG energy levels [23]. Therefore, the analysis determined the assignments of 1419 transitions of four water isotopologues and remained 138 lines unassigned in this work. Table 2 gives the summary of the band-by-band information of the observed water lines, including the number of transitions, the maximum rotational quantum number $J$ and $K_a$ for each vibrational band of four water isotopologues.

The line positions determined in this work for $H_2^{16}$O and $H_2^{17}$O isotopic species are included in Fig. 1 together with those listed in HITRAN2016. In general, the absorption intensities of the observed transitions range from $5.6 \times 10^{-24}$ to $2 \times 10^{-28}$ cm$^{-1}$ molecule$^{-1}$ around 820 nm for the $H_2^{16}$O main isotopologue in this work, while the line positions were missed here for about 50 strong transitions with intensities larger than $5.65 \times 10^{-24}$ cm$^{-1}$ molecule$^{-1}$ due to the signal saturation. These transitions belong to 11 cold bands and 9 hot bands, mainly contributed by (032) $\nu_12\nu_23\nu_3$, (112), (131), (211) and (310) cold bands. The adoption of the $^{17}$O-enriched water samples allowed the observations of $H_2^{17}$O transitions in the intensity dynamic range of $10^{-31}$ to $10^{-26}$ cm$^{-1}$ molecule$^{-1}$ in natural abundance ($3.7 \times 10^{-4}$), which are more than one times enlargement compared to the intensity cut-off of $1 \times 10^{-29}$ cm$^{-1}$ molecule$^{-1}$ for the $H_2^{17}$O isotopologue in the HITRAN2016. These $H_2^{17}$O transitions mainly come from five cold bands (as for $H_2^{16}$O species) and one hot band in this work.

Based on the line positions of the 1419 transitions determined above, a total of 894 ro-vibrational energy levels of four isotopic species were obtained and given in Supplementary Material II attached to this paper.

### 4. Comparisons with HITRAN database and IUPAC-TG

The water line positions in the studied spectral region in HITRAN2016 were calculated from the IUPAC-TG energy levels [2–4,20], or the predictions from the variational calculations by Bubukina et al. [21] and Lodi et al. [22] for $H_2^{16}$O, $H_2^{18}$O and $H_2^{17}$O using the semi-empirical potential energy surface which were the
empirical calculations, respectively. Therefore, we made two separated comparisons of the line positions between this work and those from calculations using IUPAC-TG energy levels and the empirical calculations for four isotopologues if there are two kinds of sources in HITRAN. Some corrections of line positions were given based on the comparisons. New energy levels were determined by the comparison between the obtained values in this work and those in the line lists from IUPAC-TG energy levels and our previous work. The comparisons are presented for \( \text{H}_2\text{O}^{16} \), \( \text{H}_2\text{O}^{17} \), \( \text{H}_2\text{O} \) and HD\( \text{O} \) isotopologues, respectively as follows.

4.1. \( \text{H}_2\text{O}^{16} \) isotopologue

There are more than 1300 \( \text{H}_2\text{O}^{16} \) transitions with intensities stronger than \( 2 \times 10^{-28} \text{ cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2}) \) in HITRAN2016 in the studied spectral range, in which 85% transitions were calculated from the IUPAC energy levels. There are about 51 transitions predicted by the variational calculations only with the available lower ro-vibrational assignments. And some transitions have different upper ro-vibrational assignments from ours. The comparisons were given for these transitions by sharing the same lower ro-vibrational energy levels and intensity with the same order of magnitude. Therefore, most of the observed transitions can be found in the respective values in the HITRAN2016 database from Refs. [4,21], which difference is plotted separately with circles and triangles for IUPAC-TG and empirical calculations on the upper panel of Fig. 3. In general, the calculations from IUPAC-TG energy levels present better agreements than the empirical calculations. The differences are below 0.005 cm\(^{-1}\) for over 480 transitions. While 24 transitions show significant differences against the HITRAN2016 reaching up to 0.075 cm\(^{-1}\), supplied as Supplementary Material III. Some significant discrepancy examples are shown in Fig. 4. Please note that the vibrational and rotational numbers assigned to the transitions are dominated by \( V_1, V_2, V_3 \) and \( K_a, K_c \) here. The position of the (211) 10 6 4−(000) 10 6 5 transitions in the HITRAN2016 database is shifted by 0.075 cm\(^{-1}\) compared to the same observed position at 12,129.8819 cm\(^{-1}\) since the line is much weaker in the observed spectrum shown on the left panel of Fig. 4. The second line observed at 12, 138.4761 cm\(^{-1}\) corresponds to the (051) 8 8 1−(000) 8 8 0 and (051) 8 8 0−(000) 8 8 1 transitions as shown on the right panel of Fig. 4. The corresponding line positions in the HITRAN2016 database are shifted by 0.025 and 0.023 cm\(^{-1}\) compared to the observations above. The line intensities of these three transitions in the database are \( 1.21 \times 10^{-26}, 8.15 \times 10^{-27}, \) and \( 4.39 \times 10^{-26} \text{ cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2}) \) in natural abundance from HITRAN2016. Through the comparison with the energy levels given by IUPAC-TG [2] as well as our previous work of the water vapor absorption spectrum in the 12,277−12,894 cm\(^{-1}\) region [1], 13 corrected energy levels are given in italic with differences larger than 0.008 cm\(^{-1}\) from the values published by IUPAC-TG as well as 9 new energy levels been listed in Table 3.

4.2. \( \text{H}_2\text{O}^{17} \) isotopologue

As for the \( \text{H}_2\text{O}^{17} \) isotopic species, there were more than five hundred transitions assigned in the recorded spectrum and 270 of them were reported for the first time. There are 333 transitions of \( \text{H}_2\text{O}^{17} \) species included in HITRAN2016, less than 42% are from the calculations using IUPAC-TG energy levels [2]. The lower panel of Fig. 3 shows the \( \text{H}_2\text{O}^{17} \) line position comparisons between this work and those in HITRAN2016. Similar good agreements were obtained for the \( \text{H}_2\text{O}^{17} \) transitions from the IUPAC-TG energy levels as presented on the upper panel for the \( \text{H}_2\text{O}^{16} \) transitions. While the differences of the observed line positions against the empirical calculations by Lodi et al. [22] vary from −0.102 to 0.143 cm\(^{-1}\). The differences of 75 transitions are more than 0.01 cm\(^{-1}\), summarized as Supplementary Material IV. The biggest difference is 0.143 cm\(^{-1}\), corresponding to the (310) 8 4 5−(000) 7 5 2 transition with a line intensity of \( 1.63 \times 10^{-29} \text{ cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2}) \) in natural abundance from HITRAN2016. Some of the significant discrepancies between the observed line positions and those from the HITRAN2016 database are shown in Fig. 5. The three line positions of the \( \text{H}_2\text{O}^{17} \) (211) 8 4 4−(000) 8 4 5, (211) 9 6 4−(000) 9 6 3, and (131) 9 4 6−(000) 8 4 5 transitions in the HITRAN2016 database are shifted by −0.066, −0.037 and −0.093 cm\(^{-1}\) compared to the ob-
Table 3
Corrected and new energy levels of H$_2$O-161 and 171 isotopologues.

<table>
<thead>
<tr>
<th>Vib</th>
<th>J</th>
<th>K$_a$</th>
<th>K$_c$</th>
<th>E</th>
<th>$\Delta$E</th>
<th>Vib</th>
<th>K$_a$</th>
<th>K$_c$</th>
<th>E</th>
<th>$\Delta$E</th>
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<tbody>
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<td>161</td>
<td>052</td>
<td>2</td>
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<td>11</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>052</td>
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<td>5</td>
<td>0,106</td>
<td>0.108</td>
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<td>0.0089</td>
<td>051</td>
<td>11</td>
<td>3</td>
<td>9</td>
</tr>
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<td>052</td>
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<td>0.0122</td>
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</tr>
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<td>11</td>
<td>3</td>
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<td>051</td>
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</tbody>
</table>

Notes: Vib J K$_a$ K$_c$ – vibration and rotation assignment of the energy level; E – Energy values obtained in this study (cm$^{-1}$); $\Delta$E – Energy difference between this work and the literature values from IUPAC [4] (cm$^{-1}$).
Fig. 4. Examples of $\text{H}_2^{16}\text{O}$ lines compared with the HITRAN2016 [5] using HAPI program [23]. Line intensities have been rescaled to the relative abundance shown in Table 1. Observed and calculated spectra for different isotopic species are given with dashed and solid lines, respectively. Note that $\text{H}_2^{16}\text{O}$, $\text{H}_2^{17}\text{O}$, $\text{H}_2^{18}\text{O}$ and $\text{HD}^{16}\text{O}$ are represented as 161, 171, 181 and 162 in the figure, respectively.

Fig. 5. Examples of $\text{H}_2^{17}\text{O}$ lines compared with the HITRAN2016 [5] using HAPI program [23]. Line intensities have been rescaled to the relative abundance shown in Table 1. Observed and calculated spectra for different isotopic species are given with dashed and solid lines, respectively. The stars indicate very weak absorptions contributed from other isotopic species which are not considered in our analysis. Note that $\text{H}_2^{16}\text{O}$, $\text{H}_2^{17}\text{O}$, $\text{H}_2^{18}\text{O}$ and $\text{HD}^{16}\text{O}$ are represented as 161, 171, 181 and 162 in the figure, respectively.

Observed positions at 12,116.6435, 12,116.7832, 12,116.8589 cm$^{-1}$ illustrated in the left panel of Fig. 5. The second line observed at 12,233.4731 cm$^{-1}$ corresponds to the $\text{(211) 10}_2 8_{-2}$ transition as shown in the right panel of Fig. 5. The corresponding line positions in the HITRAN2016 database are shifted by 0.053 cm$^{-1}$ comparing to the observations. Based on the 508 $\text{H}_2^{17}\text{O}$ transitions assigned in the recorded spectrum, we were able to obtain 110 new and 5 corrected energy levels using energy levels given by IUPAC-TG [2] as well as our previous work in the 12,277–12,894 cm$^{-1}$ region [1] shown in Table 3. The corrected energy
levels given in italic differ by more than 0.009 cm$^{-1}$ from the values published by IUPAC-TG [2]. Note the vibrational assignments of some energy levels for (310) and (112) states could be exchanged corresponding to IUPAC-TG adoption.

4.3. $H_2^{18}O$ and $HD^{16}O$ isotopologues

The observed transitions of $H_2^{18}O$ mainly belong to the $2\nu_1 + \nu_2 + \nu_3$ and the $3\nu_1 + \nu_2$ bands. Most of the line position differences between our observations and those from HITRAN2016 were less than 0.005 cm$^{-1}$, and the $-0.0005$ cm$^{-1}$ average difference shows the comparison in a good agreement.

The deuterium isotopic abundance in the sample is almost six times of the natural abundance, which allowed us to observe more than 40 transitions of $HD^{16}O$. Most of them come from $\nu_2 + 3\nu_3$ cold band, the strongest transition is (013) $6\ 1\ 5\ 0(000)$ $5\ 1\ 4$ at $12,062.6361$ cm$^{-1}$ with an experimental line intensity of $1.26 \times 10^{-26}$ cm$^{-1}$/molecule–cm$^2$.

5. Conclusion

The present study complements our investigation of the room temperature high resolution CRDS absorption spectrum of $^{17}$O enriched water vapor in the $12,055–12,894$ cm$^{-1}$ spectral range. More than 1400 transitions of four water isotopologues ($H_2^{17}O$, $H_2^{18}O$, $H_2^{16}O$, and $HD^{16}O$) were observed and assigned in this work. The coupling of the present and preceding studies have extended the knowledge of the near-infrared absorption spectrum of $^{17}$O enriched water vapor, which includes several aspects, the determination of new energy levels mostly for $H_2^{17}O$, corrections of some energy levels already been reported, and the high-quality data of water vapor transitions with a typical frequency accuracy of 0.002 cm$^{-1}$. Overall more than 890 precise experimental energy levels have been derived for the $H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$, and $HD^{16}O$ molecules, in which 110 of them for the $H_2^{17}O$ energy levels are obtained for the first time.

Declaration of Competing Interest

The authors declare that we have no financial and personal relationships with other people or organizations that can inappropriate influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

Acknowledgments

This work is jointly supported by NSFC (21473172, 21427804, and 21688102) and CAS (XDB21020100).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2010.06.051.

References


