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Frequency metrology in the near-infrared spectrum of H_2^{17}O and H_2^{18}O molecules: testing a new inversion method for retrieval of energy levels

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Abstract. An extensive Doppler-free spectroscopic investigation of the near-infrared absorption spectrum of the H_2^{18}O molecule was performed, for the first time, with absolute frequency calibration by using a GPS-disciplined fiber-based optical frequency comb. The investigated line pairs belong to the $\nu_1 + \nu_3$ band and have been chosen in the wavelength range from 1.38 to 1.41 μm with a lambda scheme, so as to share the excited energy level and allow an accurate determination of the rotational energy separations of the fundamental vibrational state. The measurement of the sub-Doppler line-center frequencies, also extended to the H_2^{17}O spectrum, has been performed with an overall uncertainty of ~ 30 kHz, i.e. about three orders of magnitude lower than the HITRAN data set. The retrieved energy separations agree, by less than 80 kHz, with recent findings provided by the so-called MARVEL procedure for spectral data inversion, thus yielding a very stringent test of its accuracy.

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1. Introduction

Molecular spectroscopy aided by the technology of optical frequency combs is nowadays a research subject that is very much alive for several reasons. Absolute frequency measurements of vibration–rotation transitions provide precise information on the potential energy surface and relevant perturbation effects, as recently demonstrated by an extensive study of molecular iodine [1]. Precision measurements on molecular beams or cold molecular samples allow one to check the stability of fundamental constants, such as the proton-to-electron mass ratio [2] or the fine structure constant [3]. Furthermore, narrow molecular resonances serve as high-quality frequency standards in the infrared (IR) region and knowledge of their absolute frequencies is extremely useful for the application of them in telecommunications [4] as well as for calibrating broadband molecular spectra [5]. In this respect, the spectrum of water vapor can play a very important role, being very rich in relatively strong transitions in the near- and mid-IR regions [6].

The water molecule is an important constituent of the Earth's atmosphere, being responsible for about 70% of the known atmospheric absorption of sunlight and the majority of the greenhouse effect. It has been detected in a variety of astronomical objects from the ground as well as from satellite and airborne platforms. Water vapor is also a major product of most combustion processes. Therefore, it is no surprise that the spectrum of water has been the subject of numerous experimental and theoretical studies for decades, for the purpose of achieving a full comprehension of its spectrum. This is an indispensable prerequisite in many research fields, encompassing atmospheric chemistry and physics, climatology, astrophysics, combustion science and free-space telecommunication. With its three nuclei and ten electrons, water is a relatively simple molecule for which highly accurate first-principles quantum mechanical calculations are possible [7]. In particular, very elaborate calculations based upon variational techniques have been recently reported for nuclear motion and electronic energies, and a variety of subtle physical effects arising from a fully relativistic treatment, the breakdown of the Born–Oppenheimer approximation and a quantum electrodynamics approach have also been considered [8]. From the experimental point of view, most spectroscopic investigations have been performed either by Fourier-transform spectroscopy [9, 10] or, more recently, by diode-laser-based cavity ring-down spectroscopy [11, 12], the absolute calibration of the spectra being obtained by comparison with a few selected molecular references [9]. The frequency uncertainty of the line positions remains, however, relatively high, namely at the 3–30 MHz level, mainly limited by the width of the lines. In this paper, we report the first frequency-comb-assisted characterization of the near-IR spectrum of the H_2^{18}O and H_2^{17}O water isotopologues. Sub-Doppler spectroscopy has been extensively performed in the wavelength window between

1.38 and 1.41 μm , probing a large number of line pairs, each of them sharing the excited level in a lambda scheme. To achieve saturation of the selected lines, an extended-cavity diode laser (ECDL) has been frequency locked to a high-finesse optical resonator providing strong enhancement of the power level. Absolute determination of the line-center frequencies was performed by comparing the ECDL frequency, as stabilized against the preselected sub-Doppler line, to a GPS-disciplined Rb microwave standard through a self-referenced frequency comb. The uncertainty of the measured frequencies is found to be of the order of 30 kHz. Such a high accuracy allows one to realize a very stringent test of the methods for inverting experimental transition data and retrieving energy levels of small molecules. In particular, a comparison is made with the so-called MARVEL procedure, standing for Measured Active Rotational-Vibrational Energy Levels [13], which relies on the combined use of spectroscopic data and first-principles theoretical calculations and has been recently applied for a critical and extensive evaluation of the water IR spectrum by an international task group sponsored by IUPAC [14]. The separation between the investigated energy levels is found to be in excellent agreement with that provided by MARVEL: over a set of nine line pairs, the average deviation is in fact below 80 kHz, very close to our experimental accuracy.

2. Experimental setup

Figure 1 shows the experimental setup adopted for the absolute frequency characterization of the near-IR spectrum of H_2^{18}O and H_2^{17}O . An ECDL, operating in a Littrow configuration with an emission wavelength tunable from 1.38 to 1.42 μm and a maximum output power of 35 mW, is used for Lamb-dip spectroscopy of the investigated lines. A 10% fraction of the laser beam is injected into an 86 mm long build-up resonator with an empty cavity finesse of 4450. Another fraction is combined with the output of an optical frequency-comb synthesizer on a 125 MHz bandwidth photodiode to produce the beating signal used for absolute frequency measurements. The remaining fraction is sent to a 7-digit wavemeter (Burleigh, model WA1500) for coarse frequency calibration. The Pound–Drever–Hall (PDH) technique [15] is used to lock the laser to the high-finesse cavity. For this purpose, two servo loops are used, a slow one (~ 1 kHz bandwidth) acting on the extended cavity length and a fast one (~ 1 MHz bandwidth) controlling the injection current. With such a setup the laser linewidth is narrowed down to 30 kHz in the short term (10 ms), as demonstrated in a recent work in which further details of this part of the experimental setup are provided [16].

The optical frequency-comb source is based on an amplified, commercially available, erbium-doped fiber laser (Toptica, model FFS1550) with a pulse repetition rate (f_{rep}) of 100 MHz. Its output is coupled to a highly nonlinear fiber that generates a supercontinuum (SC) spanning more than one octave at wavelengths from 1 to 2.2 μm . Two long-wavelength pass filters (LWP) are used to separate the SC into three spectral intervals. The central part (wavelengths between 1.2 and 1.7 μm) is reflected from LWP2, recombined with the ECDL output, spectrally narrowed by a grating–lens–slit assembly and then sent to the photodiode for frequency counting. The long-wavelength (above 1.7 μm) and the short-wavelength (below 1.2 μm) parts of the SC are separated by LWP1 and exploited for active stabilization of the comb carrier–envelope offset frequency (f_{CEO}) in a self-referencing scheme. In particular, the long-wavelength part is frequency doubled in a 1.8 cm long periodically poled lithium niobate crystal and, after being collinearly recombined with the short-wavelength side in a $f - 2f$ interferometer configuration, it is spectrally filtered and focused on a fast detector to produce

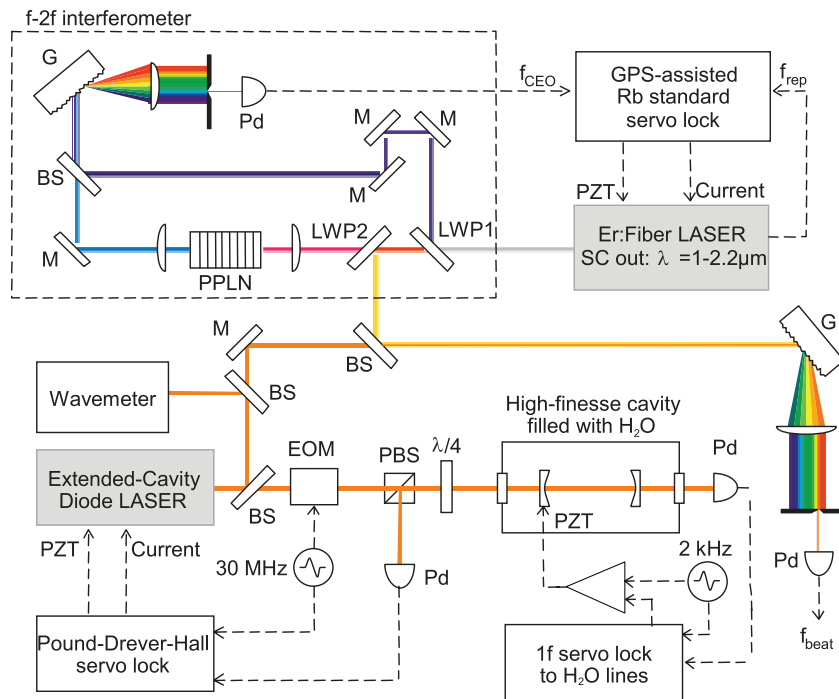


Figure 1. Schematic diagram of the experimental setup for the absolute frequency measurement of Doppler-free H₂¹⁸O and H₂¹⁷O lines. BS, beam splitter; LWP1 and LWP2, long-wavelength pass filters; EOM, electro-optic phase modulator; G, grating; $\lambda/4$, quarter wave plate; M, mirror; PZT, piezoelectric transducer; PBS, polarizing beam splitter; Pd, photodiode; PPLN, periodically poled lithium niobate crystal.

a beat note at f_{CEO} . By servo-controlling the pump diode current of the fiber oscillator, the detected beat note is locked to a GPS disciplined Rb oscillator (Symmetricom, model 4410), acting as a master clock for all electrical loops with a relative accuracy better than 10^{-12} .

The stabilization of the comb repetition rate (f_{rep}) is achieved by servo-controlling the fiber oscillator cavity length through a piezoelectric transducer (fine control) and a step motor (coarse control). The error signal of this servo-loop is obtained by comparing the f_{rep} signal given by the internal detector of the laser with the 100 MHz low-phase-noise signal coming from a quartz oscillator, also referenced to the Cs-clock primary standard through the GPS-disciplined Rb oscillator.

3. Experimental results

Examples of saturated absorption spectra, for the two isotopologues, are shown in figure 2. They were obtained by scanning the cavity resonance frequency over the absorption line and by recording the cavity transmission with a 1 kHz bandwidth low-noise InGaAs photodiode. An 80% enriched ¹⁸O water vapor sample (with a nominal purity better than 99.9%) was used, the remaining 20% being H₂¹⁷O. The total gas pressure inside the optical cavity was kept constant at about 10 Pa, as measured by a high-accuracy capacitance pressure gauge. The contrast of the Lamb-dip with respect to the Doppler-broadened envelope varied between 5 and 15%,

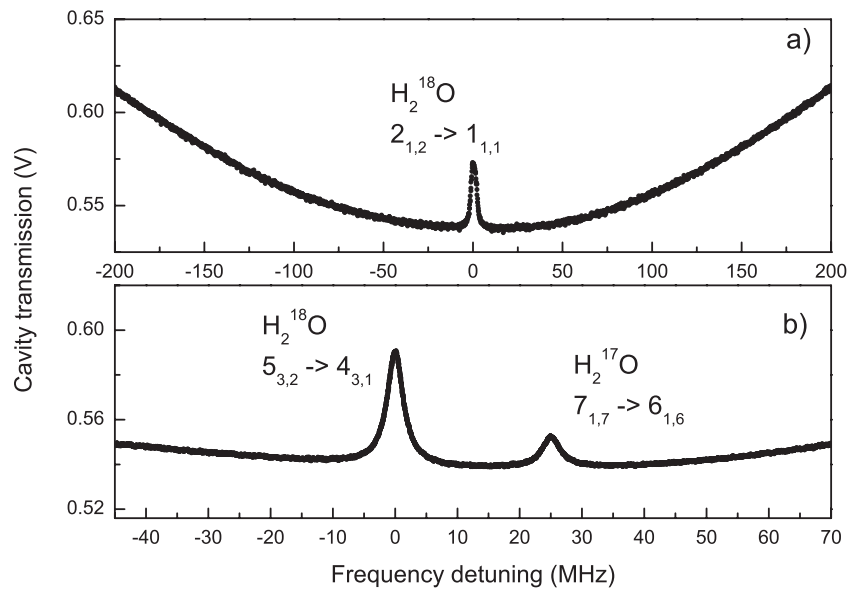


Figure 2. Examples of Doppler-free absorption lines for the H_2^{18}O molecule, at wavelengths of 1391.8938 and 1411.6320 nm, respectively, for parts (a) and (b). The latter spectrum shows that the intracavity power was sufficiently high to enable the saturation of the weaker H_2^{17}O line (whose intensity is a factor of 8 smaller, as compared to the H_2^{18}O line), the frequency separation between the two lines being equal to ~ 25 MHz. The good signal-to-noise ratio, resulting from dc detection in a 1 kHz bandwidth, demonstrates the excellent performance of the PDH locking loops.

depending on the transition dipole moment of the selected line, while its width (full-width at half maximum, FWHM) was measured to be in the range between 2 and 3 MHz, mostly resulting from the pressure broadening effect. The investigated lines are listed in table 1. All vibration–rotation transitions belong to the $\nu_1 + \nu_3$ band and have a central wavelength between 1.38 and 1.41 μm . Their saturation intensity, in our operation conditions, ranges between 2.5×10^6 and $2.5 \times 10^7 \text{ W m}^{-2}$. The H_2^{18}O lines were carefully selected within the reach of our ECDL so as to form nine different line pairs with a lambda scheme, each of them sharing the excited energy level.

The involved levels are labeled using the standard asymmetric top notation J_{K_a, K_c} , where J is the familiar quantum number of total angular momentum, K_a and K_c the projections along two of the three principal axes of inertia, the axes being distinguished on the basis of the corresponding moment of inertia, from the smallest (A -axes) to the largest (C -axes).

For a given absorption line, the ECDL emission frequency is locked to the central frequency using the procedure reported in [16]. Briefly, the cavity mode frequency is locked to the center of the Lamb-dip by using the wavelength modulation spectroscopic method. The cavity resonance is dithered by means of a sinusoidal signal at 2 kHz with a modulation depth of about 0.5 MHz. Being constantly locked to the cavity, the laser frequency follows this modulation. A lock-in amplifier performs a synchronous processing of the cavity transmitted signal, thus allowing one to retrieve an error signal given by the first derivative of the Lamb-dip. Such a signal, once properly integrated, is used to actively control the cavity length through the piezoelectric

Table 1. The absolute frequencies in comparison to the HITRAN [19] and MARVEL [14] values. The overall uncertainty of the measured values, including statistical and systematic errors, is ~ 30 kHz. The uncertainty of MARVEL data ranges between 2 and 20 MHz (at 95% confidence limits), depending on the molecule and levels.

| Line $\nu_1 + \nu_3$ band | Frequency (kHz) This work | Deviation (kHz) | |
|-------------------------------|------------------------------|---------------------------|---------------------------|
| | | This work minus HITRAN | This work minus MARVEL |
| H_2^{18}O | | | |
| $5_{3,2} \rightarrow 4_{3,1}$ | 212 372 948 620 | -9141 | -13 068 |
| $4_{3,2} \rightarrow 4_{3,1}$ | 216 163 440 240 | -9418 | -13 195 |
| $4_{3,2} \rightarrow 3_{3,1}$ | 213 284 147 000 | -11 350 | -12 309 |
| $3_{3,0} \rightarrow 3_{3,1}$ | 216 191 670 190 | -11 223 | -12 422 |
| $4_{2,3} \rightarrow 3_{2,2}$ | 213 593 222 590 | -13 689 | -109 293 |
| $3_{2,1} \rightarrow 3_{2,2}$ | 216 226 026 160 | -13 568 | -109 201 |
| $3_{2,1} \rightarrow 2_{2,0}$ | 214 200 946 980 | -2488 | -25 303 |
| $2_{2,1} \rightarrow 2_{2,0}$ | 216 519 045 920 | -2562 | -25 346 |
| $4_{1,4} \rightarrow 3_{1,3}$ | 214 079 703 410 | -5791 | -6871 |
| $3_{1,2} \rightarrow 3_{1,3}$ | 215 607 014 210 | -5656 | -6825 |
| $3_{1,2} \rightarrow 2_{1,1}$ | 214 282 880 600 | -10 841 | -17 976 |
| $2_{1,2} \rightarrow 2_{1,1}$ | 217 097 759 250 | -10 691 | -17 976 |
| $3_{2,2} \rightarrow 2_{2,1}$ | 214 338 783 640 | 3690 | -8572 |
| $2_{2,0} \rightarrow 2_{2,1}$ | 216 436 513 940 | 3718 | -8603 |
| $3_{1,3} \rightarrow 2_{1,2}$ | 214 727 582 030 | -6853 | -22 862 |
| $2_{1,1} \rightarrow 2_{1,2}$ | 216 129 993 490 | -6824 | -22 953 |
| $2_{1,2} \rightarrow 1_{1,1}$ | 215 384 571 430 | -12 026 | -8998 |
| $1_{1,0} \rightarrow 1_{1,1}$ | 216 492 761 020 | -11 852 | -9034 |
| H_2^{17}O | | | |
| $3_{2,1} \rightarrow 3_{2,2}$ | 216 520 434 422 | -13 221 | -7975 |
| $7_{1,7} \rightarrow 6_{1,6}$ | 212 372 923 640 | -5940 | -8159 |

actuator that is mounted on the cavity input mirror. As a result of an Allan variance analysis of residual laser frequency fluctuations at the lock-in amplifier output, a relative frequency stability of the order of 10^{-13} for an integration time of 1 s is typically measured.

Absolute frequency determinations are carried out by comparing the water-stabilized laser frequency to the self-referenced optical frequency-comb synthesizer. The beat note between the laser radiation and the closest comb tooth exhibits a signal-to-noise ratio of 40 dB in a 100 kHz resolution bandwidth, which is sufficient for direct counting. Figure 3 shows an example of repeated beat frequency (f_{beat}) measurements for the H_2^{18}O $2_{1,2} \rightarrow 1_{1,1}$ line, covering a time span of about 1 hour, with a 1-s gate-time. The power spectral density of the beat note is shown in the inset, along with a fit to a Gaussian function that yields a FWHM of ~ 600 kHz. This relatively large value is consistent with the depth of the sinusoidal modulation that is superimposed on the laser frequency by the cavity length dithering. The standard deviation of the data set of figure 3 is equal to 3.4 kHz. The small drift that is clearly evidenced can be explained in terms of drifts in

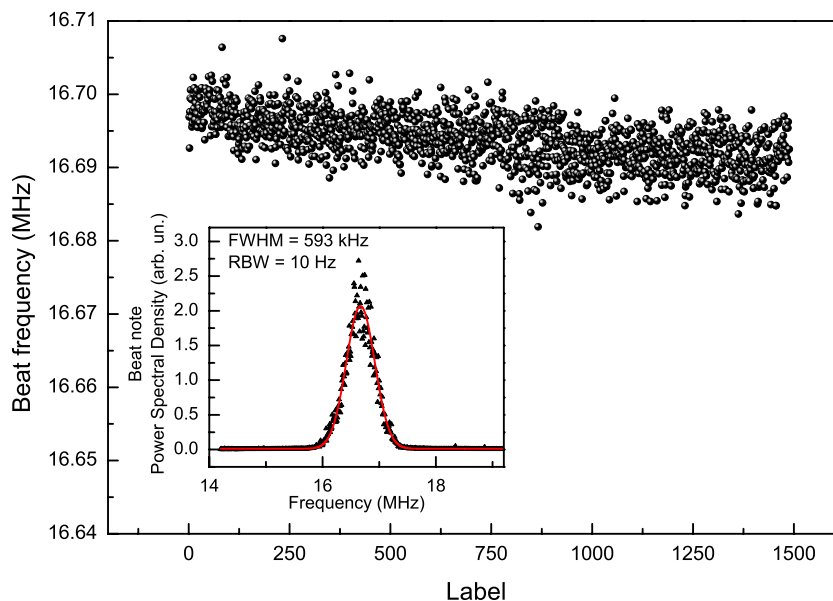


Figure 3. Repeated absolute frequency determinations for the $\text{H}_2^{18}\text{O } 2_{1,2} \rightarrow 1_{1,1}$ line. The inset shows the beat note as recorded by means of a spectrum analyzer, with a resolution bandwidth of 10 Hz.

the pressure and electronics offsets of the locking loops that shift the locking point. By removing such a drift, the standard deviation reduces to only 2.8 kHz. The absolute frequency can be retrieved using the equation $\nu_0 = n f_{\text{rep}} \pm f_{\text{beat}} \pm f_{\text{CEO}}$. The comb order, n , is easily provided by direct measurement of the laser wavelength by means of the wavemeter, whose accuracy is better than half the comb mode spacing. On the other hand, the correct signs can be determined by slightly varying f_{rep} and f_{CEO} and observing the consequent variation of f_{beat} .

In order to quantify the measurement repeatability in the long term, the absolute frequency of a predefined line, specifically the $\text{H}_2^{18}\text{O } 2_{2,1} \rightarrow 1_{2,0}$ line, was determined from several measurement runs performed over a time period of 2 weeks. Each data set encompassed 50 frequency samples of the beat note and, after each run, the chamber containing the optical resonator was evacuated and refilled at the same water pressure. In this dead time, the laser and the cavity were unlocked and the offsets properly adjusted, before locking again. The standard deviation of the mean values was found to be about 15 kHz, which includes the statistical uncertainty in the measurement of the center frequency as well as small systematic deviations (type B errors) arising from sample-handling effects and from lock-to-lock sequences. Another source of type B error is given by the pressure shift, which is expected to be of the order of a few kHz Pa^{-1} for the investigated lines [17]. Nonetheless, even adopting a very pessimistic approach, it should be sufficient to multiply the 15 kHz uncertainty by a factor of 2, in order to take into account the frequency shift due to the $\text{H}_2^{18}\text{O}-\text{H}_2^{18}\text{O}$ and $\text{H}_2^{18}\text{O}-\text{H}_2^{17}\text{O}$ collisions. Other sources of type B errors, such as the ac Stark shift or that introduced by the curvature of the wave front [18], can be neglected, being estimated to be well within the 30 kHz uncertainty. Concerning the influence of the dither amplitude (namely, the modulation depth) on the line-center frequency, we estimated it to be at the kilohertz level, on the basis of the high symmetry of the Lamb-dip and of its derivative profile. The measured frequencies are reported in the second column of table 1. A comparison with the HITRAN database [19] is also performed

Table 2. Energy separation between selected pairs of rotational levels within the (0, 0, 0) vibrational level of the H₂¹⁸O electronic ground state.

| Rotational levels | $\Delta E \text{ h}^{-1}$ (kHz) | | | $\Delta E \text{ h}^{-1}$ (kHz) | |
|------------------------------------|---------------------------------|--------------|-----------------|---------------------------------|-----------------|
| | This work | MARVEL [14] | Deviation (kHz) | HITRAN [19] | Deviation (kHz) |
| 5 _{3,2} –4 _{3,2} | 3790 491 620 | 3790 491 747 | –127 | 3790 491 897 | –277 |
| 4 _{3,2} –3 _{3,0} | 2907 523 190 | 2907 523 304 | –114 | 2907 522 164 | 1026 |
| 4 _{2,3} –3 _{2,1} | 2632 803 570 | 2632 803 478 | 92 | 2632 804 347 | –777 |
| 3 _{2,1} –2 _{2,1} | 2318 098 940 | 2318 098 983 | –43 | 2318 097 215 | 1725 |
| 4 _{1,4} –3 _{1,2} | 1527 310 800 | 1527 310 755 | 45 | 1527 310 665 | 135 |
| 3 _{1,2} –2 _{1,2} | 2814 878 650 | 2814 878 650 | 0 | 2814 877 301 | 1349 |
| 3 _{2,2} –2 _{2,0} | 2097 730 300 | 2097 730 332 | –32 | 2097 731 771 | –1471 |
| 3 _{1,3} –2 _{1,1} | 1402 411 460 | 1402 411 551 | –91 | 1402 411 131 | 329 |
| 2 _{1,2} –1 _{1,0} | 1108 189 590 | 1108 189 626 | –36 | 1108 191 815 | –2225 |

by evaluating line by line the corresponding differences. With the only exception of two H₂¹⁸O lines, the HITRAN values are slightly overestimated by a quantity that ranges between ~ 3 and ~ 14 MHz. However, these deviations are well within the uncertainty of the HITRAN values (namely, 30–300 MHz). In this respect, our data represent an improvement, by more than three orders of magnitude, in the accuracy.

4. Test of the MARVEL energies and line positions

The absolute frequencies of table 1 also provide reliable information on the rotational terms of the (0, 0, 0) vibrational level of the H₂¹⁸O electronic ground state. In fact, the frequency separation between preselected rotational levels can be retrieved from those line pairs forming a lambda scheme. The results are reported in table 2 and compared with the values taken from [14], coming from the application of the MARVEL procedure. They agree remarkably well with our values. In fact, the absolute deviations that are listed in the fourth column of table 2 exhibit a root-mean-square value of about 76 kHz, which is close to our experimental accuracy. It must be mentioned that the levels involved in this study are particularly well determined by the MARVEL procedure, all of them being classified as A+ in [14] (the grade A+ meaning that the level is involved in more than five lines and that there are at least two independent experiments probing this energy level), with a quoted uncertainty smaller than 10 MHz. However, even though limited to these types of levels, our investigation seems to provide a strong validation of the methodology adopted in the MARVEL procedure for inverting experimental transition data to give energy levels. In fact, if a similar test is carried out for the HITRAN database (see the last two columns of table 2), it turns out that the root-mean-square deviation amounts to about 1237 kHz, which is nearly a factor of 16 larger. Surprisingly, the same level of agreement is not found for the line-center frequencies, as clearly shown in the last column of table 1, in which the absolute deviations of our values with respect to those coming from [14] are listed. This is particularly evident for the two lines involving the 3_{2,2} level of the $\nu_1 + \nu_3$ vibrational state. In fact, a comparison between our values and those of [14] yields a root-mean-square deviation of about 37 MHz, which reduces to 15 MHz when removing the measurements on the line pair sharing the 3_{2,2} level. In any case, better agreement is found with the HITRAN data

set, the root-mean-square deviation being equal to only 9 MHz. Therefore, the results allow us to conclude that the MARVEL procedure, while being extremely reliable and accurate for the retrieval of energy terms belonging to the (0, 0, 0) state, does not ensure the same performance for the energies of the (1, 0, 1) vibrational state, probably because of the limited accuracy of the employed spectroscopic data. The extension of our investigation to many other absorption lines, involving different excited vibrational levels, could thus be of utmost importance for further refining the prediction capability of MARVEL and contributing to a more accurate knowledge of the H_2^{17}O and H_2^{18}O energy diagram. In this respect, it is useful to recall that the knowledge of water energy levels is of primary importance in order to calculate by explicit summation the internal partition function, Q , as well as relevant thermodynamic quantities including the specific heat capacity, the Gibbs enthalpy function, the Helmholtz function and the entropy for such a relevant molecular target [20].

5. Conclusions

Precision Lamb-dip spectroscopy was performed for H_2^{17}O and H_2^{18}O molecules using a high-finesse build-up cavity in conjunction with a self-referenced fiber-based optical frequency-comb synthesizer. This relatively complex and advanced apparatus enabled the first extensive and highly accurate investigation of the near-IR spectrum of the water isotopologues. A relative accuracy of about 10^{-10} was achieved in the absolute determination of the line-center frequencies, specifically those of 20 vibration–rotation transitions of the $\nu_1 + \nu_3$ band. Concerning the energy separations between rotational levels of the H_2^{18}O fundamental vibrational state, the retrieved values agree extraordinarily well with data provided by the recently developed MARVEL algorithms for determining energies and line positions of the main water isotopologues, based on the joint use of available experimental data and first-principles theoretical calculations. The reported results pave the way to further theoretical and experimental studies on the IR spectrum of water and its isotopologues, such as those aimed at searching for ortho–para switching transitions in the water IR spectrum [21]. A further outcome of our work is the establishment of new optical frequency standards in the spectral window between 1.38 and 1.41 μm that can be useful for calibration purposes in high-resolution molecular spectroscopy.

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