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The far infrared absorption spectrum of D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O: Experimental line positions, empirical energy levels and recommended line lists

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ABSTRACT

The far infrared absorption spectra of D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O are analyzed with improved accuracy and sensitivity in the 50–720 cm⁻¹ range corresponding to the rotational band. Four room-temperature absorption spectra of highly deuterated water vapor were recorded at the SOLEIL synchrotron by high-resolution Fourier transform spectroscopy. Line centers are reported with a typical accuracy of 5 × 10⁻⁵ cm⁻¹ for well isolated lines. The combined line list of about 9700 water lines was assigned to about 10 400 transitions of the nine stable water isotopologues (H₂^XO, HD^XO, D₂^XO, with X = 16, 17, and 18). A total of 2885 transitions of eight bands involving the first five vibrational states were assigned to D₂¹⁶O. Among them, 2057 are newly reported. The obtained set of transition frequencies was merged with literature data to generate a new set of empirical energy levels for the first five vibrational states of D₂¹⁶O. A total of 1089 transitions of the (000)–(000) and (010)–(010) bands were measured for D₂¹⁷O. They were merged with literature sources to derive 724 empirical term values of seven vibrational states, up to 8088 cm⁻¹. 348 D₂¹⁷O levels are newly determined. A set of 1150 transitions belonging to the (000)–(000) and (010)–(010) bands was measured for D₂¹⁸O. 3451 empirical energies of rotation–vibration levels up to 9222 cm⁻¹ were retrieved using our observations and literature sources. The extension and accuracy of the derived empirical energy levels allow us to recommend new line lists with empirically corrected line positions for D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O.

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1. Introduction

Doubly deuterated water (D₂O; heavy water; deuterium oxide) has a very small relative abundance in the Earth's atmosphere, on the order of 24 ppb (2.4×10^{-8}) for the D₂¹⁶O isotopologue. Nevertheless, due to the strong difference between the OD and OH stretching frequencies (about 2600 and 3600 cm⁻¹, respectively), the relative contribution of D₂O absorption to water absorption may be significantly larger than its relative abundance in some spectral windows. As a result, the D₂¹⁶O isotopologue is included in the spectroscopic databases used for atmospheric applications.^{1,2} The last version of the GEISA database² includes line lists for the three D₂^XO isotopologues (X = 16, 17, 18).

The aim of the present work is to improve our knowledge of the absorption spectrum of the D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O isotopologues in the far infrared (FIR). The FIR region corresponds to the rotational bands of the water isotopologues [purely rotational transitions in the (000) ground vibrational state and weaker rotational transitions in the first vibrational states which are much less populated at room temperature]. Water vapor absorption in the region is of major importance for the Earth's radiation budget. The thermal radiation mission FORUM³ (Far-infrared-Outgoing-Radiation Understanding and Monitoring) of the European Space Agency (ESA) to be launched in 2027 will be dedicated to the "observational gap across the far-infrared (from 100 to 667 cm⁻¹), never before sounded in its entirety from space". Since water vapor absorption is very strong in this region (line intensities up to 3×10^{-18} cm/molecule), a prerequisite for remote sensing is an accurate characterization of the water vapor spectrum, including the weak lines due to the minor isotopologues, as they may overlap absorption features used to monitor other species of interest (the so-called "spectral interferences").

As an example of the importance of the D₂O rotational transitions, absorption spectroscopy in the THz range has been proposed for atmospheric monitoring of D₂O in the emissions of nuclear plants.⁴ Astronomical observations of D₂O and HDO are important to determine the D/H ratio used to track the chemical evolution during star and planet formation and test the present chemical models of the galaxy. The pure rotational transitions $1_{11}-0_{00}$ of *ortho*-D₂O and $2_{12}-1_{01}$ transition of *para*-D₂O at 607 and 898 GHz, respectively, have been detected in solar-type protostars using the Herschel Space Observatory.⁵ Using the James Clerk Maxwell Telescope and the Caltech Submillimeter Observatory 10 m telescope, the *para*-D₂O transition $1_{10}-1_{01}$ at 316.8 GHz was detected in both absorption and emission toward the protostellar binary system IRAS 16293_2422.⁶ The D₂O abundances determined from the same $1_{10}-1_{01}$ transition measured by the Atacama Large Millimeter Array (ALMA) have been interpreted as an inheritance of the water from the prestellar environment.⁷ Finally, the $1_{10}-1_{01}$ transition was detected toward the low-mass protostar NGC 1333 IRAS2A with the IRAM Plateau de Bure Interferometer.⁸ [We use the standard normal-mode-rigid-rotor notation $(V'_1 V'_2 V'_3) J' K'_d K'_c \leftarrow (V''_1 V''_2 V''_3) J'' K''_d K''_c$ to designate the transitions, where V_1 , V_2 , and V_3 are the vibrational quantum numbers for the symmetric stretch, bend, and asymmetric stretch modes, respectively, and J , K_a , and K_c are rigid-rotor asymmetric-top quantum numbers. The single and double prime correspond to the final (upper) and initial (lower) states, respectively.]

The following elaboration of recommended line lists for D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O in the FIR is based on the analysis of a series of broadband spectra of highly deuterated water vapor combined with an exhaustive review of the literature. These high-resolution spectra covering the 50–721 cm⁻¹ range were recorded by Fourier transform spectroscopy (FTS) at the AILES beam line of the SOLEIL synchrotron near Paris (<https://www.synchrotron-soleil.fr/en>). Thanks to the unique characteristics of the synchrotron radiation in terms of brightness, stability, and spectral coverage and to the long absorption pathlength of 151.75 m used for the recordings, a considerable number of transitions could be newly measured. The achieved sensitivity combined with line center determinations having a typical accuracy of 5×10^{-5} cm⁻¹ (for well isolated lines) provides extensive and accurate line position datasets for the three considered

isotopologues. These observations merged with a review and critical evaluation of previous works by emission and absorption spectroscopies allow us to recommend sets of empirical energy levels that improve significantly on those recommended ten years ago by a task group (TG) of the International Union of Pure and Applied Chemistry (IUPAC-TG).⁹ As the main output of the present work, empirical line lists are generated in the region using as a basis the results of variational calculations by Schwenke and Partridge (SP).^{10,11} In these lists, the variational line positions were adjusted according to the empirical values of the lower and upper energy levels in order to achieve experimental accuracy.

In Sec. 2, we present the experimental details including the spectra acquisition, line list retrieval, and spectra calibration. The rovibrational assignments of our global line list are presented in Sec. 3, which includes subsections for the various isotopologues. Although transitions of H₂^XO and HD^XO are assigned, most new information concerns the D₂^XO species for which new sets of energy levels are derived and systematically compared to the literature.

2. Experiment

Extensive laboratory absorption spectroscopy in the FIR is hampered by the lack of tunable radiation sources and detectors, in particular in the terahertz frequency range (0.3–10 THz or 10–300 cm⁻¹).^{12,13} The so-called “terahertz gap” between the microwave and infrared ranges cannot be accessed using conventional electronic devices used to generate radio waves and microwaves and the traditional globar sources commonly used in the infrared have a poor brightness in the FIR. The broadband emission provided by synchrotron sources is typically one or two orders brighter than globar emission, making synchrotron radiation a suitable source for high-resolution Fourier transform absorption spectroscopy (see Fig. 1 of Ref. 14). In the fall of 2021, a one-week measurement campaign at the AILES beam line of the SOLEIL synchrotron was dedicated to the high-resolution FTS of various isotopologues of water vapor. A total of 21 spectra were recorded at different pressures for five isotopic compositions: natural, ¹⁷O enriched, D₂O, H₂O:D₂O mixture, and a mixture of the ¹⁷O enriched sample with D₂O. The analysis of the five spectra of the natural isotopic sample showed a lowering by more than three

orders of magnitude of the detectivity threshold compared to previous absorption studies.¹⁵ Similar gains in sensitivity were obtained for the ¹⁸O (Ref. 16) and ¹⁷O (Ref. 17) enriched spectra. In the present contribution, we focus on the analysis of the four spectra of heavy water for which the scarceness of previous observations makes the set of new observations particularly significant.

2.1. Spectra acquisition

A Bruker 125 interferometer with a 6 μm mylar-composite beam splitter and a 4 K cooled Si bolometer detector were used for the recordings. Synchrotron radiation emitted in the 500 mA multibunch mode was steered toward the absorption cell. This multipass cell consists of a stainless steel cylindrical vacuum chamber of 252 cm length and 60 cm diameter equipped with three mirrors in a White-type configuration. The total absorption path length, *L*, was set to 151.75 ± 1.5 m corresponding to 60 passes between mirrors and about 0.5 m of space between the 50 μm thick polypropylene film windows. Four spectra (labeled #15–#18, see Table 1) were recorded for pressure values up to 7.9 mbar, measured by a capacitance gauge (Pfeiffer 10 mbar full range with corresponding accuracy 0.01 mbar). The D₂O sample (from Sigma-Aldrich) has a stated enrichment in deuterium larger than 99.96%. The D₂O sample was frozen and liquefied several times before injection in the cell. Table 1 summarizes the sequence of the recordings and the corresponding experimental conditions. The temperature of 295.5(3) K was monitored by a pair of platinum sensors mounted on the cell external surface.

An overview of spectrum #15 recorded at 0.29 mbar is displayed on Fig. 1, which includes successive zooms. The last recorded spectrum (#18) was acquired while pumping on the cell in order to measure the strongest lines which are saturated at higher pressure (see Fig. 1). Its pressure was roughly estimated to be 35 μbar. This #18 spectrum together with spectrum #15 at 0.29 mbar were recorded with the maximum spectral resolution of 0.001 02 cm⁻¹ (defined as 0.9/MOPD where MOPD = 882 cm is the maximum optical path difference). At higher pressure (spectra #16 and #17), a spectral resolution of 0.002 cm⁻¹ was adopted as the lines are significantly broadened by pressure. The number of co-added spectra ranges between 160 and 220 (200 spectra corresponds to about 10 h acquisition time at 0.001 cm⁻¹ spectral resolution or 5 h at

TABLE 1. Experimental conditions of the four FTS spectra of deuterated water under analysis. The temperature was 295.5 K.

Label	Recording	Pressure	Resolution (cm ⁻¹)	Number of scans
#15	Sample	≈0.29 mbar	0.001	200
	Baseline	Pumping on the cell	0.05	200
#16	Sample	≈1.95 mbar	0.002	160
#17	Sample	≈7.9 mbar	0.002	200
	Baseline	Pumping on the cell	0.05	1800
#18	Sample	≈35 μbar ^a	0.001	220
	Baseline	Pumping on the cell	0.05	200

^aThe pressure gauge used does not allow measuring so low a pressure value and the given 35 μbar value is just indicative.

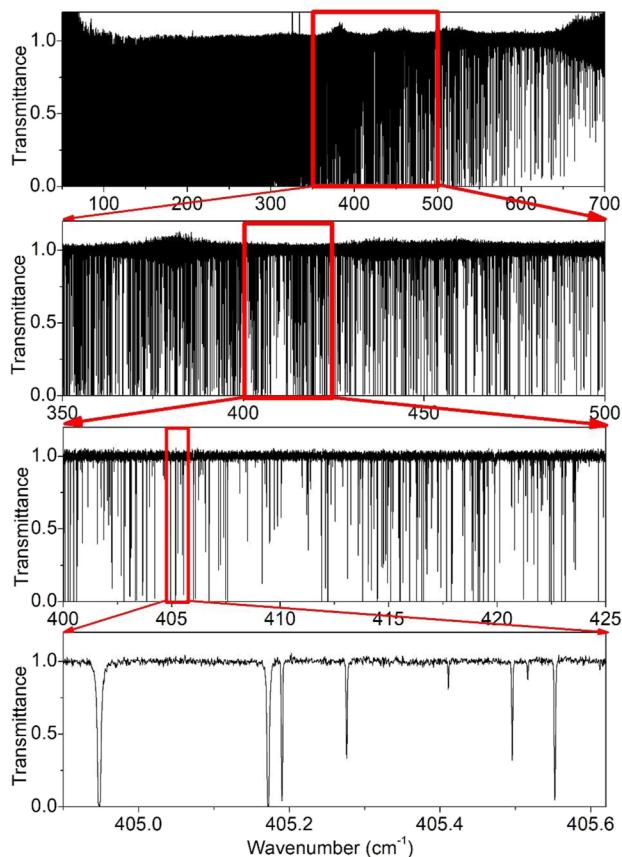


FIG. 1. Successive zooms of the FTS spectrum #15 of D_2O recorded at SOLEIL synchrotron with a pressure of 0.29 mbar between 50 and 700 cm^{-1} .

0.002 cm^{-1} resolution). No apodization of the interferogram was used (boxcar option of the Bruker software). The baseline fluctuations were corrected by division by a spectrum acquired at a lower resolution (0.05 cm^{-1}), prior to or after each high-resolution recording (see Table 1).

2.2. Global experimental line list

The line parameter retrieval followed the same procedure as described in Ref. 17. Since our work was focused on line positions, each of the four transmittance spectra was fitted independently assuming the standard Voigt profile for line shape (with adjusted Gaussian and Lorentzian widths) and no particular care was taken for the treatment of the apparatus function. The line parameters retrieval was performed using a homemade multiline fitting program written in LabVIEW with DLL written in C++. Figure 2 illustrates the line profile fitting of three spectra (#15, #16, #18) in a small spectral interval near 262 cm^{-1} . Saturated lines (transmittance at center less than a few percent) were omitted from the fit when a lower-pressure spectrum was available. The (exp. – fit) residuals of the transmittance included in Fig. 2 are close to the noise level [$\sim 1\%$ root mean square (rms)]. This value corresponds to a noise equivalent absorption on the order of $7 \times 10^{-7} \text{ cm}^{-1}$ and a detectivity threshold on the order of $10^{-25} \text{ cm}/\text{molecule}$ for the line intensities measured at the highest pressure (7.9 mbar).

We provide in the supplementary material, SM1, the global line list of water lines obtained by combining the four individual lists. For each line, the best spectrum condition was selected for the line parameter retrieval and the selected spectrum is indicated by the corresponding tag (#15–18). The spectra at 35 μbar (#18), 0.29 mbar (#15), 1.95 mbar (#16), and 7.9 mbar (#17) were used for about 2730, 5500, 970, and 500 lines, respectively. After removal of a few impurity lines (see details below), the composite list includes a total of

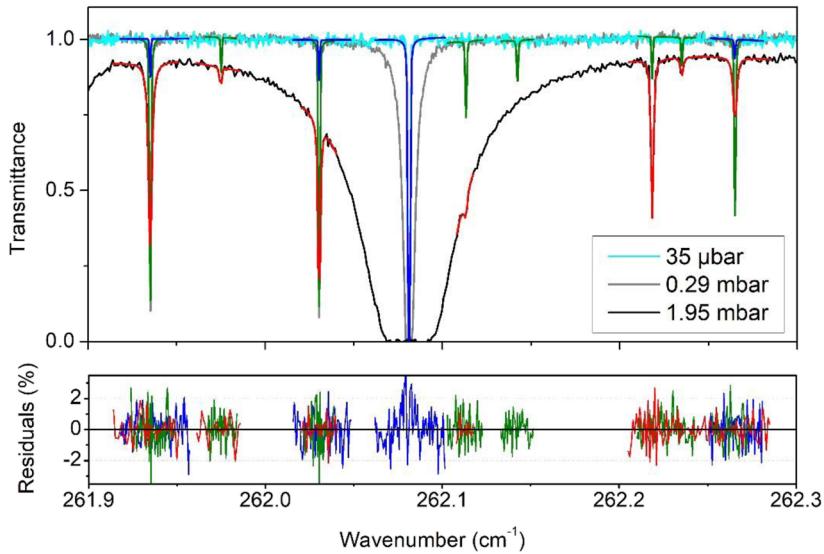


FIG. 2. Line parameter retrieval from three FTS spectra of heavy water (D_2O) near 262 cm^{-1} . The line profile fit was performed in narrow spectral intervals around the lines which are not too saturated. Upper panel: Recorded spectra at about 35 μbar , 0.29 mbar, and 1.95 mbar (#15, #16, and #18, respectively) with corresponding best fit spectra (blue, green, and red, respectively). Lower panel: Corresponding (exp. – fit) residuals in %.

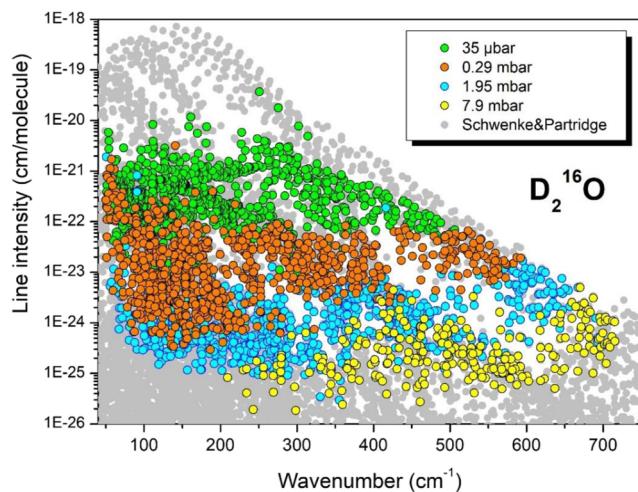


FIG. 3. Overview of the $D_2^{16}O$ lines retrieved from the four analyzed spectra of highly deuterated water between 50 and 720 cm^{-1} . The global experimental line list was obtained by combining the lists at 35 μbar , 0.29, 1.95, and 7.9 mbar (green, orange, cyan, and yellow dots, respectively). Note that the strongest lines retrieved from the lowest pressure spectrum are measured with strongly underestimated intensities (see text). Gray dots correspond to the SP variational list.^{10,11}

about 9700 water lines corresponding to transitions which have to be identified in terms of water isotopologue and rovibrational quantum numbers. The $D_2^{16}O$ lines corresponding to the four spectra are plotted with different colors on the line list overview displayed in Fig. 3.

Several comments should be made regarding our experimental intensities.

First, as is obvious from Fig. 3, many intensity values retrieved from spectrum #18 at the lowest pressure ($\sim 35 \mu\text{bar}$) are strongly underestimated. Indeed, lines with intensities larger than $10^{-20} \text{ cm/molecule}$ are completely saturated in this spectrum even if the absorption cell was continuously evacuated by pumping during the recording of spectrum #18. Although of limited position

accuracy, the corresponding lines were kept in our global line list for completeness (note that the position uncertainty as provided by the fit is included in the global list).

Our intensity values include the isotopic abundance factor. The variation of the isotopic composition of the water sample according to the spectrum is another reason to use our line intensities with much caution, in particular for the minor isotopologues. The variation of the isotopic composition is because the walls of the cell and all the gas injection system keep a “memory” of previous fillings with water vapor with different isotopic composition. The present series of recordings was performed following recordings with samples highly enriched in ^{17}O and ^{18}O (Ref. 17). Although pure $D_2^{16}O$ vapor with close to natural isotopic abundance of the oxygen atom was used for the present recordings, exchanges between $H_2^{18}O$ and $H_2^{17}O$ molecules adsorbed in the walls of the cell and fresh $D_2^{16}O$ yield an isotopic mixture highly enriched in ^{18}O , ^{17}O , and H, compared to the injected $D_2^{16}O$ sample. As indicated by the sequence of measurements of Table 1, the cell was evacuated after the recording of the first spectrum (#15 at 0.29 mbar). This spectrum is indeed the most affected by exchanges with adsorbed water while the subsequent recordings have an isotopic composition getting closer and closer to that of the injected $D_2^{16}O$ sample. The estimated range of relative abundances derived from the intensity comparison with variational calculations is given in Table 2 for the nine isotopologues contributing to the four spectra. Detailed abundance values can be found for each spectrum in the headings of the global list provided as supplementary material, SM1. This list includes for comparison the SP variational intensity values calculated by Tashkun using the results of Refs. 10 and 11. The SP line lists are available at <https://spectra.iao.ru/>. The SP variational intensities corresponding to the pure isotopologue were multiplied by a factor corresponding approximately to the maximum abundance value found for each isotopologue among the four spectra (see Table 2).

In the best cases of well isolated lines of medium intensity (i.e., in the 10^{-24} – $10^{-23} \text{ cm/molecule}$ range), we estimate that our intensity values are accurate within 5%–10% for the $D_2^{16}O$ lines retrieved from the two highest pressure spectra (#16 and #17 at 1.9 and 7.9 mbar, respectively). This relatively large error bar is mostly due to the small number of points describing the line profile [about

TABLE 2. Statistics of assigned water transitions

Molecule	Abundance, min – max, %	Factor ^a (%)	NT ^b	J_{\max}	$K_a \max$	Range (cm^{-1})
$H_2^{16}O$	0.03–3.6	4.0	679	18	12	51.434–705.361
$H_2^{17}O$	9×10^{-5} –0.1	0.1	351	16	10	53.510–634.237
$H_2^{18}O$	1.3×10^{-4} –0.07	0.1	331	15	10	53.569–633.200
$HD^{16}O$	3–25	25	1924	24	14	50.799–719.550
$HD^{17}O$	0.012–0.66	1	1000	22	12	50.133–646.383
$HD^{18}O$	0.019–0.48	1	968	21	12	50.006–654.960
$D_2^{16}O$	66.7–96.2	100	2886	29	18	50.025–715.358
$D_2^{17}O$	0.28–1.7	2	1088	25	14	50.425–543.830
$D_2^{18}O$	0.42–1.7	2	1169	25	16	51.539–586.772

^aThe calculated intensity values included in the global list were obtained by multiplying the SP variational intensity of the pure species by this factor. Note that the sum of these factors exceeds 100%.

^bNumber of assigned transitions.

four points at full width at half-maximum (FWHM)] and to the impact of the apparatus function that was roughly taken into account in the line parameter retrieval. This level of accuracy is probably insufficient for validation tests of the intensities provided by variational calculations, variational intensities being expected to be very accurate in the considered low-energy region. This is the reason why we recommend adopting variational intensities for the line list in the region (see below). In the following, we will focus on line positions (and energy levels).

2.3. Frequency calibration

The combination of the four line lists into a single global list assumes that the frequency axis was unchanged during the four spectra recordings of a total duration of about two days. The stability of the frequency axis was checked in Refs. 15 and 17 on the basis of the spectra of natural and ^{17}O enriched water vapor spectra recorded during the same measurement campaign at SOLEIL. The absolute frequency calibration of our global list was performed considering the lines of the spectra at 35 μbar (#18) and 0.29 mbar (#15) for which the self-pressure shift of the line positions is negligible (according to Refs. 18 and 19, the amplitude of the self-pressure shifts of rotational lines is less than $1.5 \times 10^{-5} \text{ cm}^{-1}$ at 0.29 mbar). We used as reference line positions the wavenumbers of 220 H_2^{16}O transitions reported in Ref. 20 with an accuracy better than $1 \times 10^{-6} \text{ cm}^{-1}$. The differences between the experimental line centers and the reference values were fitted as a linear function. The obtained empirical correction of the frequencies is $d\sigma^{\text{corr}} = +9.9 \times 10^{-5} - 7.0 \times 10^{-7}\sigma$, where σ is the measured wavenumber. An *rms* deviation of $3.15 \times 10^{-5} \text{ cm}^{-1}$ was obtained for the linear fit, thus much larger than the accuracy of the reference positions. This value gives an estimate of our typical accuracy on the reported positions of “good” lines. (Note that the calibration of the ^{17}O enriched spectra using the same procedure¹⁷ led to a correction of $d\sigma^{\text{corr}} = +7.79 \times 10^{-5} - 6.95 \times 10^{-7}\sigma$ leading to a mostly constant shift of $2 \times 10^{-5} \text{ cm}^{-1}$ between the two independent calibrations of series of spectra recorded three days apart).

In the global line list presented in the supplementary material, SM1, the fit error on the line position determination is included. For a significant fraction of the lines, the fit uncertainty was found to be smaller than $3 \times 10^{-5} \text{ cm}^{-1}$ and is believed to underestimate the real uncertainty of the line position. For all these lines, we replaced the fit uncertainty by $3 \times 10^{-5} \text{ cm}^{-1}$. Note that the position uncertainty of the weakest, highly blended lines or saturated lines can reach a value of $8 \times 10^{-4} \text{ cm}^{-1}$ in the worst cases. Note also that the hyperfine structure is at most on the order of a few MHz (about 10^{-6} cm^{-1}) in the case of D_2^{16}O (Refs. 21–23) and D_2^{17}O (Ref. 24) and thus negligible compared to our position accuracy.

3. Analysis and Comparison With Literature

Overall, about 9800 distinct lines were observed in the studied spectra. 9678 lines have been assigned to 10 396 transitions of the nine stable water isotopologues (in addition, 58 lines were assigned to CO_2 transitions, five and two lines are DF and HF features, respectively). 46 weak lines are left unassigned. The rovibrational assignments are included in the global list. In the following, we present the results obtained for the various isotopologues with a main focus on the D_2O species.

3.1. H_2^XO ($X = 16, 17, 18$)

A detailed review of the vibrational–rotational spectra of the H_2^{16}O , H_2^{17}O , and H_2^{18}O isotopologues was included in our previous analysis of the SOLEIL spectra dedicated to these species.^{15–17} These studies allowed for a significant increase of the number of observations, especially for H_2^{18}O (Ref. 16) and H_2^{17}O (Ref. 17). Since the H_2O concentration in the presently studied spectra does not exceed 4% (see Table 2), only a fraction of the absorption lines of Refs. 15–17 is observed: 679, 351, and 331 for H_2^{16}O , H_2^{17}O , and H_2^{18}O , respectively. No new transitions are detected for these species. The comparison of the present line positions to their values of Refs. 15–17 gives very good agreement: the root mean

square, $\text{rms} = \sqrt{\sum_{i=1}^N (\nu_i^{\text{TW}} - \nu_i^{\text{Ref}})^2 / N}$, is 16.2×10^{-5} , 11.4×10^{-5} , and $11.2 \times 10^{-5} \text{ cm}^{-1}$ for 738, 1346, and 1359 positions in common with Refs. 16, 15, and 17, respectively. The maximum discrepancy $d\nu = \nu^{\text{TW}} - \nu^{\text{Ref}}$ is about 0.0011 cm^{-1} for three very weak or overlapped lines.

3.2. HD^XO ($X = 16, 17, 18$)

In the series of recordings performed at SOLEIL, three spectra were dedicated to the monodeuterated isotopologues, HD^XO . Those spectra (#19–21) were recorded using a 1:1 mixture of H_2O and D_2O in order to obtain the maximum HDO abundance of 50% while, in the present spectra, the HDO abundance is significantly lower (Table 2). We thus postpone a detailed comparison to the literature and extensive energy level determinations to the future analysis of the #19–21 spectra. Here we give only a summary of the present assignments for the three HDO isotopologues.

Overall, 1924, 1004, and 967 transitions were assigned to HD^{16}O , HD^{17}O , and HD^{18}O , respectively. Despite the fact that HD^{16}O is the fourth most abundant water isotopologue (0.031% relative abundance), previous studies of its spectrum by absorption in the range of interest (50–720 cm^{-1}) are limited: (i) line positions of 60 transitions between 151 and 420 cm^{-1} were published by Kaupinen *et al.*²⁵ from absorption spectrum analysis of a natural water sample; (ii) the analysis of spectra of deuterated water by Johns,²⁶ Paso and Horneman,²⁷ and Toth²⁸ expanded the range of observed HD^{16}O lines to 50.27–719.55 cm^{-1} and the number of lines to 532; (iii) the analyses of previous SOLEIL spectra^{15–17} increasing the number of distinct observed absorption transitions to a total of 768, all belonging to the (000)–(000) and (010)–(010) rotational bands.

In emission, Janca *et al.*²⁹ reported line positions of 1422 transitions between 381 and 720 cm^{-1} involving the eight lowest vibrational states: (000), (010), (100), (020), (001), (110), (030), and (011). The analyzed emission spectra were recorded by FTS at a temperature of 1800 K. 765 of these 1422 transitions correspond to emission lines of the (000)–(000) and (010)–(010) rotational bands, but only 62 of them are observed in our and previously reported absorption spectra.

Among the 1924 absorption transitions of HD^{16}O presently reported, 1039 are observed for the first time compared to both absorption and emission studies. The lines of the (020)–(020) and (100)–(100) rotational bands are observed for the first time in absorption.

For HD^{17}O , previous observations are scarce. In previous SOLEIL studies, 364, 4, and 465 transitions were reported in Refs. 16, 15, and 17, respectively. Together with the previous absorption study of Ref. 30 and the emission measurements of Ref. 31, it leads to a total of 600 transitions ranging between 50.13 and 554.17 cm^{-1} . Of the 1000 HD^{17}O line positions measured in the present spectra, 488 are new.

The literature dataset of HD^{18}O line positions includes 1130 entries between 50 and 646 cm^{-1} from Johns,²⁶ Yu *et al.*,³² and from SOLEIL spectra.^{15–17} Here, we report 967 HD^{18}O line positions up to 655 cm^{-1} , 41 being newly measured.

A separate contribution will be dedicated to a more complete and detailed analysis of the obtained HD^XO , $X = 16, 17, 18$ line positions.

3.3. D_2^{16}O

The literature review in the 50 – 716 cm^{-1} region indicates that only 397 line positions of D_2^{16}O were previously reported by absorption, by Johns,²⁶ Paso and Horneman,²⁷ Matsushima *et al.*,³³ Michael *et al.*,³⁴ and Brünken *et al.*³⁵ Measurements in emission are more extended but less accurate: (i) Mellau *et al.*³⁶ and Mikhailenko *et al.*³⁷ reported a total of more than 1800 positions corresponding to transitions involving the five lowest states: (000), (010), (020), (100), and (001). These emission spectra were recorded by FTS at 1370, 1520, and 1940 K between 322 and 712 cm^{-1} ; (ii) about 2400 emission line positions associated with 11 vibrational states were reported by Zobov *et al.*³⁸ from FTS spectra at 1800 K between 380 and 716 cm^{-1} . We mention that this source provided more than 25 000 observations in the 380 – 4315 cm^{-1} interval representing about half of the total number of D_2^{16}O lines (about 53 500) gathered by the IUPAC-TG for the entire 0 – 14016 cm^{-1} range of the

TABLE 3. Band by band information about the D_2^{16}O transitions identified in the four analyzed SOLEIL spectra

Band	Number of transitions	J_{\max}	$K_a \max$	Region (cm^{-1})
(000)–(000)	1807	29	18	50.68–715.36
(001)–(001)	31	13	10	98.68–269.29
(001)–(100)	3	8	6	190.05–201.78
(010)–(000)	9	18	2	636.98–704.86
(010)–(010)	825	24	15	50.02–623.26
(020)–(020)	160	18	11	64.39–417.03
(100)–(001)	2	10	7	196.46–220.66
(100)–(100)	49	13	9	81.11–298.18
All	2886	29	18	50.02–715.36

D_2^{16}O observations.⁹ Due to the line overlapping and broadening of the analyzed emission spectra, the line positions of Ref. 38 are not accurate. A mean uncertainty of about $5 \times 10^{-3}\text{ cm}^{-1}$ was attached by the IUPAC-TG to the position of these emission lines.⁹ This value is about two orders of magnitude larger than the uncertainty of the positions determined from the presently analyzed absorption spectra. For this reason, our derivation of the D_2^{16}O energy levels (see below) will rely exclusively on absorption data.

The presently analyzed SOLEIL spectra at room temperature provide line positions of 2886 D_2^{16}O transitions of eight rotation and vibration–rotation bands associated with the first five vibrational states (see Table 3). As illustrated in Fig. 4, the set of observations is considerably extended: 2057 transitions are

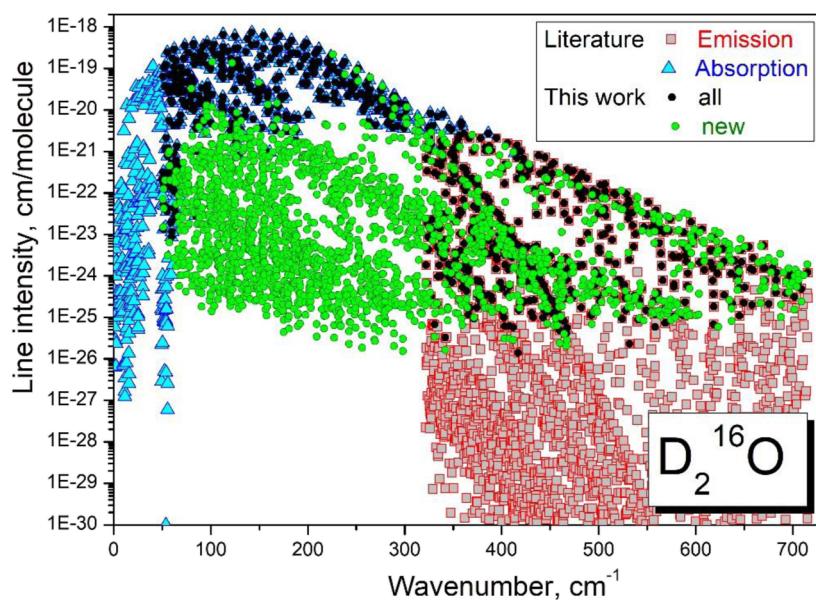


FIG. 4. Overview of observed line positions of D_2^{16}O below 720 cm^{-1} . All transitions reported in the literature and observed in this study are shown. Only transitions involving the (000), (010), (020), (100), and (001) vibrational states are considered. Variational values¹¹ have been adopted for line intensities for all the data displayed.

reported for the first time compared to both previous absorption and emission studies. From this plot, it appears that the SOLEIL observations lower by more than three orders of magnitude the detectivity threshold of previous absorption measurements (the intensity threshold is lowered from about 3×10^{-21} to about 10^{-25} cm/molecule). Note that for purpose of illustration, variational values¹¹ have been adopted for line intensities for all the data displayed in Fig. 4.

The set of 2886 SOLEIL high-precision transition frequencies was merged with literature data to generate a new set of energy levels for the first five vibrational levels of D₂¹⁶O. Only absorption data were taken into account. Thus, line positions of the pure rotation band and four rotational bands (v₁-v₁, v₂-v₂, v₃-v₃, and 2v₂-2v₂) from Refs. 21–23, 26, 27, 33, 34, and 39–50 and seven vibrational-rotational bands (v₁, v₂, v₃, 2v₂, v₁-v₂, v₃-v₂, and 2v₂-v₂) from Refs. 51–57 were used to determine empirical energy values of the (000), (010), (020), (100), and (001) vibrational states. The obtained set of 1542 empirical term values is given in the supplementary material, SM2, which includes for each level the different sources used for the determination and the statistical error bar. Although the accuracy of energy level values is believed to be significantly increased for most of the levels, only 28 levels are newly determined. Most of these 28 levels were newly determined as a result of double identifications of unresolved lines and correspond to the weakest of the two components of a doublet of the type [(J, K_a, K_c), (J, K_a - 1, K_c)] or [(J, K_a, K_c), (J, K_a, K_c - 1)]. They are listed in Table 4.

Note that the main spectroscopic network (SN1) of transitions used for the level determination involves 2876 transitions, but seventeen levels involved in nine transitions cannot be determined because they belong to different networks (SN2–SN9) (see Refs. 58 and 59 for the definition of the spectroscopic networks).

In the supplementary material, SM3, we include the results of the comparison with the D₂¹⁶O energy levels determined by Toth⁵² and recommended by the IUPAC-TG.⁹ Toth provided 1092 energy levels derived from absorption line positions. The IUPAC-TG dataset is much more complete (only 34 energy levels are missing compared to our set) because large sets of emission data^{36–38} were used for the energy derivation. Note that the IUPAC-TG energy levels were used by Kyuberis *et al.*⁶⁰ to generate a recommended list for D₂¹⁶O, which is the one provided by the high-resolution transmission molecular absorption (HITRAN) database.¹

The histograms of the differences between our energy values and those obtained by Toth and the IUPAC-TG are presented Fig. 5. Better agreement is achieved with the IUPAC-TG dataset, Toth's energy values being in general overestimated. Note that, for a large fraction of levels, the deviations of the IUPAC-TG levels are significantly larger than our claimed accuracy (see the histogram of the claimed uncertainties on our energy levels included in Fig. 5).

In order to illustrate the situation, we performed a direct calculation of the SOLEIL D₂¹⁶O transition frequencies using the different sets of energy levels. The comparison results are included in the supplementary material, SM4. Compared to our D₂¹⁶O experimental list, the calculation of 2876 frequencies leads to a weighted standard deviation, $rmw = \sqrt{\sum_{i=1}^N \left(\frac{v_i^{\text{obs}} - v_i^{\text{calc}}}{\delta v_i^{\text{obs}}} \right)^2} / N$, of 1.08 and a dimension-

TABLE 4. Newly determined empirical energy levels of the (000), (010), and (020) states of D₂¹⁶O. Vib: vibration quantum numbers V₁, V₂, V₃; J K_a K_c: rotation quantum numbers; Energy: term value in cm⁻¹. δE : 1 σ uncertainty of the term value (in units of 10⁻⁵ cm⁻¹); NT: number of line positions used for the energy determination.

Vib	J	K _a	K _c	Energy	δE	NT
000	15	11	4	2506.103 94	4	6
000	16	12	5	2880.990 35	7	5
000	16	13	4	3068.504 19	9	3
000	17	12	S	3090.231 29	8	4
000	17	13	4	3278.445 01	10	2
000	17	14	3	3475.218 63	13	2
000	18	12	7	3311.076 13	12	2
000	18	13	6	3499.953 97	11	3
000	18	14	5	3697.574 42	13	3
000	19	13	6	3732.919 50	19	3
000	20	14	7	4176.437 82	28	2
000	21	13	8	4232.767 54	27	2
000	21	14	7	4432.702 27	28	1
000	21	15	6	4640.748 59	41	1
000	22	13	10	4499.419 78	29	1
000	22	14	9	4700.024 71	52	1
000	26	2	25	3745.753 29	58	2
000	27	1	26	4016.640 08	59	3
000	28	2	27	4296.591 87	64	2
000	29	1	28	4585.566 37	69	1
010	15	10	5	3611.069 22	17	4
010	15	11	4	3791.672 57	19	2
010	15	12	3	3982.827 93	22	1
010	16	11	6	3989.108 17	19	1
010	16	12	5	4180.915 54	30	2
010	17	13	4	4592.615 31	51	1
020	11	9	2	4022.855 40	29	2
020	12	9	4	4171.778 78	21	1

sional deviation, $rms = \sqrt{\sum_{i=1}^N (v_i^{\text{obs}} - v_i^{\text{calc}})^2 / N}$, of 14.5×10^{-5} cm⁻¹.

The maximum discrepancy ($v_i^{\text{obs}} - v_i^{\text{calc}}$) is 0.00138 cm⁻¹ for the (000) 17₄13–(000) 16₁16 transition at 702.13541 cm⁻¹ observed with a poor signal-to-noise ratio and excluded from the energy determination. The calculation of 2803 frequencies using the IUPAC-TG energies⁹ gives $rmw = 11.01$ and $rms = 79.0 \times 10^{-5}$ cm⁻¹ if we exclude 22 frequencies deviating by more than 0.01 cm⁻¹. These 22 position differences range between -0.07955 cm⁻¹ for the 25₂23–25₁24 transition at 218.43457 cm⁻¹ and $+0.06642$ cm⁻¹ for the 25₁24–24₂23 transition at 252.63522 cm⁻¹. These two examples are illustrated in Fig. 5 by direct comparison to the SOLEIL spectrum. Note that deviations greatly exceed the error bars on the IUPAC-TG position (calculated as the sum of the IUPAC-TG uncertainties on the lower and upper energy levels).

The calculation of 1987 frequencies using Toth's energies⁵² gives $rmw = 9.16$ and $rms = 62.7 \times 10^{-5}$ cm⁻¹, excluding eight frequencies deviating by more than 0.01 cm⁻¹. These eight

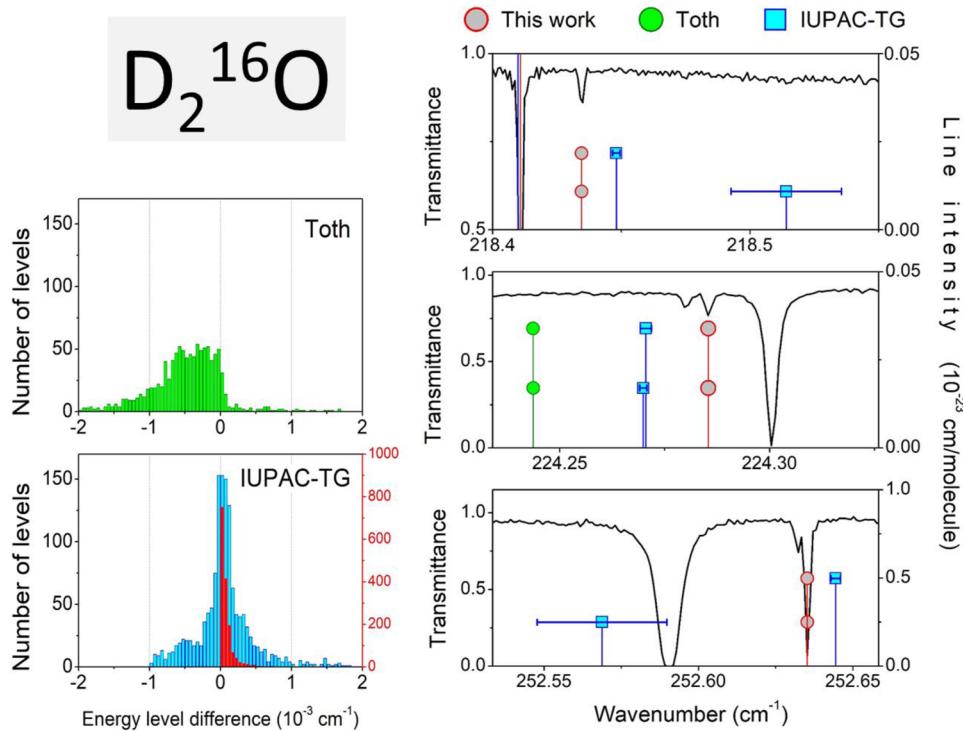


FIG. 5. Comparison of the D₂¹⁶O energy levels obtained in this work (TW) to those obtained by Toth⁵² and an IUPAC-TG.⁹ *Left panels:* Histograms of the position differences (TW–Toth) and (TW–IUPAC). On the lower panel, the histogram of the uncertainties of our energy levels is plotted (red, right-hand scale). *Right panels:* Three examples of important deviations between the recorded spectra and the D₂¹⁶O line positions calculated from energy levels of Refs. 9 and 52. Variational intensities of Ref. 11 were attached to the three sets of line positions (Toth, IUPAC, TW). The displayed stick spectra are limited to D₂¹⁶O transitions.

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large deviations range between $-0.086\,56\text{ cm}^{-1}$ for the $2v_2-2v_2$ $12_{2\,10}-11_{1\,11}$ transition at $355.126\,66\text{ cm}^{-1}$ and $+0.668\,65\text{ cm}^{-1}$ for the $2v_2-2v_2$ $9_{9\,1}-8_{8\,0}$ and $9_{9\,0}-8_{8\,1}$ transitions at $279.955\,52\text{ cm}^{-1}$.

As indicated above, the HITRAN database¹ reproduces the D₂¹⁶O line list at 296 K given by Kyuberis *et al.*⁶⁰ 3455 transitions between 50 and 720 cm⁻¹ are included in this list. The smallest intensities of the HITRAN list (including the natural isotopic abundance factor, $2.419\,740 \times 10^{-8}$) are on the order of 10^{-33} cm/molecule in our region corresponding to a value of about 4×10^{-26} cm/molecule for the pure species, slightly below our sensitivity threshold (see Fig. 4). Despite the fact that the list by Kyuberis *et al.*⁶⁰ is claimed to be limited to transitions between levels with empirically determined energies,⁹ it includes transitions corresponding to levels from Table 4, which are absent from the IUPAC-TG list of empirical energies.⁹ On the other hand, some relatively strong transitions corresponding to empirical energies⁹ are missing. First, the list⁶⁰ is limited to transitions with a maximum rotation number J of 20. Then, for an unknown reason, some pure rotation transitions are absent as for instance $10_{1\,9}-10_{1\,0}$ at $91.096\,68\text{ cm}^{-1}$ ($S^{SP} = 3.33 \times 10^{-20}$ cm/molecule), $10_{2\,8}-10_{1\,9}$ at $70.883\,12\text{ cm}^{-1}$ ($S^{SP} = 2.71 \times 10^{-20}$ cm/molecule), $10_{5\,5}-10_{4\,6}$ at $71.160\,22\text{ cm}^{-1}$ ($S^{SP} = 1.70 \times 10^{-20}$ cm/molecule), $10_{6\,4}-10_{5\,5}$ at $94.669\,33\text{ cm}^{-1}$ ($S^{SP} = 1.68 \times 10^{-20}$ cm/molecule), and $10_{7\,3}-10_{6\,4}$ at $112.017\,44\text{ cm}^{-1}$ ($S^{SP} = 1.19 \times 10^{-20}$ cm/molecule). Overall, more than 300 observed

transitions above the HITRAN intensity cutoff are missing in the line list of Ref. 60.

We provide in the supplementary material, SM5, a recommended absorption line list at 296 K for the eight bands of D₂¹⁶O involving the (000), (010), (020), (001), and (100) vibration states. This list uses as a basis the SP variational line list calculated by Tashkun using the VTET program of Schwenke.^{62,63} The potential-energy surface (PES) from Ref. 10 and dipole-moment surface from Ref. 11 were used for the line positions and line intensities, respectively. The SP line lists are available at <https://spectra.iao.ru/> since 2007. For all the transitions involving lower and upper levels with known empirical energy values, we have substituted the variational frequency by its empirical value. The intensity cutoff was fixed to 1×10^{-26} cm/molecule at 296 K. The D₂¹⁶O line list includes 19 356 transitions and spans the 0.365–3343.208 cm⁻¹ range. The overview of the recommended list is given on the upper panel of Fig. 6, where transitions with empirical and variational frequencies are presented with different symbols. Note that while in our region corresponding to the rotation bands (0–700 cm⁻¹) it has been possible to empirically correct most of the line positions in the region of the first triad (1900–3400 cm⁻¹), a significant fraction of the transitions remains with the variational value of their frequency due to the lack of knowledge of the empirical values of the involved energy levels.

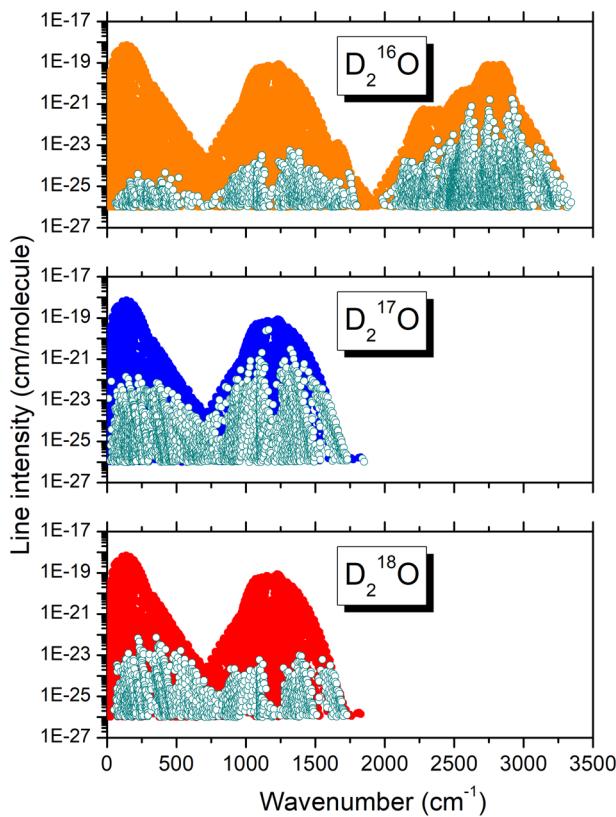


FIG. 6. Overview of the $D_2^{16}O$, $D_2^{18}O$, and $D_2^{17}O$ recommended line lists based on the variational calculations by Schwenke and Partridge.^{10,11} Transition frequencies have been empirically corrected except those corresponding to the cyan open circles.

The $D_2^{16}O$ line list of the GEISA database² is different. It includes about 7300 transitions up to $J_{\max} = 24$. The list provides the results of purely variational calculations from Shirin *et al.*⁶¹ The variational positions are systematically underestimated compared to experiment and show deviations exceeding 0.01 cm^{-1} for a large fraction of the transitions.

To the best of our knowledge, the list given by Shirin *et al.*⁶¹ is the only alternative variational list to the SP list. The variational intensities of Ref. 61 were adopted by Kyuberis *et al.*⁶⁰ For the $D_2^{16}O$ transitions of our recommended list, our systematic comparison of SP and Shirin's intensities shows a very good general agreement, although a 1.5% systematic difference is observed, the intensities of Shirin *et al.* being lower than SP values. To the best of our knowledge, no sufficiently accurate experimental data are available in the region to make a choice. We note that more than 100 high- J transitions included in our recommended list are missing in Shirin's list, some of them corresponding to relatively strong lines with intensities larger than $1 \times 10^{-22} \text{ cm}/\text{molecule}$.

3.4. $D_2^{17}O$

Among the nine stable isotopologues of water vapor, $D_2^{17}O$ is the least abundant (relative abundance of 9.02×10^{-12}). The literature survey indicates that, considering all the spectral ranges,

TABLE 5. Empirical energy levels of the (000) and (010) states of $D_2^{17}O$ newly determined from the analysis of the absorption spectra of deuterated water between 50 and 720 cm^{-1} . The ($J K_a K_c$) rotation quantum numbers are given in the first three columns, followed by the term value (Energy) in cm^{-1} . The 1σ uncertainty (δE) of the term value (in units of 10^{-5} cm^{-1}) is given in the fifth column, followed by the number of line positions (NT) used for the energy determination.

J	K_a	K_c	Energy	δE	NT
(000)					
9	7	3	982.439 99	11	7
9	7	2	982.440 58	33	6
9	8	2	1107.076 24	12	10
9	8	1	1107.076 40	33	10
9	9	1	1244.967 10	16	3
9	9	0	1244.967 24	116	3
10	4	7	822.689 64	32	9
10	5	6	902.027 81	32	9
10	5	5	903.435 56	11	11
10	6	5	996.006 18	32	6
10	6	4	996.091 28	11	7
10	7	4	1105.924 11	33	11
10	7	3	1105.926 96	12	10
10	8	3	1230.617 98	34	5
10	8	2	1230.617 76	14	6
10	9	2	1368.747 99	93	5
10	9	1	1368.747 75	16	5
10	10	1	1519.053 64	46	3
10	10	0	1519.053 45	19	4
11	3	8	932.044 43	33	7
11	4	8	957.595 22	13	11
11	4	7	977.605 19	33	8
11	5	7	1038.476 15	12	10
11	5	6	1041.823 03	33	7
11	6	6	1132.165 27	12	8
11	6	5	1132.432 52	33	7
11	7	5	1241.760 12	13	7
11	7	4	1241.772 79	34	6
11	8	4	1366.423 80	14	6
11	8	3	1366.424 25	35	5
11	9	3	1504.748 33	16	5
11	9	2	1504.748 60	78	5
11	10	2	1655.412 71	18	4
11	10	1	1655.412 94	36	4
11	11	1	1817.168 70	22	3
11	11	0	1817.168 90	67	3
12	2	11	922.140 04	34	7
12	2	10	1015.999 99	15	8
12	3	10	1018.669 18	34	8
12	3	9	1085.478 03	14	8
12	4	9	1103.657 46	34	9
12	4	8	1134.677 38	14	8
12	5	8	1187.123 07	34	8
12	5	7	1194.130 05	15	8
12	6	7	1280.782 30	34	8
12	6	6	1281.510 68	15	9
12	7	6	1389.944 59	34	6
12	7	5	1389.988 57	14	6

TABLE 5. (Continued)

J	K _a	K _c	Energy	δE	NT
12	8	5	1514.468 82	39	5
12	8	4	1514.470 44	16	6
12	9	4	1652.925 33	46	4
12	9	3	1652.925 31	18	5
12	10	3	1803.918 48	38	4
12	10	2	1803.918 33	19	4
12	11	2	1966.157 18	44	4
12	11	1	1966.156 98	22	4
12	12	1	2138.409 82	57	3
12	12	0	2138.409 64	30	3
13	1	12	1061.825 12	36	6
13	2	12	1061.905 11	16	7
13	2	11	1166.425 30	35	7
13	3	11	1167.865 98	16	8
13	3	10	1248.367 50	35	7
13	4	10	1260.442 58	15	10
13	4	9	1304.549 65	35	6
13	5	9	1347.667 76	15	10
13	5	8	1360.718 39	35	7
13	6	8	1441.790 81	15	8
13	6	7	1443.554 36	35	6
13	7	7	1550.466 80	16	7
13	7	6	1550.600 58	36	6
13	8	6	1674.725 33	18	6
13	8	5	1674.731 95	45	5
13	9	5	1813.232 12	20	4
13	9	4	1813.232 32	46	3
13	10	4	1964.509 23	23	3
13	10	3	1964.509 30	58	3
13	11	3	2127.210 51	23	4
13	11	2	2127.210 62	78	3
13	12	2	2300.075 36	28	3
13	12	1	2300.075 57	64	2
13	13	1	2481.891 96	37	2
13	13	0	2481.892 14	78	2
14	0	14	1080.238 90	22	5
14	1	14	1080.239 82	39	5
14	1	13	1211.118 34	19	6
14	2	13	1211.156 63	37	6
14	2	12	1325.908 80	18	7
14	3	12	1326.667 91	36	8
14	3	11	1420.009 58	17	8
14	4	11	1427.548 80	36	9
14	4	10	1486.091 89	18	8
14	5	10	1519.732 82	36	8
14	5	9	1541.571 82	18	8
14	6	9	1615.057 29	35	7
14	6	8	1618.898 64	17	7
14	7	8	1723.302 28	36	6
14	7	7	1723.662 88	18	6
14	8	7	1847.163 90	38	4
14	8	6	1847.185 84	21	5
14	9	6	1985.619 67	48	2

TABLE 5. (Continued)

J	K _a	K _c	Energy	δE	NT
14	9	5	1985.620 58	24	3
14	10	5	2137.121 14	98	2
14	10	4	2137.120 94	26	3
14	11	4	2300.252 78	41	3
14	11	3	2300.252 70	27	4
14	12	3	2473.716 43	40	3
14	12	2	2473.716 31	28	3
14	13	2	2656.281 26	68	2
14	13	1	2656.281 05	33	2
14	14	1	2846.757 03	95	1
14	14	0	2846.756 85	47	1
15	0	15	1229.157 70	41	4
15	1	15	1229.157 96	23	4
15	2	14	1369.845 99	40	5
15	2	13	1494.565 78	38	7
15	3	12	1494.959 45	20	8
15	3	11	1600.150 59	37	7
15	4	12	1604.632 29	19	8
15	4	11	1678.112 95	38	6
15	5	11	1702.894 22	18	8
15	6	10	1736.171 02	38	4
15	6	9	1800.367 01	19	7
15	7	9	1908.400 05	23	6
15	7	8	1909.279 35	38	5
15	8	8	2031.750 83	24	4
15	8	7	2031.815 68	39	5
15	9	7	2170.036 71	25	4
15	9	6	2170.040 09	40	4
15	10	6	2321.686 04	39	3
15	10	5	2321.686 22	63	3
15	11	5	2485.203 40	32	2
15	11	4	2485.203 60	66	2
15	12	4	2659.241 72	32	2
15	13	4	2659.241 80	63	2
15	13	3	2842.544 95	48	2
15	13	2	2842.545 07	95	2
15	14	2	3033.911 97	69	1
15	14	1	3033.912 18	119	1
16	0	16	1387.539 73	26	4
16	1	16	1387.539 87	47	4
16	1	15	1537.992 25	24	5
16	2	15	1538.001 00	44	5
16	2	14	1672.461 29	23	7
16	3	14	1672.663 78	40	6
16	3	13	1788.849 34	21	7
16	4	13	1791.421 53	39	6
16	4	12	1879.512 72	24	6
16	5	12	1896.718 86	39	6
16	5	11	1943.598 79	22	4
16	6	11	1997.424 17	40	5
16	6	10	2011.043 04	22	6

TABLE 5. (Continued)

J	K _a	K _c	Energy	δE	NT
16	7	10	2105.669 02	43	4
16	7	9	2107.627 52	23	6
16	8	9	2228.445 90	41	3
16	8	8	2228.618 22	25	4
16	9	8	2366.430 02	82	3
16	9	7	2366.440 52	28	4
16	10	7	2518.134 77	58	2
16	10	6	2518.135 14	35	3
16	11	6	2681.979 94	84	2
16	11	5	2681.979 76	47	2
16	12	5	2856.557 95	94	2
16	12	4	2856.557 75	59	2
16	13	4	3040.579 80	140	1
16	13	3	3040.579 72	70	1
16	14	3	3232.830 08	156	1
16	14	2	3232.829 96	80	1
17	0	17	1555.361 32	56	3
17	1	17	1555.361 11	28	4
17	1	16	1715.536 62	45	4
17	2	16	1715.540 82	27	4
17	2	15	1859.622 98	43	5
17	3	15	1859.726 61	25	5
17	3	14	1986.272 74	41	5
17	4	14	1987.714 18	24	6
17	4	13	2089.490 82	41	4
17	5	13	2100.797 00	24	6
17	5	12	2162.729 38	58	3
17	6	12	2205.863 61	24	6
17	6	11	2228.213 43	48	2
17	7	11	2314.961 55	27	5
17	7	10	2318.976 61	51	2
17	8	10	2437.195 19	29	3
17	8	9	2437.615 63	50	1
17	9	9	2574.743 61	35	2
17	9	8	2574.774 31	64	2
17	10	8	2726.394 75	44	2
17	10	7	2726.396 38	83	1
17	11	7	2890.496 01	55	2
17	12	6	3065.568 27	69	1
17	12	5	3065.568 45	129	1
17	13	5	3250.280 24	82	1
17	13	4	3250.280 44	160	1
18	0	18	1732.596 23	31	4
18	1	18	1732.596 26	61	3
18	1	17	1902.454 98	29	5
18	2	17	1902.456 99	46	4
18	2	16	2056.053 56	27	5
18	3	16	2056.106 56	44	5
18	3	15	2192.571 36	27	4
18	4	15	2193.367 06	44	5
18	4	14	2307.670 94	29	4
18	5	14	2314.769 67	47	4
18	5	13	2392.368 64	48	3

TABLE 5. (Continued)

J	K _a	K _c	Energy	δE	NT
18	6	13	2425.277 49	71	3
18	6	12	2459.044 54	50	2
18	7	12	2536.184 26	81	1
18	7	11	2543.664 71	39	2
18	8	11	2657.924 00	80	1
18	8	10	2658.870 64	42	1
18	9	9	2794.998 36	67	1
18	10	9	2946.393 08	61	1
18	10	8	2946.397 49	97	1
18	11	7	3110.665 04	88	1
18	12	6	3286.172 84	91	1
19	0	19	1919.218 21	74	3
19	1	19	1919.218 29	36	3
19	1	18	2098.720 62	50	4
19	2	18	2098.721 67	34	5
19	2	17	2261.740 92	46	4
19	3	17	2261.768 23	47	4
19	3	16	2407.844 54	46	3
19	4	16	2408.279 42	53	4
19	4	15	2534.033 31	62	1
19	5	15	2538.340 66	43	4
19	6	14	2655.243 25	81	1
19	7	13	2768.693 94	72	1
19	7	12	2782.000 65	89	1
19	8	12	2890.523 61	97	1
19	20	20	2115.198 54	40	3
19	20	1	2115.198 48	87	2
19	20	1	2304.305 13	38	2
19	20	2	2304.305 57	54	2
19	20	2	2476.664 17	52	2
19	20	3	2476.678 05	50	3
19	20	3	2632.142 80	72	3
19	20	4	2632.379 75	57	2
19	20	4	2768.727 90	76	2
19	21	0	2320.507 21	92	3
19	21	1	2320.507 27	46	3
19	21	1	2519.178 26	133	2
19	21	2	2519.178 32	67	2
19	21	2	2700.795 92	73	2
19	21	3	2700.803 19	60	2
19	21	3	2865.493 82	76	1
19	21	4	2865.612 33	50	1
19	21	5	3013.417 96	68	1
19	22	0	2535.113 12	51	2
19	22	1	2535.113 06	96	2
19	22	1	2743.307 37	65	2
19	22	2	2743.307 31	128	2
19	22	2	2934.105 60	55	1
19	22	3	2934.108 98	110	1
19	23	0	2758.983 30	120	2
19	23	1	2758.983 36	60	2
19	23	1	2976.659 51	269	1
19	23	2	2976.659 57	134	1

TABLE 5. (Continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	Energy	δE	<i>NT</i>
24	0	24	2992.084 02	83	2
24	1	24	2992.083 96	171	2
25	0	25	3234.379 42	319	1
25	1	25	3234.379 48	158	1
(010)					
8	7	2	2095.885 38	66	3
8	7	1	2095.884 77	34	3
8	8	1	2232.992 26	69	3
8	8	0	2232.991 76	37	3
9	6	4	2085.171 89	30	3
9	6	3	2085.188 97	49	3
9	7	3	2207.211 13	34	3
9	7	2	2207.211 54	48	3
9	8	2	2344.501 92	38	3
9	8	1	2344.502 43	64	3
9	9	1	2495.512 40	43	2
9	9	0	2495.512 90	80	2
10	3	8	1935.721 26	74	4
10	3	7	1974.465 20	43	2
10	4	7	2015.641 04	86	2
10	4	6	2025.940 91	44	3
10	5	6	2104.111 24	63	2
10	5	5	2105.237 93	34	3
10	6	5	2208.975 58	60	2
10	6	4	2209.038 82	36	3
10	7	4	2330.884 81	57	2
10	7	3	2330.886 69	36	3
10	8	3	2468.303 13	88	2
10	8	2	2468.302 73	39	3
10	9	2	2619.621 25	82	2
10	9	1	2619.620 74	43	2
10	10	1	2783.345 74	95	2
10	10	0	2783.345 24	52	2
11	2	9	2058.794 79	83	2
11	3	9	2065.604 35	38	4
11	3	8	2118.439 68	61	2
11	4	8	2150.915 42	50	3
11	4	7	2169.126 06	89	2
11	5	7	2240.693 88	49	2
11	6	6	2345.240 49	40	2
11	6	5	2345.439 66	53	2
11	7	5	2466.896 40	41	2
11	7	4	2466.905 23	70	2
11	8	4	2604.362 53	47	2
11	8	3	2604.362 93	82	1
11	9	3	2755.950 96	57	2
11	9	2	2755.951 36	103	2
11	10	2	2920.109 26	65	1
11	10	1	2920.109 77	127	1
11	11	1	3095.389 98	111	1
11	11	0	3095.390 48	222	1
12	2	11	2101.778 64	61	3

TABLE 5. (Continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	Energy	δE	<i>NT</i>
12	3	10	2205.547 41	91	2
12	3	9	2273.272 72	162	2
12	4	9	2297.471 51	71	2
12	4	8	2326.364 71	75	1
12	5	8	2389.538 83	83	1
12	5	7	2395.307 50	69	2
12	6	6	2494.496 35	95	2
12	7	6	2615.234 71	90	1
12	7	5	2615.265 39	62	2
12	8	5	2752.647 20	81	1
12	8	4	2752.648 43	68	1
12	9	3	2904.451 00	88	1
12	10	3	3069.020 27	133	1
12	10	2	3069.019 87	67	1
13	1	12	2241.331 87	69	2
13	2	12	2241.469 39	72	3
13	2	11	2353.017 91	53	2
13	4	10	2454.818 05	119	2
13	5	8	2561.372 94	76	1
13	6	8	2655.052 78	52	1
13	7	7	2775.881 11	74	1
13	8	6	2913.120 60	65	1
14	0	14	2248.873 61	51	4
14	1	14	2248.875 22	93	2
14	1	13	2390.501 80	77	3
14	2	13	2390.570 08	52	2
14	3	12	2514.607 41	62	1
14	3	11	2611.573 44	126	1
15	0	15	2396.660 43	55	2
15	1	15	2396.661 12	57	2
15	1	14	2549.015 84	83	1
15	2	14	2549.050 03	88	2
16	0	16	2553.816 24	71	2
16	1	16	2553.816 62	70	2
16	1	15	2716.866 06	63	1
17	0	17	2720.319 28	97	1
17	1	17	2720.318 90	88	1

only 760 transition frequencies have been measured for $D_2^{17}O$, all by absorption: (i) 63 purely rotational transitions in the range $0.71\text{--}53.35\text{ cm}^{-1}$ were published by Bellet *et al.*⁶⁴ and Puzzarini *et al.*,^{24,30} (ii) Toth reported 222 line positions of the v_2 fundamental band between 996 and 1390 cm^{-1} from which 213 rotational energy levels were retrieved for the (000) and (010) vibrational states,⁵² (iii) finally, more than 310 line positions of five vibrational bands (mainly of the $v_1 + v_2 + v_3$ and $2v_1 + v_3$ bands and a few transitions of the $3v_2 + v_3$, $2v_1 + v_1$ and $3v_1$ bands) were determined by Mikhailenko *et al.*⁶⁵ and Liu *et al.*⁶⁶ All these sources except for Ref. 24 were used to determine the IUPAC-TG energy levels of $D_2^{17}O$.⁹

Our present global observed list includes 1089 transitions of $D_2^{17}O$ belonging to the (000)–(000) pure rotation band and to the (010)–(010) rotation band. Most of the data were derived from

spectrum #15 as this spectrum followed recordings with highly ^{17}O enriched samples¹⁷ and thus has the highest D_2^{17}O abundance (on the order of 1.7%). All but four of our line positions are reported for the first time.

Using the Ritz principle, our set of line positions was merged with the above literature sources^{24,30,52,64–66} to derive a total of 724 term values up to 8088 cm^{-1} involving seven vibrational states. The energy values are provided in the supplementary material, SM6. The set of IUPAC-TG levels of D_2^{17}O is limited to 98 levels for the ground (000) state and 80 levels for the first excited (010) state,⁹ compared to 376 and 185 in our work, respectively. The term values of the 348 newly determined levels are listed in Table 5 with their uncertainties.

In the supplementary material, SM7, we include comparisons between our energy levels and those obtained by Toth,⁵² by the IUPAC-TG,⁹ and by Kyuberis *et al.*⁶⁰ The corresponding overview of the deviations is shown on Fig. 7 for the (000) and (010) vibrational states. An overall reasonable agreement is obtained with the IUPAC-TG dataset with $rms = 2.96 \times 10^{-3}\text{ cm}^{-1}$ and $rmw = 4.08$. The differences $dE = |E^{\text{TW}} - E^{\text{Ref.}}|$ exceeding 0.01 cm^{-1} are for four levels of the ground vibrational state: $7_{5,2}$ ($-0.010\,98\text{ cm}^{-1}$), $9_{2,7}$ ($0.015\,37\text{ cm}^{-1}$), $9_{3,6}$ ($0.011\,91\text{ cm}^{-1}$), and $10_{1,10}$ ($0.011\,23\text{ cm}^{-1}$) and one level of the (010) state: $8_{3,6}$ ($0.011\,02\text{ cm}^{-1}$). Except for (000) $9_{2,7}$, our term value of these levels is much closer to Toth's values.⁵² Nevertheless, the overall agreement with the 211 levels obtained by Toth⁵² is not optimal with $rms = 6.55 \times 10^{-3}\text{ cm}^{-1}$ and

$rmw = 8.26$ for 211 term values. Twenty-one levels differ from our value by more than 0.01 cm^{-1} , the maximum deviations being $0.034\,17$ and $0.034\,45\text{ cm}^{-1}$ for the (000) $9_{2,7}$ and (000) $12_{1,11}$ levels, respectively (our claimed uncertainty for these levels is 3.1×10^{-4} and $1.3 \times 10^{-4}\text{ cm}^{-1}$, respectively).

We also consider the D_2^{17}O line list elaborated by Kyuberis *et al.*⁶⁰ for comparison. Unfortunately, only transition frequencies were provided in that work. We thus derived the term values for the (000) and (010) states from the line list associated with Ref. 60. As Kyuberis *et al.* used both empirical and variational term values, it is mostly impossible to discriminate them from the derived dataset of 407 term values. Overall, the agreement with our energy values is not good. We obtain a large value of $33.2 \times 10^{-3}\text{ cm}^{-1}$ for the rms , probably due to the impact of the energy values with variational origin. The amplitude of the $dE = E^{\text{TW}} - E^{\text{Ref.}}$ difference exceeds 0.01 cm^{-1} for 203 levels and reaches a value of about 0.115 cm^{-1} for the $12_{3,9}$ and $13_{4,10}$ levels of the (010) state.

Similarly to D_2^{16}O , a recommended absorption line list has been elaborated for D_2^{17}O at 296 K by adjusting the SP variational positions according to empirical energy values of the upper and lower energies, when available. The obtained list provided in the supplementary material, SM8, is limited to the (000)–(000), (010)–(010), and (010)–(000) bands and includes 7047 transitions between 0.711 and 1852.768 cm^{-1} , above an intensity cutoff of $10^{-26}\text{ cm/molecule}$ at 296 K. The overview of the obtained recommended list is presented in the middle panel of Fig. 6.

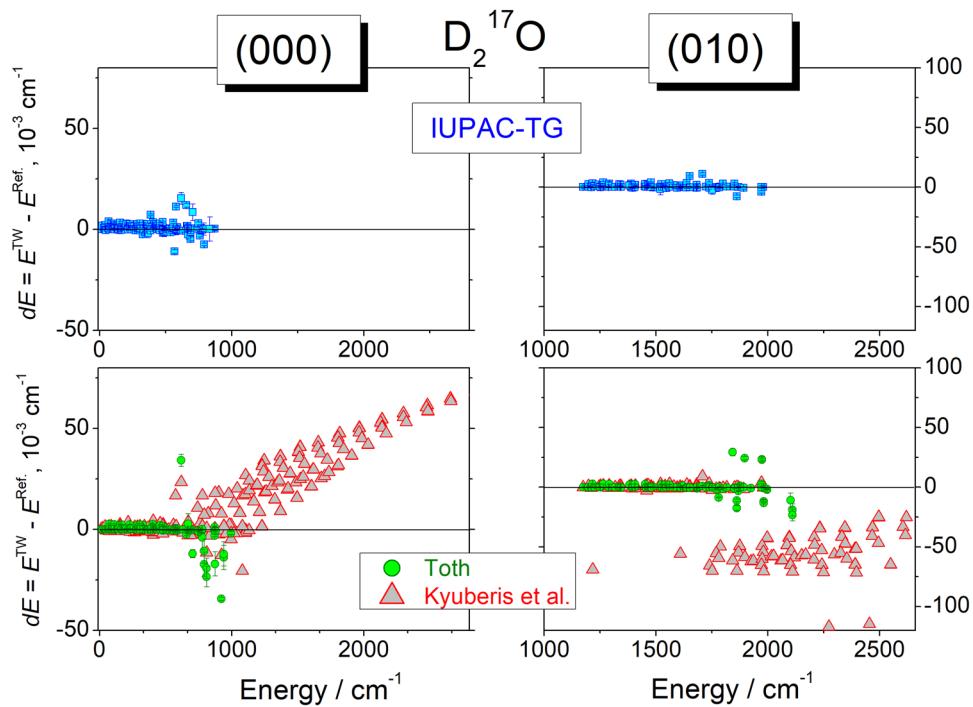


FIG. 7. Energy differences, $dE = E^{\text{TW}} - E^{\text{Ref.}}$, for the rotational levels of the (000) and (010) states of D_2^{17}O . Level energies derived in this work are compared to those obtained by the IUPAC-TG,⁹ by Toth,⁵² and by Kyuberis *et al.*⁶⁰

TABLE 6. Empirical energy levels of the (000) and (010) states of $D_2^{18}O$ newly determined from the analysis of the absorption spectra of deuterated water between 50 and 720 cm^{-1} . The ($J K_a K_c$) rotation quantum numbers are given in the first three columns, followed by the term value (Energy) in cm^{-1} . The 1σ uncertainty (δE) of the term value (in units of 10^{-5} cm^{-1}) is given in the 5th column, followed by the number of line positions (NT) used for the energy determination.

<i>J</i>	<i>K_a</i>	<i>K_c</i>	Energy	δE	<i>NT</i>
(000)					
13	12	2	2278.989 50	7	4
13	12	1	2278.989 66	13	4
13	13	1	2457.723 38	10	3
13	13	0	2457.723 61	19	3
14	12	3	2452.456 13	13	2
14	12	2	2452.455 92	8	2
14	13	2	2631.935 18	16	2
14	13	1	2631.935 02	9	2
14	14	1	2819.174 52	24	2
14	14	0	2819.174 29	12	2
15	12	4	2637.796 55	8	3
15	12	3	2637.796 72	14	3
15	13	3	2818.009 49	10	2
15	13	2	2818.009 70	22	2
15	14	2	3006.138 90	15	2
15	14	1	3006.139 06	32	2
15	15	1	3201.021 86	18	2
15	15	0	3201.022 09	37	2
16	10	7	2502.235 59	9	4
16	10	6	2502.236 05	7	4
16	11	6	2663.287 95	21	3
16	11	5	2663.287 70	8	3
16	12	5	2834.918 58	19	2
16	12	4	2834.918 39	10	2
16	13	4	3015.843 90	20	2
16	13	3	3015.843 73	13	2
16	14	3	3204.853 31	45	2
16	14	2	3204.853 10	19	2
16	15	2	3400.779 93	43	1
16	15	1	3400.779 77	20	1
16	16	1	3602.480 02	49	1
16	16	0	3602.479 79	24	1
17	8	9	2426.792 52	8	1
17	9	8	2561.377 29	18	3
17	10	8	2710.326 44	7	3
17	10	7	2710.328 67	10	3
17	11	7	2871.614 82	10	2
17	11	6	2871.614 36	20	2
17	12	6	3043.725 37	27	2
17	12	5	3043.725 62	59	2
17	13	5	3225.332 37	15	1
17	13	4	3225.332 56	28	1
17	14	4	3415.202 18	19	1
17	14	3	3415.202 35	34	1
17	15	3	3612.160 62	28	1
17	15	2	3612.160 83	58	1
18	5	14	2307.853 54	7	3

TABLE 6. (Continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	Energy	δE	<i>NT</i>
18	8	11	2646.917 06	13	1
18	8	10	2648.028 13	8	2
18	9	9	2781.476 37	8	1
18	10	9	2930.155 43	21	2
18	10	8	2930.161 18	15	2
18	11	8	3091.590 73	38	2
18	11	7	3091.588 50	39	2
18	12	7	3264.119 39	37	1
18	12	6	3264.119 85	16	1
18	13	6	3446.367 15	73	1
18	13	5	3446.366 90	37	1
19	7	13	2759.642 51	13	1
19	7	12	2774.515 37	15	1
19	8	12	2879.399 42	12	1
19	8	11	2881.617 22	19	1
19	9	11	3013.219 77	13	1
19	11	9	3323.122 58	25	1
19	11	8	3323.124 39	25	1
19	12	8	3496.000 05	49	1
19	12	7	3496.002 28	51	1
20	3	18	2468.487 84	10	4
20	3	17	2623.832 29	25	2
20	5	16	2762.948 31	14	1
20	5	15	2872.394 19	20	1
21	2	19	2691.844 08	12	2
21	5	17	3004.292 59	36	1
22	3	19	3097.905 42	28	1
23	0	23	2749.549 26	27	3
23	1	23	2749.549 33	16	3
23	1	22	2966.561 18	34	2
23	2	22	2966.560 88	21	2
24	0	24	2981.861 22	19	2
24	1	24	2981.861 15	35	2
24	1	23	3208.280 46	30	1
24	2	23	3208.280 76	47	1
25	0	25	3223.338 33	45	1
25	1	25	3223.338 40	25	1
(010)					
13	12	2	3566.816 00	19	1
13	12	1	3566.816 00	26	1
20	0	20	3264.583 40	52	1
20	1	20	3264.583 32	44	1
20	2	19	3469.522 57	19	1
21	2	21	3905.708 70	21	1

3.5. $D_2^{18}O$

Among the nine stable isotopologues of water vapor, $D_2^{18}O$ is the heaviest. To date, about 9900 experimental line positions of $D_2^{18}O$ have been published between 0.267 and 9109 cm^{-1} in 13 studies, all by absorption.^{26,39,51,64-73} Nevertheless, in our region of

interest, only 128 pure rotational transitions (up to 216.373 cm⁻¹) were published by Johns²⁶ in 1985. Here, we report line positions of more than 1150 transitions between 51.539 and 586.772 cm⁻¹. They belong to the pure (000)–(000) and the (010)–(010) rotation bands. Line positions of the (010)–(010) band are reported for the first time. This dataset was merged with literature data^{26,39,51,64–73} to extend the sets of rotational energies up to 399 and 296 term values for the ground (000) and first excited (010) states, respectively.

Empirical energies of the rotation–vibration levels up to 9222 cm⁻¹ were recovered using the Ritz principle. The complete set of 3451 term values involving 24 vibrational states can be found in the supplementary material, SM9. The term values of 90 newly determined levels belonging to the (000) and (010) vibrational states are listed in Table 6 with their uncertainties.

Empirical values of the rotational energies in the (000) and (010) states have been determined by Toth,⁵¹ Ni *et al.*,⁷⁰ Liu *et al.*,⁷² and the IUPAC-TG.⁹ More recently, Kyuberis *et al.* used a new set of empirical and variational energy levels (not provided) to calculate the D₂¹⁸O transition frequencies.⁶⁰ As with D₂¹⁷O, for comparison purposes, we derived the corresponding energy values from the published transition frequencies.⁶⁰ The energy comparisons to Refs. 9, 60, and 72 for the two lowest states (000) and (010) are provided as supplementary material, SM10, and the corresponding overviews are presented in Fig. 8. It is worth noting that our (010) energy levels are systematically lower by about 4 × 10⁻⁴ cm⁻¹ compared to literature data.

The best agreement with our values was found for the energy levels derived by Liu *et al.* from the analysis of the v₂ band:⁷² $rms = 43.5 \times 10^{-5}$ cm⁻¹ and $rmw = 1.26$ for 592 term values in common. All the energy differences $dE = E^{\text{TW}} - E^{\text{Ref.}}$ ⁷² are within ±0.003 cm⁻¹. A slightly worse agreement is observed between our values and the IUPAC-TG data:⁹ $rms = 186.2 \times 10^{-5}$ cm⁻¹ and $rmw = 2.11$ for 595 term values [excluding the (000) 23₂₂ level]. The largest differences $dE = E^{\text{TW}} - E^{\text{Ref.}}$ ⁹ with amplitude exceeding 0.01 cm⁻¹ are for four levels of the ground vibrational state: 23₂₂ ($dE = 0.230\,90$ cm⁻¹), 21₃₁₉ (0.02675 cm⁻¹), 19₃₁₇ (0.02528 cm⁻¹), and 21₂₁₉ (-0.01109 cm⁻¹). Note that while the data of Liu *et al.*⁷² were among the sources of the IUPAC-TG,⁹ the energy value for the (000) 19₃₁₉ level of Ref. 72 is much closer to our value ($dE = -0.000\,35$ cm⁻¹) than the IUPAC-TG value ($dE = 0.025\,28$ cm⁻¹).

As mentioned above, Kyuberis *et al.*⁶⁰ used both empirical and variational term values to construct their D₂¹⁸O line list. The very large value $rms = 1245.1 \times 10^{-5}$ cm⁻¹ obtained for 585 term values of the (000) and (010) states probably reflects the impact of the less accurate variational energies. Deviations from our values exceed 0.01 cm⁻¹ for 54 levels with a maximum discrepancy of -0.0638 cm⁻¹ for the (000) 24₀₂₄ and (000) 24₁₂₄ levels.

As for the D₂¹⁷O species, a recommended absorption line list has been elaborated for D₂¹⁸O by using our set of empirical energy levels to correct the SP variational line positions. The D₂¹⁸O line list provided as supplementary material, SM11, includes 7084 transitions and spans the 0.297–1827.937 cm⁻¹ range.

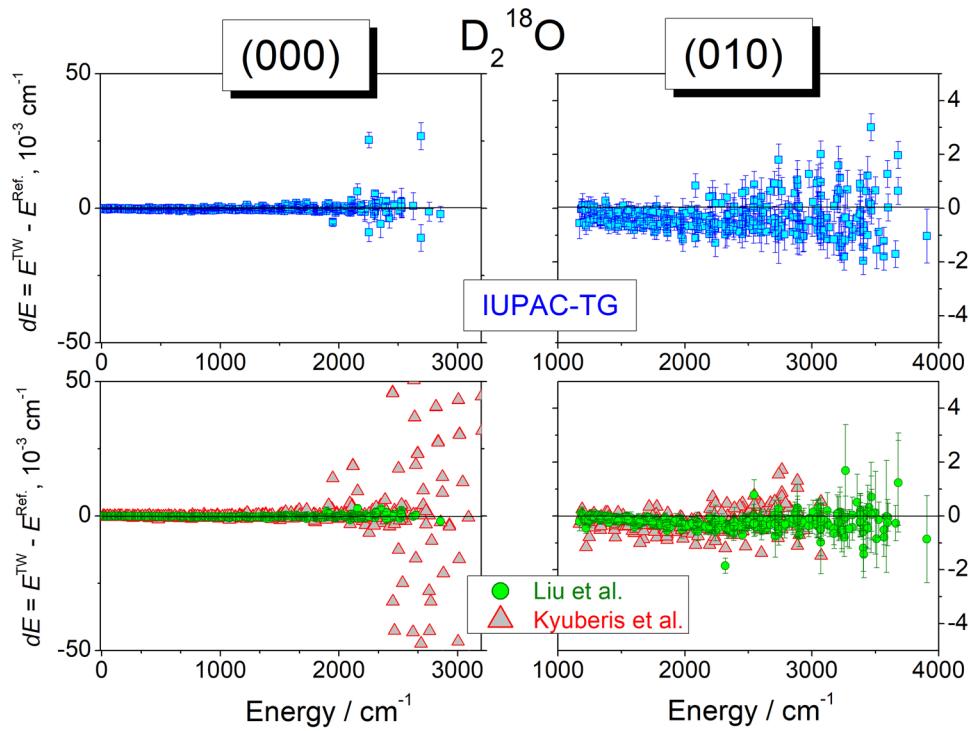


FIG. 8. Energy differences, $dE = E^{\text{TW}} - E^{\text{Ref.}}$, for the rotational levels of the (000) and (010) states of D₂¹⁸O. Level energies derived in this work are compared to those obtained by the IUPAC-TG,⁹ by Liu *et al.*,⁷² and Kyuberis *et al.*⁶⁰

An overview of the obtained recommended list is included in Fig. 6.

4. Concluding Remarks

The absorption spectrum of deuterium oxide, D_2O , has been studied by FTS in the FIR ($50\text{--}720\text{ cm}^{-1}$). The high brilliance and large spectral coverage of the SOLEIL synchrotron radiation source combined with a 151.75-m absorption pathlength has allowed lowering by more than three orders of magnitude the detectivity threshold of previous absorption studies in the region. For instance, among the 2886 transitions assigned to $D_2^{16}O$, 2057 are newly reported. A typical value of $5 \times 10^{-5}\text{ cm}^{-1}$ is estimated for the position accuracy for isolated non-saturated lines.

The extension of the observations and an exhaustive review of the literature have allowed us to propose (i) a new set of empirical energy levels for the five first vibrational levels of $D_2^{16}O$, namely

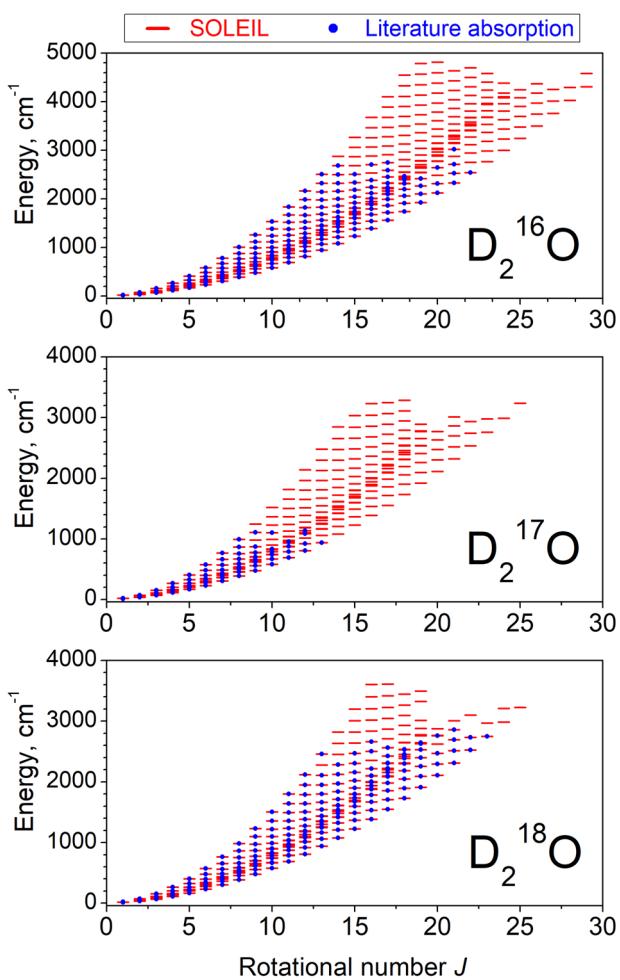


FIG. 9. Energy levels of $D_2^{16}O$, $D_2^{17}O$, and $D_2^{18}O$ in the (000) ground vibrational state determined from absorption data. The sets of energy levels presently obtained are compared to the energy levels available from previous studies by absorption spectroscopy.

(000), (010), (020), (100), and (001); (ii) an extensive set of 724 empirical energy levels up to 8088 cm^{-1} for seven vibrational states of $D_2^{17}O$; (iii) an extensive set of 3451 empirical energy levels up to 9222 cm^{-1} for 24 vibrational states of $D_2^{18}O$.

The sets of energy levels derived for the ground state is compared to previous determinations from absorption data in Fig. 9. Note that in the case of $D_2^{16}O$, our empirical set of energy levels is exclusively based on line positions measured by absorption. It includes only 28 new energy levels compared to the IUPAC-TG dataset.⁹ This is due to the fact that part of the IUPAC-TG dataset relies exclusively on emission data (which are much less accurate than the absorption data).

Because the (000) and (010) energy levels are those that are significantly populated at room temperature, they correspond to the lower states of all the transitions. Improvement or correction of their energy values has thus a direct impact on the calculated position value in all the spectral ranges. In this context, the reported sets of energy levels which are extended (348 and 90 new levels determined for $D_2^{17}O$ and $D_2^{18}O$, respectively) or improved in accuracy will be valuable to improve the status of the spectroscopic databases over the whole spectrum.

The sets of energy of the heavy water isotopologues are valuable to test, validate, and correct the PES of water vapor obtained from extensive *ab initio* calculations.^{10,61} The studied isotopologues include the heaviest of the nine stable isotopologues of water vapor ($D_2^{18}O$ has a molar mass of 22 g compared to 18 g for $H_2^{16}O$). Accurate energy values of the considered D_2O levels can be used to determine mass-dependent corrections of isotopologue-dependent PES of the water molecule, the largest mass change being suitable to refine these corrections.

Due to their small relative isotopic abundance in natural vapor, the three doubly deuterated isotopologues of water vapor have limited atmospheric interest. Nevertheless, as mentioned in Sec. 1, some strong pure rotational lines are proposed for specific atmospheric applications and for the determination of the D/H ratio from astronomical measurements in the THz range.

As main outputs of the present work, recommended line lists are provided and proposed for improving spectroscopic databases.

5. Supplementary Material

See the supplementary material for the complete line list of the analyzed FTS spectra and for the derived sets of energy levels, comparison to literature and recommended line lists elaborated for $D_2^{16}O$, $D_2^{17}O$, and $D_2^{18}O$.

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7. Author Declarations

7.1. Conflict of Interest

The authors have no conflicts to disclose.

8. Data Availability

The data that support the findings of this study are available within the article and its supplementary material.

9. References

- ¹I. E. Gordon, L. S. Rothman, R. J. Hargreaves, R. Hashemi, E. V. Karlovets, F. M. Skinner *et al.*, "The HITRAN2020 molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transfer* **277**, 107949 (2022).
- ²T. Delahaye, R. Armante, N. A. Scott, N. Jacquinet-Husson, A. Chédin, L. Crépeau *et al.*, "The 2020 edition of the GEISA spectroscopic database," *J. Mol. Spectrosc.* **380**, 111510 (2021).
- ³<https://www.forum-ee9.eu/>.
- ⁴S. S. Nabiev, V. L. Vaks, E. G. Domracheva, L. A. Palkina, S. I. Pripolzin, E. A. Sobakinskaya, and M. B. Chernyaeva, "Express analysis of water isotopomers in the atmosphere with the use of nonstationary subterahertz and terahertz spectroscopy methods," *Atmos. Oceanic Opt.* **24**, 402 (2011).
- ⁵A. Coutens, C. Vestel, S. Cazaux, S. Bottinelli, E. Caux, C. Ceccarelli *et al.*, "Heavy water stratification in a low-mass protostar," *Astron. Astrophys.* **553**, A75 (2013).
- ⁶H. M. Butner, S. B. Charnley, C. Ceccarelli, S. D. Rodgers, J. R. Pardo, B. Parise *et al.*, "Discovery of interstellar heavy water," *Astrophys. J.* **659**, L137 (2007).
- ⁷S. S. Jensen, J. K. Jørgensen, L. E. Kristensen, A. Coutens, E. F. van Dishoeck, K. Furuya *et al.*, "ALMA observations of doubly deuterated water: Inheritance of water from the prestellar environment," *Astron. Astrophys.* **650**, A172 (2021).
- ⁸A. Coutens, J. K. Jørgensen, M. V. Persson, E. F. Van Dishoeck, C. Vestel, and V. Taquet, "High D₂O/HDO ratio in the inner regions of the low-mass protostar NGC 1333 IRAS2A," *Astrophys. J.* **792**, L5 (2014).
- ⁹J. Tennyson, P. F. Bernath, L. R. Brown, A. Campargue, A. G. Császár, L. Daumont *et al.*, "IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part IV: Energy levels and transition wavenumbers for D₂¹⁶O, D₂¹⁷O, and D₂¹⁸O," *J. Quant. Spectrosc. Radiat. Transfer* **142**, 93 (2014).
- ¹⁰H. Partridge and D. W. Schwenke, "The determination of an accurate isotope dependent potential energy surface for water from extensive *ab initio* calculations and experimental data," *J. Chem. Phys.* **106**, 4618 (1997).
- ¹¹D. W. Schwenke and H. Partridge, "Convergence testing of the analytic representation of an *ab initio* dipole moment function for water: Improved fitting yields improved intensities," *J. Chem. Phys.* **113**, 6592 (2000).
- ¹²F. Sizov and A. Rogalski, "THz detectors," *Prog. Quantum Electron.* **34**, 278 (2010).
- ¹³L. Consolino, S. Bartalini, and P. De Natale, "Terahertz frequency metrology for spectroscopic applications: A review," *J. Infrared, Millimeter, Terahertz Waves* **38**, 1289 (2017).
- ¹⁴A. O. Koroleva, T. A. Odintsova, M. Y. Tretyakov, O. Pirali, and A. Campargue, "The foreign-continuum absorption of water vapour in the far-infrared (50–500 cm⁻¹)," *J. Quant. Spectrosc. Radiat. Transfer* **261**, 107486 (2021).
- ¹⁵M. Toureille, A. O. Koroleva, S. N. Mikhailenko, O. Pirali, and A. Campargue, "Water vapor absorption spectroscopy and validation tests of databases in the far-infrared (50–720 cm⁻¹). Part 1: Natural water," *J. Quant. Spectrosc. Radiat. Transfer* **291**, 108326 (2022).
- ¹⁶S. N. Mikhailenko, S. Béguier, T. A. Odintsova, M. Y. Tretyakov, O. Pirali, and A. Campargue, "The far-infrared spectrum of ¹⁸O enriched water vapour (40–700 cm⁻¹)," *J. Quant. Spectrosc. Radiat. Transfer* **253**, 107105 (2020).
- ¹⁷E. V. Karlovets, S. N. Mikhailenko, A. O. Koroleva, and A. Campargue, "Water vapor absorption spectroscopy and validation tests of databases in the far-infrared (50–720 cm⁻¹). Part 2: H₂¹⁷O and HD¹⁷O," *J. Quant. Spectrosc. Radiat. Transfer* **314**, 108829 (2024).
- ¹⁸R. A. Toth, L. R. Brown, and C. Plymate, "Self-broadened widths and frequency shifts of water vapor lines between 590 and 2400 cm⁻¹," *J. Quant. Spectrosc. Radiat. Transfer* **59**, 529 (1998).
- ¹⁹V. B. Podobedov, D. F. Plusquellec, and G. T. Fraser, "THz laser study of self-pressure and temperature broadening and shifts of water vapor lines for pressures up to 1.4 kPa," *J. Quant. Spectrosc. Radiat. Transfer* **87**, 377 (2004).
- ²⁰R. Tóbiás, T. Furtenbacher, I. Simkó, A. G. Császár, M. L. Diouf, F. M. J. Cozijn *et al.*, "Spectroscopic-network-assisted precision spectroscopy and its application to water," *Nat. Commun.* **11**, 1708 (2020).
- ²¹J. Verhoeven, H. Bluyssen, and A. Dymanus, "Hyperfine structure of HDO and D₂O by beam maser spectroscopy," *Phys. Lett. A* **26**, 424 (1968).
- ²²G. Cazzoli, L. Dore, C. Puzzarini, and J. Gauss, "The hyperfine structure in the rotational spectra of D₂O: Lamb-dip measurements and quantum-chemical calculations," *Mol. Phys.* **108**, 2335 (2010).
- ²³G. Cazzoli and C. Puzzarini, "Sub-Doppler resolution in the THz frequency domain: 1 kHz accuracy at 1 THz by exploiting the Lamb-dip technique," *J. Phys. Chem. A* **117**, 13759 (2013).
- ²⁴C. Puzzarini, G. Cazzoli, M. E. Harding, J. Vazquez, and J. Gauss, "The hyperfine structure in the rotational spectra of D₂¹⁷O and HD¹⁷O: Confirmation of the absolute nuclear magnetic shielding scale for oxygen," *J. Chem. Phys.* **142**, 124308 (2015).
- ²⁵J. Kaupinen, T. Karkkainen, and E. Kyro, "High-resolution spectrum of water vapor between 30 and 720 cm⁻¹," *J. Mol. Spectrosc.* **71**, 15 (1978).
- ²⁶J. W. C. Johns, "High-resolution far-infrared (20–350-cm⁻¹) spectra of several isotopic species of H₂O," *J. Opt. Soc. Am. B* **2**, 1340 (1985).
- ²⁷R. Paso and V. M. Horneman, "High-resolution rotational absorption spectra of H₂¹⁶O, HD¹⁶O, and D₂¹⁶O between 110 and 500 cm⁻¹," *J. Opt. Soc. Am. B* **12**, 1813 (1995).
- ²⁸R. A. Toth, "HDO and D₂O low pressure, long path spectra in the 600–3100 cm⁻¹ region. I. HDO line positions and strengths," *J. Mol. Spectrosc.* **195**, 73 (1999).
- ²⁹A. Janca, K. Tereszchuk, P. F. Bernath, N. F. Zobov, S. V. Shirin, O. L. Polyansky, and J. Tennyson, "Emission spectrum of hot HDO below 4000 cm⁻¹," *J. Mol. Spectrosc.* **219**, 132 (2003).
- ³⁰C. Puzzarini, G. Cazzoli, and J. Gauss, "The rotational spectra of HD¹⁷O and D₂¹⁷O: Experiment and quantum-chemical calculations," *J. Chem. Phys.* **137**, 154311 (2012).
- ³¹G. C. Mellau, S. N. Mikhailenko, and V. G. Tyuterev, "Hot water emission spectra: Rotational energy levels of the (000) and (010) states of HD¹⁷O," *J. Mol. Spectrosc.* **308–309**, 6 (2015).
- ³²S. S. Yu, J. C. Pearson, B. J. Drouin, C. E. Miller, K. Kobayashi, and F. Matsushima, "Terahertz spectroscopy of ground state HD¹⁸O," *J. Mol. Spectrosc.* **328**, 27 (2016).
- ³³F. Matsushima, M. Matsunaga, G. Y. Qian, Y. Ohtaki, R. L. Wang, and K. Takagi, "Frequency measurement of pure rotational transitions of D₂O from 0.5 to 5 THz," *J. Mol. Spectrosc.* **206**, 41 (2001).
- ³⁴E. A. Michael, C. J. Keoshian, S. K. Anderson, and R. J. Saykally, "Rotational transitions in excited vibrational states of D₂O," *J. Mol. Spectrosc.* **208**, 219 (2001).
- ³⁵S. Brünken, H. S. P. Müller, C. Endres, F. Lewen, T. Giesen, B. Drouin, J. C. Pearson, and H. Mäder, "High resolution rotational spectroscopy on D₂O up to 2.7 THz in its ground and first excited vibrational bending states," *Phys. Chem. Chem. Phys.* **9**, 2103 (2007).
- ³⁶G. Mellau, S. N. Mikhailenko, E. N. Starikova, S. A. Tashkun, H. Over, and V. G. Tyuterev, "Rotational levels of the (000) and (010) states of D₂¹⁶O from hot emission spectra in the 320–860 cm⁻¹ region," *J. Mol. Spectrosc.* **224**, 32 (2004).
- ³⁷S. N. Mikhailenko, G. C. Mellau, E. N. Starikova, S. A. Tashkun, and V. G. Tyuterev, "Analysis of the first triad of interacting states (020), (100), and (001) of D₂¹⁶O from hot emission spectra," *J. Mol. Spectrosc.* **233**, 32 (2005).
- ³⁸N. F. Zobov, R. I. Ovsannikov, S. V. Shirin, O. L. Polyansky, J. Tennyson, A. Janka, and P. F. Bernath, "Infrared emission spectrum of hot D₂O," *J. Mol. Spectrosc.* **240**, 112 (2006).
- ³⁹J. W. Fleming and M. J. Gibson, "Far-infrared absorption spectra of water vapor H₂¹⁶O and isotopic modifications," *J. Mol. Spectrosc.* **62**, 326 (1976).
- ⁴⁰C. I. Beard and D. R. Bianco, "Two D₂O microwave absorption lines," *J. Chem. Phys.* **20**, 1488 (1952).
- ⁴¹C. K. Jen, D. R. Bianco, and J. T. Massey, "Some heavy water rotational absorption lines," *J. Chem. Phys.* **21**, 520 (1953).
- ⁴²D. W. Posener and M. W. P. Strandberg, "Centrifugal distortion in the asymmetric top molecules. III. H₂O, D₂O, and HDO," *Phys. Rev.* **95**, 374 (1954).
- ⁴³G. Erlandsson and J. Cox, "Millimeter-wave lines of heavy water," *J. Chem. Phys.* **25**, 778 (1956).

- ⁴⁴D. A. Stephenson and R. G. Strauch, "Water vapor spectrum near 600 GHz," *J. Mol. Spectrosc.* **35**, 494 (1970).
- ⁴⁵W. S. Benedict, S. A. Clough, L. Frenkel, and T. E. Sullivan, "Microwave spectrum and rotational constants for the ground state of D₂O," *J. Chem. Phys.* **53**, 2565 (1970).
- ⁴⁶G. Steenbeckeliers and J. Bellet, "Spectre de rotation de l'eau lourde," *C. R. Acad. Sci., Ser. B* **270**, 1039 (1970).
- ⁴⁷J. Bellet and G. Steenbeckeliers, "Calcul des constantes rotationnelles des molécules H₂O, HDO et D₂O dans leurs états fondamentaux de vibration," *C. R. Acad. Sci., Ser. B* **271**, 1208 (1970).
- ⁴⁸G. Steenbeckeliers and J. Bellet, "Application of Watson's centrifugal distortion theory to water and light asymmetric tops. General methods. Analysis of the ground state and the v₂ state of D₂O¹⁶," *J. Mol. Spectrosc.* **45**, 10 (1973).
- ⁴⁹J. K. Messer, F. C. De Lucia, and P. Helmingher, "Submillimeter spectroscopy of the major isotopes of water," *J. Mol. Spectrosc.* **105**, 139 (1984).
- ⁵⁰O. I. Baskakov, V. A. Alekseev, E. A. Alekseev, and B. I. Polevoi, "New submillimeter lines of water and its isotopes," *Opt. Spectrosc.* **63**(5), 600 (1987).
- ⁵¹R. A. Toth, "D₂¹⁶O and D₂¹⁸O transition frequencies and strengths in the v₂ bands," *J. Mol. Spectrosc.* **162**, 41 (1993).
- ⁵²R. A. Toth, "HDO and D₂O low pressure, long path spectra in the 600–3100 cm⁻¹ region. II. D₂O line positions and strengths," *J. Mol. Spectrosc.* **195**, 98 (1999).
- ⁵³N. Papineau, J. M. Flaud, C. Camy-Peyret, and G. Guelachvili, "The 2v₂, v₁ and v₃ bands of D₂¹⁶O. The ground state (000) and the triad of interacting states {(020), (100), (001)}," *J. Mol. Spectrosc.* **87**, 219 (1981).
- ⁵⁴C. Camy-Peyret, J. M. Flaud, A. Mahmoudi, G. Guelachvili, and J. W. C. Johns, "Line positions and intensities in the v₂ band of D₂O improved pumped D₂O laser frequencies," *Int. J. Infrared Millimeter Waves* **6**, 199 (1985).
- ⁵⁵C. P. Rinsland, M. A. H. Smith, V. Malathy Devi, and D. C. Benner, "Measurements of Lorentz-broadening coefficients and pressure-induced line shift coefficients in the v₂ band of D₂¹⁶O," *J. Mol. Spectrosc.* **150**, 173 (1991).
- ⁵⁶C. P. Rinsland, M. A. H. Smith, V. M. Devi, and D. C. Benner, "Measurements of Lorentz-broadening coefficients and pressure-induced line-shift coefficients in the v₁ band of HD¹⁶O and the v₃ band of D₂¹⁶O," *J. Mol. Spectrosc.* **156**, 507 (1992).
- ⁵⁷R. A. Toth, NSO Spectrum 970325.2.
- ⁵⁸A. G. Császár and T. Furtenbacher, "Spectroscopic networks," *J. Mol. Spectrosc.* **266**, 99 (2011).
- ⁵⁹T. Furtenbacher and A. G. Császár, "The role of intensities in determining characteristics of spectroscopic networks," *J. Mol. Struct.* **1009**, 123 (2012).
- ⁶⁰A. A. Kyuberis, N. F. Zobov, O. V. Naumenko, B. A. Voronin, O. L. Polyansky, L. Lodi *et al.*, "Room temperature line lists for deuterated water," *J. Quant. Spectrosc. Radiat. Transfer* **203**, 175 (2017).
- ⁶¹S. V. Shirin, N. F. Zobov, and O. L. Polyansky, "Theoretical line list of D₂¹⁶O up to 16,000 cm⁻¹ with an accuracy close to experimental," *J. Quant. Spectrosc. Radiat. Transfer* **109**, 549 (2008).
- ⁶²D. W. Schwenke, "Variational calculations of rovibrational energy levels and transition intensities for tetraatomic molecules," *J. Phys. Chem.* **100**, 2867 (1996).
- ⁶³D. W. Schwenke, "Erratum to 'Variational calculations of rovibrational energy levels and transition intensities for tetraatomic molecules,'" *J. Phys. Chem.* **100**, 18884 (1996).
- ⁶⁴J. Bellet, W. J. Lafferty, and G. Steenbeckeliers, "Microwave spectra of D₂¹⁷O and D₂¹⁸O," *J. Mol. Spectrosc.* **47**, 388 (1973).
- ⁶⁵S. N. Mikhailenko, O. V. Naumenko, A. V. Nikitin, I. A. Vasilenko, A.-W. Liu, K.-F. Song *et al.*, "Absorption spectrum of deuterated water vapor enriched by ¹⁸O between 6000 and 9200 cm⁻¹," *J. Quant. Spectrosc. Radiat. Transfer* **113**, 653 (2012).
- ⁶⁶A.-W. Liu, O. V. Naumenko, S. Kassi, and A. Campargue, "CW-Cavity Ring Down Spectroscopy of deuterated water in the 1.58 μm atmospheric transparency window," *J. Quant. Spectrosc. Radiat. Transfer* **138**, 97 (2014).
- ⁶⁷G. Di Lonardo and L. Fusina, "The v₂ band of D₂¹⁸O," *J. Mol. Spectrosc.* **135**, 250 (1989).
- ⁶⁸W. F. Wang, T. L. Tan, B. L. Tan, and P. P. Ong, "The v₂ bands of HD¹⁸O and D₂¹⁸O: Rovibrational constants and additional transitions," *J. Mol. Spectrosc.* **176**, 226 (1996).
- ⁶⁹R. A. Toth, "Measurements of line positions and strengths of HD¹⁸O and D₂¹⁸O in the 2500–4280 cm⁻¹ region," *J. Mol. Struct.* **742**, 49 (2005).
- ⁷⁰H.-Y. Ni, A.-W. Liu, K.-F. Song, S.-M. Hu, O. V. Naumenko, T. V. Kruglova, and S. A. Tashkun, "High-resolution spectroscopy of the triple-substituted isotopologue of water molecule D₂¹⁸O: The first triad," *Mol. Phys.* **106**, 1793 (2008).
- ⁷¹S. N. Mikhailenko, S. A. Tashkun, L. Daumont, A. Jenouvrier, M. Carleer, S. Fally, and A. C. Vandaele, "Line positions and energy levels of the ¹⁸O substitutions from the HDO/D₂O spectra between 5600 and 8800 cm⁻¹," *J. Quant. Spectrosc. Radiat. Transfer* **111**, 2185 (2010).
- ⁷²A.-W. Liu, K.-F. Song, H.-Y. Ni, S.-M. Hu, O. V. Naumenko, I. A. Vasilenko, and S. N. Mikhailenko, "(000) and (010) energy levels of the HD¹⁸O and molecules from analysis of their v₂ bands," *J. Mol. Spectrosc.* **265**, 26 (2011).
- ⁷³M. J. Down, J. Tennyson, J. Orphal, P. Chelin, and A. A. Ruth, "Analysis of an ¹⁸O and D enhanced water spectrum and new assignments for HD¹⁸O and D₂¹⁸O in the near-infrared region (6000–7000 cm⁻¹) using newly calculated variational line lists," *J. Mol. Spectrosc.* **282**, 1 (2012).