

# Combined analysis of the high sensitivity Fourier transform and ICLAS-VeCSEL absorption spectra of D<sub>2</sub>O between 8800 and 9520 cm<sup>-1</sup>

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## Abstract

The absorption spectrum of dideuterated water, D<sub>2</sub>O, has been recorded between 8800 and 9520 cm<sup>-1</sup> by intracavity laser absorption spectroscopy (ICLAS) based on a vertical external cavity system emitting laser (VeCSEL) and by high sensitivity Fourier Transform spectroscopy. The combined analysis of the spectra has allowed attributing 1223 transitions to the D<sub>2</sub>O species. The spectrum assignment was performed on the basis of the recent results of variational calculations based on an optimized potential energy surface of D<sub>2</sub>O. A set of 687 energy levels was derived from transitions assigned to eight upper vibrational states, 577 of them being reported for the first time. A detailed line list has been generated. The line intensities were retrieved mainly from the FTS spectrum and the absolute integrated intensities of the  $2\nu_1 + \nu_2 + \nu_3$  and the  $\nu_2 + 3\nu_3$  bands dominating the spectrum have been determined.

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**Keywords:** FTS; Fourier transform spectroscopy; ICLAS; Intracavity laser absorption spectroscopy; Deuterated water; Rovibrational energy levels

## 1. Introduction

The absorption spectrum of D<sub>2</sub>O above 8100 cm<sup>-1</sup> has been the subject of a few reports:

- the 9160–9390 cm<sup>-1</sup> section was recorded and analyzed in 1982 by intracavity laser absorption spectroscopy (ICLAS) with a moderated sensitivity of 10<sup>-7</sup> cm<sup>-1</sup> using an Nd glass laser [1].

- the  $(\nu_1 + \nu_2/2 + \nu_3) = 3.5$  and 4 polyads near 9300 [2] and 10300 cm<sup>-1</sup> [3], respectively, were investigated by Fourier transform spectroscopy (FTS) with a 105 m path length.
- the 5OD region (12570–12820 cm<sup>-1</sup>) was recorded by ICLAS-Ti-Sapphire associated with a FTS detection scheme [4].

The present contribution, devoted to the 8800–9520 cm<sup>-1</sup> region, corresponds to the full coverage of the  $(\nu_1 + \nu_2/2 + \nu_3) = 3.5$  polyad which is the 2nd decade of resonating states (the 1st decade lying in the 7500–8300 cm<sup>-1</sup> region has been analyzed in Ref. [5]). As just mentioned,

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this polyad was previously investigated [1,2] but the higher sensitivity of the experimental methods presently implemented will provide a much deeper knowledge of this spectral region. The absorption spectrum was recorded in parallel in Reims by Fourier Transform spectroscopy with a 600 m path length and in Grenoble by ICLAS based on vertical external cavity surface emitting lasers (VeCSEL). An equivalent sensitivity corresponding to a detection limit  $\alpha_{\min} \sim 5 \times 10^{-9} \text{ cm}^{-1}$  was achieved in the two recordings. As discussed below, the combination of the two spectra obtained by different methods proved to be a valuable help in the species and rovibrational assignment process.

An overview of the  $\text{H}_2\text{O}$ , HDO, and  $\text{D}_2\text{O}$  stick spectra in the region of interest is presented in Fig. 1 of Ref. [6]. The  $\text{D}_2\text{O}$  spectrum is dominated by two well separated bands: the  $2\nu_1 + \nu_2 + \nu_3$  and the  $\nu_2 + 3\nu_3$  bands centered

at  $9050.349$  and  $9366.313 \text{ cm}^{-1}$  respectively. A global comparison of the absorbance in the region shows that (for the pure species), the HDO and  $\text{D}_2\text{O}$  absorbance are on the same order of magnitude while the absorbance of  $\text{H}_2^{16}\text{O}$  is much stronger than that of the  $\text{D}_2\text{O}$  and HDO isotopologues below  $9000 \text{ cm}^{-1}$ .

## 2. Experimental details

### 2.1. FTS spectrum

The FTS spectra have been recorded by the Bruxelles–Reims (BR) group and the detail of the experimental setup has been described elsewhere [7–9]. Briefly, a Bruker IFS 120M Fourier transform spectrometer was coupled to a long multiple reflection absorption cell of 50 m base

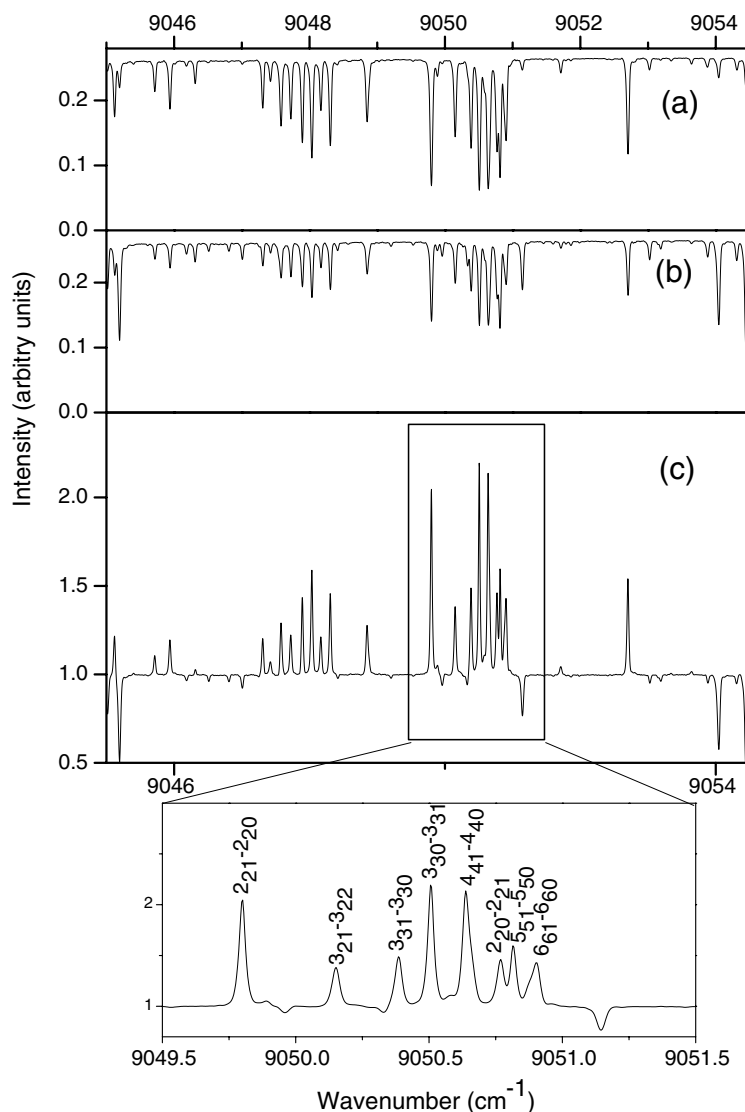


Fig. 1. Illustration of the experimental procedure used to discriminate the  $\text{D}_2\text{O}$  lines among the HDO and  $\text{H}_2\text{O}$  lines in the FTS spectrum by comparison of different spectra recorded with different  $\text{D}_2\text{O}/\text{HDO}/\text{H}_2\text{O}$  mixtures with a 600 m of path length at a resolution of  $0.03 \text{ cm}^{-1}$ : (a) and (b) correspond to spectrum B, C of Table 1, respectively; (c) presents the ratio C/B of the two spectra. As the  $\text{D}_2\text{O}$  concentration is higher in the B sample than in the C sample, the lines appearing in (c) above the baseline are those of  $\text{D}_2\text{O}$  while the  $\text{H}_2\text{O}$  and HDO lines are observed as absorption lines. This procedure is very efficient to discriminate  $\text{D}_2\text{O}$  transitions. The assignment of the strongest  $\text{D}_2\text{O}$  lines belonging to the  $2\nu_1 + \nu_2 + \nu_3$  band is indicated.

length. The unapodized resolution defined as  $0.9/\text{maximum optical path difference}$  (Bruker definition) was set to  $0.03 \text{ cm}^{-1}$ . No apodization function was used. A path length of 600 m was chosen in order to maximize the signal-to-noise (S/N) ratio. The light source was a 250 W tungsten halogen lamp (ORIEL) and the detector was a silicon diode sensitive over the whole spectral range investigated. All the spectra were recorded at room temperature ( $291 \text{ K} \pm 3 \text{ K}$ ) monitored in the cell by three platinum resistance thermometers. The temperature was not stabilized and may therefore differ by up to 2 K from one end to the other. Several spectra were recorded successively with a given sample to allow the monitoring of any change in the pressure resulting from condensation on the walls of the cell. Each spectrum was the result of the Fourier transformation of 128 co-added interferograms. To improve the S/N ratio, six spectra corresponding to a total recording time of 15 h, were co-added. A detectivity of  $\alpha_{\text{min}} \sim 4.5 \times 10^{-9}$  and  $2 \times 10^{-8} \text{ cm}^{-1}$  corresponding to an rms S/N ratio of 3600 and 800 was achieved at 9500 and  $8800 \text{ cm}^{-1}$ , respectively.

The  $\text{D}_2^{16}\text{O}$  sample was purchased from the Commissariat à l'Énergie Atomique (CEA) with a stated purity of 99.9%. In order to discriminate the transitions due to  $\text{H}_2\text{O}$ , HDO or  $\text{D}_2\text{O}$ , different  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixtures were introduced into the cell. In these mixtures, the  $\text{H}_2\text{O}$  partial pressure was first determined from the intensity of about one hundred strong and well isolated lines. Then, the HDO and  $\text{D}_2\text{O}$  partial pressures were calculated either by using the equilibrium constant given in [10],  $K_{\text{eq}} = 3.86 \pm 0.07$  for the reaction  $\text{H}_2\text{O} + \text{D}_2\text{O} \leftrightarrow 2 \text{HDO}$  or from the ratios of selected line intensities of the two species. The determined values of the relative  $\text{D}_2\text{O}/\text{HDO}/\text{H}_2\text{O}$  concentrations are reported in percentages in Table 1.

Fig. 1 shows a small section of the absorption spectra B and C (see Table 1) obtained with different experimental conditions. After their wavenumber calibration versus the Hitran 2004 database and the BR database (<http://www.ulb.ac.be/cpm/>) by using the stronger  $\text{H}_2\text{O}$  lines, the atmospheric contribution due to the absorption within the external path between the light source and the spectrometer was removed by the same procedure as described in Ref. [11]. The  $\text{D}_2\text{O}$  lines were easily identified from the variation of their intensities with the sample composition. The procedure is illustrated on Fig. 1: the  $\text{D}_2\text{O}$  lines are those appearing as peaks on the ratio of spectra B and C.

## 2.2. ICLAS-VeCSEL spectrum

The ICLAS spectra were recorded with the experimental setup based on a VeCSEL previously described in Refs. [12,13] and recently applied to the study of the HDO absorption spectrum in the same region [6]. The achieved sensitivity was on the order of  $\alpha_{\text{min}} \sim 5 \times 10^{-9} \text{ cm}^{-1}$ , which is less than the best performances achieved in other spectral regions (see for instance Refs. [13–16]) as a consequence of the poorer laser properties of the VeCSEL presently used.

The spectra were recorded with generation times up to  $130 \mu\text{s}$ , leading to equivalent absorption path lengths on the order of 23.4 km as the filling ratio of the laser cavity by the absorption cell was 60%. The spectral resolution was about  $0.04 \text{ cm}^{-1}$  slightly larger than the Doppler broadening ( $0.028 \text{ cm}^{-1}$  FWHM).

As a result of the rapid proton exchange in water and the omnipresence of the main isotopologue,  $\text{H}_2\text{O}$ , adsorbed on the walls of the filling line and of the absorption cell, it is difficult to obtain a sample of water with a largely dominant fraction of the  $\text{D}_2\text{O}$  isotopologue. This was however achieved with the ICLAS cell (about  $200 \text{ cm}^3$  volume) as the experimental procedure consisting in successively filling the cell with deuterated water, recording the spectrum, vacuuming the cell and recording the background spectrum, was performed several hundred of times and then washed out the  $\text{H}_2\text{O}$  isotopologue from the cell. Fig. 2 shows the comparison of the FTS and ICLAS spectra in a spectral section showing only HDO and  $\text{D}_2\text{O}$  lines. The  $\text{D}_2\text{O}/\text{HDO}/\text{H}_2\text{O}$  relative fractions were estimated to be 74/23/3 and 93.7/6.0/0.3 for the FTS and ICLAS samples respectively. The contribution of HDO and  $\text{H}_2\text{O}$  absorption lines was then largely reduced in the ICLAS spectrum which helps to observe  $\text{D}_2\text{O}$  lines when falling in close coincidence with HDO or  $\text{H}_2\text{O}$  transitions.

The ICLAS spectrum was obtained by adding  $12 \text{ cm}^{-1}$  wide sections of the spectrum recorded successively with the 3754 photodiode array placed at the exit of the spectrograph dispersing the VeCSEL beam. The wavenumber calibration procedure of each elementary spectrum requires the knowledge of reference line positions. We used the HDO line positions measured by FTS [17] as reference which leads to an agreement within about  $0.003 \text{ cm}^{-1}$  with the line positions measured independently on the FTS spectrum recorded in Reims.

Table 1  
Experimental conditions for the FTS spectra recorded in this work

Spectrum	Spectral range ( $\text{cm}^{-1}$ )	Total pressure (hPa)	Relative concentration $\text{D}_2\text{O}/\text{HDO}/\text{H}_2\text{O}$ (%)	$T$ (K)	Nbr of scans
<b><math>\text{H}_2\text{O} + \text{D}_2\text{O}</math></b>					
A	8500–12000	2.6	56/21/23	293	$6 \times 128$
B	8500–12000	13.3	74/23/3	293	$6 \times 128$
C	8500–12000	13.2	34/50/16	291	$6 \times 128$
<b>Pure <math>\text{H}_2\text{O}</math></b>					
D	8500–12000	18.2	0/0/100	291	$6 \times 128$

Note. The path length and resolution for all the spectra were  $602.32 \text{ m}$  and  $0.03 \text{ cm}^{-1}$ , respectively.

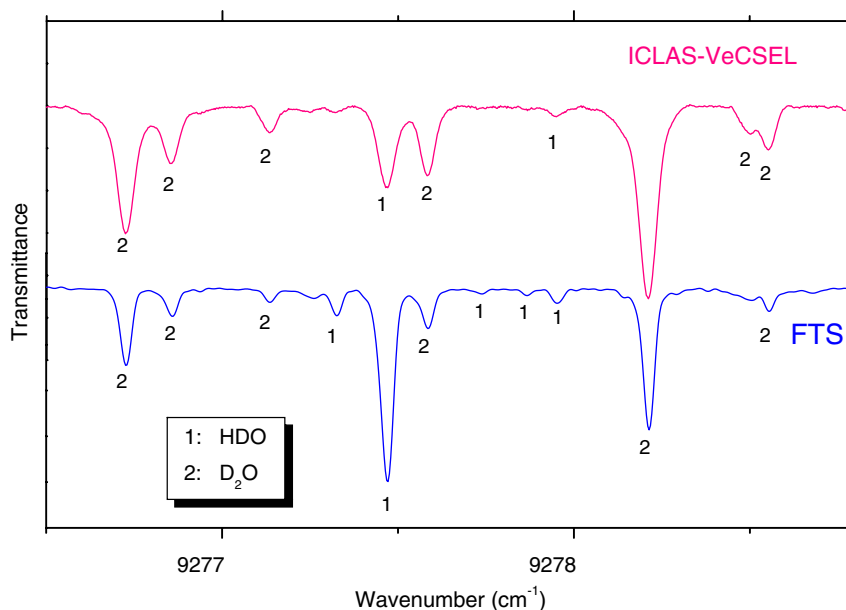


Fig. 2. Comparison of the FTS and the ICLAS-VeCSEL spectra. The experimental conditions (path length, total pressure and sample composition) were the following: FTS (spectrum B): 602.3 m, 13.3 hPa, D<sub>2</sub>O/HDO/H<sub>2</sub>O = 74/23/3 ICLAS: 20.7 km, 23.6 hPa, D<sub>2</sub>O/HDO/H<sub>2</sub>O ≈ 93.7/6.0/0.3.

### 2.3. Line list construction

The D<sub>2</sub>O lines were discriminated among the HDO and H<sub>2</sub>O lines by using the procedure illustrated in Fig. 2 or using the available H<sub>2</sub>O [9,18] and HDO [6] line lists. The D<sub>2</sub>O line list between 8800 and 9520 cm<sup>-1</sup> region was obtained by combining the FTS and ICLAS data in the 9095–9510 cm<sup>-1</sup> region where the two spectra are available. In this common region, the line positions were found to agree with a 0.004 cm<sup>-1</sup> rms deviation. The accuracy of the FTS intensities, mainly limited by the uncertainty on the D<sub>2</sub>O concentration in the FTS sample is estimated to 10 % for the lines which are not among the weakest. On the other hand, the specific laser dynamics of VeCSELS prevents their use for accurate quantitative measurements by ICLAS-VeCSEL (see Refs. [6,19] for more details about this issue). We then adopted the FTS line intensities for strong and middle intensity lines, which led to a set of 625 FT lines which was gathered with 213, mostly weak, lines measured by ICLAS. As the relative concentration of D<sub>2</sub>O compared to H<sub>2</sub>O was about 15 times higher in the ICLAS sample compared to the FTS sample with higher D<sub>2</sub>O relative concentration (spectrum B), some of the relatively strong lines were also retrieved from the ICLAS spectrum in the case of unrecoverable overlapping with strong H<sub>2</sub>O lines. Absolute intensities of the ICLAS lines were estimated from their peak absorption and scaled on the FT absolute intensities of the nearby lines. The accuracy of these ICLAS intensities is poorer and estimated to 30–50% on average.

The weakest lines which have been detected have an intensity value on the order of  $5 \times 10^{-27}$  cm/molecule both for FTS and ICLAS.

## 3. Rovibrational assignment and discussion

### 3.1. Line assignment

In the assignment process of the resulting set of 1223 D<sub>2</sub>O lines, we used the synthetic line list based on D<sub>2</sub>O potential energy surface (PES) [20] and Schwenke and Partridge *ab initio* dipole moment surface (DMS) [21]. The D<sub>2</sub>O PES was optimized by the fitting to 720 experimental energy levels with the rotational quantum number  $J=0, 2, 5,$  and  $10$ . These levels lie up to 13000 cm<sup>-1</sup> above the ground state. Morphing the original *ab initio* potential energy surface [22] using 25 constants reproduced the levels used in the fit with a standard deviation of 0.033 cm<sup>-1</sup>. This fit was presently used to generate a line list of all D<sub>2</sub>O transitions up to 11000 cm<sup>-1</sup> and  $J \leq 17$ . The DVR3D program suite [23] was used with 21 radial grid points for Morse oscillator-like basis functions and 40 angular grid points based on (associated) Legendre polynomials. A final Hamiltonian matrix of dimension 1500 was used for the vibrational calculations and  $300 * (J + 1 - p)$  for the rotational calculations, where the parity  $p=0$  or  $1$ . The masses were set at  $M_D = 2.013553$  u and  $M_O = 15.990526$  u.

In the last years, this assignment procedure based on the comparison of the observed and calculated line parameters has proven to be the most efficient for assigning the water isotopologues spectra. It takes also into account for the regular and smooth tendencies in the deviations of the observed levels from their calculated values. Though the (obs. – calc.) values may reach up to several cm<sup>-1</sup>, which leads to tens experimental lines as possible candidates for the considered assignment, the existence of evident

(obs. – calc.) tendencies combined with intensity matching still provides reliable assignments.

The deviations for all observed rotational quantum numbers (up to  $J=17$ ) were found to vary from  $0.01$  to  $0.40\text{ cm}^{-1}$ . We compared our synthetic spectrum [20,21] with that of Partridge and Schwenke [21,24] (PS), which can also be used for  $\text{D}_2\text{O}$  assignment (see, for example, [25,26]). As stated in [25] for low lying vibrational states, the (obs. – calc.) deviations for SP calculation may increase up to  $1.2\text{ cm}^{-1}$  but preserve their regular dependence on  $J$  and  $K_a$  quantum numbers up to  $J$ ,  $K_a$  values around 30 thus providing reliable criteria for assignment of the hot  $\text{D}_2\text{O}$  spectra. However, it is not the case for the spectral region under interest: the (obs. – calc.) deviations for PS calculations lose their regularity and increase much starting at  $J=10$ , (see Fig. 3), reaching  $-1.53\text{ cm}^{-1}$

for  $J=16$ . Interestingly, PS HDO synthetic spectrum is much better in the same spectral region, (obs. – calc.) values not exceeding  $0.05\text{ cm}^{-1}$  on average [6]. The reason for the poor accuracy of the PS calculations for  $\text{D}_2\text{O}$  may be caused by the fact that, contrary to HDO, the PES of  $\text{D}_2\text{O}$  [24] was not optimized by a fitting to the experimental line positions. In contrast with PS calculations, the presently used  $\text{D}_2\text{O}$  PES which was obtained in Ref. [20], shows though rather large, but regular (obs. – calc.) deviations up to  $J=17$ .

For assignment purpose, the intensity and line position matching between theory and experiment are both important. Figs. 4 and 5 illustrate the very satisfactory agreement between the experimental and calculated stick spectra, respectively, in the whole investigated spectral region and in a small interval. The calculated intensities are, on aver-

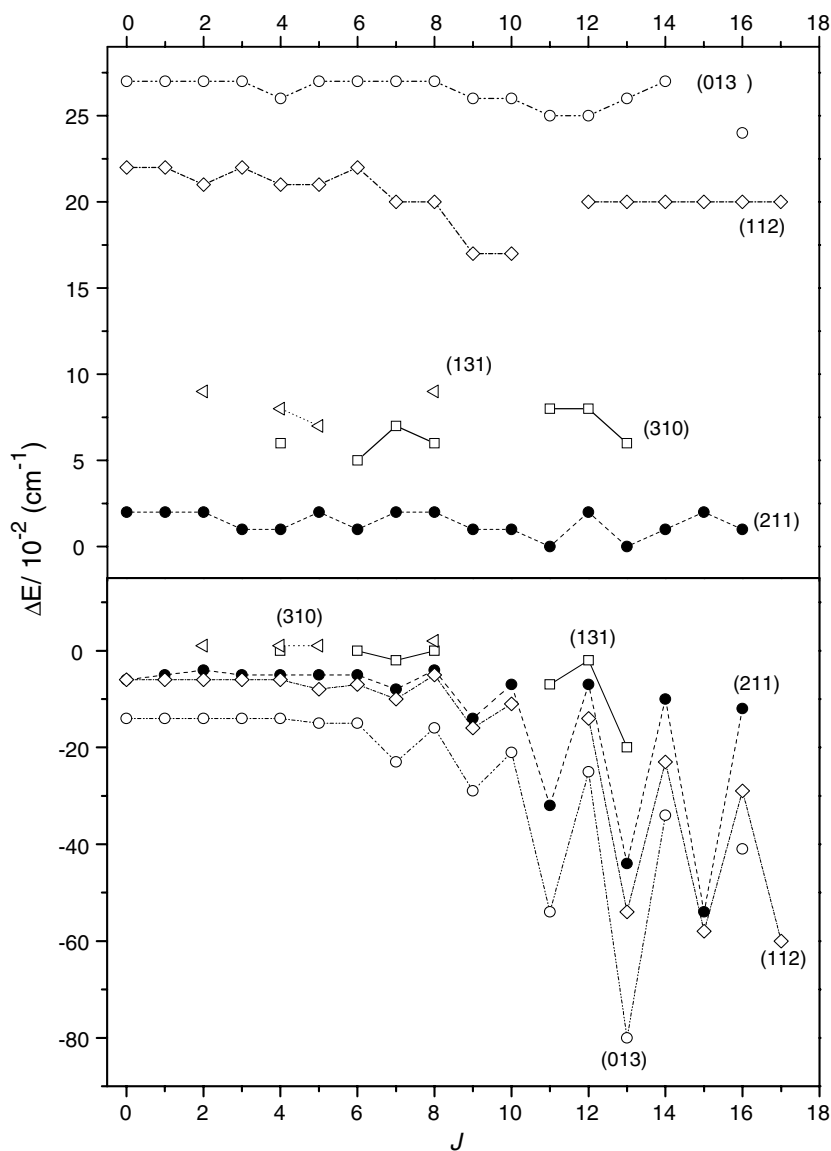


Fig. 3. Plot of the variation of the  $(E_{\text{obs.}} - E_{\text{calc.}})$  differences for the  $[J0J]$  rotational term values of the analyzed vibrational states. Note the change in the ordinate scale. Upper panel: rotational term values obtained from the  $\text{D}_2\text{O}$  optimized potential energy surface of Ref. [20]. Lower panel: calculated values from Schwenke and Partridge [24].

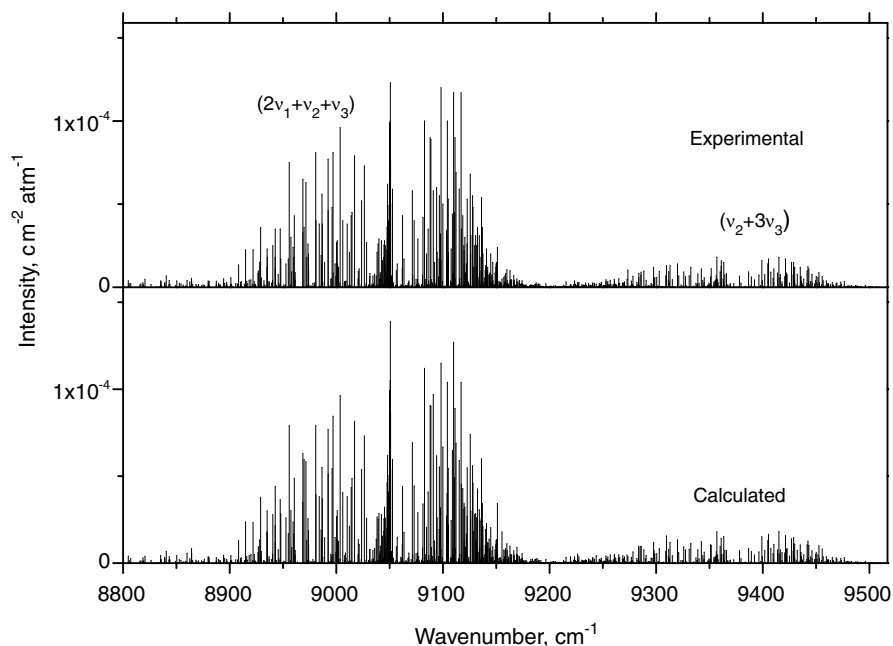


Fig. 4. Comparison of the D<sub>2</sub>O stick spectrum between 8800 and 9500 cm<sup>-1</sup>: upper panel, combined spectrum obtained from FTS and ICLAS recordings (see text); lower panel: synthetic spectrum calculated from the D<sub>2</sub>O optimized potential energy surface of Ref. [20] and SP ab initio dipole moment surface [21].

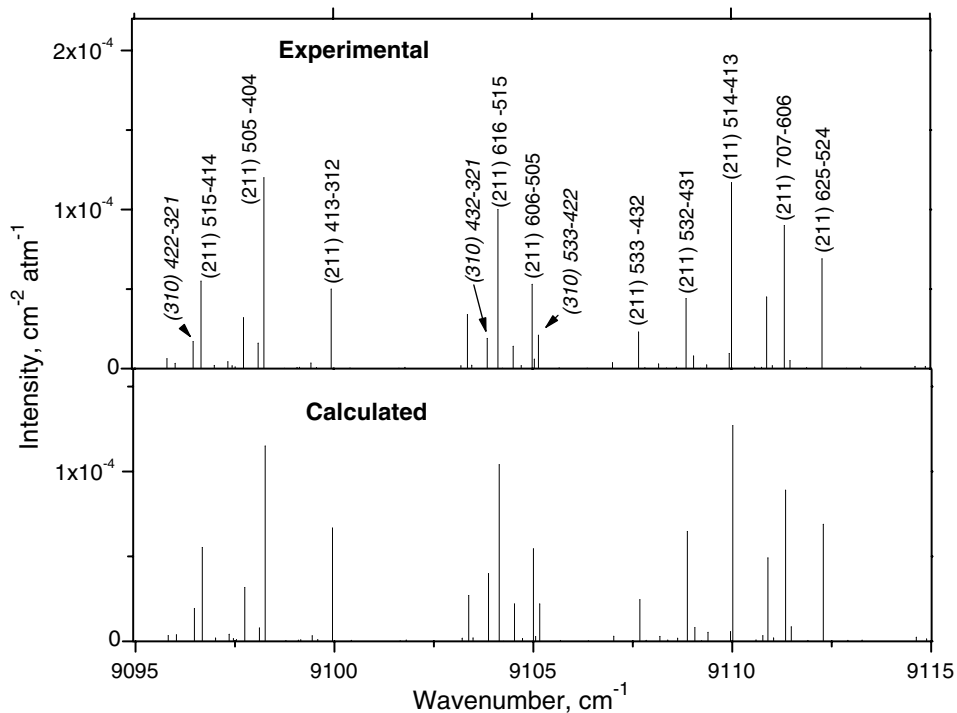


Fig. 5. Same as Fig. 3 for a small spectral section around 9105 cm<sup>-1</sup>. The  $(v'_1, v'_2, v'_3)J'K'_aK'_c - J''K''_aK''_c$  rotational assignments are given for part of the lines. The spectrum is dominated by transitions of the  $2v_1 + v_2 + v_3$  band. A few transitions of the  $3v_1 + v_2$  band are also indicated, the whole assignments being listed in the [Supplementary Material](#).

age, strongly dependent on the DMS used, and in much lesser extent on the rovibrational wave functions provided by the PES. Consequently, both sets of calculated intensities considered here coincide very well.

Nearly all (98%) experimental lines attributed to D<sub>2</sub>O were assigned. The resulting D<sub>2</sub>O line list counting 1430 lines (taking into account unresolved blends) is attached to this paper as [Supplementary Material](#). This list contains

observed positions, observed and calculated [20,21] intensities followed by their rovibrational assignment.

### 3.2. Energy levels

A summary of the quantitative information obtained in this study is given in Table 2. An important set of 687 accurate energy levels belonging to eight vibrational states listed in Table 2 was derived by adding the ground state experimental rotational energies [26] to the observed transitions. They are listed in Tables 3 and 4. Only separate energy levels were derived for the (032), (230), and (221) states. For the other five states, the number of energy levels is comparable or significantly exceeds that of the main isotopologue, H<sub>2</sub><sup>16</sup>O. The band origins for the (131) and (310) states were extrapolated from the (obs. – calc.) tendency for the [*J*0*J*] levels (see Fig. 3). That of the (221) state, presently observed through a hot band, was derived from (221)–(000) transitions assigned in the FTS spectrum between 10000 and 10485 cm<sup>−1</sup> spectral region.

In our strivings to produce as complete identification of the spectrum as possible, we admit a definite risk of less reliable assignment. The few less reliable assignments as well as the energy levels derived from them are marked as “T” (tentative) in Tables 3 and 4 and in the Supplementary Material. Tentative assignments (16 in total) concern, first of all, single weak lines not included into combination difference relations. They may either significantly deviate from the (obs. – calc.) tendency or from the calculated intensity, or they represent additional assignments to already identified transition. Finally, part of the energy levels is derived from blended lines and has poorer accuracy. These levels are marked by “B” in Tables 3 and 4.

Very weak transitions of the (230)–(000) and (032)–(000) bands seem to borrow their intensities from stronger line-partners belonging to the (310)–(000), (211)–(000) and (131)–(000) bands. In particular, a close resonance with the (211) *K<sub>a</sub>* = 3 energy levels yielded a long sequence of experimentally observed transitions involving the (032) *K<sub>a</sub>* = 4 upper levels with *J* varying from 4 to 9.

No interpolyad interactions were traced for the 2nd decade of D<sub>2</sub>O, indicating that the centrifugal distortion effect in this molecule is weaker than that for other isotopologues like H<sub>2</sub><sup>16</sup>O, HDO, H<sub>2</sub><sup>17</sup>O, H<sub>2</sub><sup>18</sup>O [27]. However, a number of the (010) energy levels of D<sub>2</sub>O with *J* > 23 is perturbed by accidental resonances with higher vibrational states [26].

We included in Table 2 a comparison of the energy levels set presently derived with that of Ref. [2] where a total of 110 levels belonging to the (211), (310), and (032) vibrational states were determined. 103 levels coincide with ours within 0.0021 cm<sup>−1</sup> while 7 outliers deviate from 0.009 up to 0.034 cm<sup>−1</sup>. Consequently, the number of newly derived energy levels is 577. The spectrum assignment in [2] was based on the Effective Hamiltonian (EH) approach; seven vibrational states were involved into a simultaneous fit, six of them being, in fact, dark levels. The band origins evaluated in [2] from the energy levels fitting are reproduced in Table 2. Band centers for all dark states excluding (310) deviate from our precise experimental or predicted [20] values by as much as 12.3 cm<sup>−1</sup>. This situation illustrates one of the most serious drawbacks of the EH method: a poor predictive ability despite the high quality of the fitting.

Despite recent advances in the analysis of the D<sub>2</sub>O line positions (see, for example, Refs. [2,4,25,26,28]), much less is known about the D<sub>2</sub>O transition intensities. We include in Table 2, the experimental integrated band intensities obtained as the sum of the intensities of all transitions assigned to a given band. (In case of a blended line, the line intensity was attributed to the vibrational level with the dominant contribution). As seen from Table 2, as well as from Fig. 4, the 2*v*<sub>1</sub> + *v*<sub>2</sub> + *v*<sub>3</sub> band, dominating the 8800–9200 cm<sup>−1</sup> region, is about seven times stronger than the *v*<sub>2</sub> + 3*v*<sub>3</sub> band dominating the 9200–9500 cm<sup>−1</sup> region.

## 4. Conclusion

High resolution Fourier Transform and ICLAS-VeC-SEL spectra of D<sub>2</sub>O molecule in the 8800–9520 cm<sup>−1</sup>

Table 2

Summary of the information obtained from the ICLAS and FT spectra of D<sub>2</sub>O recorded between 8800 and 9500 cm<sup>−1</sup>

Band	Upper state vibrational term value <sup>a</sup> (cm <sup>−1</sup> )			Band intensity (cm/molecule)	<i>J</i> <sub>max</sub>	<i>K<sub>a</sub></i> <sub>max</sub>	<i>N</i> levels
	Calc. Ref. [20]	Observed	Ref. [2]				
(230)–(000)	8712.00		8713.31	6.9E–25	10	6	11
(131)–(000)	8792.55	8792.63 <sup>b</sup>	8788.60	5.5E–24	13	9	81
(032)–(000)	8946.90		8934.60	8.2E–25	9 [7]	5 [4]	14 [1]
(310)–(000)	9005.45	9005.50 <sup>b</sup>	9005.35	1.6E–23	14 [7]	8 [3]	102 [10]
(211)–(000)	9050.34	9050.349	9050.36	2.7E–22	16 [13]	9 [6]	175 [99]
(112)–(000)	9202.50	9202.716	9201.90	1.4E–23	17	9	139
(013)–(000)	9366.04	9366.313	9365.45	4.0E–23	16	9	157
(221)–(010)	10180.04	10180.116		1.8E–25	7	2	8
Total							687 [110]

The values given in brackets in the last three columns correspond to the results of Ref. [2].

<sup>a</sup> Rovibrational term value of the [*J*, *K<sub>a</sub>*, *K<sub>c</sub>*] = [000] rotational level.

<sup>b</sup> Extrapolated value (see text).

Table 3  
 Rovibrational term values ( $\text{cm}^{-1}$ ) of the (211), (013), (112), and (310) vibrational states of  $\text{D}_2\text{O}$

$J$	$K_a$	$K_c$	$E_{\text{obs}}$	$\sigma$	$N$	$E_{\text{obs}}$	$\sigma$	$N$	$E_{\text{obs}}$	$\sigma$	$N$	$E_{\text{obs}}$	$\sigma$	$N$
			(211)			(013)			(112)			(310)		
0	0	0	9050.3491		1	9366.3131		1	9202.7161		1			
1	0	1	9062.1269	0.1	2	9378.2183	0.9	3	9214.5253	0.4	2			
1	1	1	9070.4485	0.1	2	9385.8134	0.1	2	9222.6108	0.7	3			
1	1	0	9073.0026	0.1	2	9388.4329		1	9225.1880	4.2	2			
2	0	2	9085.1652	0.4	2	9401.4525	0.7	2	9237.6197	0.9	3			
2	1	2	9091.6001	0.3	3	9407.0114	0.5	3	9243.6639		1	9046.7648		1
2	1	1	9099.1830	0.1	3	9414.8626	0.1	2	9251.3841	0.5	2			
2	2	1	9123.9822	0.2	2	9437.5497	0.2	2	9275.5375	0.6	3			
2	2	0	9124.4854	0.5	2	9438.1178		1	9276.0602	0.1	3	9080.6049		1
3	0	3	9118.5536	0.1	2	9435.0281	0.1	2	9271.0653	0.9	3			
3	1	3	9123.3248	0.2	3	9438.4713	0.1	2	9274.9322	0.1	2	9077.8118		1
3	1	2	9138.0084	0.1	3	9454.0691	0.1	2	9290.2815	0.3	3			
3	2	2	9158.2296	0.1	4	9473.2958	0.1	3	9310.9979	0.5	3	9115.1924		1
3	2	1	9160.2255	0.3	3	9475.9695	0.1	3	9313.4759	2.5	2	9116.8798	0.4	3
3	3	1	9207.0890	0.1	2	9517.6213		1	9357.6145	0.1	2	9166.2796	0.2	3
3	3	0	9207.1534	0.1	2	9517.6986		1	9357.6846		1	9165.9343	0.1	2
4	0	4	9161.3976	0.8	3	9478.0494	0.1	2	9313.9844		1	9116.2677		1
4	1	4	9162.5168	0.1	3	9479.8975	0.1	3	9316.1233	1.5	2			
4	1	3	9188.9211	0.7	3	9505.4402	0.1	3	9341.3245	0.4	3			
4	2	3	9204.1342	0.3	3	9520.4683	0.1	2	9357.8349		1	9161.5286		1
4	2	2	9208.7318	0.1	2	9527.6437	0.2	3	9364.5408	0.8	2	9169.0727	0.2	2
4	3	2	9254.3510	0.1	3	9566.2800	0.5	3	9405.8246	2.8	2	9216.1242	0.3	3
4	3	1	9254.7773	0.3	3	9566.8169	1.5	2	9406.2818	0.6	3	9214.5633	3.3	3
4	4	1	9320.0584	1.2	2	9626.3267	2.1	2	9469.1468		1	9280.5139		1
4	4	0	9320.0564 B		1	9626.3302	7.1	2	9469.1504	1.1	2	9280.5034	1.2	2
5	0	5	9213.2453	0.1	2	9530.1276	1.8	3	9365.9420		1	9168.0988		1
5	1	5	9213.9897	0.1	3	9531.1261	0.8	2	9366.9997		1	9169.3919		1
5	1	4	9251.0985	0.2	2	9568.0513	0.1	2	9403.6777	1.0	2			
5	2	4	9261.4860	0.1	3	9578.6786	0.2	2	9415.6891	2.0	2	9218.8874	0.8	3
5	2	3	9279.4461	0.1	2	9593.0575	0.1	2	9429.2720		1	9232.1989		1
5	3	3	9313.5642	0.3	3	9627.1156	0.3	2	9466.1194	1.2	4	9269.3378	0.2	3
5	3	2	9315.1482	0.2	3	9629.1143	0.6	3	9467.8545	1.6	3	9275.4248	1.6	3
5	4	2	9379.3316	0.1	4	9687.3800	0.5	2	9529.5947	2.2	3	9340.8330	1.2	2
5	4	1	9379.4193	0.1	2	9687.4597	0.4	2	9529.5547		1	9340.8207		1
5	5	1	9462.3966		1	9763.2043	2.9	2	9609.6508	0.3	3	9425.9828		1
5	5	0	9462.3961		1	9763.2068	0.1	2	9609.6534		1	9425.9771		1
6	0	6	9274.0410	0.4	3	9591.2429	0.4	2	9426.9151		1	9228.8518		1
6	1	6	9274.3852	0.3	3	9591.6053	1.1	2	9427.3554		1	9229.4717		1
6	1	5	9323.5122	0.2	2	9640.7975	0.5	3	9476.2870	0.1	2	9277.8120		1
6	2	5	9329.8748	0.7	4	9647.5028	0.1	4	9484.1648	0.1	2	9286.8947	1.1	2
6	2	4	9356.1734	0.2	3	9671.5560	0.1	2	9507.1199	1.5	2	9309.0126		1
6	3	4	9384.6231	1.0	3	9699.9032	0.2	3	9538.3289	0.4	2	9341.4772	0.9	3
6	3	3	9388.8519	0.9	2	9705.2442	0.3	3	9543.0208	1.5	3	9349.1594	0.1	2
6	4	3	9450.6924	0.2	2	9760.8272	0.1	3	9602.6223	0.5	2	9413.5424		1
6	4	2	9451.0380	0.2	3	9761.2088	0.9	2	9602.9687	0.5	3	9413.5054	0.1	2
6	5	2	9533.5363	0.5	2	9836.6913	3.6	2	9682.4428		1	9498.5718		1
6	5	1	9533.5300	0.4	2	9836.6989	3.4	2	9682.4130	0.2	2	9498.5765		1
6	6	1	9633.3519		1	9927.5318	0.2	2	9778.3592	2.9	2	9597.9416		1
6	6	0	9633.3518		1	9927.5320	0.1	2	9778.3617	0.1	2	9597.9411		1
7	0	7	9343.8657	2.4	2	9661.4995	0.1	2	9496.3264	2.4	2	9298.5873	1.0	2
7	1	7	9344.0033		1	9661.6055		1	9497.0793		1	9298.8670		1
7	1	6	9405.2075	0.3	5	9722.7787	0.2	2	9558.2255	0.4	2			
7	2	6	9408.7053	0.3	3	9726.5272	1.2	2	9562.8797	1.7	2	9365.1559	2.1	2
7	2	5	9445.4502	0.5	3	9761.9855	0.4	3	9597.2098		1			
7	3	5	9467.3258	0.1	3	9784.3029	0.6	3	9622.1383	1.2	2	9424.9222	1.8	3
7	3	4	9476.1174	0.3	3	9795.5788	0.1	3	9632.2133		1	9436.4818	0.1	2
7	4	4	9534.1445	0.4	2	9846.6435	0.6	3	9688.0755	1.2	2	9497.9309	0.1	2
7	4	3	9535.2527	0.3	2	9847.9366	1.6	2	9689.0735	2.1	2	9499.1891	2.3	2
7	5	3	9616.8332		1	9922.5705	0.6	2	9767.6405	0.1	3	9583.5619 B		1
7	5	2	9616.7882	0.1	2	9922.6295	1.0	3	9767.3439		1			
7	6	2	9716.2008	0.1	2	10013.7992	0.8	3	9863.8034		1	9681.6444		1

Note: "B" and "T" denotes an energy level derived from a blended line and with tentative assignment, respectively (see text).



Table 3 (continued)

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E<sub>obs</sub></i>	$\sigma$	<i>N</i>	<i>E<sub>obs</sub></i>	$\sigma$	<i>N</i>	<i>E<sub>obs</sub></i>	$\sigma$	<i>N</i>	<i>E<sub>obs</sub></i>	$\sigma$	<i>N</i>
			(211)			(013)			(112)			(310)		
7	6	1	9716.2006	0.1	2	10013.7993	0.7	2	9863.8029		1			
7	7	1	9832.0890		1	10118.4636		1	9974.3863	1.2	2	9801.3239		1
7	7	0	9832.0896		1	10118.4637		1	9974.3864	1.4	2	9801.3238		1
8	0	8	9422.7354	0.1	2	9741.0051	0.3	2	9576.0025	0.4	2	9377.3749	1.1	2
8	1	8	9422.8304		1	9740.9440	0.2	2	9576.1511	0.7	2	9377.4965		1
8	1	7	9495.6623	0.2	2	9813.6350		1	9649.0638	3.5	2	9450.2332	2.0	2
8	2	7	9497.4044	0.1	2	9815.4151	1.2	3	9651.5067		1	9453.3218	1.0	2
8	2	6	9546.0868	0.7	2	9861.9395	1.6	3	9698.3389		1			
8	3	6	9561.3073	0.6	4	9879.8800	1.0	3	9717.1099	2.7	2			
8	3	5	9577.6590	0.5	2	9899.8743		1	9735.3275		1	9537.7266		1
8	4	5	9629.5719	0.2	3	9944.7026 B		1	9785.6992		1	9595.3181		1
8	4	4	9632.5266	1.5	2	9948.1522		1	9788.1512	0.1	2	9595.4145		1
8	5	4	9712.4989	0.1	3	10020.8560		1	9866.5187	0.1	2	9675.0124		1
8	5	3	9712.3182	0.9	2	10021.0917	0.4	2	9864.5083	0.1	2	9675.2442		1
8	6	3	9811.1374	0.5	2	10112.4398	0.1	2	9961.2333 B	5.8	2			
8	6	2	9811.1372		1	10112.4378	2.1	2	9961.2034	1.6	2	9777.7965		1
8	7	2	9926.4057	0.2	2	10218.7196		1	10074.2845	4.2	2	9898.0059		1
8	7	1	9926.4055	0.2	2	10218.7193		1	10074.2866	2.0	2	9898.0055		1
8	8	1	10056.8914		1	10335.1032		1	10196.2738		1			
8	8	0	10056.8915		1	10335.1033		1	10196.2741		1			
9	0	9	9510.7961	0.7	2	9830.3993		1	9662.4071	0.8	4	9465.2445		1
9	1	9	9510.8264		1	9829.7153		1	9665.2776	0.7	2	9465.2930		1
9	1	8	9594.8078	0.3	2	9913.5461	1.0	2	9749.0735	2.9	2			
9	2	8	9595.6180	0.1	2	9913.9233	0.2	2	9749.8323		1	9551.0989		1
9	2	7	9656.1392		1	9978.2694		1	9809.0222		1			
9	3	7	9668.5840	0.1	2	9986.1738	0.1	2	9822.2300	2.4	4	9624.6888	2.8	2
9	3	6	9690.4669	0.7	3	10017.3094	0.2	2	9851.6868		1	9652.5353		1
9	4	6	9736.4897	0.9	2	10054.7249		1	9895.0698	2.8	4	9707.2929	0.2	2
9	4	5	9743.3842	0.3	3	10062.4006	0.8	2	9901.1331	0.6	2	9707.4509		1
9	5	5	9820.7478	0.1	2	10131.5143		1	9971.0345	2.6	3	9784.3961		1
9	5	4	9820.2921	0.5	2	10132.2593	0.5	3	9974.0199		1	9784.9530		1
9	6	4	9918.2480	1.4	2	10223.4185	0.1	2	10070.6824	0.1	2			
9	6	3	9918.2114	0.4	2	10223.4529		1	10070.6292	1.2	2			
9	7	3	10032.8708	0.5	2	10332.1106		1	10184.7204	3.8	2	10006.8093		1
9	7	2	10032.8707	0.9	2	10332.1109		1	10184.7304	5.8	2	10006.8051		1
9	8	2	10162.0657	0.4	2	10438.5545		1	10299.8881		1			
9	8	1	10162.0654	0.2	2	10438.5541		1	10299.8885		1			
9	9	1	10319.8470		1	10576.5308 T		1						
9	9	0	10319.8470		1	10576.5308 T		1						
10	0	10	9607.9739		1	9926.3652	1.0	2	9761.0745	0.5	2			
10	1	10	9607.9890	4.3	2	9925.0682	0.2	3	9760.7071	1.5	3	9562.2482		1
10	1	9	9702.7539		1	10024.0376	0.6	2	9852.1616	0.6	2	9657.8962		1
10	2	9	9703.1783		1	10021.9675	0.7	2	9857.9699		1	9658.3011	11.0	2
10	2	8	9778.2810		1	10090.7803	0.4	2	9931.0272	0.3	2			
10	3	8	9783.5173	0.3	3	10102.7588	0.1	2	9940.4828	2.0	3	9740.2731	0.8	2
10	3	7	9831.0789		1	10146.6944	7.9	2	9980.2311		1	9780.0929		1
10	4	7	9860.8982	1.9	2	10176.3631	0.7	3	10014.8335	2.3	2	9814.0393		1
10	4	6	9868.1198		1	10190.9300	1.3	2	10027.7673	3.7	2			
10	5	6	9941.6670	0.3	2	10254.4255	1.6	2	10100.3412		1	9905.4452		1
10	5	5	9941.0064	0.3	3	10256.3869	1.6	2	10096.1233		1	9906.6481		1
10	6	5	10037.6247	0.7	2	10346.7080	0.2	2	10192.2891		1			
10	6	4	10037.5239	0.1	2	10346.8331		1	10192.0971	0.2	2	10006.5790		1
10	7	4	10151.4986		1							10127.7417		1
10	7	3	10151.5634		1							10127.7221		1
10	8	3	10279.8491		1	10556.5753		1	10417.1168		1			
10	8	2	10279.8492		1	10556.5748		1	10417.1190		1			
10	9	2	10441.3162 T		1				10579.6649 T		1			
10	9	1	10441.3140 T		1				10579.6645 T		1			
11	0	11	9714.2630 B		1	10033.5529	0.5	3				9668.2602		1
11	1	11	9714.2872 B		1	10033.5675	9.2	2	9868.3353		1	9668.2831		1
11	1	10	9819.6446	1.4	2	10133.5175		1				9774.1409		1
11	2	10	9819.7981	0.7	2	10139.9244		1	9978.2241	0.8	2	9774.7241		1
11	2	9	9906.7247	0.3	2	10220.5129	5.1	2						

(continued on next page)

Table 3 (continued)

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E<sub>obs</sub></i>	$\sigma$	<i>N</i>	<i>E<sub>obs</sub></i>	$\sigma$	<i>N</i>	<i>E<sub>obs</sub></i>	$\sigma$	<i>N</i>	<i>E<sub>obs</sub></i>	$\sigma$	<i>N</i>
			(2 1 1)			(0 1 3)			(1 1 2)			(3 1 0)		
11	3	9	9909.6860	0.4	2	10229.3137	1.4	2	10066.9301	0.3	2			
11	3	8	9965.0596		1	10287.0707	0.6	2						
11	4	8	9989.3828		1	10309.1801	0.3	2	10152.6441		1	9947.9060 B	9.7	2
11	4	7	10006.3260	1.0	2	10333.3999	1.6	2	10168.2125		1	9970.2381		1
11	5	7	10074.0624	0.6	2	10389.3402		1	10232.8107		1	10038.3314	2.7	2
11	5	6	10074.8535	0.6	3	10393.3823		1						
11	6	6	10169.3910	1.2	2				10326.1487	4.1	2	10139.0419		1
11	6	5	10169.1552	1.2	2	10482.6111 T		1						
11	7	5				10594.1603		1						
11	7	4	10282.1321		1	10594.1625		1						
11	8	4	10410.0137	1.2	2							10396.1731		1
11	8	3	10410.0132	0.9	2									
12	0	12	9829.9692		1	10149.8397	5.7	2	9983.3622		1	9783.4491		1
12	1	12	9828.9798		1	10149.8462	1.6	2	9982.9097		1			
12	1	11	9945.5708		1	10263.1687	1.2	2	10098.4040	0.5	3			
12	2	11	9945.7548	1.0	2	10261.1554		1	10097.5096 T		1	9900.1132		1
12	2	10	10043.8656	0.3	2	10359.0473		1						
12	3	10	10046.4020	0.2	2	10365.7124		1				10001.5253		1
12	3	9	10120.5471		1				10273.9478		1			
12	4	9				10452.7380		1						
12	4	8	10156.4390	0.7	2	10488.9450		1						
12	5	8	10217.9891		1	10535.8544		1				10182.2374		1
12	5	7	10222.2962		1	10546.2561		1						
12	6	7	10313.6307		1	10629.9348		1						
12	7	5	10425.1681		1							10406.1659		1
13	0	13	9954.0170		1	10275.1751		1	10107.6836	0.6	2	9907.8044		1
13	1	13	9954.0217		1	10275.1798		1	10107.6810	1.3	2			
13	1	12	10080.7793		1	10399.1967		1				10034.7933		1
13	2	12	10079.8562		1	10398.9075		1	10231.4854 T		1			
13	2	11	10189.6501	1.0	2	10505.9316		1						
13	3	11	10189.0473 B		1	10512.5587		1	10355.4614		1			
13	3	10	10277.6992		1	10594.4715		1						
13	4	10	10283.3145		1	10606.6861		1				10239.6800		1
13	4	9				10656.3424		1						
13	5	9										10323.7000 T		1
13	5	8	10383.6034		1									
13	6	7	10469.9740		1									
14	0	14	10087.6493		1	10409.6433 B		1	10241.5757		1	10040.7687		1
14	1	14	10087.6517		1	10409.6457 B		1	10241.5755		1			
14	1	13	10223.9922		1							10178.7675		1
14	2	13	10224.1543	4.4	2									
14	2	12	10344.3774		1									
14	3	12	10343.6529		1	10674.8984		1						
14	4	11	10446.2183		1	10770.9180		1						
14	5	10	10540.2599		1									
14	5	9	10558.6213		1									
14	6	9	10638.8918		1									
15	0	15	10230.6034		1				10384.5040		1			
15	1	15	10230.6040		1				10384.5034		1			
15	1	14	10377.1852		1	10697.8060		1						
15	2	14	10377.2306		1	10697.7710		1						
15	6	9	10822.3077 T		1									
16	0	16	10381.8417		1	10705.8909		1	10536.4783		1			
16	1	16	10381.8805		1	10705.8911		1	10536.4781		1			
16	1	15	10538.5269 T		1									
17	0	17							10697.4908		1			
17	1	17							10697.4916		1			

region has been assigned on the basis of high quality variational calculations. The combination of these two high sensitive absorption spectra recorded independently with different experimental conditions has allowed for the deter-

mination of a precise and extensive set of 577 new rotational energy levels belonging to eight vibrational states: (2 1 1), (0 1 3), (1 1 2), (3 1 0), (0 3 2), (2 3 0), and (1 3 1). Intensity measurements were also performed and integrated intensi-

Table 4  
Rovibrational term value ( $\text{cm}^{-1}$ ) of the (131), (230), (032), and (221) vibrational states of  $\text{D}_2\text{O}$ 

$J$	$K_a$	$K_c$	$E_{\text{obs}}$	$\sigma$	$N$
(131)					
2	0	2	8827.9372		1
2	1	2	8836.9636		1
2	2	1	8878.9672		1
2	2	0	8879.4227		1
3	1	3	8868.3267		1
3	1	2	8884.9717		1
3	2	2	8915.0652		1
3	2	1	8917.2036	1.1	2
3	3	0	8977.1352		1
4	0	4	8905.5603		1
4	1	4	8909.7296		1
4	2	3	8962.8056		1
4	2	2	8968.6423		1
4	3	2	9024.9379	0.3	2
4	3	1	9025.2562		1
4	4	1	9109.8641		1
4	4	0	9109.8584		1
5	0	5	8958.2323		1
5	1	5	8961.2281		1
5	1	4	9001.0199		1
5	2	4	9021.9902		1
5	2	3	9033.9278		1
5	3	2	9086.0735	1.5	2
5	4	2	9170.1807	2.1	2
5	4	1	9170.1886	0.1	2
5	5	1	9275.7547		1
5	5	0	9275.7542		1
6	1	6	9020.6032		1
6	1	5	9075.7559		1
6	2	4	9112.8062		1
6	3	4	9156.9311		1
6	3	3	9160.0166		1
6	4	3	9242.7916		1
6	5	2	9348.1171		1
6	5	1	9348.1114		1
7	0	7	9090.1588		1
7	1	7	9090.8145		1
7	1	6	9160.2931		1
7	2	6	9166.3766		1
7	2	5	9204.6181		1
7	3	4	9247.2419		1
7	4	3	9328.0398		1
7	5	3	9432.7100		1
7	5	2	9432.7157		1
7	7	1	9704.6349		1
7	7	0	9704.6350		1
8	0	8	9169.5456		1
8	1	8	9170.0739		1
8	1	7	9253.8065		1
8	2	6	9308.3723		1
8	3	6	9337.2220		1
8	4	5	9424.9408	0.9	2
8	5	4	9529.6289		1
8	6	3	9653.0110		1
8	6	2	9653.0114		1
8	7	2	9804.5583		1
8	7	1	9804.5580		1
8	8	1	9957.7204		1
8	8	0	9957.7205		1
9	2	7	9424.3487		1
9	3	7	9444.4840 T		1
9	3	6	9476.2658		1

Table 4 (continued)

$J$	$K_a$	$K_c$	$E_{\text{obs}}$	$\sigma$	$N$
9	4	5	9537.4163		1
9	5	4	9638.9859		1
9	6	4	9761.7077 B		1
9	6	3	9761.7119 B		1
9	9	1	10238.1021		1
9	9	0	10238.1021		1
10	1	10	9355.1398		1
10	2	9	9467.9698 T		1
10	2	8	9548.9390 T		1
10	3	8	9563.3843		1
10	5	6	9760.4473	0.5	2
10	9	2	10361.0684		1
10	9	1	10361.0693		1
11	6	6	10016.3832 T		1
11	6	5	10016.4522		1
12	2	10	9825.0200		1
12	3	10	9831.8894	0.8	2
12	5	8	10039.6922		1
13	6	7	10316.4475		1
(230)					
4	3	1	8949.7629		1
5	2	4	8941.6844		1
6	3	3	9082.8504		1
6	6	0	9412.9272 B		1
7	4	4	9260.9934		1
7	6	2	9498.8748		1
7	6	1	9498.1977		1
8	6	3	9596.6980		1
8	6	2	9596.7881		1
9	6	4	9705.3255		1
10	5	5	9697.6274	1.3	2
(032)					
4	4	1	9255.7542		1
4	4	0	9255.7593		1
5	4	2	9317.3158		1
5	5	1	9416.7155		1
5	5	0	9416.7098		1
6	4	3	9391.2887		1
7	4	4	9477.7838	0.7	2
7	5	3	9577.1621		1
7	5	2	9577.2365		1
8	4	5	9575.6110	0.1	2
8	5	4	9681.3446		1
8	5	3	9681.4500		1
9	4	6	9686.2850		1
9	5	4	9792.2592		1
(221)					
1	0	1	10191.9183		1
1	1	0	10204.0985		1
2	1	2	10222.6557		1
2	2	1	10258.7775		1
3	0	3	10248.4661		1
4	0	4	10291.3992		1
4	1	4	10293.6265		1
7	1	6	10538.9828		1

Note.  $N$  is the number of lines used for the upper energy level determination and  $\sigma$  denotes the corresponding experimental uncertainty in  $10^{-3} \text{ cm}^{-1}$  units. "B" denotes the energy level derived from blended line and then with an accuracy worse than the averaged one. Energy levels marked with "T" were derived from lines with tentative assignment (see text).

ties of the considered vibrational bands were estimated. The comparison of two variational calculations: Partridge and Schwenke (PES of Ref. [24] and DMS of Ref. [21]) and that obtained by combining the PES of Ref. [20] with the DMS of Ref. [21], has shown that the PS calculation starts to diverge at  $J \geq 10$ , leading to irregular (obs. – calc.) deviations as large as  $1.53 \text{ cm}^{-1}$ , while the new one shows regular and smooth (obs. – calc.) tendencies up to  $J = 17$ . However, these new calculations deviate from the experimental rovibrational term value by up to  $0.4 \text{ cm}^{-1}$ , which may in certain cases prevent performing unambiguous assignment. The experimental data derived in this paper by combining ICLAS-VeCSEL and FTS spectra will help to further refine both the PES and the DMS of the  $\text{D}_2\text{O}$  molecule.

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### Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect ([www.sciencedirect.com](http://www.sciencedirect.com)) and as part of the Ohio State University Molecular Spectroscopy Archives ([http://msa.lib.ohio-state.edu/jmsa\\_hp.htm](http://msa.lib.ohio-state.edu/jmsa_hp.htm)).

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