

Comparison between HITRAN2012 data and a new experimental line list for water vapor in the spectral region 6450 and 9400 cm^{-1}

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Summary

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Introduction

“Water vapor line parameters from 6450 and 9400 cm^{-1} ” recently published by Regalia et al. (2014)¹ proposes new experimental dataset of water vapor lines and includes essentially comparisons with HITRAN2008 ² and GEISA2009 ³ databases.

Aim of this presentation :

- give an additional comparison between the experimental data¹ versus the HITRAN 2012 ⁴ edition
- highlight the disagreements that remain in HITRAN 2012 database with other data sources

¹ Water vapor line parameters from 6450 to 9400 cm^{-1}

L. Régalia , C. Oudot, S. Mikhailenko, L. Wang, X. Thomas, A. Jenouvrier, P. Von der Heyden, J. Quant. Spectrosc. Radiat. Transfer, 136, 119-136 (2014)

² The HITRAN 2008 molecular spectroscopic database. L.S. Rothman et al. J Quant Spectrosc Radiat Transfer, 110, 533-572 (2009)

³ The 2009 edition of the GEISA spectroscopic database. N. Jacquinet-Husson, et al. J Quant Spectrosc Radiat Transfer, 112, 2395-2445 (2011)

⁴ The HITRAN2012 molecular spectroscopic database. L.S. Rothman, et al. J Quant Spectrosc Radiat Transfer, 130, 4-50 (2013)

New experimental line list

Journal of Quantitative Spectroscopy & Radiative Transfer 136 (2014) 119–136



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt



Water vapor line parameters from 6450 to 9400 cm⁻¹



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ARTICLE INFO

Article history:

Received 15 July 2013

Received in revised form

26 November 2013

Accepted 27 November 2013

Available online 5 December 2013

Keywords:

Water vapor

Line intensity measurements

FTS spectra

Infrared spectroscopy

ABSTRACT

The spectra of natural water vapor were recorded in the spectral range 6450–9400 cm⁻¹ with a step-by-step Fourier transform spectrometer at room temperature with absorption path lengths up to 1200 m. Positions, intensities and self-broadening coefficients of about 11,000 lines were determined. This paper focuses on the intensity parameters: the lines of four isotopologues H₂¹⁶O, H₂¹⁸O, H₂¹⁷O and HD¹⁶O were observed and assigned; it presents a new experimental dataset in the 6450–9400 cm⁻¹ spectral range. Obtained results were compared to the literature data. Fifty-nine new and corrected energy levels of H₂¹⁶O and H₂¹⁷O were determined from the vibration–rotation analysis of the observed lines. A brief discussion is added for self-broadening coefficients at the end of this paper.

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Hitran2012 new edition

(6450 -9400 cm^{-1})

This list includes three data types:

- experimental or variational calculated values for both line position and line intensity
- calculated line positions from “experimental” energy levels.

The HITRAN2012 list contains 47,154 transitions of four water isotopologues (H_2^{16}O , H_2^{18}O , H_2^{17}O , and HD^{16}O) in an intensity range of 9.96×10^{-30} to 1.86×10^{-20} cm/mol at 296K.

We pointed out that the data listed in HITRAN2012 line list can be separated into **16 groups** according to their origins, independent from the absorption bands .

No	LP Ref ^a	LI Ref ^b	ISO ^c	NT ^d	Range / cm ⁻¹	S _{max} ^e / cm/mol	S _{min} ^f / cm/mol
1	[5]	[5]	11	7	8011.4 – 8423.9	1.60×10 ⁻²⁵	3.80×10 ⁻²⁷
2	[6]	[6]	11	1	8581.043	9.14×10 ⁻²⁶	9.14×10 ⁻²⁶
3	[6]	[7]	11	14	8107.6 – 9074.0	9.04×10 ⁻²⁴	2.74×10 ⁻²⁶
4	[8]	[8]	11, 14	4594	6450.8 – 7971.9	1.86×10 ⁻²⁰	2.26×10 ⁻²⁷
5	[8]	[9]	11	67	6462.3 – 7880.8	8.55×10 ⁻²³	9.98×10 ⁻²⁷
6	[8]	[10]	12, 13	1695	6556.6 – 7681.8	3.53×10 ⁻²³	1.00×10 ⁻²⁶
7	[9]	[9]	11	1371	6467.9 – 9398.7	4.69×10 ⁻²⁵	9.99×10 ⁻³⁰
8	[11]	[9]	11	482	6510.9 – 9390.4	5.40×10 ⁻²⁴	1.00×10 ⁻²⁹
9	[12]	[5]	11	79	7974.7 – 8505.1	1.10×10 ⁻²⁵	3.63×10 ⁻²⁷
10	[12]	[6]	11	110	8186.0 – 9389.0	8.54×10 ⁻²⁴	1.44×10 ⁻²⁶
11	[12]	[8]	11	164	6475.0 – 7973.1	2.22×10 ⁻²⁴	4.84×10 ⁻²⁷
12	[12]	[9]	11	20632	6450.0 – 9399.8	2.27×10 ⁻²¹	9.98×10 ⁻³⁰
13	[12]	[7]	11	1546	8057.8 – 9329.0	1.43×10 ⁻²¹	1.02×10 ⁻²⁶
14	[10]	[10]	13	6842	6451.4 – 9393.7	8.42×10 ⁻²⁵	1.00×10 ⁻²⁹
15	[13]	[10]	12	8341	6450.7 – 9394.5	4.54×10 ⁻²⁴	9.97×10 ⁻³⁰
16	[10]	[10]	12	1209	6574.9 – 9396.7	7.72×10 ⁻²⁷	9.96×10 ⁻³⁰
Totally				47154	6450.0 – 9399.8	1.86×10 ⁻²⁰	9.96×10 ⁻³⁰

Table 1

Legend

^a Line Position reference

^b Line Intensity reference

^c Isotopologue: 11 – H₂¹⁶O, 12 – H₂¹⁸O, 13 – H₂¹⁷O, 14 – HD¹⁶O

^d Number of transitions

^e Maximal intensity value

^f Minimal intensity value

16 groups

References

- The HITRAN Molecular Database: 1986 Edition L.S. Rothman, R.R. Gamache, A. Goldman, L.R. Brown, R.A. Toth, H.M. Pickett, R.L. Poynter, J.-M. Flaud, C. Camy-Peyret, A. Barbe, N.Husson, C.P. Rinsland, M.A.H. Smith, Applied Optics, 26, 4058-4097 (1987)
- H₂¹⁶O: line positions and intensities between 8000 and 9500 cm⁻¹: the second hexad of interacting vibrational states: {(050), (130), (031), (210), (111), (012)} J.-Y. Mandin, J.-P. Chevillard, J.-M. Flaud, C. Camy-Peyret, Can. J. Phys. 66, 997-1011 (1988)
- Intensity measurements of H₂¹⁶O lines in the spectral region 8000 – 9350 cm⁻¹ C. Oudot, Le Wang, X. Thomas, P. Von der Heyden, L. Daumont, L. Régalia, J. Mol. Spectrosc. 262, 22-29 (2010)
- Linelist of water vapor parameters from 500 to 8000 cm⁻¹, R.A. Toth; <http://mark4sun.jpl.nasa.gov/h2o.html>
- A high-accuracy computed water line list R.J. Barber, J. Tennyson, G.J. Harris, R.N. Tolchenov, Mon. Not. R. Astron. Soc. 368, 1087-1094 (2006)
- Line lists for H₂¹⁸O and H₂¹⁷O based on empirical line positions and ab initio intensities. L. Lodi, J. Tennyson J. Quant. Spectrosc. Radiat. Transfer, 113, 850-858 (2012)
- Private communication I.E. Gordon, Harvard-Smithsonian Center for Astrophysics (CFA), Cambridge, MA, USA (2008)
- IUPAC critical evaluation of the rotational-vibrational spectra of water vapor, Part III: Energy levels and transition wavenumbers for H₂¹⁶O. J. Tennyson, et al. J. Quant. Spectrosc. Radiat. Transfer, 117, 29-58 (2013)
- IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part I – Energy levels and transition wavenumbers for H₂¹⁷O and H₂¹⁸O. J. Tennyson, et al. J. Quant. Spectrosc. Radiat. Transfer, 110, 573-596 (2009)

Examples of disagreements between experimental or theoretical data and the HITRAN2012 edition

Group No. 1

7 H_2^{16}O transitions between 8011.4 and 8423.9 cm^{-1} :
both positions and intensities come from the **HITRAN1986** edition⁵.

All of them are in great disagreement with the observations.

⁵ The HITRAN Molecular Database: 1986 Edition

L.S. Rothman et al.

Applied Optics, 26, 4058-4097 (1987)

Comparison of line positions and line intensities from Ref. [1] (Régalia, et al. JQSRT 2014) and Ref. [5] (HITRAN1986 edition):

ν Ref. [1]	S Ref. [1]	ν Ref. [5]	S Ref. [5]	$d\nu$	R
8012.2186	6.68E-26	002 12 3 10 000 11 0 11	8011.4150 1.60E-25	.8026	.418
8180.3383	9.04E-27	041 4 2 3 010 5 2 4	8180.1400 3.80E-27	.1983	2.379
8360.2873	3.18E-26	041 6 0 6 010 5 0 5	8360.3900 3.00E-26	-.1027	1.060
8376.3210	7.42E-27	041 7 0 7 010 6 0 6	8376.5400 7.63E-27	-.2190	.972
8390.6973	1.41E-26	041 4 2 3 010 3 2 2	8390.5000 7.39E-27	.1973	1.908
8411.7103	1.97E-26	041 6 1 5 010 5 1 4	8411.6100 1.90E-26	.1003	1.037
8423.0064	9.97E-27	041 5 2 3 010 4 2 2	8423.8800 7.50E-27	-.8736	1.329

Table 2

$$d\nu = \nu^{\text{Ref. [1]}} - \nu^{\text{Ref. [5]}}, \text{ cm}^{-1}$$

$$R = S^{\text{Ref. [1]}} / S^{\text{Ref. [5]}}, S \text{ in cm/mol (T = 296K)}$$

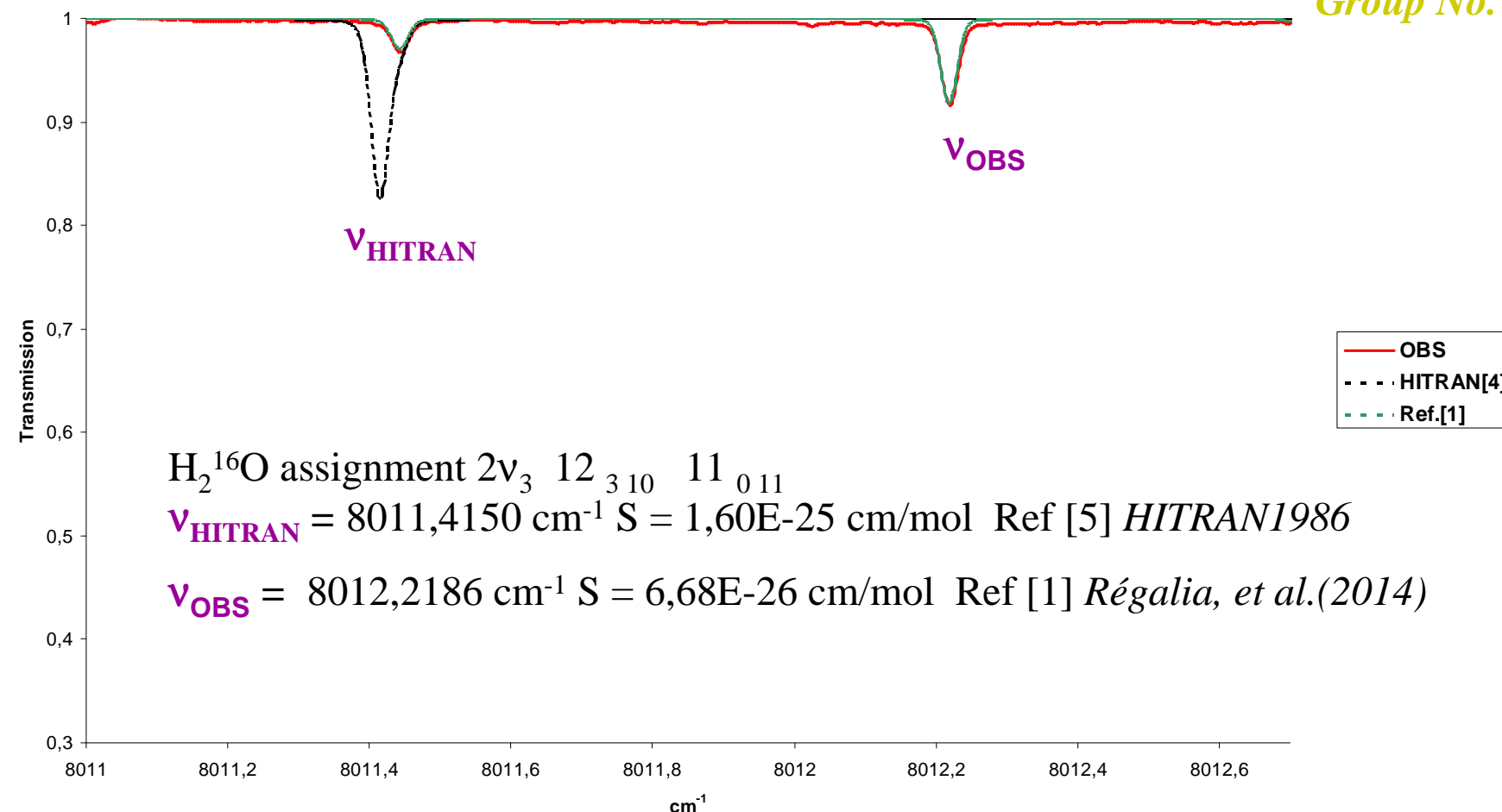


Figure 1. Observed (OBS) and calculated spectra with the HITRAN2012 edition line list near 8012 cm^{-1} . Observation: $P = 14 \text{ mbar}$, $L = 1203 \text{ m}$, $T = 294.4 \text{ K}$.

The real line position of the $2\nu_3 \ 12_{310} - 11_{011}$ is 8012.218 cm^{-1} instead of 8011.415 cm^{-1} reported in the HITRAN2012 line list.

Group No. 8

482 H₂¹⁶O transitions:

Line positions were calculated by **Gordon**¹¹ from experimentally determined energy levels.

Line intensities come from **Barber, et al.**⁹

Comparisons of 44 transitions measured by Régalia, et al. with those obtained in HITRAN2012 line list:

- Line position differences between -0.494 and +0.226 cm⁻¹: much bigger than the indicated error bars (0.001 up to 0.01 cm⁻¹; error code 3) in HITRAN2012.
- Comparison of observed and calculated line intensities is good enough.

⁹ A high-accuracy computed water line list R.J. Barber, J. Tennyson, G.J. Harris, R.N. Tolchenov, Mon. Not. R. Astron. Soc. 368, 1087-1094 (2006)

¹¹ Private communication I.E. Gordon, Harvard-Smithsonian Center for Astrophysics (CFA), Cambridge, MA, USA (2008)

Observed and calculated spectra with HITRAN2012 data (Ref[4])

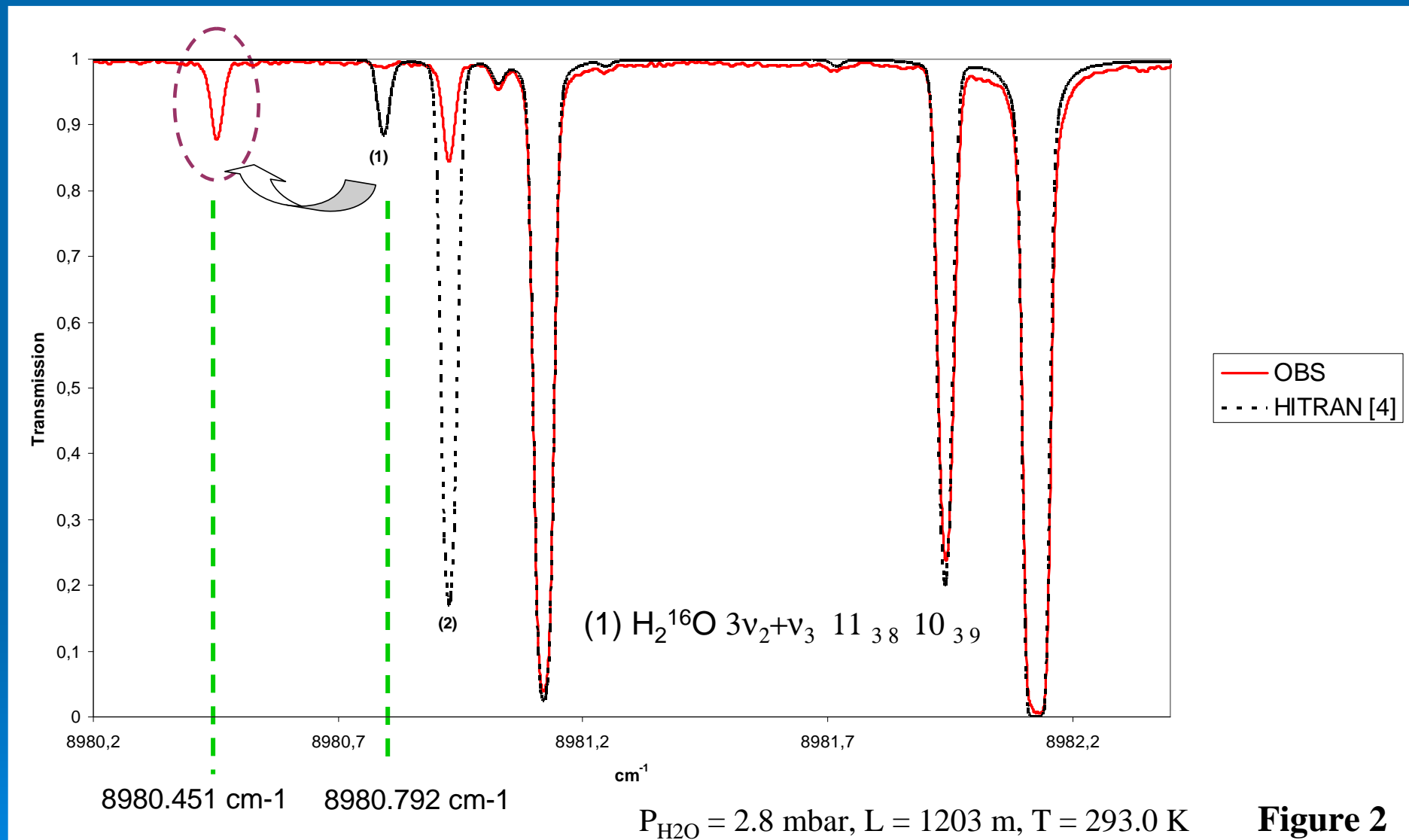


Figure 2

Observed and calculated spectra with experimental line parameters (Ref[1])

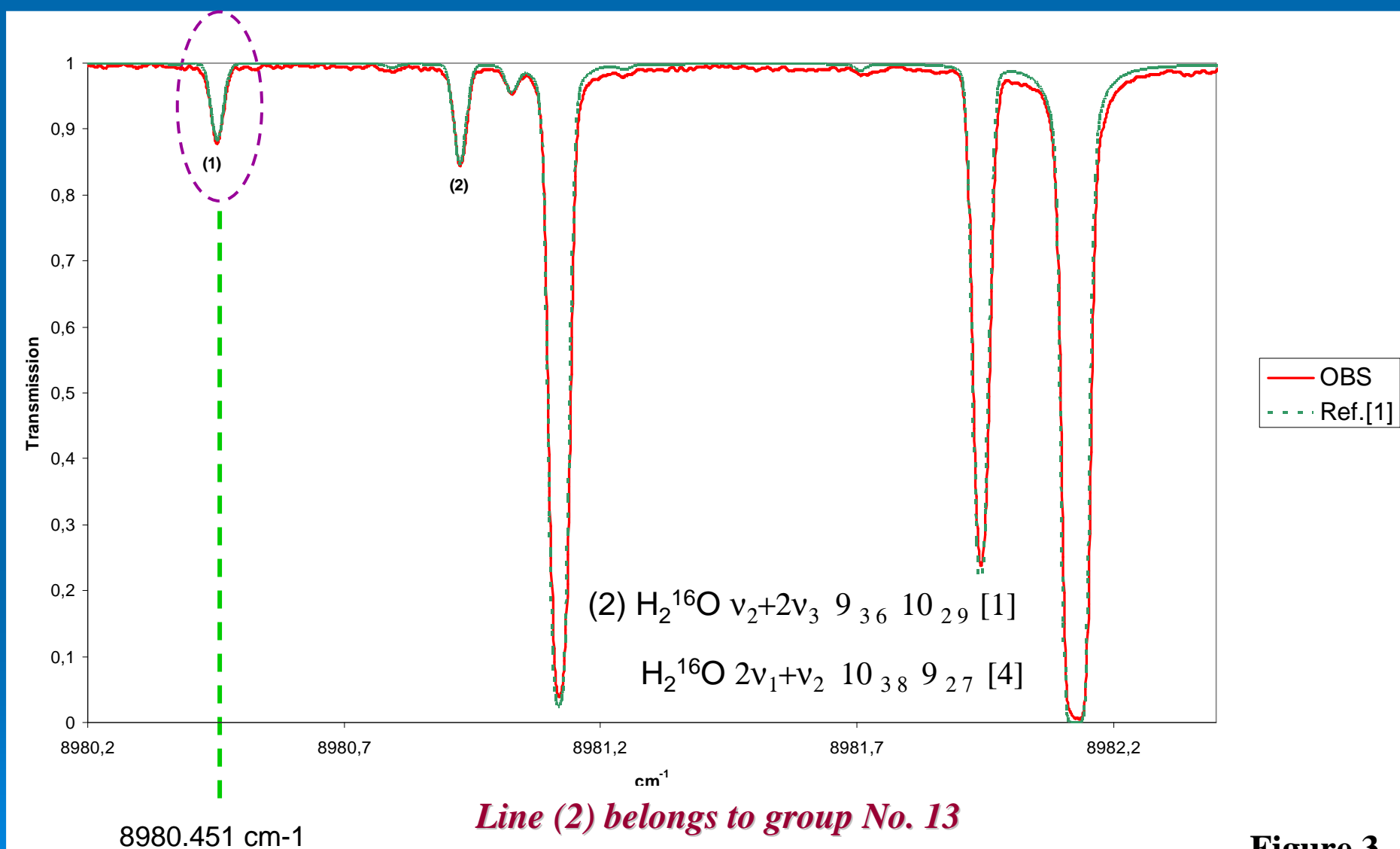


Figure 3

Group No. 13

1546 H₂¹⁶O transitions:

line positions calculated from the **IUPAC energy levels** ¹² were combined with the **experimental line intensities** of **Oudot et al.** ⁷

¹² IUPAC critical evaluation of the rotational-vibrational spectra of water vapor, Part III: Energy levels and transition wavenumbers for H₂¹⁶O.

J. Tennyson, et al. J. Quant. Spectrosc. Radiat. Transfer, 117, 29-58 (2013)

⁷ Intensity measurements of H₂¹⁶O lines in the spectral region 8000 – 9350 cm⁻¹

C. Oudot et al., J. Mol. Spectrosc. 262, 22-29 (2010)

HITRAN2012 edition				Oudot et al. (Ref. [7])	
$\nu^{\text{Ref}[4]}$	$S^{\text{Ref}[4]}$	Assignment	Elow	$\nu^{\text{Ref}[7]}$	$S^{\text{Ref}[7]}$
cm^{-1}	cm/mol				
8106.9867	7.15E-26	130 8 1 7 000 9 2 8	1080.3853		
8314.4912	1.67E-25	050 6 6 1 000 7 5 2	1059.8353		
8482.0379	1.36E-24	130 10 3 8 000 11 0 11	1327.1096		
8485.7280	6.21E-26	050 6 6 1 000 6 5 2	888.5986		
8492.1814	8.03E-25	210 10 3 8 000 11 2 9	1690.6636		
8601.5093	1.88E-25	210 10 3 8 000 10 4 7	1581.3357		
8607.2265	1.53E-25	130 10 3 8 000 9 2 7	1201.9210		
8849.3218	6.17E-24	130 6 5 2 000 6 2 5	552.9114		
8866.7083	8.99E-26	121 5 4 2 010 4 4 1	2129.5991		
8888.9795	8.23E-24	130 10 3 8 000 9 0 9	920.1680		
8889.2113	8.98E-25	210 10 3 8 000 10 2 9	1293.6337		
8901.5030	5.18E-26	012 6 3 3 000 6 4 2	757.7801		
8914.1367	8.99E-25	210 11 0 11 000 10 1 10	1114.5493		
8980.9240	6.26E-24	210 10 3 8 000 9 2 7	1201.9210		
9243.0744	1.43E-25	012 6 3 3 000 5 2 4	416.2087		
9262.6770	1.18E-25	210 10 3 8 000 9 0 9	920.1680		

Table 3

16 transitions listed above were not observed by Oudot et al. ⁷.

⁷ Intensity measurements of H₂¹⁶O lines in the spectral region 8000 – 9350 cm⁻¹
C. Oudot et al., J. Mol. Spectrosc. 262, 22-29 (2010)

Nine transitions in Table 4 have different vibration-rotation assignments and different line intensities in the HITRAN2012 ⁴ line list and in (Oudot, et al., JQSRT 2010) ⁷

HITRAN2012 edition				Oudot et al. (Ref. [7])			
ν ^{Ref[4]} cm ⁻¹	S ^{Ref[4]} cm/mol	Assignment	Elow	ν ^{Ref[7]} cm ⁻¹	S ^{Ref[7]} cm/mol	$d\nu$ ^a	dS ^b
8507.4619	6.59E-25	210 10 4 7	000 11 3 8 1813.2227	8507.4631	7.86E-25	.0012	16.2
8524.9890	7.86E-25	111 10 3 7	000 11 3 8 1813.2227	8524.9904	6.59E-25	.0014	-19.3
8685.2016	1.04E-24	130 6 4 3	000 5 3 2 508.8120	8685.2032	5.67E-25	.0016	-83.4
8874.5566	5.05E-25	210 10 4 7	000 10 3 8 1446.1279	8874.5447	6.29E-24	-.0119	92.0
8892.0838	6.29E-24	111 10 3 7	000 10 3 8 1446.1279	8892.0864	5.05E-25	.0026	-1145.5
9037.7658	5.27E-24	210 10 4 7	000 9 3 6 1282.9188	9037.7666	6.64E-24	.0008	20.6
9055.2929	6.64E-24	111 10 3 7	000 9 3 6 1282.9188	9055.2944	5.27E-24	.0015	-26.0
9241.6053	1.23E-25	210 10 4 7	000 9 1 8 1079.0792	9241.6079	1.36E-25	.0026	9.6
9259.1324	1.36E-25	111 10 3 7	000 9 1 8 1079.0792	9259.1344	1.23E-25	.0020	-10.6

^a $d\nu = \nu_2 - \nu_1$, cm⁻¹

^b

$$dS = \frac{S^{\text{Ref.[7]}} - S^{\text{Ref.[4]}}}{S^{\text{Ref.[7]}}} \times 100\%$$

Table 4

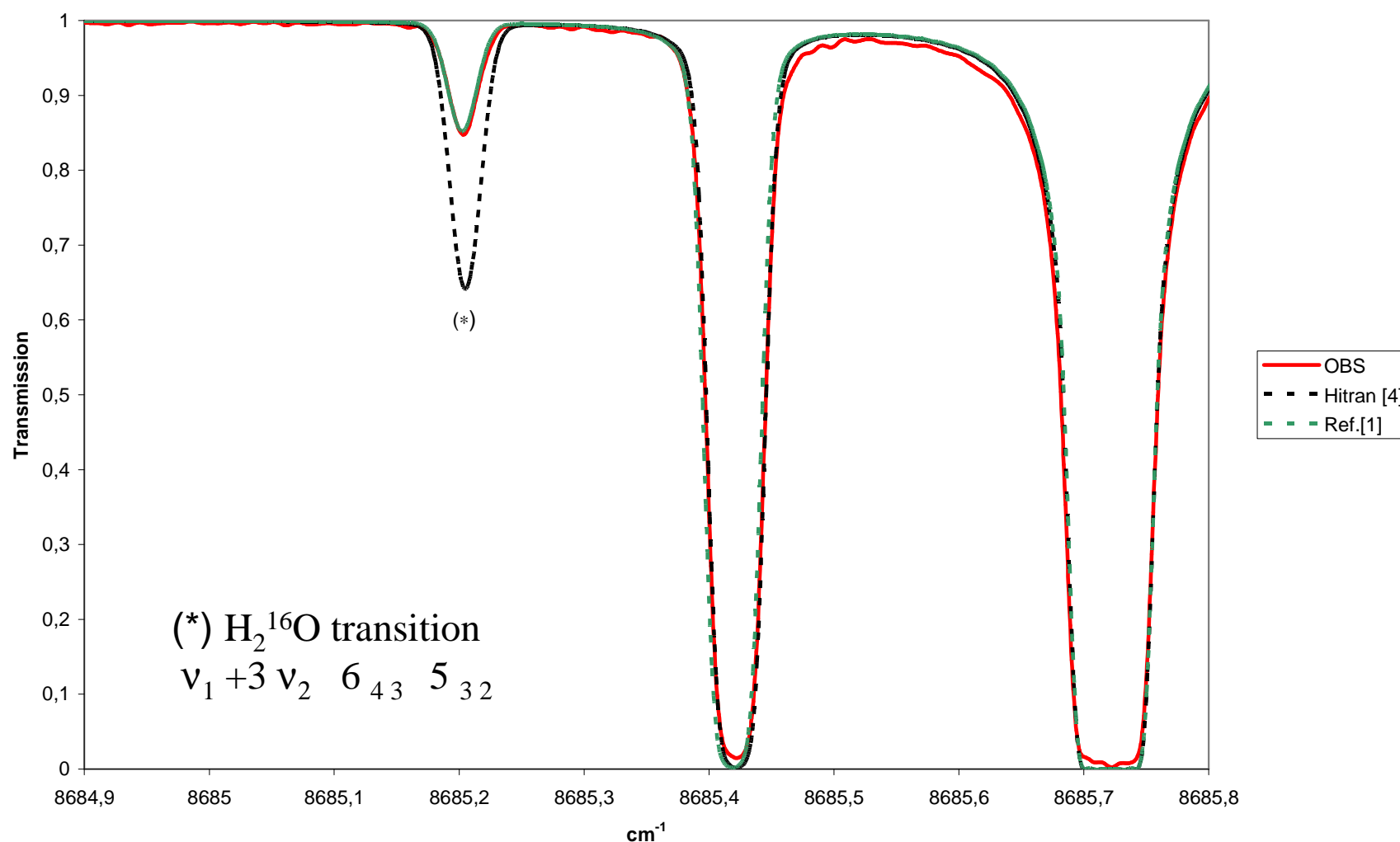


Figure 4 Observed and calculated spectra near 8685cm⁻¹. Observation: P = 2.8 mbar, L = 1203 m, T = 293.0 K Observed spectrum (OBS) is compared to the calculated spectrum obtained with the HITRAN2012 line list and with the line list (Régalia et al.) in black and in green line respectively

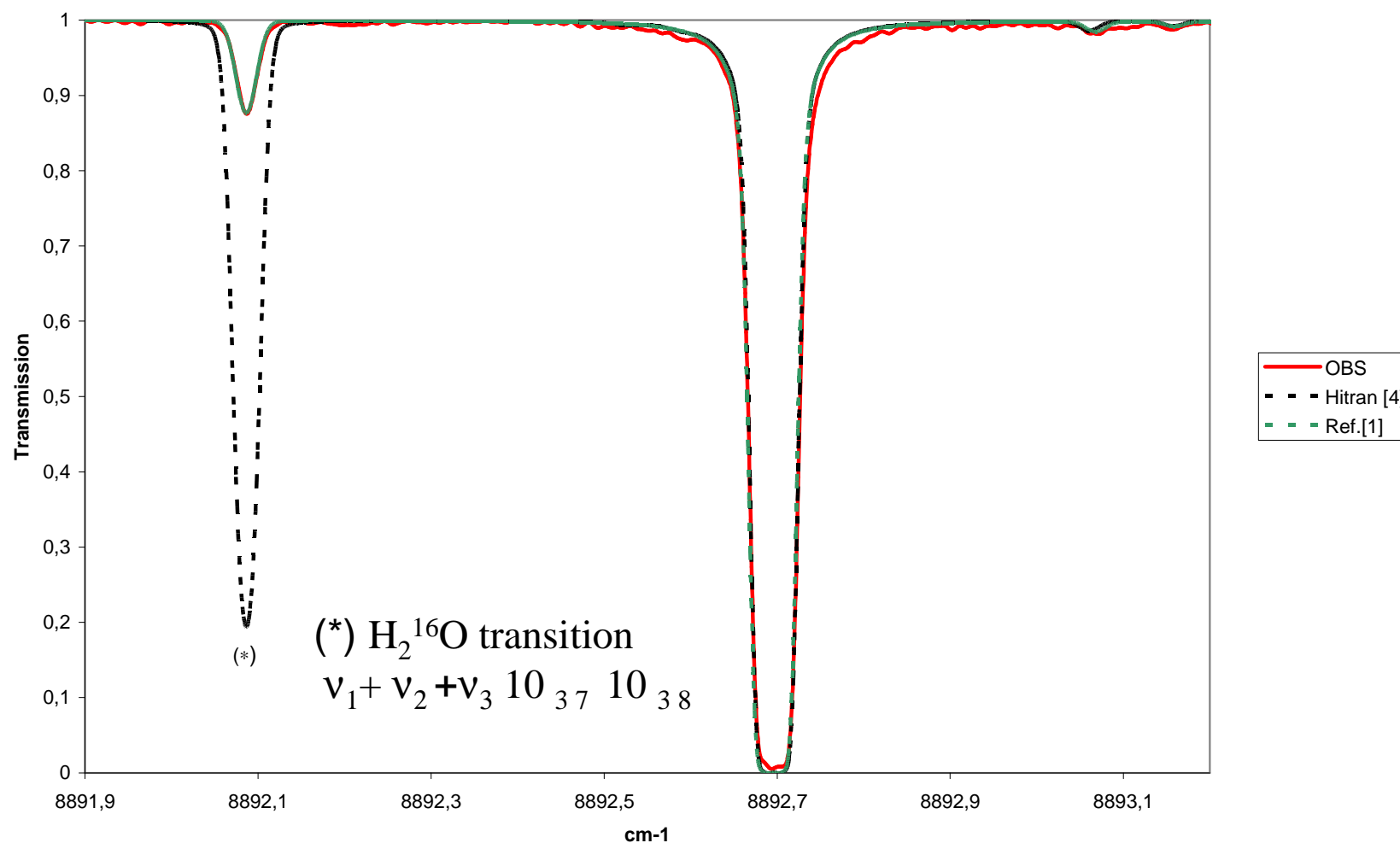


Figure 5 Observed and calculated spectra near 8892 cm^{-1} . Observation: $P = 2.8 \text{ mbar}$, $L = 1203 \text{ m}$, $T = 293.0 \text{ K}$. Observed spectrum (OBS) is compared to the calculated spectrum obtained with the HITRAN2012 line list and with the line list (Régalia et al.) in black and in green line respectively

Conclusion

- **Group 1:** All line positions mentioned above are incorrect. These parameters should be replaced by experimental ones or by calculated values.
- **Group 8:** The line positions of this group are certainly wrong. Corresponding values should be replaced by the experimental values or by the calculated ones from the IUPAC energy levels (J. Tennyson, et al. JQSRT 2013)
- **Group 13:** Sixteen line intensities of this group transitions are not really data of (Oudot, et al. JQSRT 2010). Nine line intensities in the HITRAN2012 line list are quite different compared to (Oudot, et al. JQSRT 2010).

A part of the water line list of the HITRAN2012 database need to be revised. It is true for both line parameters (positions and intensities) and their uncertainties.

Nevertheless, a part of line intensities (Régalia et al. JQSRT 2014) are not precise enough and need to be revised also.

An article is under writing to summarize these new comparisons.