IUPAC Database of Water Transitions from Experiment and Theory: $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD{}^{16}O$, $HD{}^{18}O$, $HD{}^{17}O$, $D_2{}^{16}O$, $D_2{}^{18}O$, and $D_2{}^{17}O$

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Introduction

Full characterization of the spectrum of water vapor from the microwave to the near ultraviolet is a prerequisite for the modeling and understanding of many fields in chemistry, physics and engineering,

INCLUDING

- atmospheric modeling and climate change
- remote sensing and communication-related fields using the Earth's atmosphere
- astrophysics, such as the atmospheres of most cool stars and brown dwarfs where hot water is a major constituent
- water lasers and masers (widespread in outer space)
- study of comets, based on fluorescence spectroscopy
- combustion research, such as rocket exhausts, forest fires, and turbine engines where hot steam is a major product
- spectroscopy of species of low abundance in the atmosphere or in outer space (hampered by the omnipresence of water lines).

We are reporting here results of a research effort performed by an IUPAC Task Group.[1] The procedure and code MARVEL[2, 3] have been used extensively in determining critically evaluated rovibrational levels, lines, and their self-consistent uncertainties both for cold and hot water spectra related to the nine common isotopologues.

Spectral regions (R), energy levels (E), and lines (L)

- $H_2{}^{16}O$: R = 0–25337 cm^{-1}, E = 18486, L = 184667/182156
- $H_2{}^{18}O$: R = 0–17121 cm^{-1}, E = 5131, L = 32325/31705
- $H_2{}^{17}O$: R = 0–17125 cm^{-1}, E = 2723, L = 9169/9028
- $HD{}^{16}O$: R = 0–17013 cm^{-1}, E = 8818, L = 54740/53291
- $HD{}^{18}O$: R = 0–12105 cm^{-1}, E = 1864, L = 8729/8634
- $HD{}^{17}O$: R = 0–1674 cm^{-1}, E = 162, L = 485/478
- $D_2{}^{16}O$: R = 0–14016 cm^{-1}, E = 12269, L = 53534/52842
- $D_2{}^{18}O$: R = 0–7969 cm^{-1}, E = 3351, L = 12167/12026
- $D_2{}^{17}O$: R = 0–9108 cm^{-1}, E = 338, L = 600/583

The extensive list of MARVEL lines and levels obtained are deposited in a distributed information system applied to water, W@DIS, hhtp://wadis.saga.iao.ru, and in the official MARVEL web site, http://kkrk.chem.elte.hu/marvel.

A distinguishing feature of the present evaluation of water spectroscopic data is the systematic joint utilization of all the available experimental and the best first-principles theoretical data.

MARVEL

MARVEL, standing for Measured Active Rotational-Vibrational Energy Levels, employed in this collaborative effort for collecting and critically evaluating experimental transition wavenumbers and uncertainties and for converting the wavenumbers to the best possible energy levels with uncertainties, is based on the concept of spectroscopic networks (SN).[4] MARVEL is similar to the X-matrix method[5] and the Active Thermochemical Tables (ATcT) approach.[6] MARVEL contains an iterative robust reweighting scheme[7] and it simultaneously processes *all* the available assigned experimental lines and the associated energy levels for the chosen isotopologue.

Some technical details

- contains a thorough and detailed test facility (pre-MARVEL) in order to cleanse the assembled dataset
- adjusts the experimental uncertainties via the robust reweighting scheme to achieve a self-consistent solution
- has been employed for datasets containing as much as 250,000 transitions
- computes the uncertainties of the levels through an inversion of the extremely sparse design matrix
- the memory requirements and the CPU usage of the MARVEL code scale not much worse than linear with the size of the problem, typical inversion time is a fraction of a second

Data sources

Only results from published spectroscopic measurements that include details of the experimental procedure were considered. Secondary data, such as tabulated energy levels or Hamiltonian fits, were not considered except occasionally for checking purposes.

Characteristics of selected sources, some with a large number of transitions, considered for $H_2{}^{16}O$

Tag	Range (cm^{-1})	Trans. A/V	Physical conditions T(K)	p(hPa)	Rec.
06MaToNaMo	0–165	130/130	300–900	0.01–0.6	LDFS
12YuPeDrMa	10–694	4510/4501	RT,hot		EMS-FTS
04CoPiVeLa	58–475	1708/1708	1850	1	EMS-FTS
05CoBeCaCo	540–2000	11406/11140	3000		EMS-FTS
06ZoShPoBa	722–4750	15984/15721	3000		EMS-FTS
08ZoShOvPo	4254–12361	26106/25490	3000		EMS-FTS
05ToNaZoSh	9155–25225	15566/15432	292	6–18	FTS

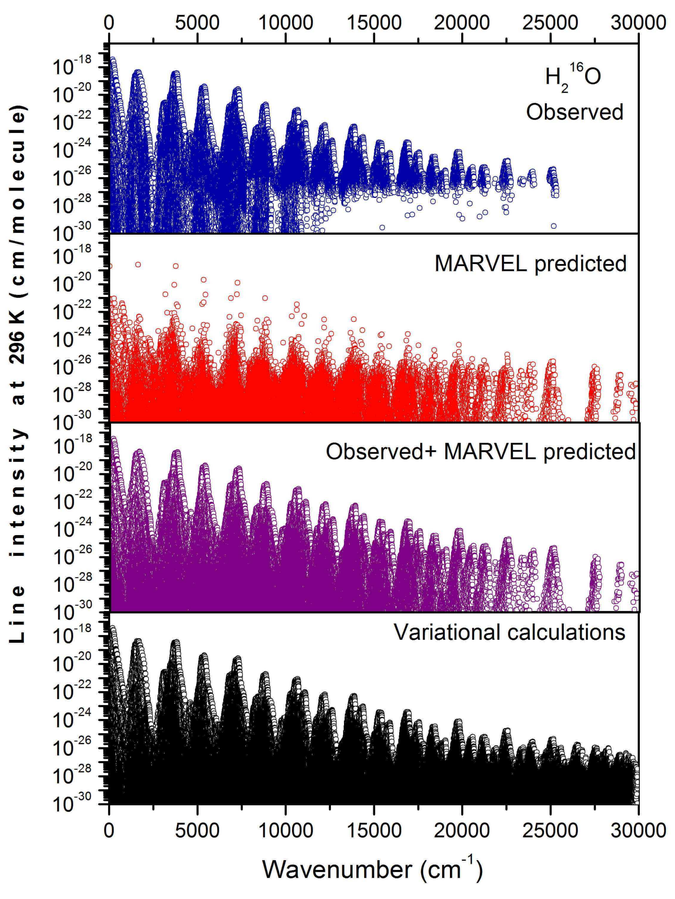
The range given corresponds to entries within the MARVEL input file; A = number of assigned transitions in the original article, V = number of transitions validated in this study. T = temperature (K), with RT = room temperature, EMS = emission spectroscopy, FTS = Fourier-transform spectroscopy, LDFS = laser difference frequency spectroscopy.

Vibrational band origins

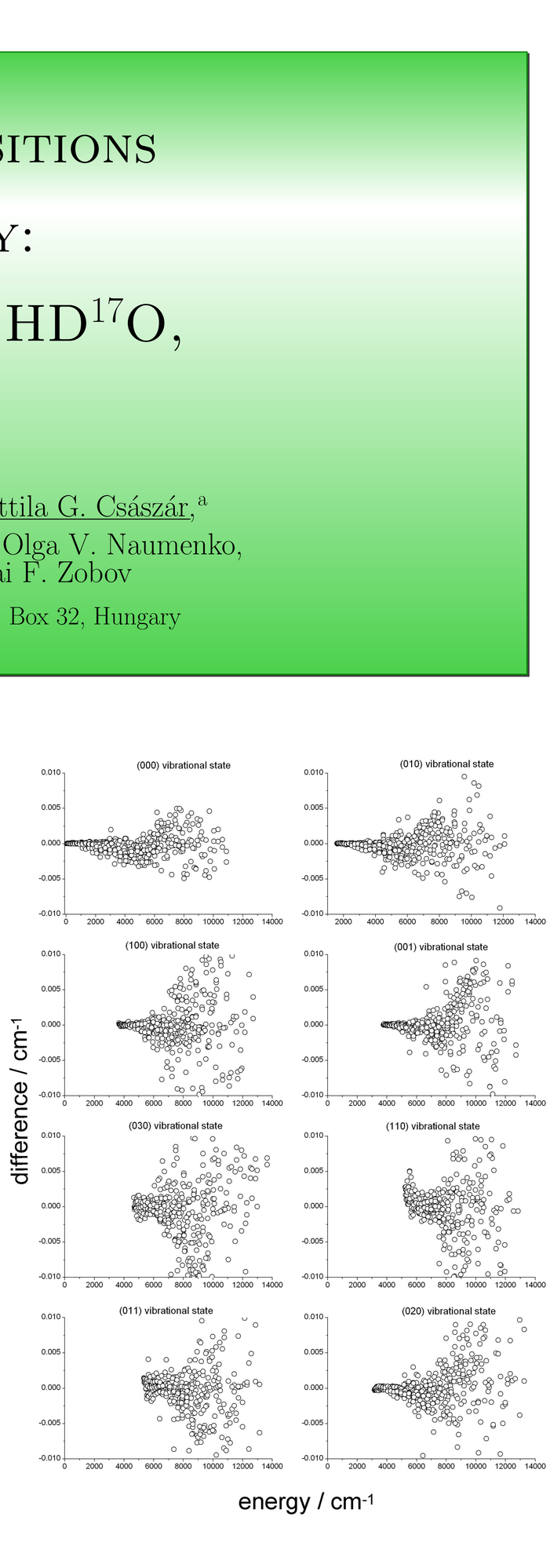
Selected vibrational band origins (VBO)

species	$v_1v_2v_3$	$(mn)^{\pm}v_2$	VBO/cm^{-1}	Unc.	RL
H2^{16}O	0 0 0	$(00)^{+}0$	0.000000	0	11171
H2^{16}O	0 1 0	$(00)^{+}1$	1594.746292	20	1063
H2^{17}O	0 1 0	$(00)^{+}1$	1591.325698	51	153
H2^{18}O	0 1 0	$(00)^{+}1$	1588.275946	33	227
H2^{16}O	0 2 0	$(00)^{+}2$	3151.629847	190	819
H2^{17}O	0 2 0	$(00)^{+}2$	3144.980503	44	78
H2^{18}O	0 2 0	$(00)^{+}2$	3139.050001	37	146
H2^{16}O	1 0 0	$(10)^{+}0$	3657.053251	200	820
H2^{17}O	1 0 0	$(10)^{+}0$	3653.142275	31	108
H2^{18}O	1 0 0	$(10)^{+}0$	3649.685416	51	192
H2^{16}O	0 0 1	$(10)^{-}0$	3755.928548	81	867
H2^{17}O	0 0 1	$(10)^{-}0$	3748.318112	31	141
H2^{18}O	0 0 1	$(10)^{-}0$	3741.566775	46	216
H2^{16}O	0 1 1	$(10)^{-}1$	5331.267252	159	680
H2^{16}O	0 6 0	$(00)^{+}6$	8869.950054	5000	119

$v_1v_2v_3$ and $(mn)^{\pm}v_2$ are normal- and local-mode labelings, respectively. Unc. = uncertainty in units of 10^{-6} cm^{-1}, RL = number of observed rotational levels within a band.



Comparison of one-photon absorption spectra with intensities at 296 K. The weakest measured intensities come from absorption spectra of hot water which are difficult to obtain directly in absorption.



Differences between MARVEL and empirical, effective-Hamiltonian-based energy levels from 04CoPiVeLa[8] for the eight lowest-energy vibrational states of $H_2{}^{16}O$

Conclusions

The protocol based on MARVEL and the use of high-accuracy variational rotational-vibrational computations covering the full spectral range of interest along with the limited spectral coverage provided by all primary experimental information collected from the literature provides a unique chance to achieve the goal of accurate and full coverage of rotational-vibrational spectra of small molecules.

Outlook

Our plans for the near future include:

- active maintainance of the IUPAC information system
- extension to intensities
- use of MARVEL energy levels, and the associated protocols, to provide new semiautomatic assignment techniques

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References

[1] J. Tennyson et al., *J. Quant. Spectrosc. Radiat. Transfer* **110**, 573 (2009); **111**, 2160 (2010); **117**, 29 (2013); **142**, 93 (2014).

[2] T. Furtenbacher, A.G. Császár, J. Tennyson, *J. Mol. Spectrosc.* **245**, 115-125 (2007).

[3] T. Furtenbacher, A.G. Császár, *J. Quant. Spectr. Rad. Transfer* **113**, 929-935 (2012).

[4] A.G. Császár, T. Furtenbacher, *J. Mol. Spectrosc.* **266**, 99-103 (2011).

[5] J.-M. Flaud, C. Camy-Peyret, J. P. Maillard, *Mol. Phys.* **32**, 499-521 (1976).

[6] B. Ruscic et al., *J. Phys. Chem. A* **108**, 9979-9997 (2004).

[7] J. K. G. Watson, *J. Mol. Spectrosc.* **219**, 326-328 (2003).

[8] L. H. Coudert et al., *J. Mol. Spectrosc.* **228**, 471-498 (2004).