Journal of Quantitative Spectroscopy & Radiative Transfer 206 (2018) 46–54

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

The 1943 K emission spectrum of $H_2{}^{16}O$ between 6600 and 7050 cm^{-1}

Eszter Czinki[a], Tibor Furtenbacher[a], Attila G. Császár[a,*], André K. Eckhardt[b], Georg Ch. Mellau[c,*]

[a] MTA-ELTE Complex Chemical Systems Research Group and Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös Loránd University, Budapest 112, P.O. Box 32, H-1518, Hungary
[b] Institut für Organische Chemie, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 17, Gießen D-35392, Germany
[c] Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 17, Gießen D-35392, Germany

ARTICLE INFO

Article history:
Received 9 August 2017
Revised 28 October 2017
Accepted 30 October 2017
Available online 1 November 2017

Keywords:
Water vapor
High-resolution emission spectroscopy
Transition wavenumbers
Energy levels
MARVEL
Spectroscopic database
Infrared spectra
`SyMath`

ABSTRACT

An emission spectrum of $H_2{}^{16}O$ has been recorded, with Doppler-limited resolution, at 1943 K using Hot Gas Molecular Emission (HOTGAME) spectroscopy. The wavenumber range covered is 6600 to 7050 cm^{-1}. This work reports the analysis and subsequent assignment of close to 3700 $H_2{}^{16}O$ transitions out of a total of more than 6700 measured peaks. The analysis is based on the Measured Active Rotational-Vibrational Energy Levels (MARVEL) energy levels of $H_2{}^{16}O$ determined in 2013 and emission line intensities obtained from accurate variational nuclear-motion computations. The analysis of the spectrum yields about 1300 transitions not measured previously and 23 experimentally previously unidentified rovibrational energy levels. The accuracy of the line positions and intensities used in the analysis was improved with the spectrum deconvolution software `SyMath` via creating a peak list corresponding to the dense emission spectrum. The extensive list of labeled transitions and the new experimental energy levels obtained are deposited in the Supplementary Material of this article as well as in the `ReSpecTh` (http://www.respecth.hu) information system.

1. Introduction

Water is the most abundant polyatomic molecule in the universe. The spectroscopic detection and quantification of the amount of water vapor in different environments is a fundamental task in several areas of chemistry, spectroscopy, astronomy, and remote sensing. Due to the numerous analytical applications there is strong interest in the detailed laboratory investigation of the high-resolution spectra of water vapor from the microwave to the ultraviolet [1–7]. For $H_2{}^{16}O$, more than 100 experimental high-resolution spectroscopic studies have been published, Tennyson et al. [4] provides a hopefully complete list up to 2013. These measurements provide an excellent coverage of the rovibrational levels of $H_2{}^{16}O$ up to 15 000 cm^{-1}. This coverage extends significantly above the barrier to linearity of $H_2{}^{16}O$, which is about 11 100 cm^{-1} [8–11]. Transitions covering the highly excited levels beyond 15 000 cm^{-1} have been measured only sporadically, though gradually more and more energy levels have become available up to the first dissociation limit [12] and even beyond [13,14].

For analytical applications of high-resolution molecular spectroscopy a list of transition wavenumbers and intensities are needed, their collection is often referred to as a line list. For some triatomic molecules, most notably HCN, it is possible to cover experimentally the complete list up to very high energy with a relative accuracy better than 10^{-7} [15,16]. The existence of a list in which not a single eigenenergy of the molecular system is missing, combined with highly accurate *ab initio* intensity computations, allows accurate analytical analysis of HCN sources even at high temperatures. The measurement and the analysis of the HCN eigenenergies originates from a single laboratory; this ensures the internal consistency and accuracy of the eigenenergy list.

For water, experimental data sets have been reported by many laboratories, they are based on different experiments with transitions measured with very different accuracy and precision. The more than 100 data sets highly overlap and the eigenenergies reported in the individual sources have been based on a limited number of experiments. As part of an IUPAC-sponsored research effort [4,5,17–19] the complete set of so far published experimental spectroscopic information obtained from the assignment of high-resolution absorption and emission spectra for nine water isotopologues, $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, $HD^{18}O$, $D_2{}^{16}O$, $D_2{}^{17}O$,

---

* Corresponding authors.
E-mail addresses: csaszar@chem.elte.hu (A.G. Császár), georg@mellau.de (G.Ch. Mellau).

https://doi.org/10.1016/j.jqsrt.2017.10.028
0022-4073/© 2017 Elsevier Ltd. All rights reserved.

and $D_2{}^{18}O$, has been collected and analyzed. The experimental spectroscopic knowledge has been organized based on the concept of spectroscopic networks (SN) [20–22]. The conversion of the measured rovibrational transitions to energy levels is based on the MARVEL (Measured Active Rotational-Vibrational Energy Levels) protocol [22–25] built upon the idea of SNs, while utilizing heavily first-principles computed data [26,27]. The current MARVEL list of $H_2{}^{16}O$ eigenenergies [4] is complete up to 7500 cm^{-1}.

High-temperature water spectra contain a huge number of transitions not observed and/or assigned to date. The analysis of hot spectra allows the characterization of new energy levels and can extend significantly the database of rovibrational levels. Accurate transition wavenumbers for which the lower and upper levels have already been determined can improve substantially the accuracy of the eigenenergies determined via the MARVEL protocol. The most significant contribution to this improvement comes from transitions connecting lower and upper levels defining new spectroscopic basic cycles [28] and from transitions connecting energy level sets of different previous measurements or those determined from measurements with low accuracy. In this work we report the analysis of a near-infrared water emission spectrum in which we assigned about 4000 transitions, connecting for the first time many previously determined energy levels. Including these transitions in the MARVEL protocol we have improved the accuracy of the energies of many highly excited rovibrational states, where the previous accuracy was only about 0.02 cm^{-1} (see Section 4.5 below).

A number of spectroscopic studies exists [8,29–50] investigating warm (between 400 and 700 K) and hot (up to 3000 K) $H_2{}^{16}O$ spectra. The hottest emission spectra of $H_2{}^{16}O$ have been recorded in the laboratory in an oxy-acetylene flame at about 3000 K [46], while the absorption spectra recorded in sunspots correspond to a temperature of about 3200 K [51]. Sunspots provide a very rich source of spectroscopic data on water [40], and many lines, which are almost certainly due to hot water, still need to be assigned. Hot spectra are rich in relatively high-J (where J is the quantum number corresponding to the overall rotation of the molecule) and hot-band transitions, often with significant bending excitation [52–54]. The transitions observed in emission often have an increased chance of misassignment and mislabeling. A significant hindrance in the utilization of hot emission spectra is that it is usually not possible to obtain line positions with the same accuracy as those coming from absorption spectra recorded at room temperature. This is due to the increased Doppler width of the transitions and, in the case of atmospheric pressure spectra such as those recorded in flames, significant pressure broadenings and pressure shifts. The extended linewidth and the high density of observable transitions also lead to a very large number of blended transitions, which places a further constraint on the accuracy with which the positions of the individual peaks can be determined.

The emission spectrum recorded in Gießen and reported in Fig. 1 has several outstanding features: constant temperature of the hot molecular gas, low gas pressure (less than 20 mbar), reproducible emission line intensities with an accuracy usually better than 10%, almost fully resolvable spectral features (after the final deconvolution analysis), and high signal to noise ratio, up to 10000, due to the very low level of the modulated and not modulated background radiation. The simultaneous fulfillment of these characteristics and the use of a special emission spectrum analysis program are the strengths of the experimental apparatus developed in Gießen. These important characteristics allow us to extract accurate line positions and intensities from up to 2000 K hot emission spectra in general and improve the MARVEL list of energy levels for $H_2{}^{16}O$ in particular.

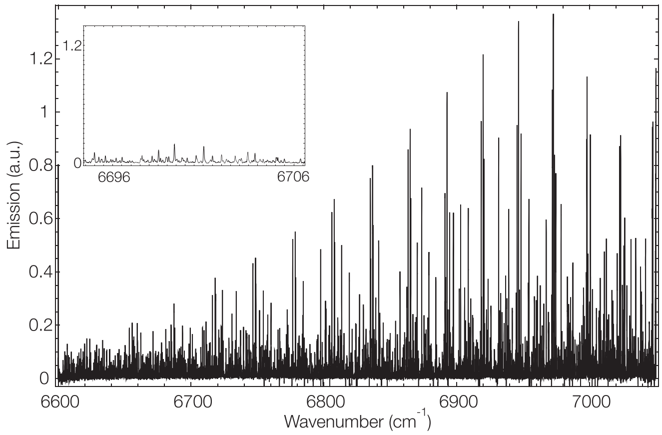

Fig. 1. Overview of the measured $H_2{}^{16}O$ emission spectrum. a.u. = arbitrary unit. The inset shows a narrow portion of the spectrum, all of the small features correspond to an emission peak. Due to the high signal to noise ratio, the noise level is smaller than the smallest feature one can see on these figures.

In this work we apply MARVEL energy levels [4,5], emission line intensities coming from the so-called BT2 database [55], and a computerized search algorithm to analyze a high-resolution emission spectrum, taken in Gießen at 1943 K, of the main water isotopologue, $H_2{}^{16}O$. It is our hope that the present study not only provides important new transition and energy-level data but also improves upon the methodology how high-resolution emission spectra of stable molecules are analyzed and assigned.

2. The MARVEL/BT2 (MB) peak list

Due to the assumed simplicity of the water molecule, it has been a favorite subject of variational nuclear motion computations [13,27,55–65]. As a result of considerable advancement in the field of computational quantum chemistry [26], systematic and mostly automated comparisons between the results of state-of-the-art variational nuclear motion computations and experiment are possible and they prove to be highly instructive.

In this study the BT2 line list [55] has been used; this line list was computed using a spectroscopically determined PES [59], an *ab initio* DMS [58], and the DVR3D [66] nuclear-motion program suite. A BT2 transition list was generated in the wavenumber range of the experiment, containing the complete set of transitions likely to be observed in the emission spectrum of Fig. 1. The emission intensities are extremely important when assigning measured emission spectra. The BT2 line list contains Einstein A_{if} coefficients for each transition; these Einstein-A coefficients have been used to compute the emission spectrum at 1943 K.

Measured spectra of $H_2{}^{16}O$ vapor are basically a superposition of two separate spectra, those of *ortho*-$H_2{}^{16}O$ and *para*-$H_2{}^{16}O$. The strongly forbidden transitions between the two nuclear-spin isomers have never been observed [67]. In the language of network theory [20,68], the transitions present in the spectra of $H_2{}^{16}O$ are part of two rooted components, o-$H_2{}^{16}O$ and p-$H_2{}^{16}O$.

For consistency and to maintain a single set of uniform labels for all levels, we chose to label rovibrational states and transitions following the recommendations of Tennyson et al. [4]. Thus, vibrations are labeled employing the usual normal-mode notation, $(v_1\, v_2\, v_3)$, while for the rotations we use the standard asymmetric-top quantum numbers $[JK_aK_c]$ or $J_{K_aK_c}$. Driven by the required uniqueness of the labels, the rotation-vibration levels of $H_2{}^{16}O$ are identified in this study by altogether six labels: $(v_1\, v_2\, v_3)$ $[JK_aK_c]$. The individual labels of the rovibrational states established by Tennyson et al. [4] were utilized unchanged.