Note

Terahertz spectroscopy of water in its second triad

Shanshan Yu *, John C. Pearson, Brian J. Drouin

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, United States

ARTICLE INFO

ABSTRACT

Terahertz absorption spectroscopy was employed to measure rotational transitions of water in its second triad $3\nu_2$, $\nu_1 + \nu_2$ and $\nu_3 + \nu_2$. Highly excited water molecules were created with a DC discharge, which allowed observation of transitions with lower state energies up to 5939 cm^{-1}. In the 0.5–2.0 THz region, 38 pure rotational transitions in the second triad were observed with MW accuracy for the first time. Additionally, 91 new rotational and ro-vibrational transitions within the ground state, ν_2, and the first triad ($2\nu_2$, ν_1 and ν_3) were measured with multiplier chains covering the 1.3–2.0 THz region.

© 2013 Elsevier Inc. All rights reserved.

Water provided the first coherent source of THz radiation once its laser action was discovered in 1964 [1]. The general features of the water spectrum have been exceptionally well sorted out after decades of high resolution spectroscopy [2]. However, the extremely non-rigid nature of the water molecule has thus far defied analysis of its Doppler limited frequency measurements to within experimental accuracy. As such, it is still necessary to frequency measure water transitions. The current effort is necessary to support the study of oxygen-rich asymptotic giant branch stars, where water observations have been detected in a number of highly excited vibrational states [3]. Water has three vibrational modes, a symmetric stretch ν_1, a bend ν_2 and an anti-symmetric stretch ν_3. We denote these modes as (ν_1, ν_2, ν_3) where the commas are omitted for quanta less than 10.

The present work follows our previous study [4] in which the rotational and ro-vibrational transitions of water in the ground state, (010), and the first triad (020), (100) and (001) were measured and analyzed with two different methods. In this study, the pure rotational transitions in the second triad (030), (110) and (011) of water were measured with terahertz absorption spectroscopy for the first time. These three vibrational levels lie high in energy, with vibrational energies of 4667, 5235, 5331 cm^{-1}, respectively. In addition, 91 new transitions in the ground state, (010), and the first triad (020), (100) and (001) were measured with our new multiplier chains covering the 1300–2000 THz region. Since the previous paper [4] provided a detailed analysis and the present data for the lowest five states is consistent with residuals from the previous work, no additional fitting of line positions was performed. The new data in the second triad are too limited to have a significant impact on molecular constants. As a result, no data analysis, i.e., fit of the measured line positions to

Hamiltonian models, was carried out and only the measured line positions are reported for the benefit of velocity resolved astronomical spectroscopy.

There is a vast literature dealing with experimental investigations of the second triad of water and we refer readers to the latest four papers [2,5–7] for details on previous studies. The obtained maximum J was 18 in Toth [5], 17 in Mikhailenko et al. [6], 18 in Coudert et al. [7]. To guide our experimental search for the line positions of pure rotation transitions in the second triad, we used the predictions from a global analysis by Coudert [8], which is based on the Bending-Rotation approach [9–12] and is still in progress.

The frequency multiplied submillimeter spectrometer (FMSS) used for the measurements is described in Ref. [13], with eight multiplier chains covering the 290–1230 and 1575–1626 GHz ranges with some small gaps in between. The present work involves four new multiplier chains covering the 1300–2000 GHz region [14,15]. The measurements were carried out with a 1.2-m-long DC discharge cell and with water pressures ranging from 100 mtorr to 180 mtorr. Typical discharge currents were 350 mA and the voltage across the electrodes was about 3 kV. Note that our frequency positions were not corrected for pressure shifts. The uncertainties were estimated to be between 50 and 500 kHz. Fig. 1 shows the observed $J'_{K'_a,K'_c} - J''_{K''_a,K''_c} = 6_{3,3} - 6_{2,4}$ rotational line in the (011) vibrational state. A few H_2O_2 transitions were also observed while we searched around the predicted H_2O transition frequencies.

Table 1 lists the assignment, observed position, experimental uncertainty, difference from the Bending-Rotation model in Ref. [8], and lower state energy for the newly measured 38 pure rotational transitions of water in the second triad (030), (110) and (011). The model results differ from the observed frequencies from -19 MHz to 14 MHz. The observed J(Max) was 6 and the observed highest energy level was at 5939 cm^{-1}. We have searched but

---

* Corresponding author.
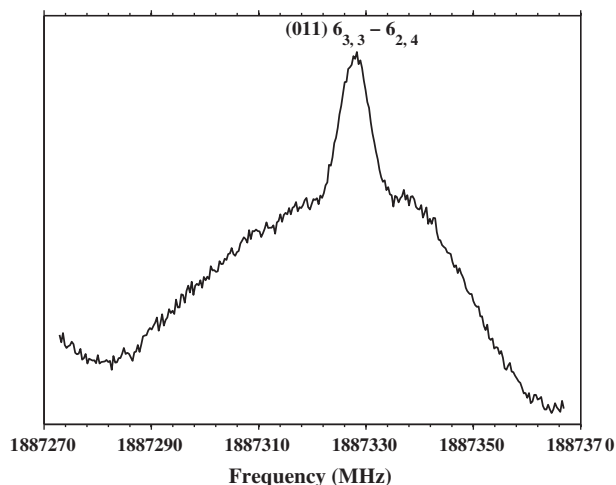 *E-mail address:* shanshan.yu@jpl.nasa.gov (S. Yu).

Fig. 1. The observed $(\nu_1 \nu_2 \nu_3) = (011)$, $J'_{K'_a,K'_c} - J''_{K''_a,K''_c} = 6_{3,3} - 6_{2,4}$ pure rotational water line together with severe baseline. The lower state energy of this transition is 5939 cm^{-1}. The integration time was 1.5 s on each point. An experimental uncertainty of 100 kHz was assigned to the measured line position.

failed to observe transitions with larger J, which has led us to believe that in Fig. 1 of our previous study [4] the tentative assignment of the 1151447 MHz line to $J = 12$ of (030)–(110) is in question. The DC discharge only modestly enhances the rotational temperature, while it provides a significant enhancement of the vibrational temperature. The result is that only the lowest rotational levels in excited vibrational states are sufficiently populated to observe. These new measurements were added to the compiled list of microwave water transitions given in our previous work [4] and the updated list is given in the "MWwaterlines.txt" file in the Supplemental Material of this note.

Table 2 lists the assignment, observed position, experimental uncertainty, difference from the Bending-Rotation model in Ref. [4], and lower state energy for the newly measured 91 rotational and ro-vibrational transitions of water in the ground state, $\nu_2 = 1$ and the first triad (020), (100), (001). Differences up to 10 MHz were found between the model results and the observed frequencies. Laser action was observed at 532644 GHz and 1312041 GHz. These new measurements were also added to the "MWwaterlines.txt" file in the Supplemental Material of this note.

To validate existing datasets, 52 previously measured transitions in the five lowest states were also re-measured. These re-measured frequencies were also included in the "MWwaterlines.txt" file in the Supplemental Material. We re-assessed experimental uncertainties for previously reported frequencies based on repeated measurements. All the remeasured positions agree well with previous values, except for the $10_{5,6}-9_{6,3}$ and $10_{6,5}-10_{7,4}$ lines of the (010) state. These two lines were measured previusly by the Cologne group in our previous work [4]. The JPL-measured vs. Cologne-measured values for these two lines are 1866271.866(50) vs. 1866269.960(300) and 1871695.115(50) vs.

Table 1

Assignment, observed position, experimental uncertainty, difference from the Bending-Rotation model in Ref. [8], and lower state energy for the newly measured 38 pure rotational transitions of water in the second triad (030), (110) and (011).

$J'_{K'_a,K'_c}$	$\nu'_1 \nu'_2 \nu'_3$	$J''_{K''_a,K''_c}$	$\nu''_1 \nu''_2 \nu''_3$	Observed (MHz)	Unc. (MHz)	O.−C. (MHz)	E'' (cm^{-1})
$1_{1,1}$	030	$0_{0,0}$	030	1519493.285	0.100	3.045	4666.7892
$1_{1,1}$	110	$0_{0,0}$	110	1174679.308	0.300	−2.876	5234.9750
$1_{1,1}$	011	$0_{0,0}$	011	1154046.217	0.100	2.475	5331.2671
$1_{1,0}$	030	$1_{0,1}$	030	988270.194	0.100	3.856	4690.5797
$1_{1,0}$	110	$1_{0,1}$	110	637714.013	0.200	−3.063	5258.3994
$1_{1,0}$	011	$1_{0,1}$	011	614348.435	0.200	2.193	5354.8709
$2_{1,2}$	110	$1_{0,1}$	110	1711840.578	0.100	−3.211	5258.3994
$2_{1,2}$	011	$1_{0,1}$	011	1695031.030	0.200	3.279	5354.8709
$2_{0,2}$	110	$1_{1,1}$	110	894833.079	0.300	9.241	5274.1582
$2_{0,2}$	011	$1_{1,1}$	011	928596.443	0.300	−6.304	5369.7619
$2_{1,1}$	030	$2_{0,2}$	030	1199093.531	0.200	2.201	4737.2026
$2_{1,1}$	110	$2_{0,2}$	110	839546.907	0.100	0.038	5304.0063
$2_{1,1}$	011	$2_{0,2}$	011	822484.021	0.100	−0.036	5400.7367
$2_{2,0}$	110	$2_{1,1}$	110	1436857.865	0.300	−8.203	5332.0105
$2_{2,0}$	011	$2_{1,1}$	011	1363583.637	0.200	5.131	5428.1719
$2_{2,1}$	110	$2_{1,2}$	110	1896020.257	0.200	−2.430	5315.5003
$2_{2,1}$	011	$2_{1,2}$	011	1826929.314	0.300	0.010	5411.4109
$3_{0,3}$	030	$2_{1,2}$	030	1375728.372	0.200	−19.458	4759.0232
$3_{0,3}$	110	$2_{1,2}$	110	1624633.034	0.200	8.769	5315.5003
$3_{0,3}$	011	$2_{1,2}$	011	1655545.358	0.300	−6.399	5411.4109
$3_{1,2}$	030	$3_{0,3}$	030	1559052.800	0.100	0.410	4804.9133
$3_{1,2}$	110	$3_{0,3}$	110	1194827.872	0.100	4.288	5369.6920
$3_{1,2}$	011	$3_{0,3}$	011	1189488.320	0.100	−3.385	5466.6342
$3_{2,1}$	110	$3_{1,2}$	110	1350535.743	0.100	−7.251	5409.5470
$2_{2,0}$	030	$3_{1,3}$	030	1062841.460	0.300	−18.554	4820.7622
$4_{1,3}$	030	$3_{2,2}$	030	1044018.072	0.200	−10.881	4926.8619
$4_{1,3}$	110	$3_{2,2}$	110	1855413.208	0.300	13.340	5449.0299
$4_{1,3}$	011	$3_{2,2}$	011	1919778.551	0.100	−5.192	5544.2486
$4_{1,3}$	110	$4_{0,4}$	110	1719294.989	0.200	6.915	5453.5701
$4_{1,3}$	011	$4_{0,4}$	011	1727231.121	0.100	−6.736	5550.6713
$4_{2,2}$	110	$4_{1,3}$	110	1406976.895	0.300	0.281	5510.9194
$4_{2,2}$	011	$4_{1,3}$	011	1341289.223	0.100	4.045	5608.2857
$3_{2,1}$	030	$4_{1,4}$	030	873631.048	0.300	−11.691	4902.1302
$5_{2,3}$	110	$5_{1,4}$	110	1560690.153	0.100	−0.112	5634.1209
$5_{2,3}$	011	$5_{1,4}$	011	1543549.888	0.200	5.927	5731.9161
$6_{2,4}$	110	$6_{1,5}$	110	1923327.454	0.100	−0.069	5776.7913
$6_{2,4}$	011	$6_{1,5}$	011	1936356.238	0.200	8.240	5874.7467
$6_{3,3}$	011	$6_{2,4}$	011	1887327.909	0.100	7.095	5939.3363