Pressure shift and broadening of 1_{10}–1_{01} water vapor lines by atmosphere gases

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Abstract

This paper is devoted to the measurement of pressure shift and broadening parameters of water-vapor lines of the pure rotational transition 1_{10}–1_{01} in the ground vibrational state of $H_2^{16}O$ at 556.936 GHz, $H_2^{17}O$ at 552.02 GHz, $H_2^{18}O$ at 547.676 GHz, and the vibrationally excited state $v_2 = 1$ line of $H_2^{16}O$ at 658.003 GHz. The broadening coefficients of the line at 556.936 GHz (for N_2 and O_2 as perturbing gases) coincide within the errors with the values obtained recently by Seta et al. [Pressure broadening coefficients of the water vapor lines at 556.936 and 752.033 GHz. JQSRT 2008;109:144–50] by means of a very different technique (THz-TDS). Pressure shift and broadening for other lines were measured for the first time. Comparison of our results with previous measurements and theoretical calculations is presented.
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1. Introduction

Spectral lines of the water molecule are used for remote sensing of the Earth's atmosphere [1]. In particular, the line 1_{10}–1_{01} of $H_2^{16}O$ at 556.936 GHz is used at the present time in satellite limb measurements of water vapor (see for example the *Odin* satellite atmospheric mission [2]). Laboratory measurements of spectroscopic parameters of the lines used for remote sensing are crucial for retrieval of atmospheric parameters from observational data. Demands for reliability of spectroscopic parameters make multiple measurements of them in different laboratories by different techniques very desirable. The necessity of multiple measurements of parameters of atmospheric spectral lines, as well as scarcity of such measurements, was pointed out in recent review papers [1,3].

In a recent paper [4], the pressure broadening coefficients of the water vapor lines at 556.936 and 752.033 GHz were measured for nitrogen and oxygen as perturbing gases. In particular, the authors of Ref. [4] pointed out significant discrepancy between their results and the earlier measurements of the 556.936 GHz water vapor line broadening by nitrogen and oxygen pressures given in Ref. [5]. The results of Refs. [4,5] were obtained by very different techniques (terahertz time-domain spectroscopy in Ref. [4] and frequency-domain

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spectroscopy with backward wave oscillator (BWO) and acoustic detector in Ref. [5]) and in very different pressure ranges (up to 900 Torr in Ref. [4] and 0.1–5 Torr in Ref. [5]). Because of the importance of water molecule lines for remote sensing of the Earth's atmosphere, it is desirable to clear up the discrepancy between data of Refs. [4,5]. In the present work, new measurements of the pressure shift and broadening coefficients of the water vapor $H_2^{16}O$ line at 556.936 GHz were performed by an improved BWO-based spectrometer with an acoustic detector [6,7]. Comparative studies of the same 1_{10}–1_{01} transitions of water isotopologues $H_2^{17}O$ at 552.02 GHz, $H_2^{18}O$ at 547.676 GHz lines, and the vibrationally excited state $v_2 = 1$ line of $H_2^{16}O$ at 658.003 GHz were performed for the first time.

2. Experiment

The present measurements of the broadening and pressure-shift parameters of the water vapor 1_{10}–1_{01} rotational lines perturbed by H_2O, O_2, N_2 as buffer gases have been performed at room temperature ($T = 299 \pm 1$ K) by the spectrometer with BWO as the radiation source and acoustic detection of absorption signal—radio-spectrometer with acoustic detector (RAD). The BWO source OB-80 (FSUE RPC "Istok", Fryazino, Russia, http://www.istok-mw.ru) operated in the frequency range 500–700 GHz and was phase locked against a reference harmonic synthesizer with a 78–118 GHz range (IEM KVARZ, Russia, http://www.kvarz.com). The synthesizer frequency itself was stabilized against the rubidium frequency standard $f = 5$ MHz, $\Delta f/f = 10^{-11}$ (IEM KVARZ) and controlled via computer. The absorption cell (the cell is 10 cm length, and 2 cm diameter) was combined with a highly sensitive membrane microphone that converted the acoustic wave into a voltage signal. The partial pressure of H_2O vapor (< 0.1 Torr), first filled into the absorption cell, provided sufficient signal-to-noise ratio, not less than 100 for measurements of weak lines. For the strong 557-GHz line, the partial pressure of water vapor in the mixture did not exceed a few mTorr. Then a controlled amount of foreign gas was added and the spectral line was recorded (half-width was determined). Further adding of a foreign gas up to partial pressures of 3–5 Torr continued this procedure. The record of spectral line shape was started only when the pressure in the cell was stable. That is important because water vapor adsorbed by cell walls is quite strong. The gases were from *Laboratory gases* with 4.5–5.0 grades of purity. The water sample was obtained from a double-distilled water source. The pressure was measured with an accuracy of 0.15% by an MKS Baratron Type 122AAX-00010ADS gauge. The details of the apparatus and method of water lines measurements used was also given in Refs. [6,7].

The amplitude modulation by a chopper was used and true absorption line shape was recorded via step-by-step frequency scan of the mm-wave synthesizer. An acoustic detection signal from the spectral line is proportional to $I_0 \cdot (1 - \exp(-\gamma(v - v_0)L))$, where I_0 is the incident radiation power, $\gamma(v - v_0)$ is the absorption coefficient, $(v - v_0)$ is the frequency detuning relative to line center v_0, and L is the optical path length that equals to L_0 (geometrical length of absorption cell) in the case of one passage of radiation through the cell. In the case of small optical depth $\gamma(v - v_0)L \ll 1$ the signal is proportional to $I_0 \cdot \gamma(v - v_0)L$; otherwise, ($\gamma(v - v_0)L \sim 1$) the exponential dependence of the experimental line profile should be taken into account in the fit procedure. In our study, we have used the Voigt model function for describing the absorption coefficient $\gamma(v - v_0)$. Line width and line center were defined from the least-squares fit of the Voigt model profile to the experimental line shape. Note that the line width was determined as the mean value over 2–5 line records at the same pressure. The scattering of the width is mainly due to acoustic noise (we used a cell with acoustic detector) and BWO radiation power drift (thermal drift of the filament current).

In practice, uncontrolled reflection of BWO radiation from the cell back window led to an increase of effective optical path length L_{eff} ($L_{eff} > L_0$) in the acoustic detection spectrometer. Although this effect is relatively small, it must be taken into consideration for precise measurements. One more difficulty for measurements with large optical depth is the correlation between fitted parameters such as I_0, L and line half width Δv increasing the error of line width determination. To minimize the uncertainty of self-broadening measurements of the 557-GHz line, two short cell lengths $L_0 = 1$ and 3 cm were used. The optical depth, one of the parameters in the line profile fit, was calculated using the HITRAN [8] value of the line intensity multiplied by L_0. Coincidence within 1% of self-broadening coefficients obtained for different cell lengths proves consistency of our measured values.

In Fig. 1, the record of the 1_{10}–1_{01} $H_2^{16}O$ line of water vapor (partial pressure about 1 mTorr) diluted by 1.14 Torr of N_2 (total pressure of 1.14 Torr) together with the Voigt profile fit are presented; the (Exp.–Calc.) residual of the fit is shown in the lower part of Fig. 1.

The line width ($\Delta \nu$) of the gas mixture is determined as $\Delta \nu = \gamma^{a-a} p_a + \gamma^{a-b} p_b$, where p_a and p_b are partial pressures of absorber and buffer gases, γ^{a-a} and γ^{a-b} self- and foreign-broadening parameters. Broadening parameters of the 557-GHz line obtained from the linear slope of width (HWHM) dependence vs. pressure of $H_2^{16}O$, N_2 and O_2 (see Fig. 2) were found to be 18.8(2), 4.590(20) and 2.470(10) MHz/Torr, respectively. The frequencies of the line center position at different pressures of H_2O, N_2 and O_2 are shown in Fig. 3. The values of the line shift parameters for N_2 and O_2 as perturbing gases are 0.280(20) and 0.135(10) MHz/Torr, respectively, while self-shifting has a negative value of $-2.235(100)$ MHz/Torr. It should be noted that the error bars in Figs. 2 and 3 are not presented, being smaller than the point size in the figures. The non-shifted central frequency ($p = 0$ Torr) 556 936.010(20) MHz, obtained as the intercept of the self shift slope with frequency ordinate in Fig. 3, is in agreement with the Lamb-dip measurement at low pressure 556 935.995(15) MHz (see Ref. [9]).

For additional verification of the self-broadening measurements (557-GHz line), we had to examine lines having low intensities ($\gamma L_0 \ll 1$). The 1_{10}–1_{01} transition lines of $H_2^{17}O$ at 552.02 GHz (0.038% of ^{17}O in natural abundance), $H_2^{18}O$ line at 547.676 GHz (0.21% of ^{18}O in natural abundance) and the vibrationally excited state $v_2 = 1$ line near 658.003 GHz (peak absorption coefficient $\gamma_0 \sim 4 \times 10^{-4}$ cm^{-1} at room temperature), because of similarity of energy level schemes, line frequencies, masses and dipole moments of molecules with those of ground state of the main isotope, might have similar broadening and shifting coefficients [10,11]. Moreover, information about these lines could be of interest for remote sensing (see, e.g., Ref. [12]).

All results of our measurements are collected in Table 1 together with data from Refs. [4,5]. The present study uncertainties given in parentheses are one standard deviation in units of the last digit quoted. Theoretical values of the broadening and shift coefficient calculated by Gamache [10] are presented as well.
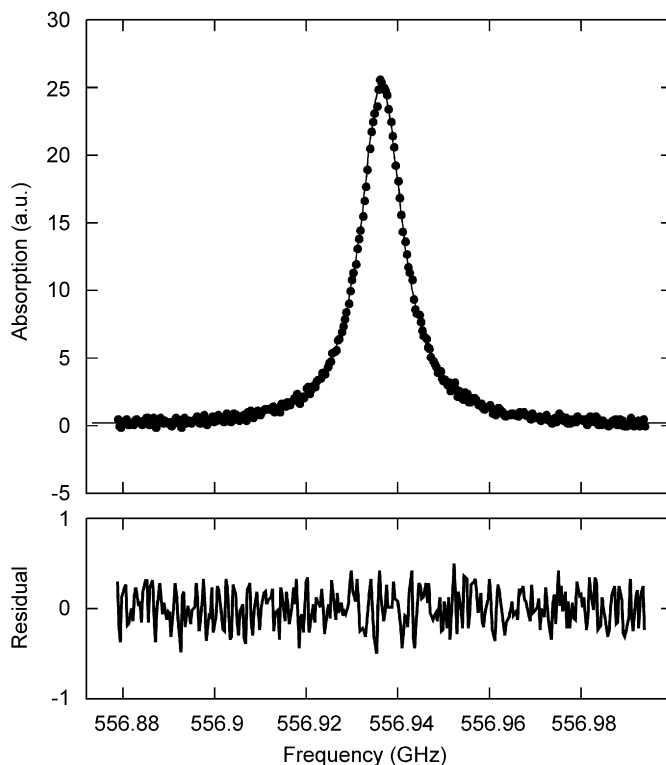

Fig. 1. The water vapor 1_{10}–1_{01} line (partial pressure $\sim$1 mTorr) in N_2 (total pressure $P = 1.14$ Torr). The (Exp.–Calc.) residual from a least-squares fit using the Voigt profile is shown below.
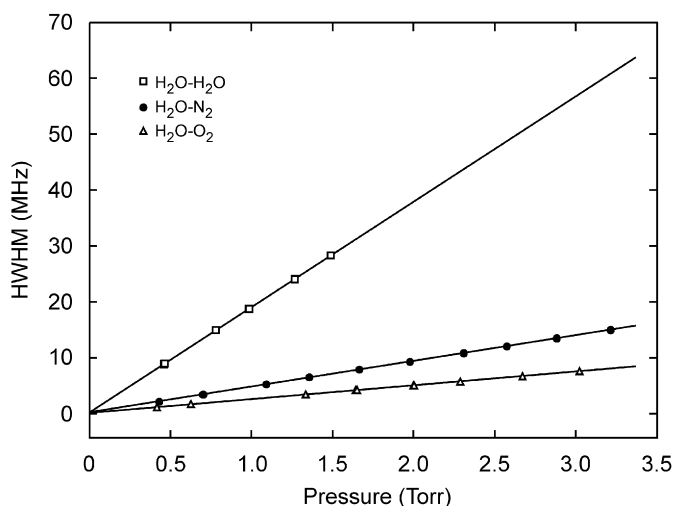
Fig. 2. The 556.936 GHz line width (HWHM) measurements. Self-broadened ($\square$), broadened by N_2 and O_2 pressure ($\bullet$ and $\triangle$). The slopes are 18.8(2), 4.590(20) and 2.470(10) MHz/Torr correspondingly. Error bars are within the points.
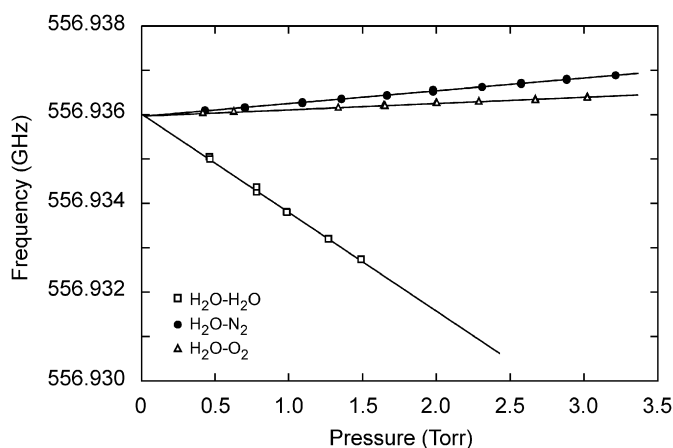

Fig. 3. Dependences of the central frequency of the 1_{01}–1_{10} $H_2^{16}O$ line on total pressure of gas mixtures are shown. Shift parameters of the line perturbed by H_2O, N_2 and O_2 are $-2.235(100)$, 0.280(20) and 0.135(10) MHz/Torr, respectively.

3. Discussion

The values obtained by us for pressure broadening and shift parameters for all transitions studied are presented in Table 1. As can be seen, the accuracies of our measurements exceed those in previous studies. To our knowledge, the experimental investigation of the collisional parameters for the 1_{01}–1_{10} $H_2^{17}O$ and $H_2^{18}O$ isotopologue lines, as well as for $v_2 = 1$ $H_2^{16}O$ line, were carried out for the first time. This gives additional information for remote sensing data treatment.

The closeness between broadening and shifting parameters of water 1_{01}–1_{10} transition of the measured lines ($H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$ ground state and $v_2 = 1$ $H_2^{16}O$) listed in Table 1 has also shown consistency of our measurements for both strong ($H_2^{16}O$ ground state) and weak lines of water isotopologues and the excited state of $H_2^{16}O$. Self-broadening parameters of measured lines are in good agreement with those tabulated in the HITRAN database [8] as 18.445 MHz/Torr for all lines studied. It should be noted that values of our broadening parameters are also very close to the ones of vibration–rotation lines (1_{10}–1_{01}) in the 1500–1700 cm^{-1} wave number range [13,14].

Table 1
Broadening and shift coefficients (MHz/Torr) of water 1_{10}–1_{01} transition lines by pressure of atmospheric gases ($T = 299 \pm 1$ K)[a]

Line	Gas	Broadening	Shifting	Reference
556.9 GHz $H_2^{16}O$	N_2	4.590(20)	0.280(20)	Present study
		4.477(36)	–	[4]
		5.40(6)	0.330(4)	[5]
		4.786	0.310	Calc. [10]
	O_2	2.470(10)	0.135(10)	Present study
		2.261(44)	–	[4]
		3.10(6)	0.170(3)	[5]
		2.648	0.175	Calc. [10]
	H_2O	18.8(2)	−2.235(100)	Present study
			−2.280(40)	[5]
552 GHz $H_2^{17}O$	N_2	4.670(100)	0.275(50)	Present study
		4.730	0.315	Calc. [10]
	O_2	2.490(50)	0.125(25)	Present study
		2.618	0.175	Calc. [10]
	H_2O	18.385(125)	−2.185(135)	Present study
547 GHz $H_2^{18}O$	N_2	4.580(30)	0.275(30)	Present study
		4.680	0.319	Calc. [10]
	O_2	2.405(30)	0.135(30)	Present study
		2.604	0.183	Calc. [10]
	H_2O	18.32(15)	−2.160(100)	Present study
658 GHz $v_2 = 1$ $H_2^{16}O$	N_2	4.650(50)	0.260(70)	Present study
	O_2	2.490(70)	0.135(30)	Present study
	H_2O	18.31(15)	−1.980(100)	Present study

[a]Uncertainties given in parentheses are in units of the last digit quoted; this work values one standard deviation.

Examination of values of N_2- and O_2-broadening parameters obtained in Ref. [4] and in the present study (see Table 1) shows a coincidence of the values within the errors quoted, while the values of broadening parameters measured in Ref. [5] are larger by approximately 25%. The reason for the discrepancy might be the frequency modulation technique used in Ref [5] and the analog data reduction. Both could lead to overestimated broadening parameters values. Nonetheless, we could not find further data to try to elucidate this problem. The general validity of the apparatus used in Ref. [5] is indirectly confirmed by the coincidence of shift parameters obtained in Ref. [5] and in the present study.

The importance of the pressure line shifts in interpretation of the remote sensing data was demonstrated in Ref. [15] in the example of the 3_{13}–2_{20} water-vapor line at 183.310 GHz obtained by MLS and MAS instruments. Introduction by authors of Ref. [15] of the pressure line shift as an adjustable parameter significantly improved the quality of retrieval of atmosphere parameters and gave for the first time an approximate value of air pressure shift parameter for this line. Pressure shifts for this line were later measured by us in the laboratory [6,16], and these laboratory measurements with better accuracy confirmed both the sign and order of magnitude of values obtained in Ref. [15] from atmospheric remote-sensing measurements. It is worth noting that the value calculated by us from experimental data for pure gases shift parameter of water vapor of the 556.936 GHz line, produced by the mixture of nitrogen and oxygen corresponding to their proportion in atmosphere, being opposite by sign to the shift value of 3_{13}–2_{20} water vapor line at 183.310 GHz, exceeds the latter almost by 2.5 times in absolute value (being equal to 0.250(20) MHz/Torr). Quite possibly, this line shift may affect remote-sensing measurements and should be taken into account in processing of the data of atmospheric remote sensing, e.g., by the *Odin* satellite using the 556.936 GHz water vapor line [2,4].

There were no data of pressure line shifts in Ref. [4]. In our opinion an attempt of measurements of pressure line shifts by the technique (THz-TDS) described in Ref. [4] would be of interest. Our experience with our resonator spectrometer [17] led to successful measurements of pressure shifts of the water vapor 183 and 325 GHz lines at atmospheric pressure [7,16].

The particular result in verification of the broadening measurements [4], carried out in the present work by another type of spectroscopic apparatus is very important, in our opinion, for providing the reliability of interpretation of remote-sensing data obtained by the use of the 556.936 GHz water vapor line. Necessity of multiple measurements of parameters of atmospheric spectral lines as well as scarcity of such measurements was pointed out many times in the review papers [1,3].

Acknowledgments

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