

Broadening and shifting of the 321-, 325- and 380-GHz lines of water vapor by pressure of atmospheric gases

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Abstract

Three spectral lines of the main water molecule isotope in the ground vibrational state located near 321, 325 and 380 GHz were studied at low pressures and room temperature using spectrometer with radio-acoustic detection of absorption. Self-, N₂- and O₂-pressure broadening and shifting parameters of these lines have been precisely measured. A number of parameters, in particular pressure shifts, were obtained for the first time. Complementary study of the 325-GHz line by resonator spectrometer at atmospheric pressure validated the low pressure experiment data and allowed measurement of the 325-GHz line intensity. Obtained results are discussed in comparison with previous experimental and theoretical data.

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1. Introduction

Water vapor is the principal absorber of millimeter- and submillimeter (MM-SubMM)-wave radiation in the terrestrial atmosphere. A number of water vapor transitions are directly used or their influence must be accounted for remote sensing of the Earth's atmosphere from satellite, airborne and ground based techniques. For correct interpretation of remote sensing measurements, it is of prime importance to know accurate line parameters (central frequency, intensity, pressure broadening and shifting parameters and their temperature dependences). To avoid domination of the total spectroscopic error in the retrieval accuracy, the air-broadening parameter should be known with uncertainty less than 5% [1]. Precise parameters of water lines are also important in view of the water vapor continuum absorption problem. The continuum study is impossible without accu-

rate accounting of resonant water vapor absorption lines that requires knowledge of precise spectroscopic parameters for each spectral line. These parameters can be obtained from laboratory measurements only.

The 325-GHz (5_{1,5}–4_{2,2}) water vapor line is one of the primary targets for space borne millimeter sensor “MASTER” [2] and the air-broadening parameter of the line is included into initial measurement priorities [3] as well as that for the 321-GHz water vapor line (10_{2,9}–9_{3,6}). Some of required broadening parameters for the 325-GHz line were measured in [4] but no experimental results were found for the 321-GHz line (probably due to its weakness: the line absorption coefficient is only $\sim 10^{-5}$ cm⁻¹). Only a few calculated values of pressure-induced shifts were found [4,5] for these two water lines and, to the best of our knowledge, no experiment confirming the calculations was carried out.

The 380-GHz (4_{1,4}–3_{2,1}) strong water vapor line is also included in MASTER database [2]. The line pressure-broadening parameters and their temperature dependence were previously studied experimentally [6–10] and theoretically [5,6,11–15]. However, except for the self-pressure

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shifting parameter measured in [6], no experimental data on atmospheric gases pressure-induced shifts are available for this line.

The present study is devoted to precise measurements of self-, N₂- and O₂-pressure broadening and shifting parameters of the 321-, 325- and 380-GHz H₂¹⁶O lines in the ground vibrational state. Measurement of the 325-GHz line integrated intensity was also performed. These measurements were carried out by use of complementary abilities of two different Backward Wave Oscillator (BWO)-based spectrometers by analogy with our previous study of the 183-GHz H₂O line [16,17], which was summarized in [18].

2. Low pressure experiment with the RAD spectrometer

2.1. Experimental details

The spectrometer with radio-acoustic detection of gas absorption (RAD spectrometer) have been proved to be one of the most suitable techniques operating in MM-Sub-MM wave range for pressure broadening and shifting investigation of spectral lines of different absorbers, e.g., H₂O [17], O₂ [19,20], CO [21]. Combination of amplitude modulation of radiation, acoustic detection of absorption and synchronous detection of output signal permits recording the true absorption profile of a line with a high signal-to-noise ratio (SNR).

The block-scheme of the experimental setup is the same as shown in Fig. 1 of [20]. BWO radiation sources of types OB-30 (258–375 GHz) and OB-32 (370–535 GHz) were used for this study. Frequency scan around each target line was performed with step by step frequency switching of the 78–118 GHz synthesizer (“KVARZ”, Nizhnii Novgorod) used as a source of reference signal in the BWO phase locked loop (PLL). Each line record contained 151 (or 301) amplitude-frequency readings with 0.5 (or 1) seconds per each reading chosen as an optimum balance between the experiment time and the line SNR. More details about the RAD spectrometer were given in [20 and references therein].

A water sample was obtained from the double-distilled water source. A partial pressure of water vapor in a foreign-gas broadening measurement was kept constant (neglecting the wall adsorption/desorption) during each measurement. The value of the pressure depended on intensity of the line under study. The 325-GHz line is stronger than 321-GHz line by about two orders of magnitude and weaker than the 380-GHz line by approximately one order of magnitude. Taking into account this difference in the line intensities, the partial pressures of water vapor for the 321-, 325- and 380-GHz lines study were kept near 0.5, 0.15 and 0.1 Torr, correspondingly. Pure nitrogen or oxygen gases of the purity better than 99.99% (supplied by Messer GmbH) were gradually added into the cell in course of the experiment; 7–10 pressure points were supposed to be enough for correct determination of pressure

broadening and shifting parameters and its uncertainties. At each pressure the line record was repeated twice to get higher accuracy and to estimate the statistical error of the measurement. For the self-pressure broadening measurement we started from highest in the series water vapor pressure and then gradually pumped out the cell. The total pressure of the gas mixture in the cell did not exceed 5 Torr in foreign-gas measurements and 2–2.5 Torr in self-broadening experiments. Influence of the spectrometer baseline on the line shape was minimal in this conditions as discussed in [22]. The 10-cm long gas cell was permanently connected to a vacuum system during the experiment. Pressure in the system was controlled with a Type 122AAX MKS Baratron having a 10-mBar full scale reading and stated accuracy of 0.15%. The experiment was carried out at room temperature measured by mercury laboratory thermometer with 0.1 °C accuracy. In course of the experiments temperature varied within 24–26 °C.

Achievement of equilibrium of the gas mixture after the next portion of foreign gas is added is a well known problem in experiments with the H₂O–*X* mixtures (*X* = N₂, O₂, ...). In our experiment this process was controlled by monitoring the line peak absorption (corresponding to the line record with zero frequency steps) through a period of time of about 20–30 min. An exponential behavior was observed and characteristic time constant τ_{chem} was evaluated. To avoid uncertainties caused by incomplete gas mixing, we waited $5\tau_{\text{chem}}$ between the pressure change and the beginning of the line record.

An example of experimental record of the studied lines at water vapor pressure of ~1.15 Torr is presented in the upper part of Fig. 1 by open circles. For convenience, each line was normalized to its maximum amplitude.

2.2. Data treatment

The output signal *S* of the RAD spectrometer is in direct proportion to radiation power absorbed inside the cell and with use of the Beer-Lambert law it can be expressed through the incident power *P*₀ and gas absorption coefficient $\alpha(\nu)$ as

$$S(\nu) = P_0 \cdot (1 - e^{-\alpha(\nu) \cdot L}), \quad (1)$$

where *L* is the gas cell length. For a small optical depth ($\alpha L \ll 1$) Eq. (1) can be simplified as

$$S(\nu) = P_0 \cdot \alpha(\nu) \cdot L. \quad (2)$$

Within the experiment pressure range, normalized Lorentz profile was found to be sufficient for describing molecular absorption line. The spectrometer baseline as described, for example, in [19,22] was taken into account by including multiplicative and additive constant- and linear-with-frequency terms. So the spectrometer output signal in vicinity of the line center can be approximated by

$$S(v) = A_0 \cdot (1 + A_1 \cdot (v - v_0)) \cdot \frac{\Delta v}{(v - v_0)^2 + (\Delta v)^2} + A_2 + A_3 \cdot (v - v_0), \quad (3)$$

where A_i , Δv , v_0 are adjustable parameters for approximation the function (3) to experimental record. It should be noticed, that use of simplified model (2) for the relatively strong 380-GHz line (peak absorption $\alpha(v_0) \cdot L \sim 0.1$ for 10-cm gas cell) results in about 3% systematic error in self-broadening parameter. To avoid this error, shorter gas cell of ~ 0.6 cm was used for the 380-GHz line study.

An example of fitting of the theoretical profile (3) to the experimental data is shown in the upper part of Fig. 1 by solid lines. Residuals of the fit are presented in the lower part of the figure. Note that residuals for the 325- and 380-GHz lines are shown magnified by 5 \times to keep variations of residual in the same scale for all lines. The SNR for the 321-GHz line was about 200 and for the 325- and 380-GHz lines it was better than 1000. The residual variations observed near the center of strong lines and indicating small deviation of observed line shape from Lorentz profile did not exceeded 0.3% from line amplitudes.

2.3. Results and discussions

Obtained in the experiment pressure dependences of the 325-GHz line half-width at half maximum (HWHM) and the line central frequency are plotted in Figs. 2 and 3, respectively. Triangles, squares and circles correspond to H_2O , N_2 and O_2 foreign gases, correspondingly. Pressure broadening γ and shifting δ parameters were obtained as a result of linear regression of the experimental data and shown in Figs. 2 and 3 by solid lines. It is worth to note that the fitted intercept for self-broadening dependences constitute less than 0.5–1.5% from the broadening parameter that is practically zero considering the experimental accuracy. This indicates a lack of any parasitic line broadening caused, e.g., by the line saturation by power or by baseline influence. The non-shifted frequency of the line was obtained as an intercept both from self-shifting dependence and from foreign gas-shifting dependences. In the

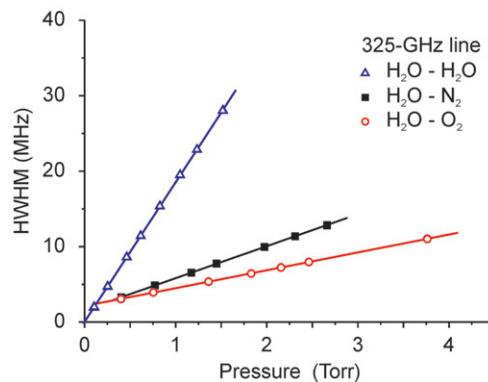


Fig. 2. Dependence of the half-width of the 325-GHz water line broadened by H_2O , N_2 and O_2 versus total pressure in the gas cell. Solid lines are result of linear regression of experimental points.

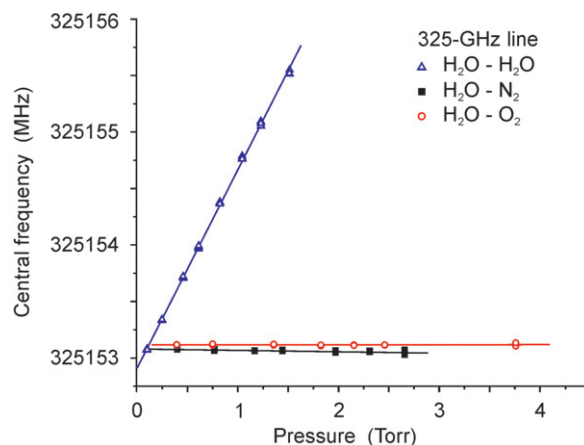


Fig. 3. Dependence of central frequency vs. total pressure for the 325-GHz water line for H_2O , N_2 and O_2 as a collision partners. Solid lines are result of linear regression of experimental points.

second case the self-shift value was taken into account. The absolute values of central frequency obtained from different dependences coincided within experimental accuracy.

Results of our low pressure experiment are presented in Table 1 along with other experimental and theoretical values. Measured broadening parameters were recalculated to 25 °C using common expression $\gamma(T) = \gamma(T_0)(T/T_0)^n$ and

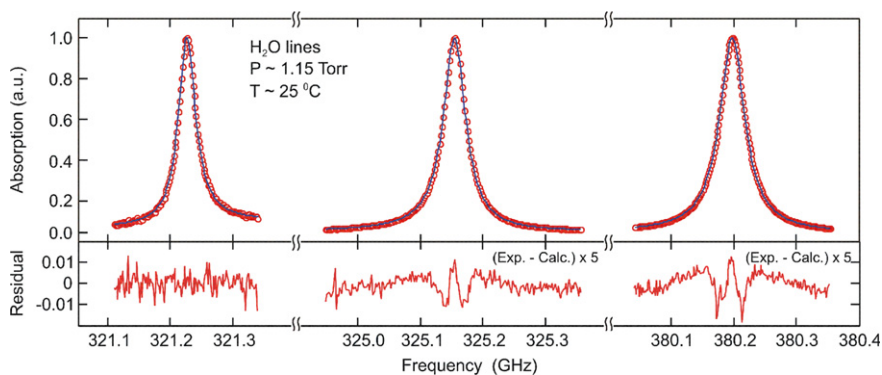


Fig. 1. Normalized experimental records of the studied lines (circles) and result of their treatment by model function (3) (solid line). Residuals of the fit are shown in the lower part.

Table 1
Measured and calculated parameters for studied water transitions at room temperature

Transition	Frequency (MHz)		Broadening (MHz/Torr)						Shifting (MHz/Torr)					
			H ₂ O	Ref.	N ₂	Ref.	O ₂	Ref.	H ₂ O	Ref.	N ₂	Ref.	O ₂	Ref.
3 _{1,3} –2 _{2,0}	183310.075(5)	[17]	19.50(4)	[17]	4.230(7)	[17]	2.580(5)	[17]	+0.230(30)	[17]	−0.092(10)	[17]	−0.097(5)	[17]
	183310.087(1)	[24]			4.409	[15]	2.459	[15]			−0.140	[5]	−0.099	[5]
10 _{2,9} –9 _{3,6}	321225.630(40)	tw^a	14.15(25)	tw	3.58(7)	tw	1.85(6)	tw	+0.370(100)	tw	−0.240(30)	tw	+0.000(30)	tw
	321225.644(150)	[25]			3.370	[15]	1.84	[15]			−0.104	[5]	−0.054	[5]
	321225.676(6)	[24]												
5 _{1,5} –4 _{2,2}	325152.888(5)	tw	18.51(3)	tw	4.17(3)	tw	2.33(2)	tw	+1.764(8)	tw	−0.020(7)	tw	−0.007(5)	tw
	325119.2(353)	[8]			4.011(30)	[4]	2.212(16)	[4]			−0.170	[4]	−0.082	[4]
	325153.8	[29]			4.140	[4]	2.176	[4]			−0.101	[5]	−0.107	[5]
	325152.919(150)	[25]			4.203	[14]	2.725	[14]						
	325152.899(1)	[24]			4.157	[15]	2.226	[15]						
4 _{1,4} –3 _{2,1}	380197.365(5)	tw	19.50(10)	tw	4.21(5)	tw	2.42(3)	tw	+0.315(20)	tw	−0.098(6)	tw	−0.082(6)	tw
	380196.4(96)	[8]	20.54(6)	[6]	4.24(7)	[6]	2.33(4)	[6]	+0.70(10)	[6]	−0.150	[5]	−0.112	[5]
	380196.800	[29]	21.7(2)	[8]	4.18(17)	[7]	2.42(10)	[7]						
	380197.372(150)	[25]	20.83	[11]	3.75(30)	[8]	2.63	[6]						
	380197.38(3)	[6]	20.59	[12]	3.94	[6]	2.693	[14]						
	380197.356(5)	[24]	19.96	[12]	3.74	[13]	2.335	[15]						
					4.155	[14]								
					4.275	[15]								

Results obtained in this work are displayed in bold. Experimental data are given with accuracy declared by authors. Theoretical data are shown in italic.

^a tw, this work.

the averaged value for temperature exponent $n = 0.75$ from Table 9 of [4] for all data. Small systematical error that can appear from the conversion due to inaccurate value of n is much less than estimated experimental uncertainty of the data. Shifting parameters are given without correction because of unknown temperature dependence. Uncertainties of our data given in parentheses correspond to one standard deviation ($1 - \sigma$) in the units of the last given digit. Results of our previous study of the 183-GHz line [17] were also included in Table 1 for comparison. In general, our data are in reasonable agreement with other results. However, detailed analysis allows one to make following conclusions:

First conclusion concerns line center frequencies. All these water lines were recently studied using Lamb-dip technique [24]. Our non-shifted frequencies agree within experimental errors with weighted average frequency of hyperfine components of these lines measured in [24]. It must be emphasized that this coincidence between our measurements and by Lamb-dip techniques excludes the problem of apparent line shift in our experiments and proves consistency of our line shift study results. Our frequencies are in a good agreement also with previous measurements performed at low pressure using conventional video-spectrometer by DeLucia et al. [25] and recommended by NIST as rest frequencies for observed interstellar molecular lines [26]. Differences between these data and our frequencies are much less than 150 kHz uncertainty given by authors of [25].

Second conclusion can be made about pressure broadening parameters. It is worth to note that, to our knowledge, self-, N_2 - and O_2 -pressure broadening parameters for the 321-GHz line and self-broadening of the 325-GHz line were measured for the first time. Most of the previously known experimental broadening parameters for each studied line coincide with our data within $3-\sigma$ uncertainty. The best agreement of our broadening parameters in comparison to calculated ones are found for the most recent theoretical data obtained by Gamache [15] for most cases. Results of the present study are also in good general agreement with data of previous investigation of the 183-GHz line of water molecule by RAD spectrometer [17]. Third conclusion is related to the line center pressure-induced shift that is the most unexplored effect for these water lines. As far as we know, self-, N_2 - and O_2 -pressure shift parameters were measured for the first time for all studied lines except for the 380-GHz line self-shift measured by Bauer et al. [6] as $+0.7(1)$ MHz/Torr. This value is twice larger than one obtained from our experiment. It looks similar to results of our investigation of the 183-GHz water vapor line [17] where the self-shift parameter measured as $+0.230(30)$ MHz/Torr was found to be a few times smaller than $+0.7$ MHz/Torr obtained by Bauer et al. in [27]. Measured shift parameters vary from positive to negative depending on buffer gas. This tendency is appeared for each water line studied in this work as well as for previously investigated the 183-GHz line [17]. It seems interesting to

note that the self-shift for the 325-GHz line is much bigger than those for the 183-, 321- and 380-GHz lines. Interesting difference in the N_2 - and O_2 -pressure shifting parameters was also observed. The N_2 -shifting varies more than ten times from $-0.02(7)$ MHz/Torr for the 325-GHz line to $-0.270(30)$ MHz/Torr for the 321-GHz line; although the O_2 -shifting for these lines fall down to practically to zero that was not predicted by any theoretical calculation. However, shift calculations developed by Gamache [15] seem to be reasonable in prediction of order of magnitude of the effect. Thus, we believe our measurements of pressure-induced shifts can be useful as reference data for further development of intermolecular interaction theory.

The broadening and shifting parameters for dry air can be easily estimated in binary collisions approximation from measured parameters assuming air composition as 21% O_2 and 79% N_2 . The values obtained for the 321-, 325- and 380-GHz lines are respectively 3.22(7), 3.78(3) and 3.83(5) MHz/Torr for air-broadening and $-0.190(30)$, $-0.017(7)$ and $-0.095(6)$ MHz/Torr for air-shifting.

3. Atmospheric pressure experiment with resonator spectrometer

3.1. Experimental details

Recent extension of the working frequency range of our millimeter-wave resonator spectrometer up to 370 GHz [18] allowed us investigate the absorption of H_2O-N_2 and H_2O-O_2 mixtures in the range of 290–370 GHz including the 325-GHz water vapor line. The procedure of gas absorption measurement is described in detail in [16] and based on measurement of the width of resonance response of Fabry-Perot cavity that is in direct proportion to absorption of the sample filling the cavity. The sample substitution by non-absorbing gas was used for the apparatus function accounting. Absorption coefficient α measured at eigen-frequencies of the resonator can be obtained from

$$\alpha = (2\pi/c) \cdot (\Delta f - \Delta f_0), \quad (4)$$

where Δf and Δf_0 are, respectively, widths of resonance response of the Fabry-Perot resonator with sample and filled by non-absorbing gas (nitrogen), directly measured in the experiment; c is the speed of light. Plastic film isolation was used to fill the resonator either with pure nitrogen or with sample mixtures. H_2O-N_2 and H_2O-O_2 mixtures were obtained by permanent flow of nitrogen or oxygen through the bulb with double distilled liquid water. Amount of water vapor in a mixture was controlled by the gas flow speed and varied in the range from 2.5 to 10 g/m³. In a few hours of blowing we were able to get satisfactory stable sample conditions inside the resonator isolation. The sample humidity and temperature monitoring during the experiment was performed by “TESTO-645” meter equipped with highly accurate humidity/temperature probe which was placed nearby the inter-mirror space of the Fabry-Perot resonator. Guaranteed by manufacturer accuracy

of relative humidity measurement is $\pm 1\%$ (10–90% RH from +15 to +30 °C) and $\pm 2\%$ in the remaining range. The accuracy of temperature measurement is ± 0.2 °C. Technical grade oxygen from local supplier with declared purity better than 98% was used. Pure nitrogen was obtained by its evaporation from liquid stage. The experiment was carried out at atmospheric pressure which was measured by pressure meter (600–800 Torr scale) calibrated with an accuracy of 0.5 mmHg. The absorption spectrum was recorded a few times during five days for both H₂O–N₂ and H₂O–O₂ mixtures to estimate statistical errors of the experiment. Measurements were performed at different humidity of the gas sample. The laboratory temperature varied from day to day from 23 to 25 °C. Day-to-day pressure variations were from 753 to 759 Torr.

3.2. Data treatment

An example of experimental record of the absorption spectrum of H₂O–N₂ mixture having absolute humidity of 5.3 g/m³ at 25.2 °C and the sample pressure of 754 Torr is presented in Fig. 4 by points. The following components contribute to the sample absorption in the recorded spectrum: (1) the 321- and 325-GHz water vapor lines highly overlapped at atmospheric pressure; (2) the wing of the strong neighboring 380-GHz water vapor line; (3) non-resonance absorption of summed wings of other water lines and continuum absorption. Each component was taken into account as described below. The Van Vleck–Weisskopf (VW) profile has been previously shown [16,28,29] to be appropriate as a line shape for a single isolated line at atmospheric pressure and was used in the present study. The 321- and 380-GHz lines absorption contribution could

not be accurately derived from the record of experimental spectrum. Therefore the contribution was calculated using line parameters from the low pressure experiment (Table 1) and line intensities from HITRAN [23]. Corresponding absorptions are shown in Fig. 4 by solid and dashed curves. A polynomial function with constant, linear and square with frequency terms was found to be sufficient for taken into account the non-resonance absorption in far wings of other water lines (as well as absorption in wings of weak oxygen lines in the case of experiments with H₂O–O₂ mixture) and the continuum absorption [16]. Thus the total model profile can be expressed as

$$F(v) = A \cdot \left(\frac{v}{v_c} \right)^2 \cdot \left(\frac{\Delta v}{(\Delta v)^2 + (v - v_c)^2} + \frac{\Delta v}{(\Delta v)^2 + (v + v_c)^2} \right) + B_0 + B_1 \cdot v + B_2 \cdot v^2 + \text{VW}(321) + \text{VW}(380), \quad (5)$$

where VW(321) and VW(380) are VW function with corresponding parameters for the 321- and 380-GHz water lines; A , Δv and v_c are the 325-GHz line amplitude, half-width and central frequency, correspondingly; B_i are non-resonance absorption characterizing constants. Values of these six parameters were obtained from fitting function (5) to experimental data.

The residual of the fit is shown in lower part of Fig. 4 magnified by 2- \times and shifted down to –5 dB/km for clarity of the picture. Obtained from the fit contribution of non-resonance absorption is plotted in Fig. 4 by dotted line. The noise-like residual proves appropriateness of the function (5) for the experimental data treatment. The SNR for the 325-GHz line records was usually ~ 100 or higher.

3.3. Results

Line half-width Δv and central frequency v_c determined from the fit are related to pressure-broadening γ and pressure-shifting δ parameters as

$$\Delta v = \gamma^{a-a} \cdot p_a + \gamma^{a-b} \cdot p_b$$

$$v_c = v_0 + \delta^{a-a} \cdot p_a + \delta^{a-b} \cdot p_b, \quad (6)$$

where γ^{a-a} , γ^{a-b} are self- and foreign-gas broadening parameters; δ^{a-a} , δ^{a-b} are self- and foreign-gas shifting parameters; p_a and p_b are partial pressures of water vapor and buffer gas in a mixture, respectively; v_0 is non-shifted position of the line center.

The N₂- and O₂-pressure broadening and shifting parameters for the 325-GHz water line were derived from the observed line half-width and central frequency using equation (6) and values of self-broadening, self-shifting parameters and v_0 from the low pressure experiment (Table 1). Broadening parameters were recalculated to 24 °C as mentioned in Section 2.3 and averaged over all experiments at atmospheric pressure. No temperature correction was used for shifting parameters but they were also averaged over all experiments. Results are presented in Table 2.

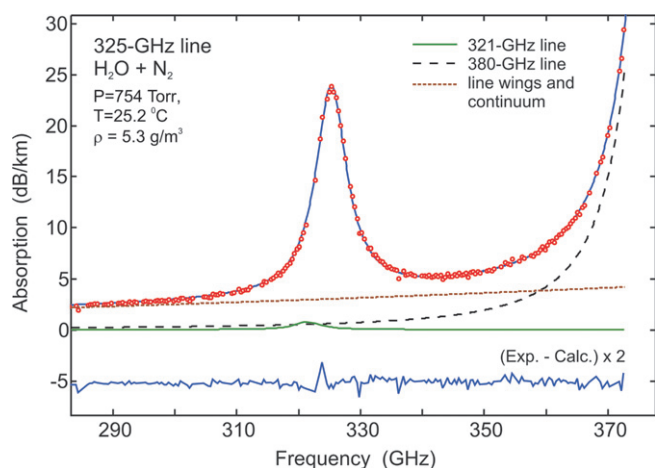


Fig. 4. An experimental absorption spectrum (points) of H₂O–N₂ mixture around the 325-GHz line recorded by the resonator spectrometer at atmospheric pressure, room temperature and absolute humidity of the gas sample of 5.3 g/m³. Weak absorption line plotted by solid line represents contribution of the 321-GHz line of water vapor. The 380-GHz line wing is shown by dashed line. Dotted line combines absorption in the wings of the other H₂O lines and continuum absorption obtained from the fit of the experiment (see text for details). Zoomed in factor of 2 residual of the fit is shown in the lower part shifted to –5 dB/km.

Table 2

Results of the room temperature study of the 325-GHz water vapor line at atmospheric pressure by resonator spectrometer and at a few Torr pressure range by RAD spectrometer

	Broadening (MHz/Torr)		Shifting (MHz/Torr)		Normalized integrated intensity (cm/molecule)
	H ₂ O–N ₂	H ₂ O–O ₂	H ₂ O–N ₂	H ₂ O–O ₂	
Resonator	4.09(5)	2.29(4)	−0.037(11)	0.000(40)	$8.55(35) \times 10^{-23}$
RAD	4.17(3)	2.33(2)	−0.020(7)	−0.007(5)	—

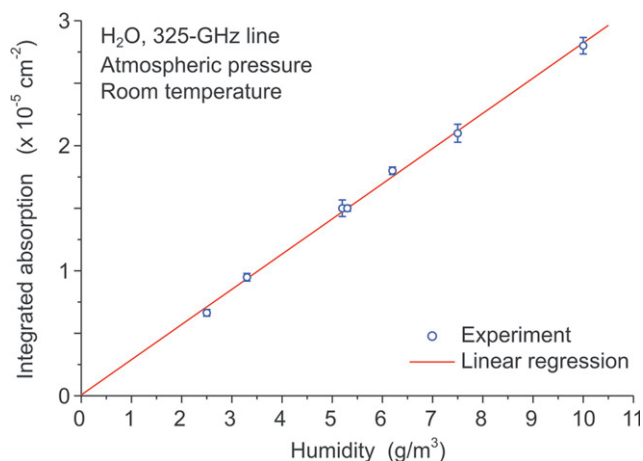


Fig. 5. Integrated absorption coefficient of the 325-GHz water vapor line at 24 °C measured at atmospheric pressure experiments and plotted as a function of the sample humidity (points). Error bars correspond to one standard deviation ($1 - \sigma$) of measured parameter. Solid line is a result of linear regression of the experimental points.

Air-broadening and shifting parameters for the 325-GHz line calculated as in Section 2.3 from the results of the experiment are 3.71(5) and $-0.029(17)$ MHz/Torr, respectively. The low pressure study data are also given in Table 2 for comparison. The line parameters measured by entirely different techniques at pressures differing by factor of ~ 300 coincide within the experimental uncertainties confirming that sources of systematical errors in both spectrometers data and in the way of their treatment are minimized.

The integrated absorption coefficient of the 325-GHz line was determined from the atmospheric pressure experiment results as π times the line absorption at the line center frequency times the line HWHM ($\pi \alpha(v_c) \cdot \Delta v$) and plotted as a function of humidity in Fig. 5 with error bars corresponding to one standard deviation ($1 - \sigma$) of the parameter. Both H₂O–N₂ and H₂O–O₂ mixture measurement results were included into dependence in Fig. 5 since the line integrated absorption is independent from foreign gas concentration but is determined by a number of water molecules. The line intensity was determined as a slope of linear regression of experimental points (solid line in Fig. 5) and constituted $8.55(35) \times 10^{-23}$ cm/molecule (at 24 °C as average experimental temperature). Zero within experimental accuracy intercept of the dependence confirmed the lack of systematic error. The measured line intensity is of about 6%

less than the value 9.076×10^{-23} cm/molecule calculated for the same temperature using HITRAN database [23]. The agreement can be considered as reasonably good however the difference is slightly bigger than $3 - \sigma$ experimental uncertainty.

4. Conclusions

The experimental study of the 321-, 325- and 380-GHz spectral lines of the main isotope of the water molecule in the ground vibrational state was performed at room temperature and low pressure by the RAD spectrometer and validated by investigation of absorption in H₂O–N₂ and H₂O–O₂ mixtures at atmospheric pressure by the resonator spectrometer in the frequency range 290–370 GHz. The 321-GHz line collisional parameters were experimentally studied for the first time. Self-, N₂- and O₂-pressure broadening and shifting parameters were precisely measured for all mentioned lines at room temperature. To the best of our knowledge, the line center shift induced by pressure of main components of atmosphere for the 321-, 325- and 380-GHz lines was studied by the first time (except for the self-pressure shifting of the 380-GHz line). Systematical variations of obtained data compare to theoretical calculations results indicate necessity of further improvement of theoretical model. Measured central frequencies agree within experimental errors with weighted average frequency of hyperfine components of these lines measured in [24] using Lamb-dip technique.

Intensity of the 325-GHz line determined from results of atmospheric pressure experiments with the resonator spectrometer was found about six percents smaller than the value tabulated in HITRAN database. We believe that collisional parameters of water lines measured in this work are of interest for Earth's atmosphere remote sensing applications as well as for further development of the molecular interaction theory and also for refinement of existing atmospheric radiation transfer models.

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References

- [1] J. Urban, N. Lautie, D. Murtagh, Y. Kasai, E. Dupuy, J. de La Noe, L. El Amraoui, P. Eriksson, U. Frisk, C. Jimenez, E. Le Flochmoen, M. Olberg, P. Ricaud, in: Proceedings of the International Workshop on Critical Evaluation of mm/sub-mm-Wave Spectroscopic Data for Atmospheric Observations, Ibaraki, Japan, 2004, pp. 69–74.
- [2] A. Perrin, C. Pizzarini, J.-M. Colmont, C. Verdes, G. Wlodarczak, G. Cazzoli, S. Buehler, J.-M. Flaud, J. Demaison, J. Atmos. Chem. 51 (2005) 161–205.
- [3] A. Bauer, M. Birk, S.A. Buehler, J.M. Colmont, A. von Engeln, K. Kuenzi, A. Perrin, D. Priem, G. Wagner, G. Wlodarczak, Final Report, ESTEC Contract No 11581-95-NL-CN, 1998 (available from <http://www.sat.uni-bremen.de/members/sab/publications/spectro/db_fr.ps.gz/>).
- [4] J.-M. Colmont, D. Priem, G. Wlodarczak, R.R. Gamache, J. Mol. Spectrosc. 193 (1999) 233–243.
- [5] <http://faculty.uml.edu/Robert_Gamache/>.
- [6] A. Bauer, M. Godon, M. Kheddar, J.M. Hartmann, J. Bonamy, D. Robert, J. Quant. Spectrosc. Radiat. Transfer 37 (1987) 531–539.
- [7] T.M. Goyette, F.C. DeLucia, J.M. Dutta, C.R. Jones, J. Quant. Spectrosc. Radiat. Transfer 49 (1993) 485–489.
- [8] R. Emery, Infrared Phys. 12 (1972) 65–79.
- [9] V.Y. Ryadov, N.I. Furashov, Optics and Spectroscopy 24 (1968) 93–97.
- [10] J.E. Pearson, D.T. Llewellyn-Jones, R.J. Knight, Infrared Phys. 9 (1969) 53–58.
- [11] W.S. Benedict, L.D. Kaplan, J. Quant. Spectrosc. Radiat. Transfer 4 (1964) 453–469.
- [12] J.Y. Mandin, J.M. Flaud, C. Camy-Peyret, G. Guelachvili, J. Quant. Spectrosc. Radiat. Transfer 23 (1980) 351–370.
- [13] W.S. Benedict, L.D. Kaplan, J. Chem. Phys. 30 (1959) 388–399.
- [14] K.L. Lam, J. Quant. Spectrosc. Radiat. Transfer 17 (1977) 351–383.
- [15] R.R. Gamache, J. Fischer, J. Quant. Spectrosc. Radiat. Transfer 78 (2003) 289–304.
- [16] M.Yu. Tretyakov, V.V. Parshin, M.A. Koshelev, V.N. Shanin, S.E. Myasnikova, A.F. Krupnov, J. Mol. Spectrosc. 218 (2003) 239–245.
- [17] G.Yu. Golubiatnikov, J. Mol. Spectrosc. 230 (2005) 196–198.
- [18] M.Yu. Tretyakov, V.V. Parshin, M.A. Koshelev, A.P. Shkaev, A.F. Krupnov, J. Mol. Spectrosc. 238 (2006) 91–97.
- [19] M.Yu. Tretyakov, M.A. Koshelev, V.V. Dorovskikh, D.S. Makarov, P.W. Rosenkranz, J. Mol. Spectrosc. 231 (2005) 1–14.
- [20] A.F. Krupnov, G.Yu. Golubiatnikov, V.N. Markov, D.A. Sergeev, J. Mol. Spectrosc. 215 (2002) 309–311.
- [21] V.N. Markov, G.Yu. Golubyarnikov, V.A. Savin, D.A. Segeev, A. Guarnieri, H. Maeder, J. Mol. Spectrosc. 212 (2002) 1–5.
- [22] M.Yu. Tretyakov, G.Yu. Golubiatnikov, V.V. Parshin, M.A. Koshelev, S.E. Myasnikova, A.F. Krupnov, P.W. Rosenkranz, J. Mol. Spectrosc. 223 (2004) 31–38.
- [23] L.S. Rothman, D. Jacquemart, A. Barbe, D.C. Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chakerian Jr., K. Chance, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J.-M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, G. Wagner, J. Quant. Spectrosc. Radiat. Transfer 96 (2005) 139–204.
- [24] G.Yu. Golubiatnikov, V.N. Markov, A. Guarnieri, R. Knochel, J. Mol. Spectrosc. 240 (2006) 191–194.
- [25] F.C. DeLucia, P. Helminger, R.L. Cook, W. Gordy, Phys. Rev. A 5 (1972) 487–490.
- [26] <<http://physics.nist.gov/cgi-bin/micro/table5/start.pl/>>.
- [27] A. Bauer, M. Godon, M. Kheddar, J.M. Hartmann, J. Quant. Spectrosc. Radiat. Transfer 41 (1989) 49–54.
- [28] A.F. Krupnov, M.Yu. Tretyakov, V.V. Parshin, V.N. Shanin, S.E. Myasnikova, J. Mol. Spectrosc. 202 (2000) 107–115.
- [29] M. Lichtenstein, V.E. Derr, J.J. Gallagher, J. Mol. Spectrosc. 2 (1966) 391–401.