



Line shape parameters of the 22-GHz water line for accurate modeling in atmospheric applications



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ABSTRACT

The paper concerns refining parameters of one of the major atmospheric diagnostic lines of water vapor at 22 GHz. Two high resolution microwave spectrometers based on different principles of operation covering together the pressure range from a few milliTorr up to a few Torr were used. Special efforts were made to minimize possible sources of systematic measurement errors. Satisfactory self-consistency of the obtained data was achieved ensuring reliability of the obtained parameters. Collisional broadening and shifting parameters of the line in pure water vapor and in its mixture with air were determined at room temperature. Comparative analysis of the obtained parameters with previous data is given. The speed dependence effect impact on the line shape was evaluated.

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1. Introduction

Water vapor is the main atmospheric absorber having a dominant influence on the Earth's radiation balance. Moreover, water vapor is the basic greenhouse gas affecting the weather and climate of the planet [1]. A vertical concentration profile of atmospheric water can be retrieved by remote sensing measurements, which requires accurate knowledge of diagnostic line shape parameters. The 22-GHz line corresponding to the pure rotational transition $J'_{Ka'Kc'} \leftarrow J_{KaKc} = 6_{16} \leftarrow 5_{23}$ of an H_2O molecule is one of the major diagnostic lines used in the microwave range. Spectroscopic parameters of this line are known from several laboratory investigations [2–8]. Comparative analysis of the parameters obtained in those studies can be found in [9] and includes also related data obtained from laboratory studies in the IR range and from direct atmospheric radiometry.

The most recent thorough laboratory investigation of the line [8] was performed with the use of a classical video-type spectrometer having a 2 m long gas cell (P-band thermo-stabilized wave guide). The line was studied in pure water vapor and in mixtures with two main atmospheric constituents O_2 and N_2 within the pressure range of 10–120 milliTorr. The retrieved value of the air pressure broadening parameter was found to be much smaller (from 3 up to 10%) than in all other known studies. Besides, the value of the self-pressure shifting parameter of the line center was also found to be much smaller (~40%) than in the earlier study

[4] performed with the use of the dispersion resonator spectrometer at pressures up about 6 Torr. In this respect, measurements performed at atmospheric pressure with the use of an “echo-box” should be also mentioned [2]. The self-shifting parameter determined from those earlier data has approximately the same magnitude as in [4,8] but the opposite sign.

These inconsistencies demonstrate the problem of unknown systematic measurement errors discussed in many previous studies. The results of even most careful investigations may differ from each other, going significantly beyond the limits of measurement error range given by different authors. That is why multiple measurements under different experimental conditions using instruments based on different principles are believed to be required for determining a reliable value of the parameter (see, e.g., overview articles [10,11]).

In this work we revise the line shape parameters at room temperature using two spectrometers with complementary abilities, namely, the spectrometer with radio-acoustic detection (RAD-spectrometer) [12,13] and the video spectrometer [14]. Section 2 presents experimental details and methods of raw data treatment. The obtained parameters are compared with the known data and discussed in Section 3. Concluding remarks are given in Section 4.

2. Experimental details

2.1. Video spectrometer

A stainless steel tube (2 m long, 11 cm in diameter) with conical high-density polyethylene windows was used as a gas cell. The

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Table 1
Experimental conditions for the self- and air-pressure broadening study.

		RAD	Video
Self	P _{water} (mTorr)	29–890	0.8–32.14
	T, °C	22.7–23.3	23.0–26.0
Air	P _{water} (mTorr)	39–170	9.7
	P _{air} (mTorr)	126–1340	7.9–83.2
	T, °C	22.7–23.3	23.7–25.5

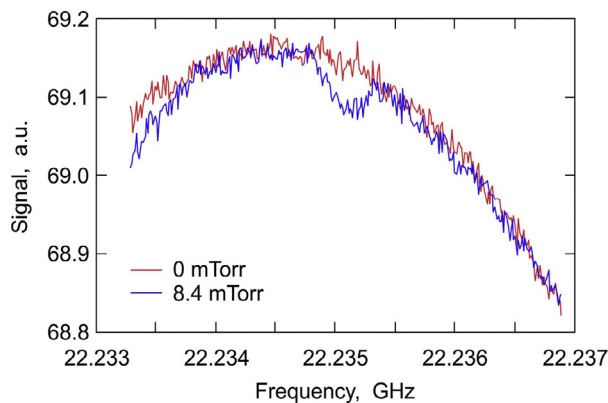


Fig. 1. Video spectrometer output signals recorded using 100% AM of radiation power with 8.4 mTorr of water vapor (blue trace) and with gas cell evacuated (red trace).

geometrical path length was ~ 196 cm. The cell had no temperature stabilizing circuit. All measurements were performed at room temperature (see Table 1 for details). A radiation source (frequency synthesizer, Keysight E8267D) and a detector (commercial point-contact Si diode, D608A) were coupled with the cell using two horn antennas at opposite ends of the cell. A radiation beam phase front was corrected by dielectric lenses having 20 cm focal length. The beam size diameter was comparable with the cell diameter. The radiation power did not exceed 5 mW (the corresponding Rabi frequency is about 15 kHz) to minimize transition saturation and the corresponding distortion of the line shape at the lowest pressure of the experiment. For the pressure of 1 mTorr, additional line broadening due to this effect was estimated to be 6–7 kHz. The spectrometer baseline within a frequency range of the line recording was explicitly controlled by the use of the radiation amplitude modulation (AM) method and synchronous detection of the signal at the (1f) modulation frequency (200 Hz). This method allowed choosing either positive or negative slope of the baseline at the line central frequency or flat area corresponding to minimum or maximum of the standing waves forming the baseline fringes. The baseline was observed with a signal-to-noise ratio (SNR) of the order of 10^4 – 10^5 . Repeated recordings revealed satisfactory stability of the baseline in spite of a rather small contrast of molecular absorption (Fig. 1). Multiple recording of the absorption spectrum with different baselines allowed evaluating the corresponding systematic influence on the retrieved parameters of the line.

The amplitude modulation method allowed direct measurement of the gas absorption coefficient value using the basic spectroscopic equation

$$\alpha = -\frac{1}{L} \ln \left(\frac{W}{W_0} \right),$$

where W and W_0 are, respectively, the detected power with and without absorbing gas and L is the gas cell path length. Such measurements were used as a consistency check of experimental data.

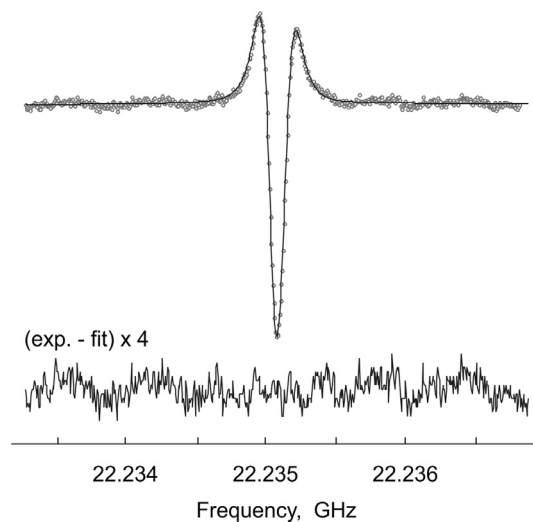


Fig. 2. Line recording in pure water vapor at 4.75 mTorr obtained with video spectrometer using FM regime (upper trace) and the result of model function fitting to the observed spectrum (lower trace).

The detector response versus radiation power was calibrated using our synthesizer. Taking into account the result of this calibration we found that the absorption coefficient at the line central frequency at pure collisional regime coincides within statistical experimental uncertainty (10%) with the value $9 \times 10^{-6} \text{ cm}^{-1}$ reported in HITRAN [15] at 296 K on the basis of Refs. [16,17].

The frequency modulation (FM) regime of spectrum recording and synchronous detection at doubled (2f) frequency was used for the line shape parameters determination. The modulation frequency was 4 kHz, which is much less than the line width (the Doppler half width is 32 kHz at 296 K). The amplitude of frequency deviation was less than 15% from the line width to reduce apparent broadening of the observed line due to the modulation. A typical example of the line recording is given in Fig. 2.

The instrumental baseline was taken into account by (i) its experimental recording and further subtraction from the observed spectra and (ii) by inclusion of the multiplicative and the additive terms varying linearly with frequency to the line shape fitting function. The function took into account the hyperfine structure of the line related to the spin-rotational interaction in the H_2^{16}O molecule. Relative intensity and central frequency of the hyperfine components were taken from [6]. The sum of Voigt profiles was used assuming identical collisional broadening for all lines of the structure. It should be noted that the structure can be resolved at pressures below ~ 1.3 mTorr. At pressures within 5–50 mTorr it manifested itself by asymmetry of the observed line profile, which is clearly seen in Fig. 2. No deviation from the Voigt profile was revealed. All spectral recordings were treated separately (the so called one-by-one spectrum fitting procedure).

It was found that the baseline influence on the line shape parameters was insignificant until the collisional line width exceeded a value of about 400–600 kHz. This was used as a sample upper pressure limitation criterion.

Double distilled water (natural abundance of isotopologues) degassed by freezing and deep pumping of the sample was used for the study. High purity dry synthetic atmospheric air was bought from the local supplier. The sample pressure in the cell was controlled by the capacitance diaphragm gauge Inficon (CDG025D, 0.1 Torr) and MKS Baratron (626B, 1 Torr). For air-broadening experiments we filled the cell with about 10 mTorr of water vapor and waited for more than 20–30 min until the pressure became stable.

Then dry air was gradually added. Several back and forth frequency sweeping recordings were collected at each sample pressure.

2.2. RAD–spectrometer

The spectrometer design and method of measurement were described in detail in [13]. The principle of line shape parameters investigation can be found in [18]. A microwave synthesizer (Agilent E8257D) synchronized with GPS-based time and frequency standard was used as a source of highly coherent CW radiation. Amplitude modulation of radiation by a mechanical chopper and subsequent synchronous detection of the absorption signal at 1f modulation frequency was used. The chopping frequency was carefully adjusted so that the radioacoustic signal remained out of characteristic mechanical resonances in the setup elements (table, vacuum system, etc.) and was kept near 80 Hz. A copper gas cell (~10 cm long, 2 cm diameter) was used. The cell was permanently connected with Julabo FP-50 thermostat (<http://www.julabo.de/>) that provided stable temperature of a coolant inside the thermostat within ± 0.1 °C around the chosen value. The cell was isolated from ambient atmosphere by a foamed polyethylene case. Four copper temperature sensors of ± 0.5 °C stated uncertainty were mounted on the cell surface and ensured temperature control of the gas sample inside the cell. No temperature gradients were revealed in the cell. Gas pressure in the cell was permanently monitored using MKS Baratron (Type 626B, 10 Torr) and Inficon (CDG025D, 0.1 Torr) gauges having a declared accuracy of reading of 0.25% and 0.5%, respectively. No differences between gauges readings exceeding uncertainties stated by manufacturers were revealed. Small pressure variations caused by water sorption processes were observed in case of a pure water sample ('cold-finger' was not used), even half an hour after gas filling. The value of these variations was about 1–2 mTorr, which is comparable with the gauges inaccuracy. In air-broadening experiments the variations were even smaller.

Special efforts were focused on achieving sufficient SNR for accurate determination of parameters of the studied weak water line. The influence of external acoustic and mechanical noise was reduced by placing the cell inside a pot filled with about 25 kg of small lead balls (3 mm in diameter each). This resulted in about tenfold increase of the initial cell weight and in sevenfold increase of the SNR of the experimental spectra.

Temperature stability of the whole setup was provided by the room air conditioning. High stability of radiation parameters (frequency and power), studied gas sample conditions (temperature and pressure) and related electronic circuits allowed averaging a large number of repeated experimental recordings without noticeable distortions in the observed spectra. As an illustration of a possibility of high sensitivity recordings of molecular spectra we present in Fig. 3 the results of analysis of the spectrum of water vapor strongly diluted by argon in the vicinity of the 22-GHz line. The spectrum contained 100 frequency points and was recorded for about 8 h. The spectrum averaged over 300 sequential recordings revealed in the high frequency wing of the studied 22-GHz line another very weak line corresponding to the pure rotational transition 5_{32} – 5_{33} of HDO molecule contained in our water sample in natural abundance. The shape of this line after the baseline subtraction can be well described by the Lorentz function (Fig. 4). The central frequency retrieved from the fit was 22307.46(10) MHz, which is in perfect coincidence with the tabulated value of 22307.53(2) MHz calculated on the basis of early measurements of the HDO rotational spectrum in deuterium-enriched sample [19]. The collisional width (HWHM) of the line was found to be 3.1(3) MHz, which is in agreement with the estimated value of 3.53 MHz obtained assuming the same self-broadening parameter as of the 22 GHz line and 0.141 efficiency of the line broadening by argon [5]. Thus, identification of the line causes no doubts. Known inten-

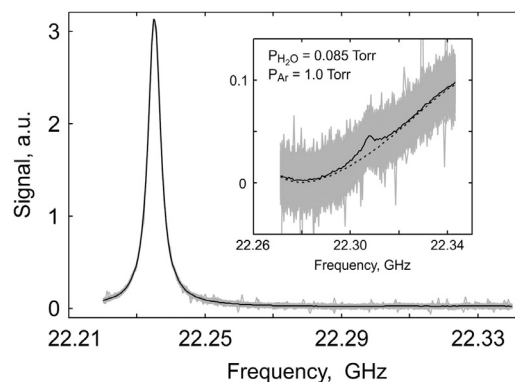


Fig. 3. Three hundred experimental spectra (lock-in time constant is 0.5 s) of the mixture of water vapor with argon are shown by grey curves. Averaged spectrum is shown by solid black curve. Dotted curve in the inset is a fitted polynomial function demonstrating baseline.

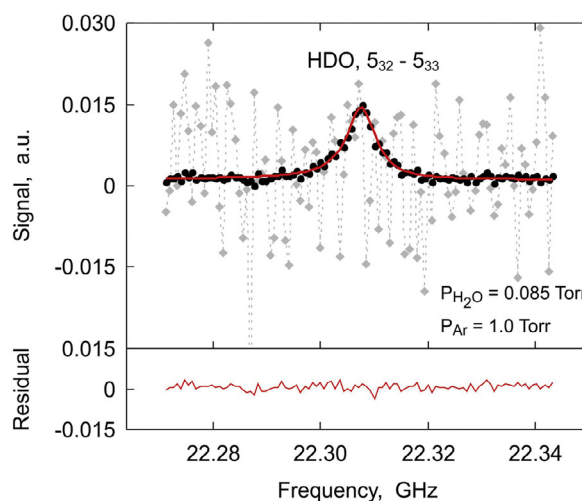


Fig. 4. Upper part: typical single experimental recording of the spectrum after baseline subtraction (grey diamonds connected by dotted lines), result of 300 recordings averaging (black points) and model function (Lorentz plus linear with frequency function) fitted to the points (red solid curve). The fit residual is shown by blue curve in the lower part. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sity of the line (5.483×10^{-28} cm/mol [15]), SNR of its recording (Fig. 4) and known partial pressure of water vapor allowed evaluating the spectrometer sensitivity to the absorption coefficient to be 2×10^{-10} cm $^{-1}$. Standard deviation of experimental points from the fitted curve in the single recording of the spectrum (grey traces in Figs. 3 and 4, each recording took about 90 s) corresponded to the sensitivity of 3.3×10^{-9} cm $^{-1}$. Note that the signal accumulation gain amounted to about 16.5, which is very close to the value of square root from the number of averaged traces expected from statistics.

The signal accumulation method was used for the 22 GHz line investigation. Typical SNR of a single spectrum recording with 1 s lock-in time constant varied from 100 for pressures below 50 mTorr up to 800 for higher pressures. Averaging of several sequential recordings of the line at permanent thermodynamic conditions allowed achieving SNR up to 1600.

Low radiation frequency and, correspondingly, large wavelength (which becomes comparable with gas cell dimensions and therefore causes a more pronounced interference pattern) entailed a stronger than usual problem with the spectrometer baseline related to the non-resonance heating of the cell elements and sec-

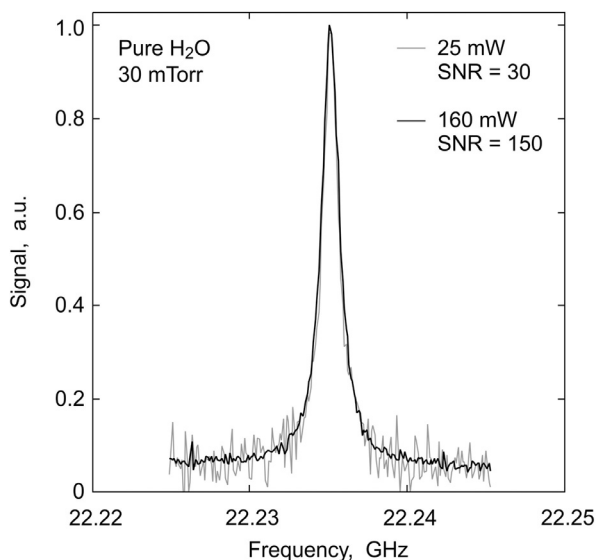


Fig. 5. Experimental recordings of pure water vapor spectra at two significantly different radiation power levels (shown in the figure). Both spectra are normalized to line amplitude.

ondary heating of gas. This baseline was determined experimentally in every experimental cycle by replacing the studied sample by a non-absorbing gas and subtracting from experimental recordings. The remaining minor variations of the baseline as well as unknown minor variation of the radiation power absorbed by the gas sample were taken into account in the spectrometer signal model function by additive and multiplicative to the line shape terms (both terms were functions changing linearly with frequency and with adjustable parameters), respectively. Very good linearity of collisional line width versus pressure could be obtained if displacement of the spectrometer elements remained unchanged. However, every slight move of the cell led to uncontrolled change of the interference pattern, causing a slight change of the slope of the line width versus pressure without worsening the quality of linearity. This change is expected to be periodical and, therefore, an unperturbed value of the slope can be determined by averaging, if a sufficiently large number of cell positions (uniformly spread along the radiation beam axis within the radiation wavelength interval) are probed. In the present study the line recordings at different pressures were obtained at 7 and 5 different cell positions for self- and air-broadening, respectively.

The principle of the RAD spectrometer operation allows increasing SNR of the experimental spectra (or the spectrometer sensitivity) by increasing the radiation power [20]. Fig. 5 clearly demonstrates a better quality of the 22 GHz line recording at increased radiation power.

However, high power requires careful consideration of the transition saturation effect. Special study was performed to exclude the influence of this effect on the retrieved line shape parameters. The essence of the effect is local violation of thermodynamic equilibrium if molecules absorb more radiation energy than they can dissipate via collisions with each other. The effect manifests itself by additional broadening of the observed spectral lines, which may be especially significant at low pressures. If the line shape perturbation is small, it can be characterized by the following dependence of the collisional line width (Γ) on radiation power (W) [21]:

$$\Gamma(W) = \Gamma(0) \sqrt{1 + \frac{aW}{\Gamma(0)^2}}, \quad (1)$$

where a is an empirically found coefficient dependent on the properties of molecular transition and radiation beam. To determine

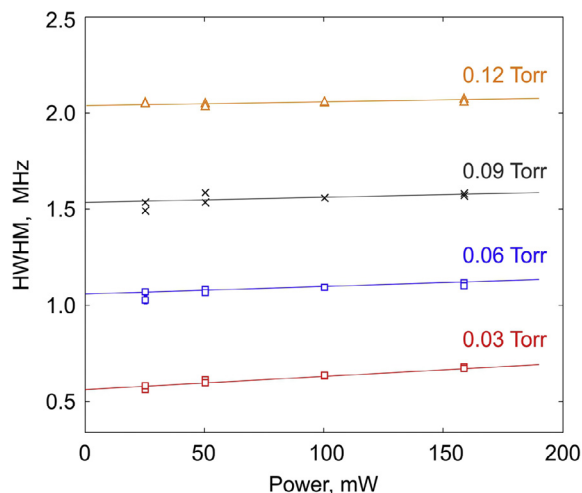


Fig. 6. Measured width of 22-GHz line versus preset radiation power at different pressures of water vapor (different symbols correspond to different pressure values) and result of fitting Eq. (1) to these points (solid lines).

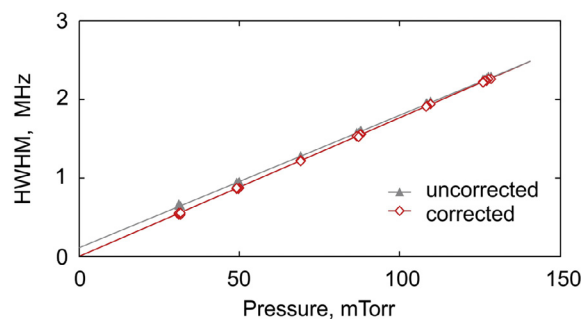


Fig. 7. Collisional half width at half maximum (HWHM) of 22-GHz line in pure water vapor as measured by RAD spectrometer without (grey triangles) and with (red diamonds) power saturation correction applied. See text for details. Solid lines are results of linear regression of corresponding points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the value of this coefficient in our experiment we found the line width from its profile recorded at four pressures (30, 60, 90 and 120 mTorr) using four levels of the synthesizer output power (25, 50, 100 and 160 mW). The result of fitting Eq. (1) to these data is presented in Fig. 6.

The found value of the coefficient a was used for correction of the line collisional width determined from the experimental data. The correction result is shown in Fig. 7. The linear dependence of the uncorrected line width on pressure has a noticeable intercept at the Y axis, which is completely eliminated if the power saturation correction is applied.

That experiment demonstrated in particular that the impact of the power saturation effect is practically negligible at sample pressures above 150 mTorr, even if full power supplied by our synthesizer is used.

All experimental recordings were treated one by one using the Voigt profile, which allowed direct comparison of the obtained values with the video spectrometer data or unified dataset treatment, which will be reported in the next section. This also allowed minimizing uncertainty caused by the pressure variations mentioned above.

High SNR of experimental recordings achieved by data accumulation allowed observation and evaluation of the “fine” line shape effect, namely speed dependence (SD) of the collisional cross section. However, the back side of a longer experimental time was a

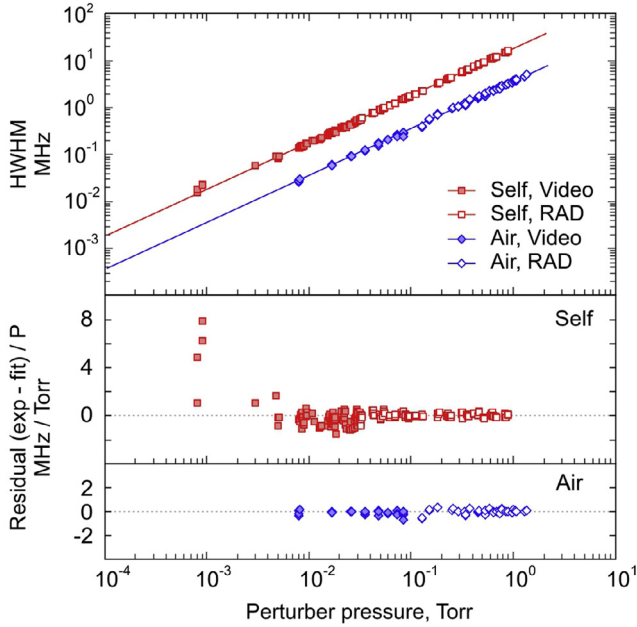


Fig. 8. Upper panel: Collisional width of 22-GHz line in water vapor (upper series of points) and dry air (lower series of points) at 296 K. Bright symbols are for RAD data and dim symbols are for video-spectrometer data. Solid lines are the best fit of $y = k \times x$ function to corresponding points. Lower panel is deviation of experimental points from these straight lines.

larger pressure uncertainty (up to ± 5 mTorr) due to water sorption processes in the cell in the case of self-broadening experiments, which caused additional uncertainty of the retrieved line shape parameters. The HTP model in the qSDVP limit [22,23] suitable for experimental conditions was employed for the obtained spectra analysis.

A short summary of the experimental conditions for both setups is given in Table 1.

3. Data analysis

Variations of the studied sample temperature corresponding to different spectral recordings were taken into account. The obtained parameters were recalculated to 296 K assuming their temperature dependence in the form $(T/296)^n$, where n was taken to be 0.7 as a rough estimate for all data [9]). Note that possible uncertainty of this value makes a negligible contribution to the retrieved parameters error budget.

We assumed that the collisional width and frequency shift of the line center retrieved from the fit depend linearly on the gas pressure. Self-pressure contributions of the line width and shift were subtracted from each air-related data point, thus supplying expected zero intercepts for the dependence of all studied parameters on perturber pressure. The frequency of 22235079.85 kHz calculated as a “center of gravity” of the line using position and relative intensity of the line hyperfine components from the work [6] was subtracted from the experimentally observed center of the line at each pressure and only deviation from this value was considered.

All data points obtained from both spectrometers are combined in Fig. 8 for pressure broadening and in Fig. 9 for pressure shifting. Line width and shift data in pure water vapor and in air are plotted versus pressure of collisional perturber in Figs. 8 and 9, respectively, together with the retrieved linear $y = k \times x$ functions. All points were assumed to have the same weights.

Good linearity of the experimental data related to all four line shape parameters studied in a very broad pressure range is

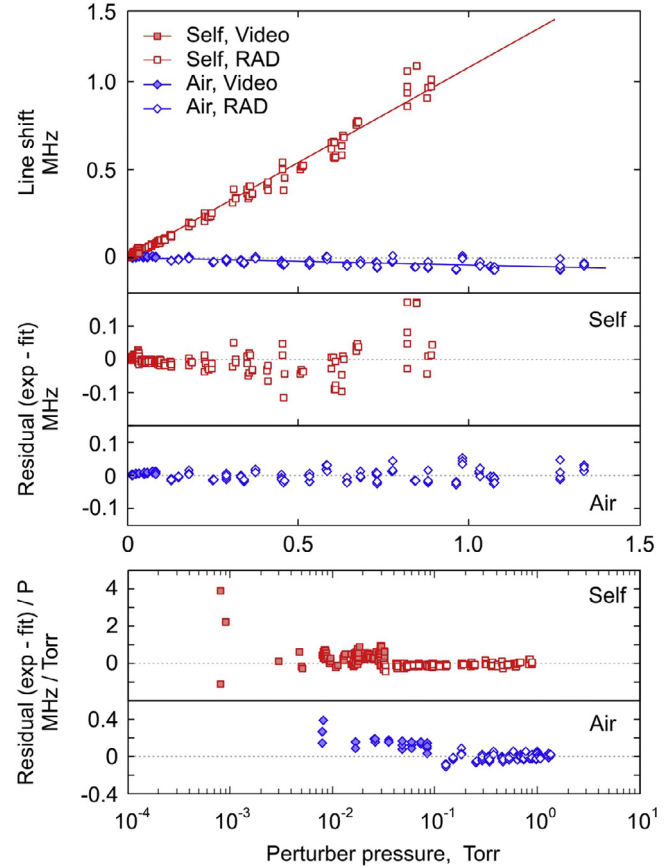


Fig. 9. Upper panel: Collisional shifting of central frequency of 22-GHz line from 22235079.85 kHz [6] in water vapor (upper series of points) and dry air (lower series of points) at 296 K. Solid lines are the best fit of the $y = k \times x$ function to corresponding points. Lower panels are the deviation of experimental points from these straight lines on linear and logarithmic scales, respectively.

observed. The slopes of the lines corresponding to the pressure broadening parameters determined from the unified data of both experiments are given in Table 2. The remaining minor systematic deviations of data from different spectrometers can be revealed in the residuals (lower panels in Figs. 8 and 9). These deviations are more prominent in the line shifting data (Fig. 9). This could be expected because the line shift is much more sensitive to possible inaccuracy of the spectrometer baseline accounting than the width. The results of separate treatment of each spectrometer dataset with their statistical uncertainties are also presented in Table 2. The 6-kHz power broadening (see section 2.1) was taken into account for the video spectrometer data. The error sources and the corresponding relative parameter errors contributing to the total uncertainty of the line shape parameters determination are presented in Table 3. Combined total uncertainty of each parameter was calculated as a square root of the sum of squared errors. General agreement of the results within the total uncertainties can be stated even without taking into consideration the aforementioned systematic deviations.

A typical example of experimental recordings obtained by the RAD spectrometer data accumulation and used for evaluation of the impact of SD effect on the studied line shape is given in Fig. 10 together with two line shape model fitting results.

The as-obtained values of collisional parameters Γ_0 and Γ_2 used in the HTP model for representing SD broadening of the line in water vapor and air are presented in Fig. 11 and the corresponding line shifting data are shown in Fig. 12. It can be seen that the SD shifting parameter is practically undetectable, especially for the air

Table 2

Parameters of 22-GHz line shape at 296K determined from both spectrometers. Total uncertainties (see Table 3) are given in parentheses in the last quoted digit.

Parameter	Self-broadening MHz/Torr			Air- broadening MHz/Torr		
	RAD	Video	Combined	RAD	Video	Combined
<i>Voigt profile</i>						
γ	17.713(15)	17.35(12)	17.707(45)	3.598(22)	3.397(79)	3.584(52)
δ	1.085(11)	1.530(60)	1.099(79)	-0.044(5)	0.081(15)	-0.032(38)
<i>Speed-dependent Voigt profile (RAD)</i>						
γ_0		18.17(3)			3.653(22)	
γ_2		2.55(6)			0.580(19)	
δ_0		0.968(10)			-0.045(6)	
δ_2		0.060(60)			-0.002(8)	

Table 3

Retrieved parameter error budget. Errors for RAD, video and combined values of γ and δ are separated by slashes.

Parameter	Fit error (%)		Pressure uncertainty (%)	Temperature uncertainty (%)	Total uncertainty (%)	
	Self	Air			Self	Air
γ	0.08 / 0.70 / 0.25	0.6 / 2.3 / 1.45	0.25	0.2	0.33 / 0.77 / 0.5	0.68 / 2.32 / 1.51
δ	1.01 / 3.92 / 7.19	11.4 / 18.5 / 119	0.25	0.35	1.10 / 3.94 / 7.2	11.4 / 18.5 / 119
γ_0	0.17	0.60	0.25	0.2	0.36	0.68
γ_2	2.35	3.28	0.25	0.2	2.37	3.30
δ_0	1.0	13.0	0.25	0.35	1.08	13.0
δ_2	100	400	0.25	0.35	100	400

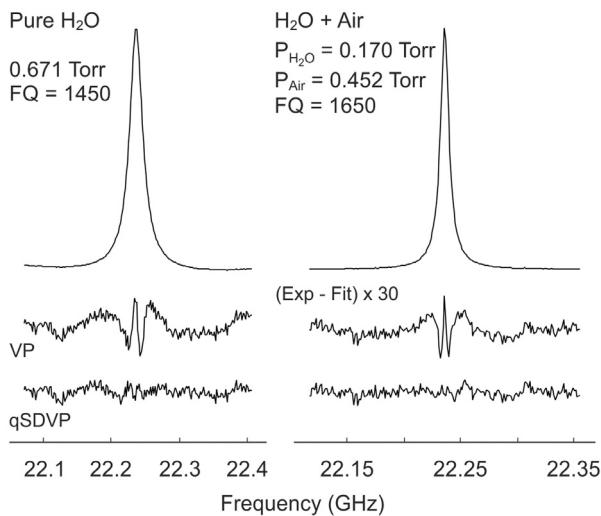


Fig. 10. 22-GHz line recordings in pure water vapor (left) and air (right) at 296K. Residuals of fitting line shape function based on Voigt (VP) and quadratic speed-dependent Voigt (qSDVP) profiles to recordings are given below on magnified vertical scale.

related data. However, its inclusion in the model improves the fit quality.

4. Discussion

The 22-GHz line parameters obtained in this work based on the Voigt profile model were used for comparison with the data of earlier studies. They include results of all known from literature studies of this line in laboratory and field experiments, theoretical calculations and related measurements in the IR range. This concerns broadening parameter of vibration-rotational transitions with the same change of rotational quantum numbers which is expected to be similar to broadening of the studied line [24]. Detailed description of information sources for the comparison can be found in [9]. Data from these sources related to the line broad-

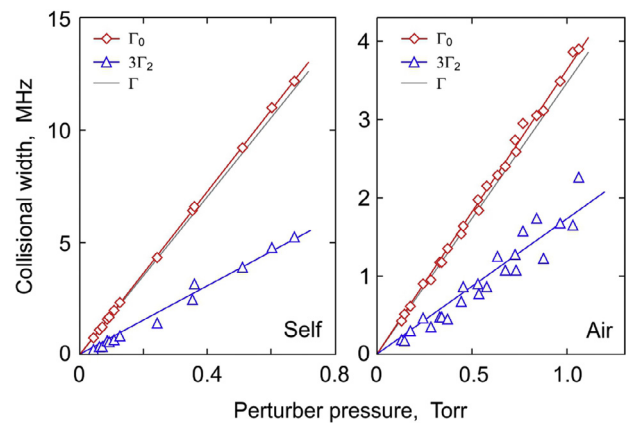


Fig. 11. Collisional broadening parameters of 22-GHz line in pure water vapor (left) and in air (right). Solid lines are for linear regression of corresponding data points. Black lines obtained by fitting Voigt profile to the same data are given for comparison.

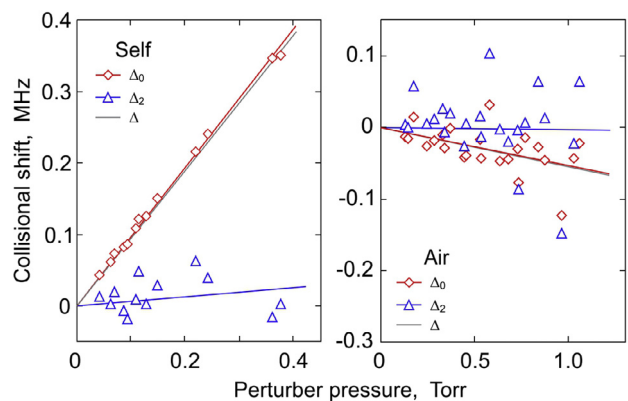


Fig. 12. Collisional shifting parameters of 22-GHz line in pure water vapor (left) and in air (right). Solid lines are for linear regression of corresponding data points. Black lines obtained by fitting Voigt profile to the same data are given for comparison.

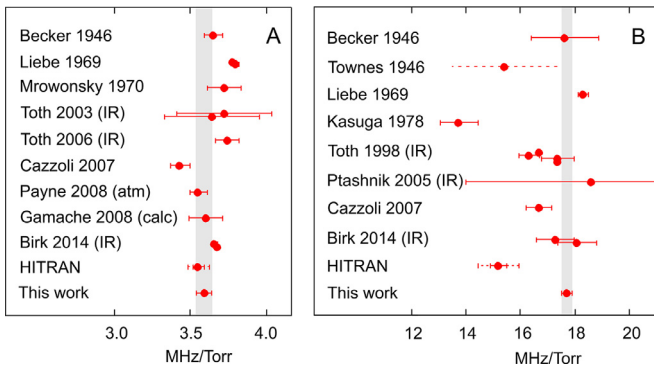


Fig. 13. Collisional broadening parameter of 22-GHz line by pressure of dry air (panel A) and pure water vapor (panel B) at 296 K in accordance with results of various studies, in chronological order. The shaded area corresponds to the parameter confidence interval determined in this work.

Table 4

The 22-GHz line center frequency shifting coefficients $\delta = (\nu - \nu_0)/P$ in MHz/Torr. The classical (non-SD) line profile (Voigt, Lorentz, Van Vleck–Weisskopf or similar) is assumed.

δ_{self}	δ_{air}	References
+1.51(7)	+0.081(15)	This work (video data)
+1.085(11)	−0.044(5)	This work (RAD data)
+1.099(79)	−0.032(38)	This work (final)
−1.61(14) ^a		[2]
+1.38(15)		[4]
+0.82(10)	+0.02(50) ^a	[8]
	−0.035	Calc. by R. Gamache and co-workers [26]
	−0.032(39) ^b	HITRAN

^a estimated from experimental data reported by the authors.

^b the uncertainty interval estimate is 0.039–0.39 MHz/Torr.

ening are shown in Fig. 13. Several details can be pointed out: (a) First of all, we note that our air- and self-broadening parameters are in a very good agreement with the results of the pioneer study performed at atmospheric pressure using the “echo-box” [2]. The radiation power, huge by spectroscopic standards, available in that work and careful preparation of the experiments minimizing possible sources of systematic error provided a very high, even by modern standards, quality of the spectroscopic data. (b) Our data points lie just in between the results of two most thorough laboratory investigations [4,5,8] having smaller error bars than other laboratory studies in this frequency range. (c) Agreement with the IR range results is pronounced, especially with the most recent data from [25]. (d) Our air broadening parameter is almost in perfect agreement with the result of calculations performed by R. Gamache on the basis of extensive collection of experimental data (the result is reported in [26]).

All currently known data on the line center pressure shifting are summarized in Table 4. Note there may arise a confusion as a result of different definition of the parameter responsible for the shifting effect in the works [4] and [8]. The line center frequency increases with pressure increase in both studies (violet shifting) but the parameters reported have opposite signs. Our self-shifting coefficient has a considerably smaller uncertainty and is found just in between the values taken from those studies, thus confirming the direction of the shifting and the order of magnitude of the effect.

As far as the value from [2] is concerned, we should note that the absolute value of the frequency shift observed in the experiment constituted only about one fifth part of the radiation frequency uncertainty interval stated by the authors and about one half of the 1σ confidence interval of the determined line center position. Small statistical uncertainty of the shifting param-

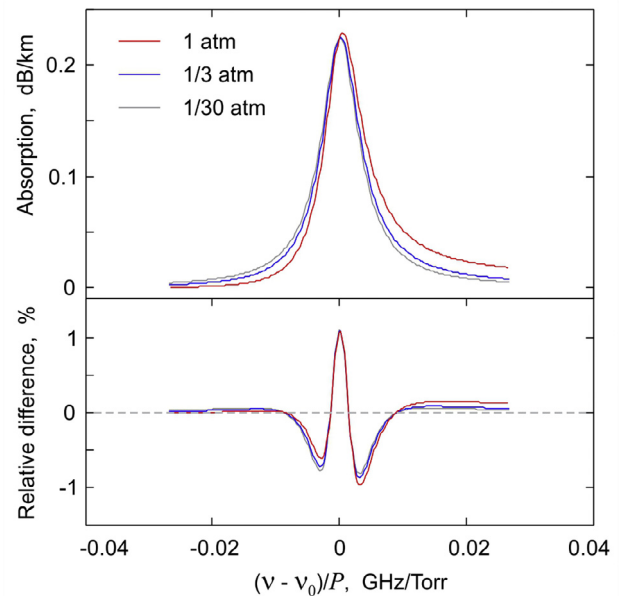


Fig. 14. Expected manifestation of SD effect in 22-GHz line shape in atmospheric air. See text for details.

ter determined from these data and presented in parenthesis in Table 4 is supplied only by the clear and almost perfect linear decrease of the line center frequency with increasing humidity.

The agreement of our air shifting parameter with the result calculated by R. Gamache can be considered to be almost perfect taking into account the very small value of the effect which does not exceed its limits set in [8].

The manifestation of the SD effect observed and studied in this work allows assessing the deviation of the line observed in the real atmosphere from the Van Vleck–Weisskopf (VW) profile traditionally used in propagation models. This may be done using the line shape parameters determined in this work and the speed dependent Van Vleck–Weisskopf (SDVW) profile (see e.g., [18]). The results of such evaluation are shown in Fig. 14. The upper part of the figure demonstrates the evolution of the 22-GHz line profile with pressure decrease as if we took air at room temperature, atmospheric pressure and 50% relative humidity and pumped it down to 1/3 and 1/30 atm. The calculated absorption is plotted versus frequency detuning from the line center normalized by pressure of the mixture. Notable asymmetry of the initial profile (which is a special feature of the VW model related to the frequency squared multiplier) practically disappears at low pressures. The difference between the profiles calculated using the SDVW and VW profiles and normalized by the line amplitude is shown in the lower part of the figure. It demonstrates that the deviation from the VW profile characteristic for the SD effect linearly scales with pressure and may be up to about 1% of the line amplitude. This result may be useful for retrieved data uncertainty evaluation in atmosphere remote sensing applications.

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