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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.

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

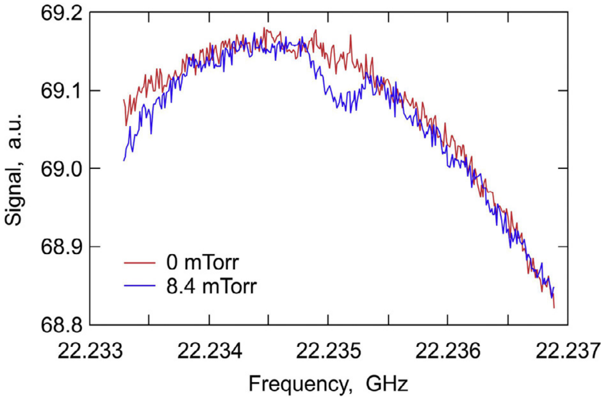

Fig. 1. Video spectrometer output signals recorded using 100% AM of radiation power with 8.4 mTorr of water vapor (blue trace) and with gas cell evacuated (read trace).

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.

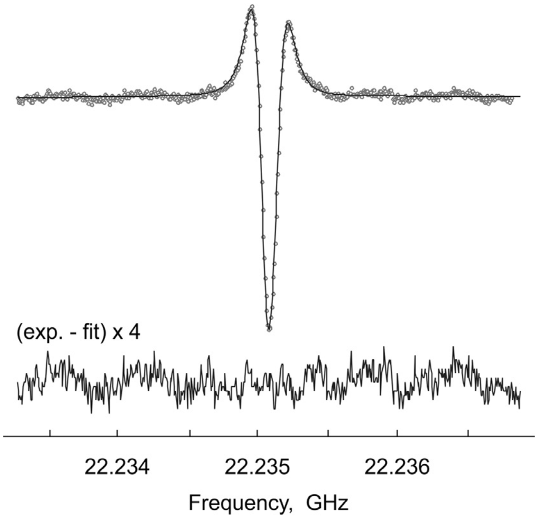

Fig. 2. Line recording in pure water vapor at 4.75 mTorr obtained with video spectrometer using FM regime (upper trace) and the result of model function fitting to the observed spectrum (lower trace).

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 9×10^{-6} 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.