

Letter to the editor

Shifting and broadening parameters of the water vapor 183-GHz line ($3_{13-2_{20}}$) by H_2O , O_2 , N_2 , CO_2 , H_2 , He , Ne , Ar , and Kr at room temperature

The water molecule spectrum is the subject of permanent interest in view of the importance of the molecule. The broadening of the water vapor 183-GHz line was studied earlier by different methods of microwave spectroscopy, but there are practically no laboratory measurements of the shifts of this spectral line. The present paper is a result of low-pressure verification of recent studies [1] of the 183-GHz line shifted by N_2 , O_2 , and air, performed in situ with a resonator spectrometer, where the line center was shifted down at about 53 MHz (at 24.5 °C and 755.8 mm Hg), corresponding to $-0.07(2)$ MHz/Torr. As shown in [2], the value of the water line shift can also be found by analyzing satellite limb-sounding data. The retrieved values of pressure shifts reported in [2] depend on computing procedures and were obtained as $-0.187(40)$, $-0.267(53)$, or $-0.13(4)$ MHz/Torr. The calculated value quoted, as a personal communication, in [2] for the H_2O –air lineshift, performed by R. Gamache, is -0.13 MHz/Torr.

The present measurements of the broadening and shifting parameters of the 183-GHz line ($3_{13-2_{20}}$) of H_2O molecule perturbed by H_2O , O_2 , N_2 , CO_2 , H_2 , He , Ne , Ar , and Kr as buffer gases were performed at room temperature with the RAD technique (using a spectrometer with BWOs and acoustic detector). The advantage of the RAD spectrometer is recording the true absorption profile of a line by means of amplitude modulation with a signal-to-noise ratio (SNR) on the order of 1000, as demonstrated earlier in a study of the rotational spectrum and broadening and shift parameters of O_2 and CO molecules [3–5]. A water sample was obtained from a double-distilled water source. The gases were from the Messer MG Company with 4.5–5.0 grades of purity. The gas pressure in the cell was measured with an MKS Baratron gauge.

The partial pressure of H_2O , first filled into the sample cell, was about 20 mTorr to obtain sufficient SNR. Then a controlled amount of foreign gas was added (usually no more than 3 Torr). The linewidth and the line center were defined from the fit of the experimental lineshape to the Voigt profile model.

The measured line centers plotted versus pressure are shown in Fig. 1 (for perturbing molecules H_2O , O_2 , He , Ne , H_2 , and CO_2). The fittings to the pressure linear dependence function and the residuals of the fits are also presented in Fig. 1 (bottom traces). The residuals show good accuracy and reproducibility. The shift and broadening parameters of the 183-GHz line obtained in this work and some previously measured ones are listed in Table 1.

The very good consistency with data of [1] obtained by the resonator technique under real atmospheric conditions should be pointed out. The present work line-shift coefficients of H_2O – O_2 , and H_2O – N_2 are $-97(5)$ and $-92(10)$ kHz/Torr; in [1] the values are $-84(30)$ and $-91(24)$ kHz/Torr, correspondingly. As one can see, the shifts are within the error limits quoted. The broadening parameters of H_2O – O_2 and H_2O – N_2 obtained in the present work, 2.580(5) and 4.230(7) MHz/Torr, agree within 10 kHz/Torr with the values obtained in [1]—2.57(5) and 4.24(4) MHz/Torr.

The 183-GHz water vapor line pressure-induced self-shift is measured as $+230(30)$ kHz/Torr. In the paper [7] the self-shift H_2O – H_2O was determined to be just positive and lower than $+700$ kHz/Torr; calculations of [12] gave $+576$ kHz/Torr. The measured shift coefficients (see Table 1 and Fig. 1) are varied from positive ones, for H_2O – H_2O and H_2O – He , to negative ones for H_2O – X (where $\text{X} = \text{O}_2$, N_2 , H_2 , CO_2 , Ar , Kr). There is a very small shift of the H_2O – Ne mixture, measured as $-7(7)$ kHz/Torr. The maximum negative shift value $-935(20)$ kHz/Torr is observed for H_2O – CO_2 . The shift and broadening parameters are important for the calculation of water absorption in the 200–300 GHz spectral window used for remote sensing of the troposphere.

The line center has been determined as 183 310.075(5), in comparison with earlier measurements, $\nu_{\text{line}} = 183\,310.0906(15)$ MHz [13], 183 310.074(15) MHz [7,14], and 183 310.117(2) MHz [15]. The center line measurements were also performed using the Lamb dip technique. The true Lamb dip in the Doppler line with amplitude modulation has been observed. The dip was about 10% of the line amplitude; the water vapor was strongly diluted by Ne (for the H_2O – Ne mixture there is an extremely low broadening parameter 1.046(10)

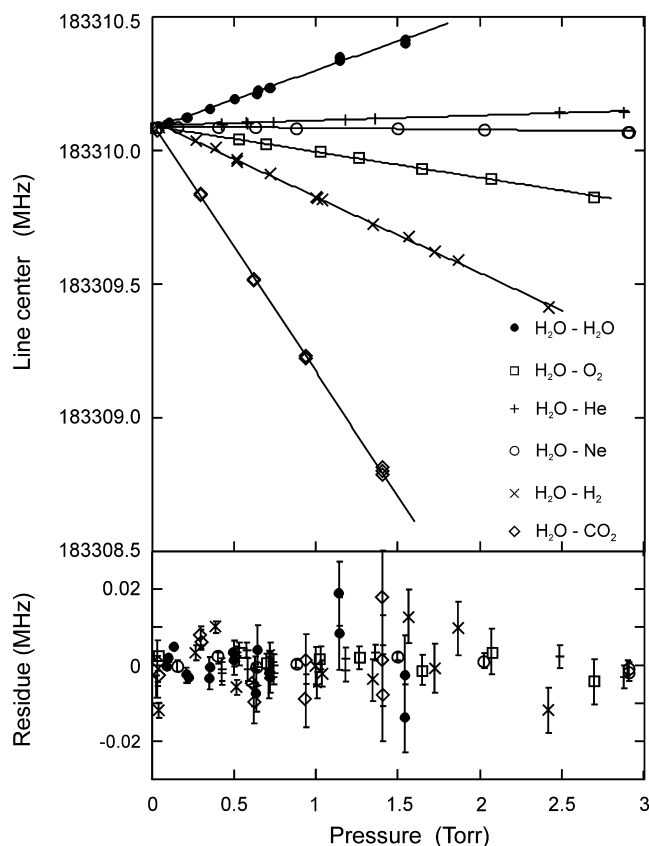


Fig. 1. Line positions versus buffer gases pressure of H₂O (●), He (+), Ne (○), O₂ (□), H₂ (×), and CO₂ (◇). The residuals of the fits to the linear dependence function with error bars are shown below.

MHz/Torr compared with self-broadening 19.50(4) MHz/Torr, and practically no shift, $-7(7)$ kHz/Torr) at a pressure of about 20 mTorr. The partial pressure of water vapor did not exceed a few milliTorrs, but there was not much improvement in the accuracy of line center determination because of insufficient sensitivity of the acoustic detector at low pressures and the time limitation of the line record due to desorption of the water molecules from cell walls.

These measurements of the 183-GHz water line center show the advantages of the RAD spectrometer for lineshift experiments. To the author's knowledge, this is the first systematic study of pressure shifts of this water vapor line.

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Table 1
Broadening and line shifting parameters for 183.310-GHz water line ($3_{13}-2_{20}$) at room temperatures

Perturber	Broadening parameter (MHz/Torr)	Temperature exponent (n(T))	Shifting parameter (kHz/Torr)	Temperature (K)	Refs.
H ₂ O	19.50(4)		+230(30)	300	This work
	19.47(5)			298	[6]
	19.88(8)	0.85(5)	<+700	300	[7]
	21.69(45)	0.66(6)		297	[8]
	19.06(20)			298	[9]
O ₂	2.580(5)		-97(5)	301	This work
	2.57(5)		-84(30)	298.6	[1]
	2.77(10)	0.85(3)		300	[10]
	2.54(2)	0.77(10)		300	[7]
	2.72(3)			300	[9]
N ₂	4.230(7)		-92(10)	302	This work
	4.24(4)		-91(24)	299	[1]
	4.19(15)	0.74(3)		300	[10]
	4.07(7)	0.63(10)		300	[7]
	3.76(5)			300	[9]
CO ₂	6.180(20)		-935(20)	300	This work
	6.1(3)			300	[9]
H ₂	3.50(2)		-284(10)	301	This work
	3.20(8)	0.95(7)		300	[11]
He	0.945(20)		+18(6)	299	This work
	0.95(3)	0.49(2)		300	[10]
Ne	1.046(10)		-7(7)	298	This work
Ar	2.055(10)		-46(7)	299	This work
	1.98(3)	0.72(20)		300	[7]
	1.97(6)			300	[9]
Kr	2.360(7)		-66(10)	302	This work
Air	3.97		-94	300, 30% of H ₂ O	(Calc.)
	3.89		-95	1% of H ₂ O	(Calc.)
	3.84(4)		-70(20)	298	[1]
	3.75(6)	0.64(10)		300	[7]
	4.6		-130(40)	300	[2]

Note. Some values of previous measurements are given.

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