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Pressure broadening of oxygen fine structure lines by water

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ABSTRACT

The results of measuring water broadening coefficients of oxygen fine structure lines are considered. Together with the data from the work [Drouin BJ, et al. JQSRT 2014;133:190–8] they provide accurate and reliable information for atmospheric applications. Water pressure shifts are shown to be less than 15 kHz/Torr. The results of cross-checking the pressure shifts from the work [Drouin BJ, et al. JQSRT 2014;133:190–8] are presented.
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1. Introduction

The 60-GHz oxygen band is a unique spectroscopic object because any pair of fine structure transitions forming the band is coupled collisionally (see, e.g., [1,2] and references therein). The effect is so strong that even at atmospheric pressure the band shape deviates from the sum of individual lines by about 25%. The band as well as the single 118-GHz fine structure line is also of interest for a number of applications such as remote sensing of terrestrial atmosphere, wireless communications, broadband networks and services, etc. Knowledge of parameters of the lines forming the band is required for accurate modeling. Modern requirements for the quality of laboratory measurements of these parameters have become very rigorous [3]. Moreover, only multiple measurements of the same parameter using different spectroscopic techniques can provide reliable data for its practical use. Pressure broadening of the lines is supposed to be a crucial parameter affecting accuracy of atmospheric applications. Self-, nitrogen and air broadening coefficients and their rotational dependence have been accurately studied in our recent work [4]. In this paper we present results of the measurements of water broadening coefficients of oxygen fine structure lines. Our data are complementary to the data set obtained recently using the Zeeman modulation technique [5] and to the earlier results on the $1-$ [6,7] and $9+$ lines [8]. Together they provide accurate and reliable data for the atmospheric applications.

2. Experimental details

The spectrometer with a backward-wave oscillator and a radio-acoustic detector of absorption (RAD spectrometer) [9] proved to be a powerful tool for precise and accurate measurements of collisional parameters of lines [10] including relatively weak oxygen lines in the millimeter [4] and submillimeter [11] wave ranges. The small size of the gas cell ($\sim$10 cm length, $\sim$2 cm diameter) allows its easy demagnetizing and shielding from the external magnetic fields, thus avoiding distortion of the shape of the magnetic-dipole oxygen lines. The spectrometer and the

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measurement method are similar to those described in Ref. [4]. The improvements include, in particular, connection of the cell with Julabo FP-50 thermostat (http://www.julabo.de/) that provides gas temperature stability within $\pm 0.1\ ^\circ$C around its mean value (296.0 ± 0.5 K in this work). Gas pressure in the cell was monitored using a 10-Torr range MKS Baratron (type 626B) gauge having a declared accuracy of 0.25% of reading. Partial pressure of oxygen in the O_2–H_2O mixture was set to be from 0.5 to 1 Torr depending on the studied line intensity. Then the high-purity water vapor was gradually added into the cell by steps of 0.3–0.4 Torr until the total pressure of the O_2–H_2O mixture of about 2.5 Torr was attained. Line recording at each step started on achieving the mixture equilibrium controlled using exponential time-behavior of the spectrometer output signal at line center frequency, which took about 30–40 min.

3. Experimental data and analysis

A typical example of the data set is presented in Fig. 1. The signal-to-noise ratio for the majority of recordings was 100 and higher, reaching 500–600 for the most intense lines. Line width and center position were obtained from the fit of the Lorentz profile to experimental spectra at each pressure. To achieve better accuracy, measurements of each line were repeated several times using different positions of the cell relative to the radiation source and different values of partial pressure of oxygen in the mixture. Pressure broadening coefficients found from the repeated measurements for each particular line were then averaged to obtain the reported value (Table 1; Fig. 2). The presented errors combine the statistical uncertainty of fitting and the dispersion of values in repeated measurements.

To check reliability of the experimental data, test measurement of the self-broadening coefficient for 5+ line was performed. The obtained value of 1.916(12) MHz/Torr is in a good agreement with the previous results of 1.890(10) and 1.920(10) MHz/Torr for 5+ and 5− lines, respectively [4]. This proves that the influence of possible systematic errors including lineshape distortion due to baseline and external magnetic fields is negligible.

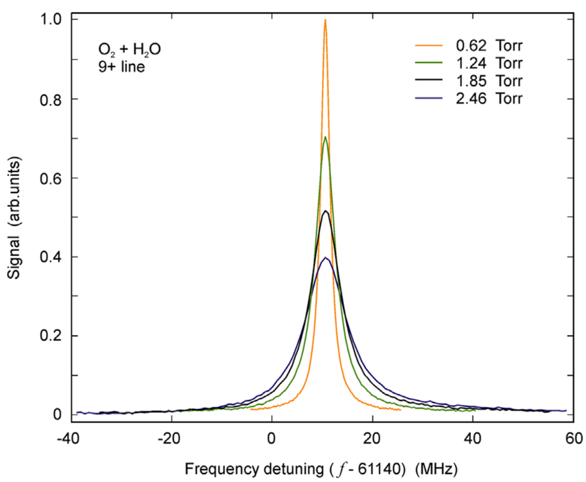

Fig. 1. Experimental recordings of 9+ line at different pressures of O_2–H_2O mixture. Partial pressure of oxygen is 0.62 Torr.

Table 1
Measured pressure broadening coefficients (MHz/Torr) of oxygen lines by water for 296 K.

$N\pm$	Broadening coefficient γ	
	Present study	Ref. [5]
1−	2.520 (40)	3.053 (48)
1+	2.531 (60)	2.507 (03)
3−	2.375 (40)	2.293 (09)
3+	2.385 (67)	2.444 (12)
5−	2.224 (30)	2.254 (10)
5+	2.223 (29)	2.061 (06)
7−	2.162 (27)	2.209 (04)
7+	2.139 (32)	2.180 (05)
9−	2.108 (26)	2.086 (04)
9+	2.125 (27)	2.090 (03)
11−	2.083 (23)	2.109 (04)
11+	2.082 (15)	2.115 (06)
13−	2.014 (31)	2.033 (10)
13+	2.040 (25)	2.026 (05)
15−	1.985 (35)	1.995 (12)
15+	1.997 (24)	1.958 (04)
17−	1.928 (53)	1.911 (08)
17+	1.910 (19)	1.915 (05)
19+	1.841 (49)	1.749 (05)
21+	1.754 (27)	1.922 (15)
23+	1.690 (44)	1.614 (22)*
25+	1.582 (61)	1.522 (17)

* The value corresponds to 23− line.

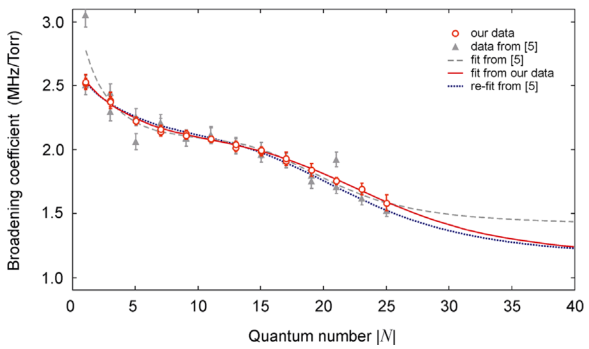

Fig. 2. Broadening coefficient of fine structure oxygen lines by water pressure at 296 K as a function of rotational quantum number N. Designation of symbols and curves is shown in the figure inset. See text for details.

Data from Ref. [5] are given in Table 1 and Fig. 2 for comparison. One should note a very good coincidence within experimental uncertainties of both data sets, demonstrating high precision and high accuracy of the presented data.

Analysis of the rotational dependence of the obtained broadening parameters was made using the same function as in the work [5]:

$$\gamma(N) = A_\gamma + \frac{B_\gamma}{1 + c_1 N + c_2 N^2 + c_3 N^4} \tag{1}$$

that is similar to the Padé approximation applied, for example, to the OCS pressure broadening in our work

Table 2
Fitted coefficients for Eq. (1). See the text for details.

Parameter	Our data	Data from Ref. [5]	
		Initial fit	Our re-fit
A_g	1.140 (129)	1.409 (210)	1.154 (202)
B_g	1.528 (118)	1.854 (246)	1.486 (176)
c_1	0.101 (18)	0.382 (236)	0.093 (36)
c_2	$-4.78\ (115) \times 10^{-3}$	$-2.50\ (194) \times 10^{-2}$	$-4.63\ (271) \times 10^{-3}$
c_3	$7.40\ (233) \times 10^{-6}$	$4.06\ (388) \times 10^{-5}$	$9.32\ (587) \times 10^{-6}$

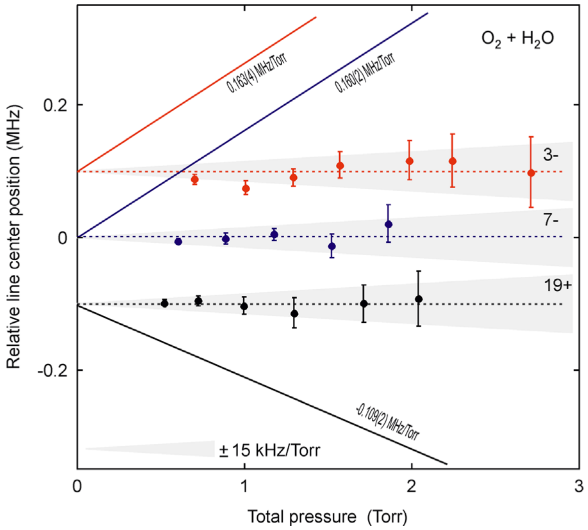

Fig. 3. Measured position of line center for 3− (red), 7− (blue) and 19+ (black) oxygen lines as a function of pressure (circles). Measured non-shifted positions of the transitions (62486.267(14), 59164.211(11) and 64127.765(11) MHz for 3−, 7−, and 19+ line, respectively) are shown by the dotted horizontal lines. For clarity, data for 3− and 19+ lines are shifted up and down by 0.1 MHz. The solid lines correspond to pressure shifts measured in the work [5]. Gray areas indicate the estimated experimental uncertainty of ± 15 kHz/Torr.

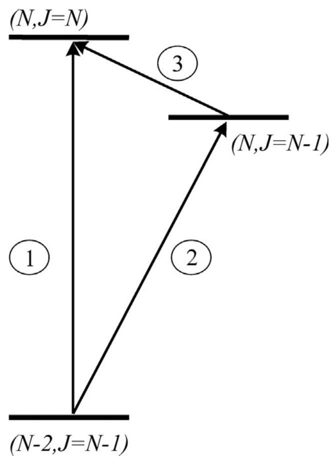

Fig. 4. Part of energy diagram and possible transitions in oxygen molecule for cross checking interpretation.

[12]. The fitted coefficients are listed in Table 2. The result of the fit of the function (1) to our O_2–H_2O data is shown in Fig. 2 by the solid line. The fitted curve from the work [5] is also given for comparison by the dashed line. It is interesting to note that our re-fit of the data from Ref. [5] excluding 1−, 5+ and 21+ lines (which are the most diverging points from the expected smooth dependence) gives almost the same function as for our data fit (the dotted line in Fig. 2). The use of the re-fitted curve instead of the initial one [5] gives significant changes in the pressure broadening coefficient for the lines with $|N|=1$ and $|N|>25$.

The mean value of the water-to-air broadening ratio was calculated to be 1.20(5) using current results and data from Ref. [4] for N ranging from 1 to 19 and can be easily introduced in the millimeter wave propagation model [13] (instead of the current 1.1) for consideration of water broadening of oxygen lines without any modifications of the program code.

Our previous studies of the oxygen fine-structure lines perturbed by different atmospheric gases made at both low [4,7] and high [14] pressures employing different techniques did not reveal any noticeable pressure shifts within experimental accuracy of ± 15 kHz/Torr. Contrary to that, the value of the H_2O-shift coefficients measured in the work [5] reaches 150–180 kHz/Torr, which is at least 10 times larger than the aforementioned uncertainty typical for the RAD spectrometer measurements. This means that such shifts should be easily detectable by this technique. Three typical sets of our measurements for the 3−, 7− and 19+ line positions are shown in Fig. 3. The experimental accuracy of ± 15 kHz/Torr is indicated by gray areas. They demonstrate that water-pressure shift coefficients are not detectable. The corresponding pressure shifts from Ref. [5] are presented for comparison by solid lines in Fig. 3.

The experimental data set obtained in the work [5] allows a simple cross check for these data. It follows from the energy diagram and selection rules for oxygen molecule [15] (see Fig. 4) that three series of spin-rotational transitions, namely

1) $(N,J=N)\leftarrow(N-2,J=N-1)$ (pressure shift δ_1)
2) $(N,J=N-1)\leftarrow(N-2,J=N-1)$ (pressure shift δ_2)
3) $(N,J=N)\leftarrow(N,J=N-1)$ (pressure shift δ_3)

form close energy loops, which may be used for the cross check procedure based on obvious relation between

Table 3
Result of cross check for pressure shifts from Ref. [5]. Uncertainties are a sum of errors of shifts δ_1, δ_2 and δ_3.

$N=J$	$\delta_1-\delta_2-\delta_3$ kHz/Torr
3	−230 (30)
5	46 (12)
7	−96 (20)
9	94 (26)
11	20 (22)

pressure shifts of the involved lines:

$$\delta_1-\delta_2-\delta_3=0.$$

Here, N and J are quantum numbers characterizing pure rotational moment and total angular momentum, respectively. The result of the cross check is presented in Table 3. The frequency shifts practically in all available close loops are nonzero. This is an indication that the water pressure shifts of oxygen lines observed in the work [5] more likely result from the experimental artifacts (e.g., baseline influence, instabilities, low signal-to-noise ratio, etc.) rather than have real physical meaning. However, this result does not affect accuracy of the broadening coefficients measured in Ref. [5], since the line position and line width parameters are not correlated.

The broadening coefficients measured in the current study and supported by a good coincidence with the results of the work [5] provide highly accurate and reliable spectroscopic data in a wide range of rotational quantum numbers for atmospheric applications.

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References

[1] Makarov DS, Tretyakov MYu, Rosenkranz PW. 60-GHz oxygen band: precise experimental profiles and extended absorption modeling in a wide temperature range. J Quant Spectrosc Radiat Transf 2011;112:1420–8.
[2] Makarov DS, Tretyakov MYu, Boulet C. Line mixing in the 60-GHz atmospheric oxygen band: comparison of the MPM and ECS model. J Quant Spectrosc Radiat Transf 2013;124:1–10.
[3] Harrison JJ, Bernath PF, Kirchengast G. Spectroscopic requirements for accurate, a microwave and infrared-laser occultation satellite mission. J Quant Spetrosc Radiat Transf 2011;112:2347–54.
[4] Tretyakov MYu, Koshelev MA, Dorovskikh VV, Makarov DS, Rosenkranz PW. 60-GHz oxygen band: precise broadening and central frequencies of fine structure lines, absolute absorption profile at atmospheric pressure, revision of mixing coefficients. J Molec Spectrosc 2005;231:1–14.
[5] Drouin BJ, Payne V, Oyafuso F, Sung K. Pressure broadening of oxygen by water. J Quant Spetrosc Radiat Transf 2014;133:190–8.
[6] Setzer BJ, Pickett HM. Pressure broadening measurements of the 118.750 GHz oxygen transition. J Chem Phys 1977;67:340.
[7] Golubiatnikov GYu, Koshelev MA, Krupnov AF. Reinvestigation of pressure broadening parameters at 60-GHz band and single 118.75 GHz oxygen lines at room temperature. J Mol Spectrosc 2003;222:191–7.
[8] Liebe HJ. Molecular transfer characteristics of air between 40 and 140 GHz. IEEE Trans Microw Theory Tech 1975;MT23:380–6.
[9] Tretyakov MYu, Koshelev MA, Makarov DS, Tonkov MV. Precise measurements of collision parameters of spectral lines with a spectrometer with radioacoustic detection of absorption in the millimeter and submillimeter ranges. Instrum Exp Tech 2008;51:78–88.
[10] Krupnov AF, Tretyakov MYu, Belov SP, Golubiatnikov GYu, Parshin VV, Koshelev MA, et al. Accurate broadband rotational BWO-based spectroscopy. J Molec Spectrosc 2012;280:110–8.
[11] Golubiatnikov GYu, Krupnov AF. Microwave study of the rotational spectrum of oxygen molecule in the range up to 1.12 THz. J Molec Spectrosc 2003;217:282–7.
[12] Koshelev MA, Tretyakov MYu. Collisional broadening and shifting of OCS rotational spectrum lines. J Quant Spectrosc Radiat Trans 2009;110:118–28.
[13] Liebe HJ. MPM – an atmospheric millimeter-wave propagation model. Int J Infrared Milli 1989;10:631–50.
[14] Tretyakov MYu, Golubiatnikov GYu, Parshin VV, Koshelev MA, Myasnikova SE, Krupnov AF, et al. Experimental study of line mixing coefficient for 118.75 GHz oxygen line. J Molec Spectrosc 2004;223:31–8.
[15] Gordy W, Cook RL. Microwave molecular spectra. 3rd ed. New York: Wiley; 1984.