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## Pressure broadening of oxygen fine structure lines by water

M.A. Koshelev<sup>a,b,\*</sup>, I.N. Vilkov<sup>a</sup>, M.Yu. Tretyakov<sup>a,b</sup><sup>a</sup> Institute of Applied Physics, Russian Academy of Sciences, 46 Ulyanov street, Nizhny Novgorod 603950, Russia<sup>b</sup> Lobachevsky State University of Nizhny Novgorod, 23 Gagarin Avenue, Nizhny Novgorod 603950, Russia

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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 (~10 cm length, ~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

\* Corresponding author at: Institute of Applied Physics, Russian Academy of Sciences, 46 Ulyanov street, Nizhny Novgorod 603950, Russia. Fax: +7 831 4363792.

E-mail address: [koma@appl.sci-nnov.ru](mailto:koma@appl.sci-nnov.ru) (M.A. Koshelev).

URL: <http://www.mwl.sci-nnov.ru> (M.A. Koshelev).

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  $\pm 0.1$  °C around its mean value ( $296.0 \pm 0.5$  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<sub>2</sub>–H<sub>2</sub>O 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<sub>2</sub>–H<sub>2</sub>O 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,

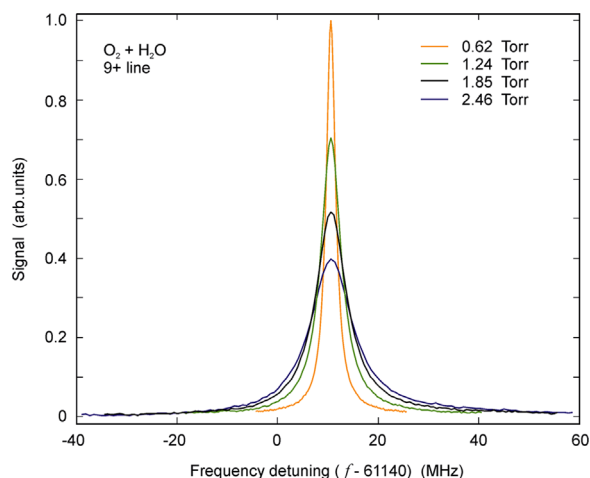


Fig. 1. Experimental recordings of 9+ line at different pressures of O<sub>2</sub>–H<sub>2</sub>O mixture. Partial pressure of oxygen is 0.62 Torr.

Table 1

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

N ±	Broadening coefficient $\gamma$	
	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.

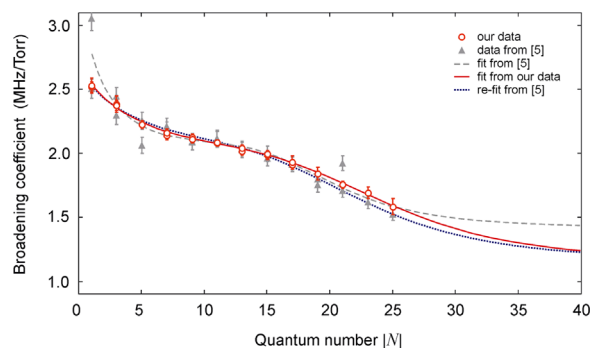


Fig. 2. Broadening coefficient of fine structure oxygen lines by water pressure at 296 K as a function of rotational quantum number  $N$ . Designation of symbols and curves is shown in the figure inset. See text for details.

respectively [4]. This proves that the influence of possible systematic errors including lineshape distortion due to baseline and external magnetic fields is negligible.

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]:

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

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

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