



Collisional broadening of oxygen fine structure lines: The impact of temperature



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ABSTRACT

The temperature dependence of self-, nitrogen- and air-broadening coefficients of oxygen fine structure lines was studied. Temperature exponents of a series of oxygen lines with rotational quantum number N ranging from 1 to 19 were measured with high accuracy for the first time. The obtained parameters were compared with the results of the earlier studies. This information is of high importance for atmospheric applications.

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1. Introduction

The significant role for different applications of the oxygen fine structure lines forming the 60-GHz atmospheric band is well known. In particular, the band is widely used for retrieving vertical pressure and/or temperature profiles from remote sensing data obtained by ground based, airborne and satellite instruments. These applications require knowledge of the line parameters with high enough accuracy [1,2]. Pressure broadening of the lines is known to be a crucial parameter affecting accuracy of the retrieved data. Broadening of the fine structure lines by pressure of the principal atmospheric gases (nitrogen, oxygen and water vapor) and rotational dependence of the corresponding coefficients have been accurately studied at room temperature in our recent works [3,4]. However, their temperature dependence has

not been studied for most of the band lines. The majority of the papers devoted to measurements of the temperature exponent n_γ of the oxygen fine structure line width [5–8] (see Fig. 4) concerns the single $N=1$ – line at 118 GHz [6–8]. We are familiar only with two studies of the 9+ fine structure line and the 425-GHz pure rotational line carried out by Liebe [5] and Drouin [7], respectively. The value of n_γ in all of the aforementioned measurements varies within the 0.61–0.9 range (corresponding to about $\pm 19\%$ deviation from the mean value) for self-broadening and within the 0.79–1.04 range (about $\pm 14\%$) for nitrogen broadening. Results of the study of pressure broadening in oxygen A-band [9] demonstrate some smooth rotational dependence of the temperature exponent (see Fig. 4) which varies within 0.6–0.77 (about $\pm 12\%$) with the estimated uncertainty of about $\pm 15\%$. Such a large spread of available data and insufficiency of systematic measurements in both microwave and visible regions impede accurate evaluation of the rotational dependence of the temperature exponent.

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The present study is devoted to measurements of the temperature exponent for self-, nitrogen- and air-broadening of the oxygen fine structure lines.

2. Experimental details

The spectrometer with a backward-wave oscillator and a radio-acoustic detector of absorption (RAD spectrometer) was employed for the current investigation. The spectrometer design and the corresponding method of measurements are described in detail in Refs. [10,11]. Similar studies of pressure broadening performed at room-temperature are described in Refs. [3,4,12]. The copper gas cell (~ 10 cm length, ~ 2 cm diameter) was placed inside a double shield made of annealed permalloy to avoid distortion of the shape of the magnetic-dipole oxygen lines by external magnetic fields. The cell was permanently connected with Julabo FP-50 thermostat (<http://www.julabo.de/>) that provides stable temperature of a coolant inside the thermostat within ± 0.1 °C of the chosen value. The cell as well as both shields were additionally 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 allowed temperature control of the gas sample inside the cell. Temperature gradients along the cell were estimated to be less than 0.2 °C. Gas pressure in the cell was permanently monitored using a 10-Torr range MKS Baratron (Type 626B) gauge having a declared accuracy of 0.25% of reading.

Temperature dependence studies are time consuming, so some optimization of the number of studied lines and temperature points is unavoidable. Transitions for the study were chosen on the basis of a uniformly covered, maximum possible range of rotational quantum numbers limited from the large $|M|$ side by decreasing intensity and therefore insufficient signal-to-noise ratio for accurate study. The total of 12 transitions were selected ranging from 1 to 19.

Measurements of pressure broadening coefficients of oxygen lines were carried out at 12 temperatures in the range from -35 °C to $+75$ °C with 10 °C step. At each temperature, spectra were recorded at 8–10 pressures in the interval of 0.3–3.3 Torr. In the case of foreign broadening, partial pressure of oxygen in the mixture was set to be from 0.5 to 1 Torr depending on the studied line intensity. Then foreign gas was gradually added into the cell by steps of 0.3–0.4 Torr and line recording started after achieving the mixture equilibrium (the corresponding time was experimentally estimated to be about 15 min).

3. Data analysis

A typical example of the experimental data is shown in Fig. 1. The signal-to-noise ratio (SNR) for the majority of recordings was about 200–300, reaching 800 for the most intense lines. In quite a few cases (less intensive lines and high temperatures) SNR decreased down to 70. About 13,000 spectrum recordings for 12 oxygen fine structure lines were obtained and analyzed within the frames of the present investigation. The ratio of the Lorentz-to-Doppler width for oxygen lines of the 60-GHz band under the

conditions of our experiment was at least 10, therefore the Lorentz profile was used for fitting the experimental spectra. For the 118-GHz line this ratio is twice less and a Voigt profile was used. The noise-like residuals shown in Fig. 2 confirm correspondence of the model function to the experiment. Pressure broadening coefficient was determined as a result of linear regression of the width pressure dependence (see Fig. 2).

One of the main sources of uncertainties in any spectrometer is its baseline originating mainly from the radiation interference effect. In the acoustic detection method the signal is produced by absorbed power only (the so-called “zero level detection”) and interference is efficiently averaged over the cell volume. The baseline is reduced considerably in comparison with the classical video-spectrometers but is still present. A false signal is produced by radiation absorption in windows and wall surfaces of a gas cell [10,11]. The major part of this signal can be removed by a repeated record of the spectrum with replacement of the sample by gas that is not absorbing in this frequency range [3,4]. Its remaining part is taken into account by additive plain terms to the model function. The part of the baseline related to frequency dependence of incident radiation can be taken into account by including a multiplicative term (linear frequency function was shown to be sufficient in most cases [3]) to the model function. The change of the cell position changes the interference pattern and, respectively, its contribution to the output signal. This may give significant systematic uncertainty to the fitting results if the model function is inadequate. In the current study pressure broadening coefficients were measured at several different positions of the cell relative to the radiation source. This allows not only minimizing the influence of standing waves on the retrieved line parameters but also assessing possible baseline-related systematic errors. The final value of the pressure broadening coefficient for each particular line at a given temperature was found by averaging the values obtained from the repeated measurements. The corresponding errors are combinations of statistical uncertainties and a standard deviation σ of the spread of parameters obtained in the repeated measurements. Experimental values of the self-broadening coefficients γ_{self} for the three selected lines are plotted in Fig. 3 as a function of temperature T which is described by the phenomenological power law

$$\gamma(T) = \gamma(T_0) \left(\frac{T_0}{T} \right)^{n_\gamma}$$

$$\lg(\gamma) = \lg(\gamma_0) + n_\gamma \cdot \lg\left(\frac{T_0}{T}\right), \quad (1)$$

where $\gamma_0 = \gamma(T_0)$; T_0 is reference temperature ($T_0 = 296$ K in our case). In total, pressure broadening coefficients $\gamma(296)$ and their temperature exponents n_γ were measured for 12 fine structure lines with the rotational quantum number N ranging from 1 to 19. Results are presented in Table 1 and in Figs. 4 and 5.

Air-broadening parameter $\gamma_{air}(296)$ and its temperature exponent n_γ^{AIR} were calculated for each oxygen line studied using the corresponding self- and nitrogen-broadening

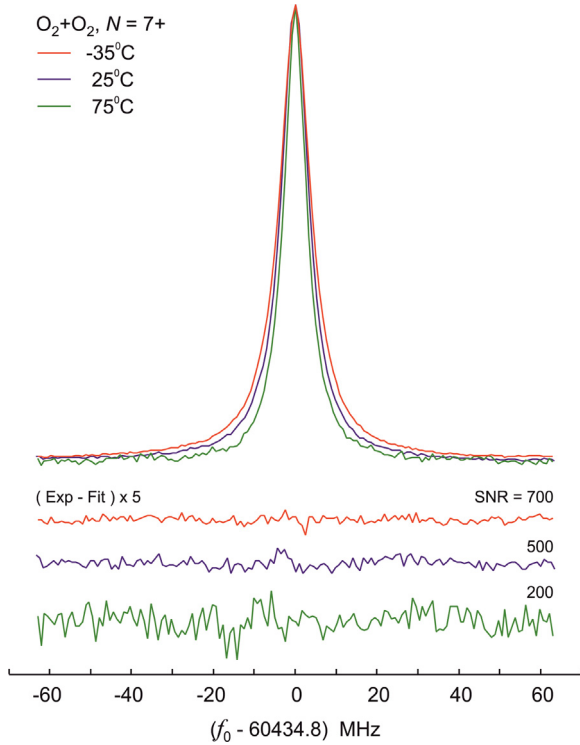


Fig. 1. Experimental recordings of 7+ line normalized by maximum amplitude at 2.1 Torr of pure oxygen and different temperatures. Fit residuals are shown at the bottom.

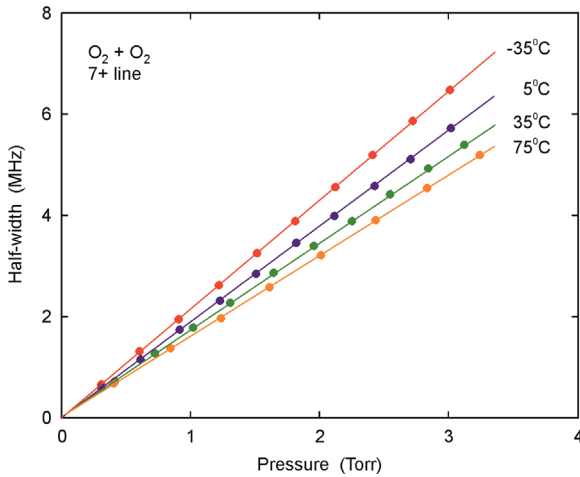


Fig. 2. Measured half-widths of 7+ line are plotted as a function of oxygen pressure at different temperatures (points). Errors are less than the point size. Solid lines are results of linear regression of the experimental data.

coefficients and their temperature exponents from Table 1 as

$$\begin{aligned} \gamma_{AIR}(T) &= 0.79 \cdot \gamma_{N_2}(T) + 0.21 \cdot \gamma_{O_2}(T) \\ \gamma_{AIR}(T) &= \gamma_{AIR}(296) \left(\frac{296}{T} \right)^{n_{AIR}^{AIR}} = 0.79 \cdot \gamma_{N_2}(296) \left(\frac{296}{T} \right)^{n_{N_2}^{N_2}} \\ &\quad + 0.21 \cdot \gamma_{self}(296) \left(\frac{296}{T} \right)^{n_{self}^{self}} \end{aligned} \quad (2)$$

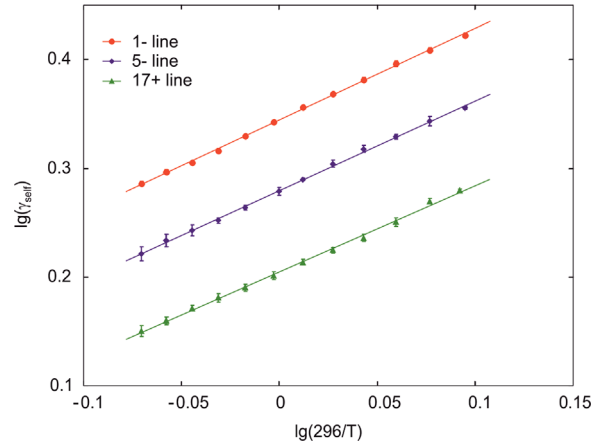


Fig. 3. Dependence of $\lg(\gamma_{self})$ on $\lg(296/T)$ for 1–, 5– and 17+ oxygen lines. Error bars are combinations of several uncertainties (see text for details). For some points errors are less than the point size. Solid lines are results of the fit of Eq. (1) to experimental data. Slopes are temperature exponents n_{γ}^{self} and intercepts are $\lg(\gamma_{self}(296))$.

The results are presented in Table 1. In addition, $\gamma_{air}(296)$ and n_{γ}^{AIR} were measured directly (the preliminarily prepared 79/21-composition mixture of N_2/O_2 was used) for the 1– line as 2.267(4) MHz/Torr and 0.771 (14). These values coincide within statistical uncertainty with the calculated parameters 2.270(2) MHz/Torr and 0.778(6), respectively, which proves high reproducibility and precision of the data obtained.

4. Discussion

Results of all published (to the best of our knowledge) measurements of pressure broadening temperature exponents of oxygen fine structure lines are collected in Table 2 and shown graphically in Fig. 4 together with the corresponding results for the oxygen A-band lines [9]. Generally, the obtained results demonstrate substantially less scatter compared to other microwave data proving their high precision. Best agreement of measured parameters is observed with the data obtained for 1– line in our earlier study [8] using the resonator spectrometer at atmospheric pressure (i.e. approximately 300 times higher than pressure in this study) at temperatures ranging from -30°C up to $+60^\circ\text{C}$. Coincidence of the results obtained by principally different techniques and methods at significantly different pressures demonstrates that possible systematic errors are minimized in both studies. For the rest of the earlier data, the difference from our results exceeds significantly total measurement errors. However, it is interesting to note that the majority of n_{γ}^{AIR} coefficients presented in Table 2 and in Fig. 4 are in better agreement with each other within the measurement accuracy.

To the best of our knowledge, there were no theoretical predictions of the rotational behavior of n_{γ} for oxygen fine structure lines. Therefore, we cannot assume that the weak rotational dependence (deviation of points from the mean value) of our measured temperature exponents observed in Fig. 4 has real physical meaning. A coincidence of the

measured coefficients within $2\text{-}\sigma$ interval allows using for all oxygen fine structure lines the averaged values of the temperature exponents presented at the bottom of Table 1 and by dashed horizontal lines in Fig. 4.

For further analysis, the obtained $\gamma(296)$ parameters were combined with our previous highly accurate results from Ref. [3]. Fig. 5 demonstrates good coincidence of both datasets. Then, we followed the procedure from work [4]. In particular, the rotational dependence of the obtained broadening parameters was described by the function

$$\gamma(N) = A_\gamma + \frac{B_\gamma}{1 + c_1 N + c_2 N^2 + c_3 N^4}. \quad (3)$$

Results of the weighted fit of Eq. (3) to the experimental data are shown in Fig. 5 by dashed lines. The value of the inversed squared error was used as a weight. The fitted coefficients are listed in Table 3 and allow both

interpolating and extrapolating the results to uninvestigated lines.

Our present study of the oxygen fine structure lines as well as our earlier measurements [3,4,8] did not reveal any noticeable pressure shifts within the experimental accuracy of ± 15 kHz/Torr.

Pressure broadening coefficients and their temperature exponents measured in this and our earlier [3,4,8] works provide the most full and accurate set of spectroscopic parameters for oxygen fine structure lines in a wide range of rotational quantum numbers. The obtained data can be used to improve accuracy of atmospheric radiation transfer codes used for remote sensing and other spectroscopic applications. It should be noted that the phenomenological dependence (1) is supposed to be valid within about $\pm 100^\circ$ of T_0 [13]. Applicability of Eq. (1) for nitrogen and oxygen pressure broadening of the water lines was

Table 1

Measured pressure broadening coefficients $\gamma(296)$ (MHz/Torr) and their temperature exponents n_γ for oxygen fine structure lines. Errors are estimated statistical uncertainty of the fit of Eq. (1) to experimental data.

$N \pm$	$\gamma_{\text{self}}(296)$	n_γ^{self}	$\gamma_{N_2}(296)$	$n_\gamma^{N_2}$	$\gamma_{\text{AIR}}(296)^a$	$n_\gamma^{\text{AIR}^a}$
1 –	2.239(2)	0.765(7)	2.278(2)	0.781(6)	2.270(2)	0.778(6)
3 +	2.034(3)	0.743(10)	–	–	–	–
5 –	1.938(3)	0.757(14)	1.928(3)	0.738(13)	1.930(3)	0.742(13)
7 +	1.840(2)	0.755(6)	1.819(3)	0.759(13)	1.823(3)	0.758(11)
9 +	1.791(3)	0.784(11)	1.773(2)	0.755(9)	1.777(2)	0.761(9)
9 –	1.811(2)	0.781(6)	–	–	–	–
11 +	1.757(1)	0.773(6)	–	–	–	–
13 –	1.734(2)	0.760(8)	1.649(2)	0.733(9)	1.667(2)	0.739(9)
15 –	1.685(2)	0.775(9)	1.610(4)	0.739(19)	1.626(3)	0.747(17)
17 –	1.641(3)	0.771(14)	–	–	–	–
17 +	1.631(2)	0.758(8)	–	–	–	–
19 +	1.586(2)	0.763(14)	1.455(3)	0.752(17)	1.483(3)	0.754(16)
Mean value		0.765(11) ^b		0.751(15) ^b		0.754(12) ^b

^a Calculated values (see text for details).

^b Mean value and its standard deviation of all values in the column.

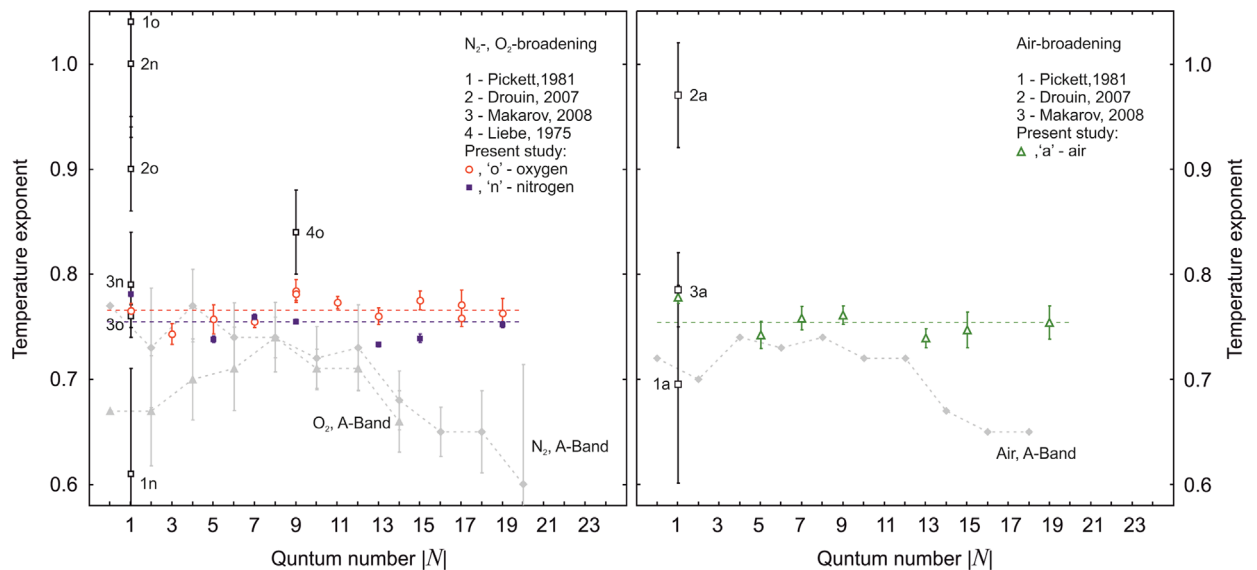


Fig. 4. Measured temperature exponents n_γ for (left) self- and N_2 - and (right) air-broadening coefficients of oxygen fine structure lines in comparison with previous data. Designations are shown in the figure insets. Uncertainties of the A-band lines air-broadening were estimated in [9] to be $\pm 15\%$.

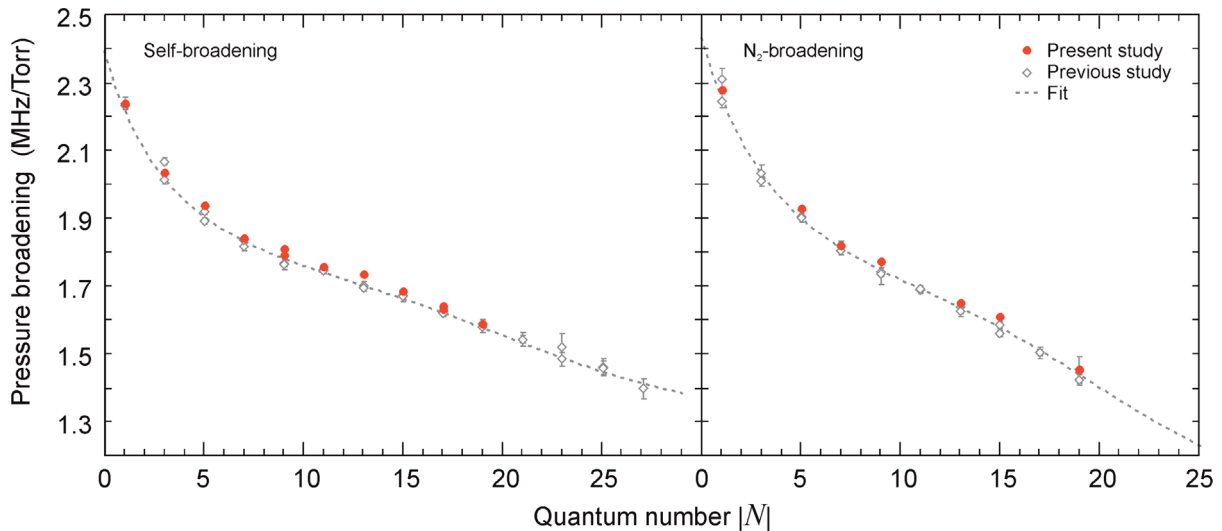


Fig. 5. Measured self- and N_2 -broadening coefficients $\gamma(296)$ (filled circles) together with the results of our previous study [3] (open diamonds). Dashed curves are results of weighted fit of the function (3) to the whole set of experimental data. For some points errors are less than the point size.

Table 2

Review of measured n_γ for oxygen fine structure lines.

$N \pm$	n_γ^{self}	$n_{N_2}^{\text{N}_2}$	$n_{\text{AIR}}^{\text{AIR}}$	Reference
1 –	0.765(7)	0.781(6)	0.778(6)	Present study
	1.04(11)	0.65(11)	0.695(94)	[6]
	0.90(4)	1.00(5)	0.97(5)	[7]
	0.760(11)	0.79(5)	0.785(35)	[8]
9 +	0.784(11)	0.755(9)	0.761(9)	Present study
	0.84(4)	–	–	[5]

Table 3

Results of the weighted fit of Eq. (3) to the measured broadening coefficients $\gamma(296)$.

Parameter	$\gamma_{\text{self}}(296)$	$\gamma_{N_2}(296)$	$\gamma_{\text{AIR}}(296)$
A_γ	1.263(48)	0.960(180)	1.132(150)
B_γ	1.129(40)	1.471(165)	1.348(131)
c_1	0.186(21)	0.141(33)	0.188(44)
c_2	–0.0071(11)	–0.0059(15)	–0.0077(20)
c_3	1.249(315) $\times 10^{-5}$	1.170(534) $\times 10^{-5}$	1.660(877) $\times 10^{-5}$

demonstrated experimentally in the works [14,15] in a temperature range from about 150 K to 600 K. This suggests that n values obtained in this work can be used with high accuracy in remote sensing applications even for the most extreme Earth's atmosphere conditions.

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