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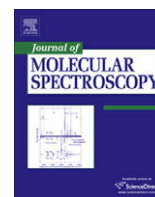
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## Journal of Molecular Spectroscopy

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## Letter to the Editor

**Collisional parameters of the 118-GHz oxygen line: Temperature dependence**

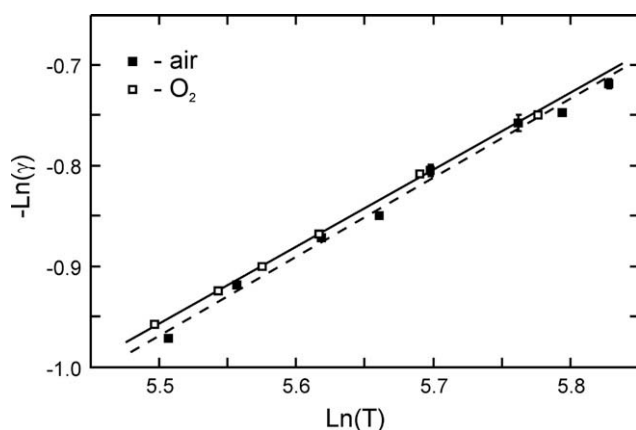
The present study is a continuation of our series of papers (see [1] and references therein) related to the investigation of the microwave spectrum of oxygen. Here, we report on the results of laboratory investigations of the temperature-dependent collisional parameters of the single isolated 118-GHz,  $N = 1$ —oxygen line performed by a resonator technique. The experimental technique and measurement method have been described in detail in reference [1]. A Fabry-Perot resonator of 70 cm geometrical length provided about 100 measurement frequency points in the 110–130 GHz range. A 3  $\mu\text{m}$  thick polyethylene terephthalate film (instead of the previously used 6  $\mu\text{m}$  thick teflon film) coupling resonator with a radiation source (a backward wave oscillator) and a detector provided good repeatability of the spectrometer baseline and consequently a good signal-to-noise ratio (SNR) up to the previously inaccessible value of 800 in pure oxygen. The most essential improvement of the experimental setup described in [1] consisted of the development of a climate chamber for the resonator equipped by cooling and heating elements which provide an experimental temperature range from  $-30$  up to  $60$  °C with  $0.2$  °C accuracy. The resonator mirrors and gas sample temperatures were monitored by a set of copper and platinum thermo-sensors with  $0.2$ – $0.5$  °C manufacturer stated accuracy. A low speed fan placed inside the chamber supplied effective sample intermixing while also minimizing temperature gradients. All of these factors allowed extension of the working temperature range by more than a factor of two and essentially improved the experimental accuracy in comparison with [1], where the ambient atmosphere served as a sample cooler. The measurements were started with the baseline recording in pure nitrogen after thermal equilibrium between the mirrors and the sample was reached. Technical grade oxygen from a local supplier (nominal purity  $>98\%$ ) and dried atmospheric air blown slowly through the chamber at atmospheric pressure were used as the studied samples. A pressure meter (600–800 mmHg range) calibrated with  $\pm 0.05$  mmHg accuracy was used. Each temperature point required one day for preparation and performing the measurements. Variations of the sample pressure during the course of the measurements were less than 1 mmHg. Sample pressures were in the 730–777 mmHg range corresponding to a slow variation of atmospheric pressure during our two-week experimental cycle.

Line parameters obtained from the fit of the Rosenkranz absorption line profile (Eq. (1) of [1]) to the recorded experimental spectrum are shown as functions of temperature in Figs. 1 and 2 for the pressure broadening  $\gamma$  and pressure-normalized line mixing  $y$  parameters, respectively. A standard empirical expression was used to determine the temperature dependence of the measured parameters:

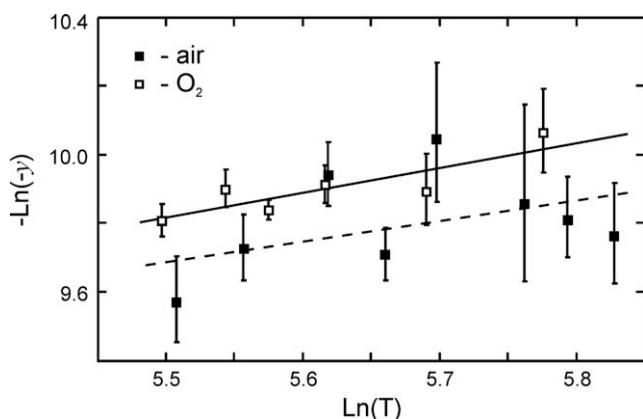
$$\gamma(T) = \frac{\Delta\nu(T)}{P} = \gamma(T_0) \left( \frac{T_0}{T} \right)^{n_\gamma}, \quad y(T) = \frac{Y(T)}{P} = \frac{Y(T_0)}{P} \left( \frac{T_0}{T} \right)^{n_y},$$

where  $\Delta\nu(T)$  and  $Y(T)$  are the measured half-width and mixing of the line at temperature  $T$  and pressure  $P$ ,  $n_\gamma$  and  $n_y$  are the temperature exponent for  $\gamma$  and  $y$ , respectively, and  $T_0$  is the fixed temperature (usually 300 K). From the measured half-width and mixing at different temperatures, the corresponding temperature exponents were determined by a least-squares analysis of the slopes of the plots of  $-\ln(\gamma)$  vs.  $\ln(T)$  (Fig. 1) and  $-\ln(y)$  vs.  $\ln(T)$  (Fig. 2).

The results of the study are presented in Table 1. Errors are  $1 - \sigma$  statistical uncertainties obtained from the least-squares fit. Both the broadening and mixing parameters at 300 K are in good agreement with our previous measurement [1] but these data have better accuracy. The value of the temperature exponent for the self-broadening parameter coincides well with our previous result of  $n_\gamma = 0.74(5)$  [1]. The temperature dependence of the air-broadening coefficient of the 118-GHz oxygen line was measured for the first time. The nitrogen broadening parameter and its temperature exponent were calculated as 2.255(14) MHz/Torr and 0.79(5), respectively, using the measured parameters and an air composition of 21% of  $\text{O}_2$  and 79% of  $\text{N}_2$ . It should be mentioned that the obtained broadening parameters also coincide within experimental error with the results of our previous study [2] where the 118-GHz line was investigated by two spectrometers that were essentially different by principal of operation. The study in reference [2] demonstrated coincidence of the broadening parameters measured by a RAD spectrometer (in the pressure range 0.2–3.5 Torr) and a resonator spectrometer (at one atmospheric pressure point), confirming that systematic errors are minimized for both instruments. Comparison of our results with very recent measurements by B.J. Drouin [3] of the same 118-GHz line shows quite a large discrepancy. The oxygen- and air-broadening parameters obtained in [3] are smaller by 8% and 10%, but the temperature exponents are larger by 18% and 24%, respectively, in both cases exceeding the summed error of the two experiments compared. At the same time, the temperature exponent for the  $\text{O}_2$ -broadening of the pure rotational 425-GHz oxygen line measured in [3] is exactly the same as our value for the 118-GHz line, and the air-broadening exponent is smaller by just 6%, which can still be considered as coinciding within the given experimental errors. Thus, the results of [3] seem to be puzzling because one would expect a similar value of the temperature exponent for those lines having insignificant differences in quantum numbers. One of the most probable sources of potential systematic errors of our measurements was the composition of the studied sample. For  $\text{O}_2$  content control, we used a DK-21 oxygen sensor (“INSOVT” St. Petersburg, Russia). The sensor operates from  $-20$  °C up to  $+50$  °C and has  $\pm 1\%$  specified accuracy for  $\text{O}_2$ -concentration measurements within the 10–30 °C temperature range. A TESTO-645 humidity meter equipped by a highly accurate humidity probe (“Testo” GmbH & Co, Germany) operating from  $-20$  °C up to  $+70$  °C was used for additional



**Fig. 1.** Temperature dependence of the air- and oxygen-pressure broadening parameters of the 118-GHz oxygen line. The experimental points are shown by filled and blank squares, respectively. The solid and dotted lines are fit by an exponential function. The slope of the straight line fitting the  $-\ln(\gamma)$  vs.  $\ln(T)$  plot is the value of the exponent  $n_\gamma$ . The error bars are  $1 - \sigma$  statistical uncertainties (for some points, the bars are smaller than the symbol size).



**Fig. 2.** Temperature dependence of the mixing parameters of the 118-GHz oxygen line in dry air and in oxygen. The experimental points are shown by filled and blank squares, respectively. The solid and dotted lines are the exponential functions fitted to the experiment. The slope of the straight line fitting the  $-\ln(\gamma)$  vs.  $\ln(T)$  plot is the value of the exponent  $n_\gamma$ . The error bars are  $1 - \sigma$  statistical uncertainties.

**Table 1**  
Measured parameters of the 118-GHz oxygen line

Experiment	Pressure broadening $\gamma(300)$ (MHz/Torr)	Temperature exponent $n_\gamma$	Line mixing $y(300)$ (1/Torr)	Temperature exponent $n_y$	Intensity at 300 K (cm/mol)
Dry air	2.250(10)	0.785(35)	$-5.5(3) \cdot 10^{-5}$	0.60(45)	$9.79(4) \cdot 10^{-25}$
Pure oxygen	2.230(5)	0.760(11)	$-4.7(1) \cdot 10^{-5}$	0.72(22)	$9.62(2) \cdot 10^{-25}$

sample control. Since the indices of refraction of oxygen and nitrogen are different, we could also control the equilibrium conditions of the sample measuring frequency of the working eigenmode of the resonator. However, since the experimental temperature range exceeded the specified range of the sensors, and because of the impossibility of their calibration in the course of our measurements, there may be some uncertainty in the determined  $O_2$  con-

centration. Fortunately, our experiment allows measurement of the integrated intensity of the observed line, enabling determination of the real concentration assuming a known value of the line strength.

The integrated line intensity obtained for each line record at different temperatures was used as a natural indicator of the experimental consistency. The measured intensities shown in Table 1 agree within  $3 - \sigma$  statistical uncertainty with each other and with the result of our previous measurements of  $9.73(29) \cdot 10^{-25}$  cm/mol [1]. However, they are 2–4% smaller than the value quoted in HITRAN [4]. A lower value of the line intensity could be caused either by the gas purity or by nitrogen remaining after the baseline was recorded. Since  $O_2$ - and  $N_2$ -broadening parameters of the 118-GHz line, as well as their temperature exponents, are very close to each other, such a small dilution of the sample by nitrogen may lead to systematic errors in the determination of the temperature exponent of only 0.2%, which is much smaller than our statistical error. Therefore, this was not taken into account in either determination of the parameter value or in its error.

The temperature dependence of the line mixing parameter is the most unexplored characteristic of the 118-GHz oxygen line due to the weakness of this effect, even at atmospheric pressure. However, the high signal to noise ratio achieved for the studied line in the present study allowed us, for the first time, a reliable determination of the temperature exponent for the line mixing parameter presented in Table 1. One can see the closeness of the corresponding temperature exponents for the broadening and mixing parameters that proves the appropriateness of using an aggregate value of 0.8 for the temperature dependence of both parameters in the Millimeter-wave Propagation Model [5].

## Acknowledgments

The authors thank Dr. P.W. Rosenkranz for informal review of the manuscript. The present work was supported in part by the Grant of Russian Fund for Basic Research No. 06-02-16082.

## References

- [1] M.Yu. Tretyakov, M.A. Koshelev, I.A. Koval, V.V. Parshin, L.M. Kukin, L.I. Fedoseev, Yu.A. Dryagin, A.F. Andriyanov, J. Mol. Spectrosc. 241 (2007) 109–111.
- [2] M.Yu. Tretyakov, G.Yu. Golubiatnikov, V.V. Parshin, M.A. Koshelev, S.E. Myasnikova, A.F. Krupnov, P.W. Rosenkranz, J. Mol. Spectrosc. 223 (2004) 31–38.
- [3] B.J. Drouin, J. Quant. Spectrosc. Radiat. Transfer 105 (2007) 450–458.
- [4] L.S. Rothman, D. Jacquemart, A. Barbe, D.C. Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chakerian Jr., K. Chance, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J.-M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, G. Wagner, J. Quant. Spectrosc. Radiat. Transfer 96 (2005) 139–204.
- [5] H.J. Liebe, P.W. Rosenkranz, G.A. Hufford, J. Quant. Spectrosc. Radiat. Transfer 48 (5/6) (1992) 629–643.

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