Journal of Molecular Spectroscopy **215,** 309–311 (2002)
doi:10.1006/jmsp.2002.8672

Pressure Broadening of the Rotational Line of Oxygen at 425 GHz

A. F. Krupnov, G. Yu. Golubiatnikov, V. N. Markov, and D. A. Sergeev

Institute of Applied Physics of RAS, 46 Uljanova str., 603950 Nizhnii Novgorod, Russia

E-mail: kru@appl.sci-nnov.ru

Received May 12, 2002; in revised form July 19, 2002

The pressure broadening of the $^{16}O^{16}O$ rotational line $(N, J) = (3, 2)$–$(1, 2)$ at 425 GHz by oxygen and nitrogen perturbers at room temperatures have been reported. A spectrometer with BWO and acoustic detector was employed with a double magnetically shielded cell. The signal-to-noise ratio on the line was about 200–250 for self-broadening and about 100 for broadening by N_2 measurements. The pressure-broadening parameters of the line at room temperature $(23 \pm 0.5°C)$ were measured as 2.19 ± 0.01 MHz/Torr for self-broadening and 2.215 ± 0.02 MHz/Torr for broadening by nitrogen. Values of these parameters significantly (by about 25%) differ from ones previously measured by H. M. Pickett, E. A. Cohen, and D. E. Brinza, (*Astrophys. J.* **248**, L49–L51 (1981)). The results of the present work show the necessity for correction of broadening parameters of this line for the purpose of Earth atmosphere remote sensing. The central frequency of the transition $(N, J) = (3, 2)$–$(1, 2)$ was measured as 424 763.023 ± 0.020 MHz.

Key Words: oxygen; submillimeter; spectrum; broadening.

INTRODUCTION

The $^{16}O_2$ transition $(N, J) = (3, 2)$–$(1, 2)$ of the $^3\Sigma$ ground electronic state at 425 GHz belongs to the lowest rotational transitions of this nonpolar molecule. The transition is planned for use in airborne remote sensing by the NAST-M apparatus (*1*) and is being considered for use in future satellite remote sensing of Earth's atmosphere (*2*). Nevertheless laboratory studies of the broadening parameter of this transition were given only in the paper (*3*). The evident cause of such limited studies of this line of O_2 as an important component of atmosphere is the weakness of the magnetodipole transition and the difficulty of spectroscopic studies in the submillimeter-wave range. In the present paper laboratory measurements of this line are reported. Self- and nitrogen broadening parameters were measured with the accuracy significantly better than in previous measurements (*3*). The central frequency of the $^{16}O_2$ $(N, J) = (3, 2)$–$(1, 2)$ transition was measured also with significantly better accuracy than in previous measurements. Comparisons with previous measurements are presented.

EXPERIMENTAL DETAILS

For the study of the oxygen line at 425 GHz the submillimeter RAD spectrometer with backward wave oscillator (BWO) and acoustic cell (*4*) was employed. The block-scheme of the experimental setup is presented in Fig. 1. The frequency of the BWO source of the range 370–535 GHz was phase-locked against a harmonic of the fundamental output frequency of a 78–118 GHz synthesizer of type (*5*). The synthesizer frequency itself was stabilized against a rubidium standard and the final accuracy of the measurements was tested by measurement of the central frequencies of CO lines. The measurements of the CO $J =$ 4–3 transition showed agreement with a well–known frequency within 5 kHz. The BWO frequency and signal acquisition system were controlled via computer. Details of such a spectrometer were given in (*6*). For the study of the oxygen transition sensitive to ambient magnetic field a double magnetic shell was made of annealed permalloy to shield the cell filled by the oxygen sample. The small size of the acoustic cell permitted convenient and compact construction of the shell. The gas pressure in the cell was measured by an MKS Baratron gauge. Pure gas samples from the Messer MG Company were used in the investigations. A record of the typical lineshape with fitting to the Voigt profile and the residue is presented in Fig. 2. As can be seen, the signal-to-noise ratio on the record is no less than several hundreds, which advantageously differ from that obtained in other studies of this submillimeter oxygen line (*7, 8*).

RESULTS OF EXPERIMENT

The oxygen collisional line half width at half maximum height (HWHM) was defined from the fit of the experimental lineshape to the Voigt line profile (Fig. 2). The Doppler broadening linewidth was used at the calculated value of 462 kHz at room temperature. A linear regression fit of line HWHM (MHz) versus oxygen pressure (Torr) together with the residue of this fit is presented in Fig. 3. The collisional self-broadening parameter of the $(N, J) = (3, 2)$–$(1, 2)$ oxygen line was then found as 2.19 ± 0.01 MHz/Torr. The small value of the intercept, 9 kHz, of the linear dependence of the pressure broadening line HWHM in Fig. 3 at zero pressure shows the practical absence of residual

0022-2852/02 $35.00

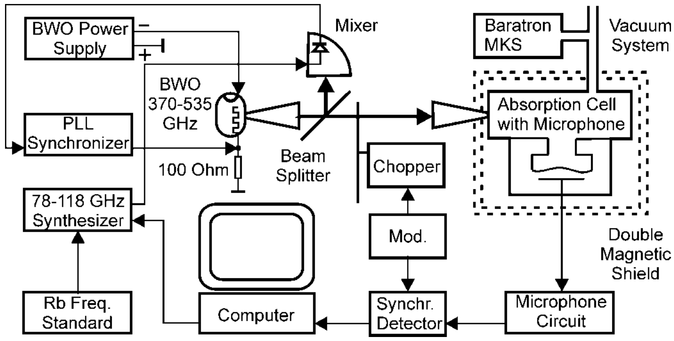

FIG. 1. Block diagram of the experimental setup of the RAD spectrometer for oxygen line measurements.

magnetic splitting of the line in addition to the internal consistency of measurements.

The nitrogen broadening parameter was defined from a similar fit procedure as 2.215 ± 0.02 MHz/Torr.

This work was not aimed principally at measurement of the central line frequency but comparison of the obtained frequency value at low pressures (0.2–0.7 Torr) with measured earlier ones (McKnight and Gordy (*7*), Steinbach and Gordy (*8*)) and a calculated frequency (Zink and Mizushima (*11*)) has also been of interest from the point of view of measurement consistency. The central frequency of the $^{16}O_2$ $(N, J) = (3, 2)$–$(1, 2)$ transition was measured in this work as $424\,763.023 \pm 0.02$ MHz.

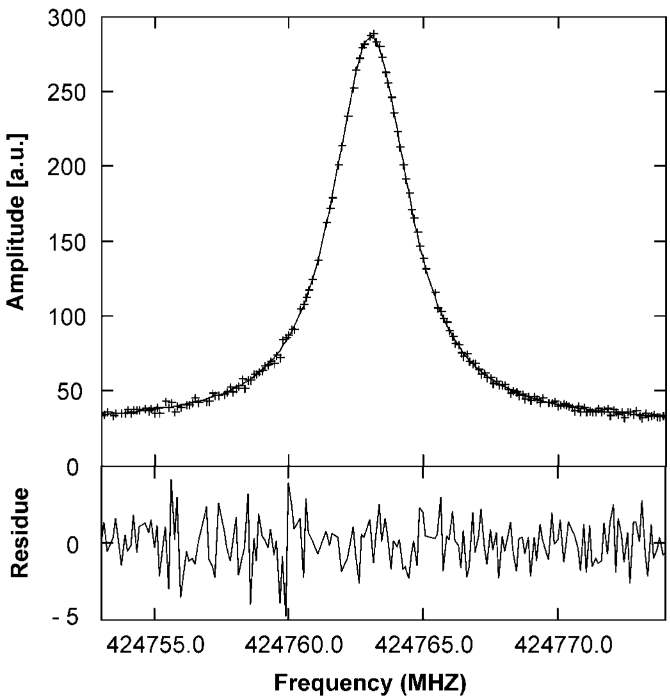

FIG. 2. Record of the $(N, J) = (3, 2)$–$(1, 2)$ rotational line of the oxygen molecule. Experimental points are denoted by crosses (+); the line (—) represents the fit to the Voigt line profile; the bottom trace is the residuum of the fit. Pressure in the cell was $p = 0.83$ Torr.

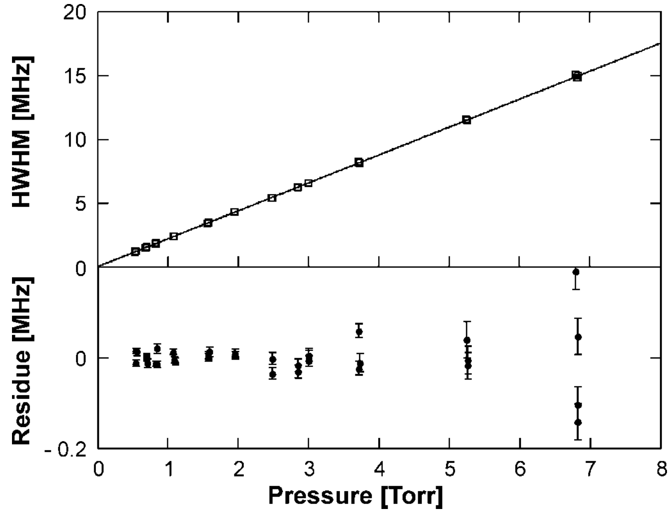

FIG. 3. Experimental line HWHM values (□) represent the pressure broadened collisional part of linewidth while the linear regression fit to this pressure dependence is depicted by a solid line (—). The slope of this line is 2.19 ± 0.01 MHz/Torr; the intercept at $p = 0$ Torr is +9 kHz. The residuum resulting from the fit with error bars are shown below.

DISCUSSION

The broadening parameters obtained in the present work are given in Table 1 together with those reported by Pickett *et al.* (*3*). Comparison shows significant differences amounting to roughly 25% in opposite directions for self- and nitrogen broadening parameters. These differences exceed the quoted errors. The values of broadening parameters obtained in the present work for the 425-GHz line resemble more closely the values obtained earlier for the 118-GHz line of oxygen (see (*3, 9*)) than the values of (*3*) for the same 425-GHz line. In our opinion, for remote sensing purposes the values of broadening parameters previously used for the 425-GHz oxygen line (see, e.g., (*3, 10*)) must be significantly corrected in accordance with the results obtained in the present work.

The measured line frequency is given in Table 2 together with values obtained by McKnight and Gordy (*7*) and Steinbach and Gordy (*8*). The comparison also shows that our value of the central frequency is slightly outside of the errors quoted in (*7, 8*) and has a better accuracy. The measured frequency value lies nearer to the one calculated by Zink and

TABLE 1
Broadening Parameters for 425-GHz Oxygen Line at Room Temperature (MHz/Torr)

O_2 and Perturber	Broadening parameter (MHz/Torr)	References
O_2	1.6 ± 0.16	(*3*)
N_2	2.86 ± 0.31	(*3*)
O_2	2.19 ± 0.007	this work
N_2	2.215 ± 0.02	this work

TABLE 2
Center Frequency of the Oxygen Line
$(N, J) = (3, 2)$–$(1, 2)$

Frequency (MHz)	References	
424 763.80 ± 0.20	(*7*)	[Meas.]
424 763.210 ± 0.100	(*8*)	[Meas.]
424 763.023 ± 0.02	this work	[Meas.]
424 763.124	(*11*)	[Calc.]

Mizushima (*11*) from fitting many rotational transitions of the oxygen molecule.

No evident pressure self-shift of the central line at 425 GHz was noticed. The upper limits of the probable pressure line self-shift could not exceed a magnitude of ±40 kHz/Torr; the statistical self-shift value over many measurements was determined as +5 ±40 kHz/Torr.

CONCLUSION

In the present paper the investigation of the pressure broadening 425-GHz oxygen line by oxygen and nitrogen has been described. Corresponding broadening parameters were measured. A comparison of the results with those obtained earlier by other authors is given. The accuracy of the present measurements exceeded the accuracy quoted earlier for the self–broadening parameter and up to the order of magnitude for nitrogen broadening one. There is significant difference (by 25%) of the present broadening parameters with obtained earlier in the only previous measurements of (*3*). This difference exceeds the limits of the quoted error. The significance of the results for Earth atmosphere remote sensing of this perspective oxygen line is pointed out. The central frequency of the line was also measured with higher accuracy.

ACKNOWLEDGMENTS

The present work was supported in part by a Grant of the Russian Fund for Basic Studies (RFBR), No. 00-02-16604, and a Contract with the Ministry of Industry, Science and Technology of Russian Federation, No. 40.020.1.1.1160. To both these sources of support the authors express their deep gratitude.

REFERENCES

1. *Available at* http://rseg.mit.edu/nastm/HTML/mts.html, P. W. Rosenkranz, personal communication.
2. M. Klein and A. J. Gasiewski, *J. Geophys. Res. D* **105**(13), 17 481–17 511 (2000).
3. H. M. Pickett, E. A. Cohen, and D. E. Brinza, *Astrophys. J.* **248,** L49–L51 (1981).
4. A. F. Krupnov, *in* "Modern Aspects of Microwave Spectroscopy" (G. W. Chantry, Ed.), pp. 217–256. Academic Press, San Diego, 1979.
5. A. F. Krupnov and O. P. Pavlovsky, *Int. J. Infrared Millimeter Waves* **15,** 1611–1624 (1994).
6. V. N. Markov, G. Yu. Golubyatnikov, V. A. Savin, D. A. Sergeev, A. Guarnieri, and H. Maeder, *J. Mol. Spectrosc*, in press.
7. J. S. McKnight and W. Gordy, *Phys. Rev. Lett.* **21,** 1787–1789 (1968).
8. W. Steinbach and W. Gordy, *Phys. Rev. A*, **8,** 1753–1758 (1973).
9. M. Yu. Tretyakov, V. V. Parshin, V. N. Shanin, S. E. Myasnikova, M. A. Koshelev, and A. F. Krupnov, *J. Mol. Spectrosc.* **208,** 110–112 (2001).
10. H. J. Liebe, *Radio Sci.* **20,** 1069–1089 (1985); H. J. Liebe, *Int. J. Infrared Millimeter Waves* **10,** 631–650 (1989); H. J. Liebe, P. W. Rosenkranz, and G. A. Hufford, *J. Quant. Spectrosc. Radiat. Transfer* **48,** 629–643 (1992).
11. L. R. Zink and M. Mizushima, *J. Mol. Spectrosc.* **125,** 154–158 (1987).