High precision measurement of ultraweak transitions of the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (0, 0) band of molecular oxygen

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Abstract

We have used a highly sensitive cavity-enhanced frequency modulation spectroscopy technique to measure different parameters of the ultraweak transitions of $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (0, 0) band of molecular oxygen in the range 7640 cm$^{-1}$ to 7917 cm$^{-1}$. The self-broadened half-width and air-broadened half-width of the transitions have been measured for three different pressures for both $^{16}$O$_2$ and $^{18}$O$_2$. To measure the line intensity and self-broadened half-width we have used ultra pure oxygen sample and air-broadened half-width was measured with dry air sample. The (0,0) band of $^{16}$O$_2$ and $^{18}$O$_2$ show weak quadrupole transitions with line intensities ranging from $1 \times 10^{-30}$ to $1.9 \times 10^{-28}$ cm/molecule. The measurements are in excellent agreement with the recent measurement of Rothman et al. [1].

Keywords: Oxygen, Line intensities, Widths, Cavity-enhanced frequency modulation spectroscopy

1. Introduction

The precise measurement of different parameters in the infrared spectrum in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (0, 0) band of oxygen is of fundamental interest to the atmospheric scientists for modelling and calculating different physical parameters like radiation transfer, heat distribution due to the greenhouse gases, ozone abundances and hence providing a comparative study of different atmospheric models available. Oxygen transitions are often used as a calibrator on the spectra obtained from the satellite instruments. Furthermore taking the ratio of column abundances of CO$_2$ or CH$_4$ to that of O$_2$ cancels many common systematic errors which are related to the instruments [2]. So there
is a constant demand that all the spectroscopic parameters corresponding to this a-X (0,0) transition are precisely measured.

Due to the importance, magnetic dipole transitions in this band were tabulated in the HITRAN database [3]. Since these parameters have been continuously updated through different experimental results as HITRAN was evolving. The intensities of the a$^1\Delta_g \leftarrow X\,3\Sigma_g^{-} (0,0)$ band for $^{16}$O$_2$ in HITRAN (modified for HITRAN2000 using experimental parameters from Lafferty et al. [4]). However it were found to be inadequate for atmospheric retrievals such as the one in Ref.[2]. The updated list of $^{16}$O$_2$ intensities recently adopted for HITRAN was derived by Orr-Ewing based on experimental results from Newman et al. [5]. These intensities are much accurate in application to atmospheric retrievals [2]. In order to improve the retrievals, Washenfelder et al. [2] used an empirical scaling to HITRAN2008 intensities of $^{16}$O$^{18}$O. These intensity improvements have served as a basis for an interim update of the HITRAN oxygen file that was placed on the HITRAN website in November 2009. There is still space for substantial improvement of spectral parameters of the $^1\Delta_g \leftarrow X\,3\Sigma_g^{-} (0,0)$ band of molecular oxygen. Recently Gordon et al. [6] have shown the importance of including quadrupole lines in this region to the HITRAN line list to improve the residuals of the solar absorption spectrum.

The line position of the a$^1\Delta_g \leftarrow X\,3\Sigma_g^{-} (0,0)$ band transitions of $^{16}$O$_2$ in HITRAN, the X $3\Sigma_g^{-}$ spectroscopic constant from Rouillié et al. [7] and a$^1\Delta_g$ rotational constants determined from the microwave spectrum by Hilling et al. [8] were used. Gamache et al. [9] describe that the term energy of a$^1\Delta_g$ was taken from Krupenie [10]. The term values of Krupenie were corrected in HITRAN to match the unpublished FTS spectrum measured by Brault [11]. In HITRAN2008, line position of $^{16}$O$^{18}$O were calculated using ground state constant of Yamamoto et al. [12] and excited-state rotational constants reported by Herzberg et al. [13].

Though the HITRAN line positions are well accepted universally till today, a much more precise measurement of the a$^1\Delta_g \leftarrow X\,3\Sigma_g^{-} (0,0)$ band is required. Furthermore, a recent measurement of Rothman et al. [1] and the measurement Cheah et al. [14] differs significantly though Chech et al. [14] claim that their measurement are better than those in HITRAN. This discrepancies also invite attention for further investigation and precise measurement parameters of this a$^1\Delta_g \leftarrow X\,3\Sigma_g^{-} (0,0)$ band transitions.

In this paper, we present measurement of the a$^1\Delta_g \leftarrow X\,3\Sigma_g^{-} (0,0)$ band electronic transitions using a high sensitive cavity-enhanced frequency modu-
lation spectroscopy. The present work measures different parameters i.e. the self-broadened half-width, air-broadened half-width, line-center frequency and line intensity of the O$_2$ a-X (0,0) band using ultra pure oxygen sample and dry air sample at three different pressures (200 mbar, 400 mbar and 600 mbar). Our measurement of the line positions of the transitions are used to determine improved molecular constants which are of significance for the correct interpretation of the atmospheric phenomena.

2. Experimental setup

To record our data we use the ultrasensitive technique of noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) [15, 16]. NICE-OHMS is a technique in which frequency modulation spectroscopy (FMS) is performed within a high-finesse cavity, thereby increasing the effective sample path length by $\frac{2 \times \text{finesse}}{\pi}$. The laser frequency is locked to a longitudinal cavity mode and the modulation frequency is locked to exactly match the cavity free spectral range ($f_{FSR}$). This ensures all the frequency components of the light are affected identically by the cavity. The light transmitted by the cavity is incident on a fast photodiode and the output is demodulated to produce a cavity-enhanced FMS signal. A second level of modulation, at low frequency, is applied to the cavity (and hence the laser), and this signal is demodulated by a lock-in amplifier to produce the NICE-OHMS signal.

Details of our NICE-OHMS experimental setup are described in an earlier work from our laboratory [17]. Briefly, our experimental setup uses an external cavity diode laser with a wavelength range from 1260 nm to 1310 nm, and a high finesse cavity with a free spectral range of 540 MHz. The cavity has a finesse $\approx 16000$ and thus an effective path length of over 2.8 km. The cavity output mirror is mounted on a piezoelectric transducer (PZT) to allow scanning of the cavity length. The cavity lies within an ultrahigh vacuum chamber, evacuated to a base pressure of $10^{-7}$ mbar before being filled with molecular oxygen sample (ultra pure oxygen) or dry air sample. The intra-cavity pressure was measured using a capacitance manometer (Pfeiffer Vacuum TPG 261) with a range of 1-1100 mbar and a precision of 0.1%. Over the period our measurements were taken the temperature of the vacuum chamber drifted with the variation in room temperature between 22.4 and 23.3°C.
We used a National Instruments PCI-6259 M-series data-acquisition card to perform frequency scans and to collect our NICE-OHMS data. A voltage ramp from an analog output was fed to the cavity PZT, producing a scan of the cavity length and hence the laser frequency. Each scan took 40s and spanned up to 0.42 cm$^{-1}$. The cavity PZT does not produce a linear scan with voltage, so a frequency scaling measurement was made for each data set. Each 42 cm$^{-1}$ wide spectrum recorded with one single laser (New Focus TLB 6324-D Velocity Laser) was calibrated independently on the basis of the wavelength values provided by a Michelson-type wavemeter (Bristol 621A NIR, absolute accuracy ±0.002 cm$^{-1}$ @ 10,000 cm$^{-1}$). Furthermore we applied lambda meter reading corrections as described in an earlier work by Perevalov [18]. After the correction, the entire spectrum become linear in terms of frequency. For the data presented in this paper, the output of the lock-in amplifier (the NICE-OHMS signal) was averaged over 12 consecutive scans. The typical uncertainty in the line position is estimated to be less than $1 \times 10^{-3}$ cm$^{-1}$.

We used Matlab to perform a fit of the collected data to a theoretical NICE-OHMS lineshape function [17]. The theoretical lineshape is based on a Voigt lineshape and accounts for the effect of the two levels of frequency modulation. As the experiment is performed at room temperature, we calculate the Gaussian width at 23°C which causes the Doppler broadening, and the fitting routine produced best fit parameters for the peak absorption, the Lorentzian half-width due to pressure broadening, and thus the line intensity. We estimate the experimental precision for each of the transitions on a case by case basis, determining the range over which fitted parameters are reasonable. A detailed discussion of the sources of error is discussed in an earlier work from our laboratory [17]. For stronger, well-resolved, transitions we estimate an experimental precision of 4% for the linewidth and 7% for the line intensity, whereas for the weakest, least resolved, transitions we have estimated errors of up to 40% for the linewidth, and 70% for the line intensity. In addition, the uncertainty in our detection system gain in 8% so the overall accuracy of the line intensities is there experimental precision plus 8%, while the overall accuracy of the linewidths is equal to the experimental precision. For our experiment we have used ultra pure oxygen and a dry air mixture to measure the self-broadened and air-broadened half-width respectively.
3. Result and analysis

The overview of the transitions in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band of oxygen is shown in Fig. 1. The transitions reported within this paper lie between 7640 to 7917 cm$^{-1}$ and it is clear that from the overview spectra that the line strength of these transitions are very low. We were able to measure only the symmetric isotopologues i.e. $^{16}\text{O}_2$ and $^{18}\text{O}_2$, since the line strengths for the transitions of asymmetric isotopologues are much lower than the resolution limit of our experimental set up.

3.1. Lines of $^{16}\text{O}_2$

We have measured 14 transitions in the $O$ branch, 7 transition in the $R$ branch, 36 transitions in the $P$ branch and 53 transition in the $Q$ branch of $^{16}\text{O}_2$ in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (0,0) band. Our measured parameters and corresponding experimental uncertainty of these transitions are given in Table 1, Table 2, Table 3 and in Table 4 respectively. The uncertainties for some of the transitions are larger. Since many of the transitions overlap and hence the fitting become more difficult. In Fig. 2 and Fig. 3 we compared our measured line intensities for these transitions with the calculated values in the HITRAN database. Furthermore, we have measured the self-broadened linewidth (measurement with ultra pure oxygen sample) and the air-broadened linewidth (measurement with dry air sample) for these transitions at three different pressure i.e. 200 mbar, 400 mbar and 600 mbar which are shown in Fig. 4, Fig. 5, Fig. 6 and in Fig. 7 along with the calculated values in the HITRAN database. It is to be noted that, the measured line positions, line intensities, self-broadened and air-broadened Lorentzian half width are in good agreement with the predictions in the HITRAN database.

3.2. Lines of $^{18}\text{O}_2$

We have measured 14 transitions in the $O$ branch, 13 transition in the $R$ branch, 3 transition in the $S$ branch, 40 transitions in the $P$ branch, and 60 transition in the $Q$ branch of $^{18}\text{O}_2$ in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (0,0) band. Our measured parameters and corresponding experimental uncertainty of these transitions are given in Table 5, Table 6, Table 7 and in Table 8 respectively. In Fig. 8, Fig. 9 we compared our measured line intensities for these transitions with the calculated values in the HITRAN database. Furthermore, we have measured the self-broadened linewidth (measurement with ultrapure oxygen sample) and the air-broadened linewidth (measurement with dry air sample).
sample) for these transitions at three different pressure i.e. 200 mbar, 400 mbar and 600 mbar which are shown in Fig. 10, Fig. 11, Fig. 12 and in Fig. 13 along with the calculated values in the HITRAN database. It is to be noted that, the measured line positions, line intensities, self-broadened and air-broadened Lorentzian half width are in good agreement with the predictions in the HITRAN database.

3.3. Data fitting

We used Matlab to perform a Voigt lineshape fit on each transition to a theoretical NICE-OHMS lineshape function [17]. The lineshape is accounts for the effect of the two levels of frequency modulation.

The energy of a transition from the ground state \((N', J')\) to the excited state \((J)\) is given by the equation

\[
\tilde{\nu}_{J\leftarrow N', J'} = \tilde{\nu}_{0\leftarrow 0} + B_0 J(J + 1) - D_0 [J(J + 1)]^2 - F'(N', J')
\]

where the lower state energy \(F'(N', J')\) is calculated with the molecular constant in a recent publication [1]. \(\tilde{\nu}_{J\leftarrow N', J'}\) is the measured line position, and \(\tilde{\nu}_{0\leftarrow 0}, B_0\) and \(D_0\) are the molecular constants of the excited state, \(a(\tilde{\nu} = 0)\) which we measured.

3.3.1. \(^{16}\text{O}_2\) parameters

We have measured 111 lines of the \(^1\Delta_g \leftarrow X^3\Sigma_g^-\) (0, 0) band of \(^{16}\text{O}_2\). To extract the parameters of each individual transition we fit Eq. (1) to the line position of the measured transition. The results of the fit are given in Table 9, where the \(^1\Delta_g\) state constants compared with those from Olaga [1], Amiot [19] and Rothman [20].

3.3.2. \(^{18}\text{O}_2\) parameters

We have measured 130 lines of the \(^1\Delta_g \leftarrow X^3\Sigma_g^-\) (0, 0) band of \(^{18}\text{O}_2\). To extract the parameters of each individual transition we fit Eq. (1) to the line position of the measured transition. The results of the fit are given in Table 10, where the \(^1\Delta_g\) state constants compared with those from Olaga [1].

4. Conclusion

Our work characterized 241 ultraweak transitions in molecular oxygen by measuring their line positions, self-broadened and air-broadened linewidths
and line intensities using NICE-OHMS. The precise value of the parameters provide a path to improve the existing HITRAN database. It is to be noted that the $a^1 \Delta g \leftarrow X^3 \Sigma_g^-$ electric quadrupole transitions of $^{16}$O$_2$ and $^{18}$O$_2$ are important to atmospheric modelling. The NICE-OHMS measurement of different $a^1 \Delta g \leftarrow X^3 \Sigma_g^-$ transitions in this work provide one of the best set of spectroscopic parameters for the $a^1 \Delta_g$ state of $^{16}$O$_2$ and $^{18}$O$_2$.

5. Acknowledgements

We are grateful to Tzahi Grunzweig for his help with labview for automation of the experiment. This research is supported by the New Zealand Foundation for Research, Science and Technology, Otago University.
Table 1: Measured transition parameters of the $O$ branch of $^{16}$O$_2$.

| Transition | Position | Line intensity | Self-broadened half-width |
|------------|----------|----------------|---------------------------|
| $\Delta N \, \Delta N'$ | $\Delta J \, \Delta J'$ | cm$^{-1}$ | $10^{-8}$cm$^{-2}$atm$^{-1}$ | cm$^{-1}$ at 400 mbar |
| O31P30 | 7692.459(2) | 0.139(18) | 0.0136(14) |
| O29P28 | 7706.069(2) | 0.338(10) | 0.0140(12) |
| O27P26 | 7719.552(2) | 0.722(14) | 0.0144(9) |
| O25P24 | 7732.894(2) | 1.372(11) | 0.0155(6) |
| O23P22 | 7746.031(2) | 3.062(10) | 0.0163(6) |
| O21P20 | 7759.092(2) | 5.125(10) | 0.0167(6) |
| O19P18 | 7772.052(2) | 7.369(10) | 0.0167(6) |
| O17P16 | 7784.807(2) | 10.173(10) | 0.0175(6) |
| O15P14 | 7797.435(2) | 13.147(10) | 0.0179(6) |
| O13P12 | 7809.917(2) | 16.335(10) | 0.0186(6) |
| O11P10 | 7822.243(2) | 18.934(10) | 0.0194(6) |
| O9P8 | 7834.445(2) | 18.041(10) | 0.0198(6) |
| O7P6 | 7846.459(2) | 14.563(10) | 0.0202(6) |
| O5P4 | 7858.330(2) | 8.204(10) | 0.0214(6) |

Table 3: Measured transition parameters of the $P$ branch of $^{16}$O$_2$.

| Transition | Position | Line intensity | Self-broadened half-width |
|------------|----------|----------------|---------------------------|
| $\Delta N \, \Delta N'$ | $\Delta J \, \Delta J'$ | cm$^{-1}$ | $10^{-8}$cm$^{-2}$atm$^{-1}$ | cm$^{-1}$ at 400 mbar |
| P37P37 | 7750.151(2) | 0.037(5) | 0.0119(25) |
| P37Q36 | 7751.843(2) | 0.032(5) | 0.0120(16) |
| P35P36 | 7758.676(2) | 0.209(17) | 0.0120(14) |
| P35Q34 | 7760.315(2) | 0.067(5) | 0.0127(22) |
| P33P33 | 7767.024(2) | 0.186(19) | 0.0133(15) |
| P33Q32 | 7768.760(2) | 0.148(22) | 0.0126(14) |
| P31P31 | 7775.219(2) | 0.318(17) | 0.0139(14) |
| P31Q30 | 7776.958(2) | 0.381(18) | 0.0137(13) |
| P29P29 | 7783.193(2) | 0.711(14) | 0.0148(8) |
| P29Q28 | 7785.02(2) | 0.878(13) | 0.0149(8) |
| P27P27 | 7791.141(2) | 2.251(10) | 0.0149(6) |
| P27Q26 | 7792.931(2) | 1.622(10) | 0.0156(6) |
| P25P25 | 7798.861(2) | 3.629(10) | 0.0146(6) |

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### Table 3 – Continued from previous page

| Transition | Position | Line intensity | Self-broadened half-width |
|------------|----------|----------------|---------------------------|
| Δ N N' Δ J J' V | | cm⁻¹ | 10⁻⁸ cm⁻² atm⁻¹ | cm⁻¹ at 400 mbar |
| P25Q24 | 7800.622(2) | 3.631(10) | 0.0148(6) |
| P23P23 | 7806.475(2) | 5.960(10) | 0.0157(6) |
| P23Q22 | 7808.213(2) | 6.657(10) | 0.0158(6) |
| P21P21 | 7813.861(2) | 10.867(10) | 0.0164(6) |
| P21Q20 | 7815.716(2) | 10.859(10) | 0.0170(6) |
| P19P19 | 7821.099(2) | 13.731(10) | 0.0177(6) |
| P19Q18 | 7822.939(2) | 16.290(10) | 0.0171(6) |
| P17P17 | 7828.202(2) | 20.672(10) | 0.0177(6) |
| P17Q16 | 7830.106(2) | 24.296(10) | 0.0174(6) |
| P15P15 | 7835.216(2) | 27.187(10) | 0.0167(6) |
| P15Q14 | 7837.104(2) | 33.127(10) | 0.0179(6) |
| P13P13 | 7841.963(2) | 34.795(10) | 0.0183(6) |
| P13Q12 | 7843.927(2) | 42.831(10) | 0.0189(6) |
| P11P11 | 7848.657(2) | 39.733(10) | 0.0193(6) |
| P11Q10 | 7850.604(2) | 49.796(10) | 0.0192(6) |
| P9P9 | 7855.182(2) | 40.231(10) | 0.0195(6) |
| P9Q8 | 7857.122(2) | 53.482(10) | 0.0196(6) |
| P7P7 | 7860.503(2) | 35.064(10) | 0.0197(6) |
| P7Q6 | 7863.463(2) | 52.423(10) | 0.0199(6) |
| P5P5 | 7867.711(2) | 23.739(10) | 0.0205(6) |
| P5Q4 | 7869.706(2) | 41.412(10) | 0.0209(6) |
| P3P3 | 7873.700(2) | 7.952(10) | 0.0227(6) |
| P3Q2 | 7875.785(2) | 19.828(10) | 0.0219(6) |

### Table 4: Measured transition parameters of the Q branch of \(^{16}\text{O}_2\).

| Transition | Position | Line intensity | Self-broadened half-width |
|------------|----------|----------------|---------------------------|
| Δ N N' Δ J J' V | | cm⁻¹ | 10⁻⁸ cm⁻² atm⁻¹ | cm⁻¹ at 400 mbar |
| Q3R2 | 7884.298(2) | 40.095(10) | 0.0219(6) |
| Q3Q3 | 7882.217(2) | 64.156(10) | 0.0212(6) |
| Q3P4 | 7884.141(2) | 8.482(10) | 0.0211(6) |

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| Transition | Position (cm⁻¹) | Line intensity (10⁻⁸ cm⁻² atm⁻¹) | Self-broadened half-width cm⁻¹ at 400 mbar |
|-----------|----------------|---------------------------------|------------------------------------------|
| Q5R4      | 7883.870(2)    | 43.470(10)                      | 0.0203(6)                                |
| Q5Q5      | 7881.834(2)    | 99.431(10)                      | 0.0202(6)                                |
| Q5P6      | 7883.822(2)    | 16.293(10)                      | 0.0197(6)                                |
| Q7R6      | 7883.285(2)    | 43.599(10)                      | 0.0203(6)                                |
| Q7Q7      | 7881.326(2)    | 116.910(10)                     | 0.0194(6)                                |
| Q7P8      | 7883.318(2)    | 20.976(10)                      | 0.0205(6)                                |
| Q9R8      | 7882.631(2)    | 40.629(10)                      | 0.0196(6)                                |
| Q9Q9      | 7880.664(2)    | 118.606(10)                     | 0.0200(6)                                |
| Q9P10     | 7882.704(2)    | 22.926(10)                      | 0.0196(6)                                |
| Q11R10    | 7881.713(2)    | 35.100(10)                      | 0.0184(6)                                |
| Q11Q11    | 7879.818(2)    | 107.894(10)                     | 0.0188(6)                                |
| Q11P12    | 7881.892(2)    | 22.012(10)                      | 0.0194(6)                                |
| Q13R12    | 7880.716(2)    | 28.214(10)                      | 0.0182(6)                                |
| Q13Q13    | 7878.812(2)    | 89.421(10)                      | 0.0177(6)                                |
| Q13P14    | 7880.908(2)    | 19.084(10)                      | 0.0181(6)                                |
| Q15R14    | 7879.564(2)    | 20.762(10)                      | 0.0183(6)                                |
| Q15Q15    | 7877.646(2)    | 68.931(10)                      | 0.0172(6)                                |
| Q15P16    | 7877.798(2)    | 15.592(10)                      | 0.0189(6)                                |
| Q17R16    | 7878.227(2)    | 14.756(10)                      | 0.0174(6)                                |
| Q17Q17    | 7876.317(2)    | 49.824(10)                      | 0.0172(6)                                |
| Q17P18    | 7878.490(2)    | 11.131(10)                      | 0.0178(6)                                |
| Q19R18    | 7876.714(2)    | 9.569(10)                       | 0.0169(6)                                |
| Q19Q19    | 7874.846(2)    | 33.174(10)                      | 0.0176(6)                                |
| Q19P20    | 7877.008(2)    | 8.197(10)                       | 0.0174(6)                                |
| Q21R20    | 7875.053(2)    | 6.005(10)                       | 0.0167(6)                                |
| Q21Q21    | 7873.214(2)    | 20.530(10)                      | 0.0162(6)                                |
| Q21P22    | 7875.399(2)    | 5.245(10)                       | 0.0168(6)                                |
| Q23R22    | 7873.172(2)    | 3.728(10)                       | 0.0166(6)                                |
| Q23Q23    | 7871.393(2)    | 12.400(10)                      | 0.0162(6)                                |
| Q23P24    | 7873.571(2)    | 3.341(10)                       | 0.0153(6)                                |
| Q25R24    | 7871.260(2)    | 1.981(10)                       | 0.0155(6)                                |
| Q25Q25    | 7869.429(2)    | 6.520(10)                       | 0.0150(6)                                |
| Q25P26    | 7871.593(2)    | 2.112(10)                       | 0.0151(6)                                |
| Q27R26    | 7869.050(2)    | 1.628(10)                       | 0.0149(6)                                |

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Table 4 – Continued from previous page

| Transition | Position | Line intensity | Self-broadened half-width |
|------------|----------|----------------|--------------------------|
| ∆ N N' ∆ J J' V | cm⁻¹ | 10⁻⁸ cm⁻² atm⁻¹ | cm⁻¹ at 400 mbar |
| Q27Q27    | 7867.299(2) | 3.566(10) | 0.0147(6) |
| Q27P28    | 7869.517(2) | 0.783(13) | 0.0146(8) |
| Q29R28    | 7866.741(2) | 0.476(16) | 0.0141(11) |
| Q29Q29    | 7865.008(2) | 1.717(10) | 0.0144(6) |
| Q29P30    | 7867.212(2) | 0.401(16) | 0.0139(11) |
| Q31R30    | 7864.257(2) | 0.293(18) | 0.0135(14) |
| Q31Q31    | 7862.492(2) | 0.833(12) | 0.0135(8) |
| Q31P32    | 7864.728(2) | 0.186(19) | 0.0145(14) |
| Q33R33    | 7861.57(2)  | 0.165(19) | 0.0133(15) |
| Q33Q33    | 7859.856(2) | 0.342(17) | 0.0139(12) |
| Q33P34    | 7862.130(2) | 0.109(20) | 0.0139(15) |
| Q35R35    | 7858.739(2) | 0.072(6)  | 0.0101(22) |
| Q35Q35    | 7857.004(2) | 0.157(20) | 0.0120(15) |
| Q35P36    | 7859.310(2) | 0.038(6)  | 0.0126(21) |
| Q37R37    | 7853.988(2) | 0.159(21) | 0.0129(15) |
| Q39Q39    | 7850.825(2) | 0.064(7)  | 0.0127(23) |

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Table 7 – Continued from previous page

| Transition | Position cm⁻¹ | Line intensity 10⁻⁶cm⁻²atm⁻¹ | Self-broadened half-width cm⁻¹ at 400 mbar |
|------------|--------------|-------------------------------|------------------------------------------|
| P18Q17     | 7831.084(2)  | 0.044(5)                      | 0.0182(14)                               |
| P17P17     | 7832.571(2)  | 0.046(7)                      | 0.0177(14)                               |
| P17Q16     | 7834.393(2)  | 0.055(6)                      | 0.0181(14)                               |
| P16Q16     | 7835.876(2)  | 0.054(4)                      | 0.0170(14)                               |
| P16Q15     | 7837.756(2)  | 0.056(4)                      | 0.0190(12)                               |
| P15P15     | 7839.164(2)  | 0.061(5)                      | 0.0188(14)                               |
| P15Q14     | 7841.035(2)  | 0.070(7)                      | 0.0180(12)                               |
| P14P14     | 7842.543(2)  | 0.062(4)                      | 0.0182(14)                               |
| P14Q13     | 7844.284(2)  | 0.081(7)                      | 0.0182(12)                               |
| P13P13     | 7845.528(2)  | 0.068(3)                      | 0.0191(14)                               |
| P13Q12     | 7847.487(2)  | 0.087(4)                      | 0.0193(12)                               |
| P12P12     | 7848.723(2)  | 0.078(5)                      | 0.0189(12)                               |
| P12Q11     | 7850.656(2)  | 0.095(5)                      | 0.0195(10)                               |
| P11P11     | 7851.817(2)  | 0.076(4)                      | 0.0197(12)                               |
| P11Q10     | 7853.783(2)  | 0.098(4)                      | 0.0198(10)                               |
| P10P10     | 7854.912(2)  | 0.077(6)                      | 0.0193(12)                               |
| P10Q9      | 7856.884(2)  | 0.121(29)                     | 0.0197(9)                                |
| P9P9       | 7858.003(2)  | 0.076(4)                      | 0.0191(12)                               |
| P9Q8       | 7859.914(2)  | 0.115(29)                     | 0.0190(9)                                |
| P8P8       | 7861.020(2)  | 0.072(3)                      | 0.0206(12)                               |
| P8Q7       | 7862.962(2)  | 0.147(32)                     | 0.0207(9)                                |
| P7P7       | 7863.980(2)  | 0.070(5)                      | 0.0207(13)                               |
| P7Q6       | 7865.945(2)  | 0.098(3)                      | 0.0198(12)                               |
| P6P6       | 7866.943(2)  | 0.060(6)                      | 0.0222(14)                               |
| P6Q5       | 7868.863(2)  | 0.090(3)                      | 0.0214(12)                               |
| P5P5       | 7869.786(2)  | 0.049(4)                      | 0.0203(14)                               |
| P5Q4       | 7871.769(2)  | 0.078(4)                      | 0.0213(12)                               |
| P4P4       | 7872.687(2)  | 0.032(5)                      | 0.0211(15)                               |
| P4Q3       | 7874.676(2)  | 0.061(3)                      | 0.0210(12)                               |
| P3P3       | 7875.457(2)  | 0.015(5)                      | 0.0223(15)                               |
| P3Q2       | 7877.569(2)  | 0.044(5)                      | 0.0229(14)                               |
### Table 2: Measured transition parameters of the $R$ and $S$ branch of $^{16}\text{O}_2$.

| Transition | Position $\Delta N N'$ $\Delta J J'$ | Line intensity $10^{-8}\text{cm}^{-2}\text{atm}^{-1}$ | Self-broadened half width $\text{cm}^{-1}$ at 400 mbar |
|------------|--------------------------------------|---------------------------------|---------------------------------|
| R1R1       | 7888.092(2) 71.688(10)              | 0.0222(6)                       |
| R1Q2       | 7889.930(2) 18.870(10)              | 0.0210(6)                       |
| R3R3       | 7893.558(2) 82.862(10)              | 0.0210(6)                       |
| R3Q4       | 7895.457(2) 41.828(10)              | 0.0198(6)                       |
| R5R5       | 7898.879(2) 88.711(10)              | 0.0198(6)                       |
| R5Q6       | 7900.841(2) 58.952(10)              | 0.0194(6)                       |
| R7R7       | 7904.023(2) 91.036(10)              | 0.0194(6)                       |
| S1R2       | 7898.470(2) 37.062(10)              | 0.0214(6)                       |

### Table 5: Measured transition parameters of the $O$ branch of $^{18}\text{O}_2$.

| Transition | Position $\Delta N N'$ $\Delta J J'$ $\Delta V$ | Line intensity $10^{-8}\text{cm}^{-2}\text{atm}^{-1}$ | Self-broadened half-width $\text{cm}^{-1}$ at 400 mbar |
|------------|---------------------------------------------|---------------------------------|---------------------------------|
| O19P18     | 7779.627(2) 0.013(5)                        | 0.0171(15)                     |
| O18P17     | 7785.657(2) 0.021(5)                        | 0.0176(14)                     |
| O17P16     | 7791.669(2) 0.022(5)                        | 0.0183(15)                     |
| O16P15     | 7797.647(2) 0.025(5)                        | 0.0177(15)                     |
| O15P14     | 7803.528(2) 0.033(5)                        | 0.0177(14)                     |
| O14P13     | 7809.441(2) 0.027(4)                        | 0.0193(15)                     |
| O13P12     | 7815.363(2) 0.043(4)                        | 0.0193(14)                     |
| O12P11     | 7821.190(2) 0.042(4)                        | 0.0186(14)                     |
| O11P10     | 7827.009(2) 0.039(5)                        | 0.0202(14)                     |
| O10P9      | 7832.777(2) 0.042(3)                        | 0.0195(14)                     |
| O9P8       | 7838.509(2) 0.032(4)                        | 0.0195(14)                     |
| O8P7       | 7844.231(2) 0.042(4)                        | 0.0204(14)                     |
| O7P6       | 7849.877(2) 0.035(4)                        | 0.0212(14)                     |
| O6P5       | 7855.489(2) 0.029(5)                        | 0.0212(14)                     |
Table 6: Measured transition parameters of the R and S branch of $^{18}$O$_2$.

| Transition | Position $\Delta N N' \Delta J J'$ | Line intensity $10^{-8}$cm$^{-2}$atm$^{-1}$ | Self-broadened half-width cm$^{-1}$ at 400 mbar |
|------------|-----------------------------------|---------------------------------|---------------------------------|
| R1R1       | 7889.051(2)                      | 0.151(32)                      | 0.0230(11)                     |
| R1Q2       | 7890.971(2)                      | 0.036(5)                       | 0.0219(14)                     |
| R2R2       | 7891.679(2)                      | 0.191(31)                      | 0.0222(11)                     |
| R2Q3       | 7893.593(2)                      | 0.056(4)                       | 0.0215(14)                     |
| R3R3       | 7894.221(2)                      | 0.191(30)                      | 0.0219(11)                     |
| R3Q4       | 7896.199(2)                      | 0.082(4)                       | 0.0215(12)                     |
| R4R4       | 7896.781(2)                      | 0.221(31)                      | 0.0211(11)                     |
| R4Q5       | 7898.773(2)                      | 0.097(4)                       | 0.0210(12)                     |
| R5R5       | 7899.278(2)                      | 0.300(32)                      | 0.0204(11)                     |
| R5Q6       | 7901.264(2)                      | 0.238(35)                      | 0.0211(11)                     |
| R6R6       | 7901.729(2)                      | 0.198(31)                      | 0.0206(11)                     |
| R6Q7       | 7903.717(2)                      | 0.253(32)                      | 0.0204(11)                     |
| R7R7       | 7904.157(2)                      | 0.247(30)                      | 0.0204(11)                     |
| S0R1       | 7893.632(2)                      | 0.059(4)                       | 0.0225(12)                     |
| S1R2       | 7899.001(2)                      | 0.070(4)                       | 0.0219(12)                     |
| S2R3       | 7904.325(2)                      | 0.076(4)                       | 0.0214(12)                     |
Table 8: Measured transition parameters of the $Q$ branch of $^{18}$O$_2$.

| Transition | Position $\Delta N \Delta N'$ cm$^{-1}$ | Line intensity $\Delta J \Delta J'$ $10^{-8}$cm$^{-2}$atm$^{-1}$ | Self-broadened half-width $V$ cm$^{-1}$ at 400 mbar |
|------------|----------------------------------------|-------------------------------------------------|-----------------------------------------------|
| Q2R1       | 7885.814(2)                           | 0.064(5)                                        | 0.0223(12)                                    |
| Q2Q2       | 7883.661(2)                           | 0.140(29)                                      | 0.0216(10)                                    |
| Q3R2       | 7885.623(2)                           | 0.081(7)                                        | 0.0219(12)                                    |
| Q3Q3       | 7883.539(2)                           | 0.139(51)                                      | 0.0214(10)                                    |
| Q3P4       | 7885.485(2)                           | 0.021(5)                                        | 0.0200(13)                                    |
| Q4R3       | 7885.414(2)                           | 0.083(4)                                        | 0.0211(12)                                    |
| Q4Q4       | 7883.378(2)                           | 0.218(33)                                      | 0.0216(10)                                    |
| Q4P5       | 7885.322(2)                           | 0.028(5)                                        | 0.0206(13)                                    |
| Q5R4       | 7885.216(2)                           | 0.085(3)                                        | 0.0212(12)                                    |
| Q5Q5       | 7883.168(2)                           | 0.201(38)                                      | 0.0217(10)                                    |
| Q5P6       | 7885.191(2)                           | 0.035(5)                                        | 0.0200(13)                                    |
| Q6R5       | 7884.96(2)                             | 0.082(5)                                        | 0.0206(12)                                    |
| Q6Q6       | 7882.980(2)                           | 0.227(36)                                      | 0.0202(10)                                    |
| Q6P7       | 7884.975(2)                           | 0.037(5)                                        | 0.0203(13)                                    |
| Q7R6       | 7884.664(2)                           | 0.083(4)                                        | 0.0210(12)                                    |
| Q7Q7       | 7882.689(2)                           | 0.242(32)                                      | 0.0190(10)                                    |
| Q7P8       | 7884.695(2)                           | 0.041(5)                                        | 0.0201(13)                                    |
| Q8R7       | 7884.331(2)                           | 0.087(7)                                        | 0.0195(12)                                    |
| Q8Q8       | 7882.443(2)                           | 0.245(38)                                      | 0.0192(10)                                    |
| Q8P9       | 7884.394(2)                           | 0.046(6)                                        | 0.0197(13)                                    |
| Q9R8       | 7884.052(2)                           | 0.077(4)                                        | 0.0196(12)                                    |
| Q9Q9       | 7882.072(2)                           | 0.250(32)                                      | 0.0198(10)                                    |
| Q9P10      | 7884.124(2)                           | 0.050(6)                                        | 0.0198(13)                                    |
| Q10R9      | 7883.598(2)                           | 0.078(5)                                        | 0.0188(12)                                    |
| Q10Q10     | 7881.699(2)                           | 0.250(30)                                      | 0.0200(10)                                    |
| Q10P11     | 7883.744(2)                           | 0.043(4)                                        | 0.0201(13)                                    |
| Q11R10     | 7883.19(2)                            | 0.068(4)                                        | 0.0196(13)                                    |
| Q11Q11     | 7881.273(2)                           | 0.253(33)                                      | 0.0197(10)                                    |
| Q11P12     | 7883.342(2)                           | 0.043(4)                                        | 0.0194(13)                                    |
| Q12R11     | 7882.734(2)                           | 0.065(6)                                        | 0.0184(13)                                    |
| Q12Q12     | 7880.819(2)                           | 0.249(30)                                      | 0.0190(10)                                    |
| Q12P13     | 7882.927(2)                           | 0.044(5)                                        | 0.0191(14)                                    |

Continued on next page
| Transition | Position cm⁻¹ | Line intensity 10⁻⁸ cm⁻² atm⁻¹ | Self-broadened half-width cm⁻¹ at 400 mbar |
|------------|---------------|-------------------------------|------------------------------------------|
| Q13R12     | 7882.263(2)   | 0.059(7)                      | 0.0186(13)                              |
| Q13Q13     | 7880.326(2)   | 0.234(28)                     | 0.0194(10)                              |
| Q13P14     | 7882.433(2)   | 0.041(5)                      | 0.0182(14)                              |
| Q14R13     | 7881.726(2)   | 0.054(4)                      | 0.0184(13)                              |
| Q14Q14     | 7879.845(2)   | 0.165(29)                     | 0.0181(10)                              |
| Q14P15     | 7881.898(2)   | 0.038(5)                      | 0.0183(14)                              |
| Q15R14     | 7881.138(2)   | 0.047(5)                      | 0.0180(13)                              |
| Q15Q15     | 7879.247(2)   | 0.147(29)                     | 0.0181(10)                              |
| Q15P16     | 7881.361(2)   | 0.034(5)                      | 0.0178(14)                              |
| Q16R15     | 7880.536(2)   | 0.041(5)                      | 0.0181(14)                              |
| Q16Q16     | 7878.644(2)   | 0.160(43)                     | 0.0167(10)                              |
| Q16P17     | 7880.767(2)   | 0.027(5)                      | 0.0178(14)                              |
| Q17R16     | 7879.864(2)   | 0.035(5)                      | 0.0172(15)                              |
| Q17Q17     | 7878.009(2)   | 0.163(28)                     | 0.0176(10)                              |
| Q17P18     | 7880.122(2)   | 0.024(5)                      | 0.0175(14)                              |
| Q18R17     | 7879.166(2)   | 0.029(5)                      | 0.0175(15)                              |
| Q18Q18     | 7877.326(2)   | 0.085(3)                      | 0.0174(12)                              |
| Q18P19     | 7879.414(2)   | 0.022(5)                      | 0.0174(15)                              |
| Q19R18     | 7878.482(2)   | 0.020(5)                      | 0.0174(15)                              |
| Q19Q19     | 7876.581(2)   | 0.073(4)                      | 0.0178(12)                              |
| Q19P20     | 7878.708(2)   | 0.020(5)                      | 0.0168(15)                              |
Table 9: Comparison of molecular constants in cm$^{-1}$ of the $\nu = 0$ levels of the $a^{1}\Delta_g \rightarrow X^{3}\Sigma_g^-$ state of $^{16}$O$_2$.

| Constants | This work | Olaga [1] | Amiot [19] | Rothman [20] |
|-----------|-----------|-----------|------------|--------------|
| $\nu_{0\rightarrow0}$ | 7883.756662(142) | 7883.756645(113) | 7883.76179(28) | 7882.4288(3) |
| $B_0$ | 1.417832166 (66) | 1.417839039 (38) | 1.41784020(82) | 1.4178442(19) |
| $D_0 \times 10^{-6}$ | 5.102159(351) | 5.102256(243) | 5.1074(24) | 5.11144(139) |

Table 10: Comparison of molecular constants in cm$^{-1}$ of the $\nu = 0$ levels of the $a^{1}\Delta_g \rightarrow X^{3}\Sigma_g^-$ state of $^{18}$O$_2$.

| Constants | This work | Olaga [1] |
|-----------|-----------|-----------|
| $\nu_{0\rightarrow0}$ | 7886.512585(200) | 7886.409277(117) |
| $B_0$ | 1.260406188(110) | 1.260409499 (56) |
| $D_0 \times 10^{-6}$ | 4.011059(850) | 4.029678(664) |

References

[1] O. Leshchishina, S. Kassi, I.E. Gordon, L.S. Rothman, L. Wang, A. Campargue, High sensitivity CRDS of the $a^{1}\Delta_g \rightarrow X^{3}\Sigma_g^-$ band of oxygen near 1.27 $\mu$m: Extended observations, quadrupole transitions, hot bands and minor isotopologues, J. Quant. Spec. Rad. Trans. 111 (2010) 22362245.

[2] R.A. Washenfelder, G.C. Toon, J.F. Blavier, N.T. Allen, P.O. Wennberg, et al. Carbon dioxide column abundances at the Wisconsin Tall Tower site. J. Geophys. Res. 111 (2006) 22305.

[3] L.S. Rothman, I.E. Gordon, A. Barbe, D.C. Benner, P.F. Bernath, M. Brik et al. The HITRAN 2008 molecular spectroscopic database. J. Quant. Spectrosc. Radiat. Transfer. 110 (2009) 533-72.

[4] W.J. Lafferty, A.M. Solodov, C.L. Lugez, G.T. Fraser, Rotational line strength and self-pressure-broadening coefficients for the 1.27 $\mu$m $a^{1}\Delta_g \rightarrow X^{3}\Sigma_g^-$ (0, 0) band of O$_2$. Appl. Opt. 37 (1998) 2264-70.

[5] S.M. Newman, I.C. Lane, A.J. Orr-Ewing, D.A. Newmham, J. Ballard, Integrated absorption intensity and einstein coefficients for the O$_2$ $a^{1}\Delta_g \rightarrow X^{3}\Sigma_g^-$ (0, 0) transitions: a comparison of cavity ringdown and high resolution Fourier transformation spectroscopy with a long path absorption cell. J Chem. Phys. 110 (1999) 10749-57.

17
Figure 1: Overview of the transitions in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band of oxygen recorded by CW-CRDS ($P = 400$ mbar, $T = 300$ K).

Figure 2: Intensity of the $O, R$ branch of $^{16}$O$_2$.

Figure 3: Intensity of the $P, Q$ branch of $^{16}$O$_2$. 
Figure 4: Width of $O, R$ branch $^{16}$O$_2$.

Figure 5: Width of $O, R$ branch $^{16}$O$_2$.

Figure 6: Width of $P, Q$ branch $^{16}$O$_2$.

Figure 7: Width of $P, Q$ branch $^{16}$O$_2$.
Figure 8: Intensity of the $O, R$ branch of $^{18}$O$_2$.

Figure 9: Intensity in the $P, Q$ branch of $^{18}$O$_2$.

Figure 10: Width of $O, R$ branch $^{18}$O$_2$.

Figure 11: Width of $O, R$ branch $^{18}$O$_2$. 
Figure 12: Width of $P, Q$ branch $^{18}$O$_2$.

Figure 13: Width of $P, Q$ branch $^{18}$O$_2$.

[6] I.E. Gordon, S. Kassi, A. Campergue, G.C. Toon, First identification of the $\text{a}^1\Delta_g \leftarrow \text{X} \ 3\Sigma_g^-$ electric quadrupole transition of oxygen in the solar and laboratory spectra. J. Quant. Spectrosc. Radiat. Transfer. 111 (2010) 1174-83.

[7] G. Rouillié, G. Millot, R. Saint-Loup, H. Berger, High-resolution stimulated Raman spectroscopy. J. Mol. Spectrosc. 154 (1992) 372-82.

[8] K.W. Hillig, C.C.W. Chiu, W.G. Read, E.A. Cohen, The pure rotation spectrum of $\text{a}^1\Delta_g$ O$_2$. J. Mol. Spectrosc. 109 (1985) 205-6.

[9] R.R. Gamache, A. Goldman, L.S. Rothman, Improved spectral parameters for the three most abundant isotopomers of the oxygen molecule. J. Quant. Spectrosc. Radiat. Transfer. 59 (1998) 495-509.

[10] P.H. Krupenie, The spectrum of molecular oxygen. J. Phys. Chem. Ref. Data. 1 (1972) 423-534.

[11] J. Brualt, Private Communication (1982).

[12] M. Mizushima, S. Yamamoto, Microwave absorption lines of $^{16}$O$^{86}$O in its ($^3\Sigma_g^-, \nu=0$) state. J. Mol. Spectrosc. 148 (1991) 447-52.

[13] L. Herzberg, G. Herzberg, Fine structure of the infrared atomospheric oxygen bands. J. Astrophys. 105 (1947) 353.
[14] S-L. Cheah, Y-P. Lee, J.F. Ogilvie, Wavenumber, strength, widths and shift with pressure of lines in four bands of gaseous $^{16}$O$_2$ in the systems $a^1\Delta_g \leftarrow$X $^3\Sigma_g^-$ and $b^1\Sigma_g^+ \leftarrow$X $^3\Sigma_g^-$. J. Quant. Spectrosc. Radiat. Transfer. 64 (2000) 467-82.

[15] J. Ye, L.S. Ma, J.L. Hall, Ultrasensitive detections in atomic and molecular physics: demonstration in molecular overtone spectroscopy, J. Opt. Soc. Am. B-Opt. Phys. 15 (1) (1998) 615.

[16] L.S. Ma, J. Ye, P. Dube, J.L. Hall, Ultrasensitive frequency modulation spectroscopy enhanced by a high-finesse optical cavity: theory and application to overtone transitions of C$_2$H$_2$ and C$_2$HD, J. Opt. Soc. Am. B-Opt. Phys. 16 (12) (1999) 2255 - 2268.

[17] N.J. van Leeuwen, A.C. Wilson, Spectroscopic measurement of pressure-broadened ultra-weak molecular transitions using NICE-OHMS, J. Opt. Soc. Am. B-Opt. Phys. 21 (10) (2004) 1713 - 1721.

[18] B.V. Perevalov, S. Kassi, D. Romanini, V.I. Perevalov, S.A. Tashkun, A. Camparague, CW-cavity ringdown spectroscopy of carbon dioxide isotopologues near 15. $\mu$m. J. Mol. Spectrosc. 238 (2006) 241 - 55.

[19] C. Amiot, J. Vergèes, The magnetic dipole $a^1\Delta_g \leftarrow$X $^3\Sigma_g^-$ and $b^1\Sigma_g^+ \leftarrow$X $^3\Sigma_g^-$ transition in the oxygen afterglow. Can. J. Phys. 59 (1981) 1391.

[20] L.S. Rothman, Magnetic dipole infrared atmospheric oxygen bands. Appl. Optics. 21 (1982) 24281-31.