Intensities of lines in the band $a^{1}\Delta_{g}(v'=0) - X^{3}\Sigma_{g}^{-}(v''=0)$ of ¹⁶O₂ in absorption

Y. T. HSU, Y. P. LEE* and J. F. OGILVIE*†

Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan

Abstract—Line-strengths in the band $a^{1}\Delta_{g}$ (v'=0) – $X^{3}\Sigma_{g}^{-}$ (v''=0) of gaseous ${}^{16}O_{2}$ in absorption near 7.9×10⁵ m⁻¹ have been remeasured in the laboratory under conditions of pressure less than 101,000 Pa and temperature near 300 K. The band-strength is estimated to be $(2.1 \pm 0.3) \times 10^{-26}$ m, and the coefficient for self-broadening of individual lines near the band centre is (10 ± 1) m⁻¹ bar⁻¹. No evidence of an underlying continuum was found.

INTRODUCTION

DIOXYGEN molecules O_2 contribute not only directly to the radiative properties of the terrestrial atmosphere throughout the optical spectral range from the microwave region to the vacuum-UV, but also indirectly through their chemical relationship to oxygen atoms and ozone $O_3[1]$. Although the transitions of O_2 , except the electronic ones in the UV region, are relatively weak, the great abundance of O_2 in air assigns the IR transitions a measurable role in the mechanism whereby solar energy affects the radiative balance of the atmosphere in the IR spectral region.

In our previous investigation [2] we demonstrated for the first time that absorption spectra at high resolution could be measured for the band $a^{1}\Delta_{g}(v'=0) - X^{3}\Sigma_{g}^{-}(v''=0)$ in the laboratory with relatively standard optical components—namely an interferometric spectrometer having a spectral resolution of at least 2 m^{-1} and a multiple-pass gas cell having a maximum absorbing path of about 20 m. Under those conditons, with gaseous O_{2} about atmospheric pressure or less, the measurements nevertheless approached the limit of the instrumental capability because of the extreme weakness of this band; for instance, the then estimated oscillator strength $\sim 10^{-12}$ of this single band may have been the smallest value so far derived from a quantitative estimate of absorption in the individual rovibronic lines of any molecule. Since those measurements, we have been able to improve the photometric accuracy of our interferometric system, in particular by the use of optical filters, but also in combination with a superior data-processing system and associated software. Therefore we deemed it advisable to repeat the previous measurements because of the importance of this molecular species O_{2} in atmospheric phenomena.

RESULTS AND DISCUSSION

The experimental system based on an interferometric spectrometer (Bomem DA3.002) differed from that described previously [2] in a few notable respects. Most importantly, an optical filter passing only the band $(7.72-8.12) \times 10^5 \text{ m}^{-1}$ (points of 50 per cent transmission relative to the maximum transmission) served to prevent saturation of the InSb detector by light from the incandescent W lamp throughout its effective range of emission (2.4-25) $\times 10^5 \text{ m}^{-1}$ in combination with a beam-splitter of crystalline SiO₂. Secondly, the effectively increased sensitivity of the system bestowed by the renovated

^{*} Also at Academia Sinica, Institute of Atomic and Molecular Sciences, P.O. Box 23-166, Taipei 10764, Taiwan.

[†] Author to whom correspondence should be addressed.

Table 1. Experimental line-strengths $S_1/10^{-28}$ m of lines in the band $a^1\Delta_g(v'=0) - X^3\Sigma_g^-(v''=0)$ of O₂ in absorption at 302 K

N	°P	PP	"Q	٩P	٩Q	₽ R	'Q	'R	۶R
1							1.0	3.4	2.0
3		1.6	0.6	1.2	3.4	2.3	2.9	5.2	3.0
5	0.5	2.0	2.2	*	*	*	3.4	5.0	*
7	0.6	1.9	3.1	*	7.4	*	3.8	5.6	3.2
9	1.1	2.9	3.1	*	•	*	3.9	4.8	3.7
11	0.7	3.1	4.6	*	•	*	3.3	4.8	2.6
13	0.6	2.5	2.6	2.0	6.2	*	*	4.4	1.2
15		1.7	2.7	*	6.3	1.5	2.2	4.0	1.0
17		1.1	1.4	1.5	3.2	1.0	1.9	2.2	0.8
19			1.1	0.9	1.8	0.9	1.7	1.3	
21			0.8	0.8	1.7		1.0		
23			0.7		0.8				

* Overlapping lines are denoted by an asterisk; the lines involved within the specified range of wavenumber/ m^{-1} and the total linestrength/ 10^{-28} m are respectively:

78,8373-78,8392	2.9
78,8320-78,8340	3.5
78,8252-78,8274	3.6
78,8160-78,8203	9.3
78,8047-78,8081	9.4
78,7959-78,7994	7.5
79,2040–79,2080	6.9
	78,8373-78,8392 78,8320-78,8340 78,8252-78,8274 78,8160-78,8203 78,8047-78,8081 78,7959-78,7994 79,2040-79,2080

electronics meant that a decreased period of measurement could be used, thus to tend to decrease drift of the temperature and the consequent effects on optical and electronic components. Thirdly, the new software made it possible to estimate the integrated intensity (area under the curve of absorbance vs wavenumber) of a particular rovibronic line using an inclined base line (to take into account any effects of underlying interference fringes due to optical components such as windows or the filter). Under these conditions we have remeasured the line-strengths of the lines in the specified band. To verify the accuracy of the software, we have also plotted some lines on an expanded scale and weighed the area under the curves of some individual lines cut from the chart paper, relative to the area of a standard rectangle for calibration purposes. These tests proved the accuracy of the integration program provided in the Bomem software within the uncertainty caused by the only moderate ratio of signal to noise.

The pressures, varied only in the range 66,000-101,000 Pa so as to maintain a practicable ratio of signal to noise, of gaseous dioxygen (natural O₂, 99.97 per cent chemical purity, but effectively entirely ${}^{16}O_2$) within the multipass cell at a fixed absorption path of 18.75 m, were measured with a capacitance manometer with a relative precision of 0.1 per cent. The temperatures, about ambient, were monitored ± 0.5 K during measurements by means of a digital thermocouple attached to the metallic body of the gas cell. As the wavenumbers of the measured lines were consistent with previous measurements [2], no new analysis of these data was necessary. From the reproducibility in various experiments at different pressures (near 300 K), we estimate the accuracy of the measurements of individual line-strengths to be $\pm 4 \times 10^{-27}$ m or 30 per cent, whichever is greater; because of partial cancellation of errors in the summation of the line-strengths, the band-strength is estimated to be accurate to ± 15 per cent.

In Table 1 we present the line-strengths of the lines measured in the nine branches of the band within the spectral range of wavenumber $7.8 < \tilde{\nu}/10^5 \text{ m}^{-1} < 8.0$. The lines are classified according to the quantum number N of the ground vibrational state; N denotes the quantum number for the total angular momentum except for electronic spin. The branches are denoted P, Q or R according to the change, -1, 0 or +1, respectively, of the quantum number J for total angular momentum; the prefixed superscript indicates

the change in N during the transition, with o, p, q, r and s implying $\Delta N = -2, -1, 0, +1$ or +2, respectively. The line-strength S_1 is defined according to the relation

$$S_1 = \int \ln(I_0/I) \mathrm{d}\tilde{\nu}/(Nb),$$

in which I_0 is the incident intensity and I the intensity of light transmitted at wavenumber \hat{v} through the sample, N is the number of molecules per unit volume and b is the length of the optical path through the sample; for any particular line, the integral was taken over the full width of the line between the limits at which the (visually smoothed) profile of the line became indistinguishable from the baseline. Being the sum of all these line-strengths, the band-strength thus determined is $(2.12 \pm 0.32) \times 10^{-26}$ m. Related measures of the intensity are the Einstein coefficient for absorption, $B \sim 1.2 \times 10^{10}$ m kg⁻¹, for emission, $A \sim 2.9 \times 10^{-4}$ s⁻¹, and the oscillator strength $f \sim 2.5 \times 10^{-12}$. As this electronic band is known to arise as mostly a magnetic-dipole transition [3], the corresponding transition moment is 2.6×10^{-26} J T⁻¹, although there may also be a weak component of electric-quadrupole transition as in the other near IR rovibronic transition [4]. The intensity distribution in the various branches is approximately consistent with that expected from the Honl-London factors [3, 5], but the limited accuracy of the line-strengths precludes a quantitative treatment to deduce the appropriate parameters [5].

The present estimate of the Einstein coefficient for spontaneous emission, $(2.9\pm0.4)\times10^{-4}\,\mathrm{s}^{-1}$, is within experimental error indistinguishable from that, $2.58\times10^{-4}\,\mathrm{s}^{-1}$ [6], also determined in the laboratory less directly (because of the poorer optical resolution and the presence of the pressure-induced continuum), a value which was in turn larger than previous ones from atmospheric measurements having larger uncertainties.

The increased optical stability of the interferometric spectrometer made possible a test, which was more stringent than before [2], for the possible existence of a continuum underlying the discrete rovibronic lines of the (v'=0) - (v''=0) band. No evidence of such a continuum was found within the pressure range up to 101,000 Pa, consistent with an upper limit $0.5 + 10^{-26}$ m for the potential contribution to the band-strength; recent measurements of the emission spectrum also indicated the absence of such a continuum under these conditions of concentration [7], although previous measurements at much greater pressures had attributed a continuum absorption proportional to pressure of collision complexes (O₂)₂ [6]. Under atmospheric conditions, other origins of a possible continuum may be applicable [8].

Our measurements of the line-widths over the range of pressures indicated that a selfbroadening coefficient $\sim (10 \pm 1) \text{ m}^{-1} \text{ bar}^{-1}$ is applicable for the stronger lines near the band centre; there was slight evidence that lines in the wings of the bands were subject to a smaller collisional broadening, but the poor ratio of signal to noise for these weaker lines precluded a more quantitative estimate. Our value appears slightly larger than that $(8 \text{ m}^{-1} \text{ bar}^{-1})$ estimated previously [6] under much worse conditions of resolution (25 m^{-1}) than our effective resolution of 2 m^{-1} .

GREENBLATT et al. [9] measured the absorption of compressed gaseous dioxygen in the spectral range $9 > \bar{\nu}/10^5 \,\mathrm{m}^{-1} > 30$, hence not overlapping our measurements. The absorption that they observed as a broad line near $9.388 \times 10^5 \,\mathrm{m}^{-1}$ may be due to the transition $a^1\Delta_g$ $(v'=1)-X^3\Sigma_g^-$ (v''=0); because that transition within single molecules of O₂ is much weaker (in fact undetectable in our experiments) than the origin band that we here report, that intensity is undoubtedly due mostly to double molecules, according to which effectively one of the subunits of the $(O_2)_2$ complex underwent the transition specifed above, as GREENBLATT et al. described [9]. Because in our experiments the intensity of absorption appeared linearly proportional to the pressure, we estimate that a negligible fraction of the reported band-strength is due to collision complexes. In other investigations of the absorption of compressed O₂ near $7.9 \times 10^5 \,\mathrm{m}^{-1}$, the ordinate intercept of SA(A) 48:9-C

Y. T. Hsu et al.

the plot of the ratio of absorbance to density vs the density is therefore expected to equal our value of the band-strength.

In conclusion, our present estimates of the strengths and widths of individual lines in the band $a \, {}^{1}\Delta_{g} (v'=0) - X^{3}\Sigma_{g}^{-} (v''=0)$ of dioxygen ${}^{16}O_{2}$ represent a contribution to the body of data on which the radiative properties of the terrestrial atmosphere in the near IR region can be based.

REFERENCES

- [1] T. G. Slanger and P. C. Cosby, J. Phys. Chem. 92, 267 (1988).
- [2] L. B. Lin, Y. P. Lee and J. F. Ogilvie, J. Quant. Spectrosc. Radiat. Transfer 39, 375 (1988).
- [3] I. Kovacs, Rotational Structure in the Spectra of Diatomic Molecules. Adam Hilger, Bristol (1969).
- [4] J. W. Brault, J. Molec. Spectrosc. 80, 384 (1980).
- [5] V. P. Bellary and T. K. Balasubramanian, J. Molec. Spectrosc. 126, 436 (1987).
- [6] R. M. Badger, A. C. Wright and R. F. Whitlock, J. Chem. Phys. 43, 4345 (1965).
- [7] J. Wildt, E. H. Fink, P. Biggs and R. P. Wayne, Chem. Phys. 139, 401 (1989).
- [8] I. C. McDade, E. J. Llewellyn, R. G. H. Greer and D. P. Murtagh, Planet. Space Sci. 35, 1541 (1987).
- [9] G. D. Greenblatt, J. J. Orlando, J. B. Burkholder and A. R. Ravishankara, J. Geophys. Res. 95 (D11), 18,577 (1990).