LINESTRENGTHS OF THE BAND
$a^1\Delta_g(v'=0)-X^3\Sigma_g^-(v''=0)$ OF $^{16}O_2$

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Abstract—The strengths of some absorption lines in the nine rotational branches of the $v'=0\leftarrow v''=0$ band of the electronic transition $a^1\Delta_g\leftarrow X^3\Sigma_g^-$ of $^{16}O_2$ have been measured at 296 K. The bandstrength is thus determined to be $(9.4 \pm 2.4) \times 10^{-27}$ m and the band origin is at $(788,809.53 \pm 0.82)$ m^{-1}. These values are compared with previous results.

INTRODUCTION

In the infrared region, the dioxygen molecule has two well established electronic transitions in absorption from the ground state $X^3\Sigma_g^-$, to the $a^1\Delta_g$ state at wavelength $\sim 1.26\,\mu$m and to the $b^1\Sigma_g^+$ state at $\sim 0.77\,\mu$m.[1] Because of the importance of O_2 in the atmosphere and in many chemical systems, both these bands and related bands with additional vibrational excitation have been studied extensively.[1] Although the latter system lies in a convenient region for study by both photographic and photoelectric methods, the $a–X$ system occurs farther into the infrared and thus, in combination with its smaller absorption cross-section, is more difficult to observe. Some studies of the band $v'=0\leftarrow v''=0$ in absorption have been made for the $a\leftarrow X$ electronic transition, but not with good resolution except for the photographic observations made with the sun as source and the terrestrial atmosphere as sample, with the consequent variability of pressure, temperature and chemical composition along the absorbing path.[2] In contrast, many studies, summarized by Krupenie,[1] have been made of both systems at densities greater than atmospheric or in the liquid and solid phases, and at relatively poor resolution.

In emission spectra, several measurements have been made of the glows from an electronic discharge and from the day and twilight sky,[3] in which the $a\rightarrow X$ transition appears, but again because of the weakness of the transitions only moderate resolution was possible, except for the recent work of Amiot and Verges.[4] In this laboratory investigation, it was possible to obtain a spectrum of the band $v'=0\rightarrow v''=0$ with a resolution ~ 2 m^{-1} and thus to measure precisely the wavenumbers of some resolved lines in the various branches. Many Rydberg states of the O_2 molecule are known to exist; recently a spectrum between two of these has also been observed in the infrared in emission from O_2 gas at a small pressure in an electric discharge.[5]

We have made some new measurements of the absorption spectrum of O_2 also under laboratory conditions, using a resolving power sufficient to separate the rotational fine structure in the $a(v'=0)\leftarrow X(v''=0)$ band. By this means we have for the first time been able to make some quantitative estimates of the linestrengths in this band. Our results are described in the following sections.

EXPERIMENTAL RESULTS

All spectra were recorded on a Bomem DA3.002 spectrometer, a Fourier-transform interferometer. The wavenumber scale was calibrated against the precisely measured band $2\leftarrow 0$ of CO.[6] Integrated intensities were measured by means of the computer routines supplied with the spectrometer. A multipass cell of path length 20.25 m contained the sample of O_2 gas (nominal purity $\sim 99.97\%$) at pressures varied in the range $4.6 \leqslant P/10^4\,\text{N m}^{-2} \leqslant 13.3$.

The spectrum of the band $a^1\Delta_g(v'=0)-X^3\Sigma_g^-(v''=0)$ is shown in Fig. 1; the band $v'=1\leftarrow v''=0$ was not observable under the conditions in these experiments. The wavenumbers of the measured

transitions are listed in Table 1, and the linestrengths are given in Table 2. The very weak nature of this transition precluded use of the full resolving power of the spectrometer, but the resolution used (2–$10\ m^{-1}$) was sufficient to resolve most of the rotational fine structure. As in the previous photographic study,[2] some lines in the ${}^qP$ and ${}^qR$ branches were not entirely separated, and of course elsewhere some lines of one branch overlapped fortuitously those of other branches where the two branches crossed. No density dependence of the wavenumbers of the absorption maxima was detected; at a concentration $19\ mol\ m^{-3}$ (corresponding to $4.7 \times 10^4\ N\ m^{-2}$), the linewidths, approx. 4–$5\ m^{-1}$ for unblended lines, were significantly greater than the instrumental resolution, $2\ m^{-1}$ in the best cases. The effect of the overlapping lines on the integrated intensities is more severe, because, although two lines might be effectively resolved at the absorption maxima, any overlapping in the shoulders interfered with the measurement of the separate intensities; the asterisks on some values of the linestrength in Table 2 indicate those lines thus affected. The estimated absolute accuracy of the linestrengths in Table 2 is only $2 \times 10^{-29}\ m$, or 30% relative accuracy, whichever is greater, due to the small extent of absorption even at the maximum available path length; the accuracy of the linestrengths relative to one another should be somewhat better, although the scatter in the data in Table 2 indicates that a greater improvement in both the relative and absolute precision of the linestrengths requires a greatly increased length of absorption path. There was detected no density dependence of the linestrengths within the range of pressures used, and no significant continuum of absorption beneath the lines was observable.

Additional explanation of the results in Table 2 is required. Under the best conditions of measurement, the maximum absorbance $[\ln(I_0/I)]$ of any line in the band was still <0.02; because the ratio of signal to noise for the least intense lines under these conditions was approx. 1, the measurement of the integrated area of the absorption was much more difficult than that of the wavenumber of the absorption maximum. Moreover, the overlapping of a few lines precluded the estimate of separate linestrengths; in these cases, the total intensity was apportioned between the affected lines in the ratio of the total intensities of the branches, also indicated in Table 2. The lines with measurements of either wavenumber maximum or integrated intensity affected by this overlapping are indicated by asterisks in Tables 1 and 2.
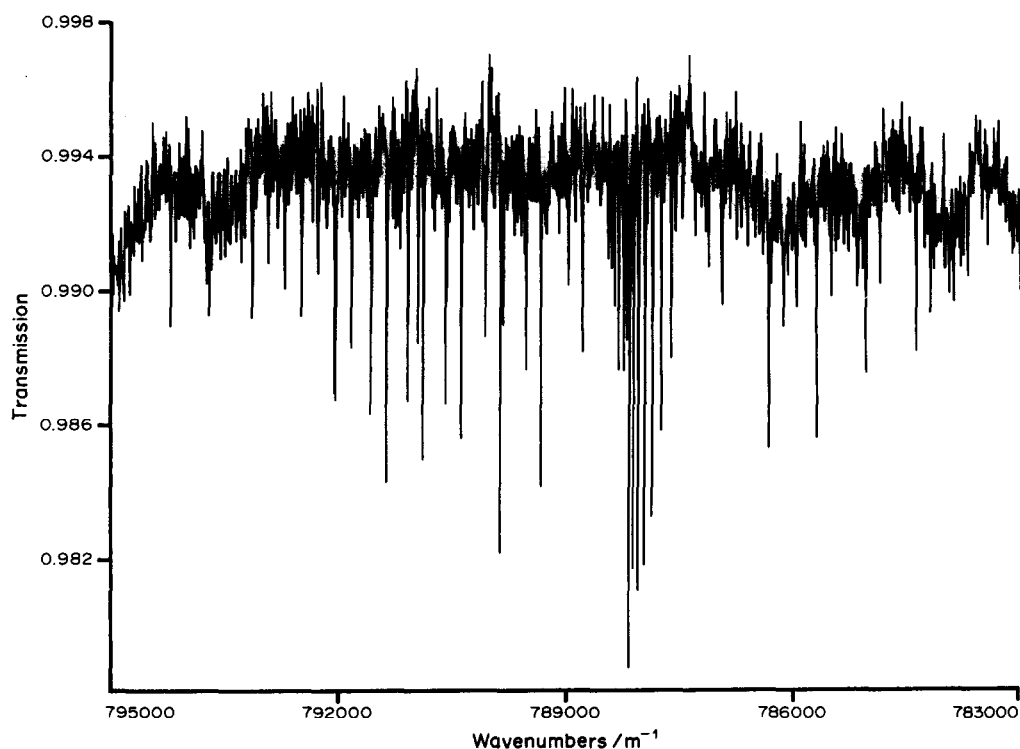

Fig. 1. Absorption spectrum of the band $a^1\Delta_g(v' = 0)$–$X^3\Sigma_g^-(v'' = 0)$ at 296 K; resolution $\sim 2\ m^{-1}$. The irregular baseline is an instrumental artifact.

Table 1. Transition wavenumbers/m^{-1} of the lines in the band $a^1\Delta_g(v'=0)-X^3\Sigma_g^-(v''=0)$ of $^{16}O_2$.†

$\Delta N=$	+2	+1	+1	0	0	0	-1	-1	-2
$\Delta J=$	+1	+1	0	0	+1	-1	0	-1	-1
R\	${}^sR$	${}^rR$	${}^rQ$	${}^qQ$	${}^qR$	${}^qP$	${}^pQ$	${}^pP$	${}^oP$
1	789844.1	788804.5	788996.9	—	—	—	—	—	—
3	790966.0	789353.0	789547.3	788218.9	788426.5*	788414.5*	787576.4	787371.0	—
5	792067.9	789884.2	790083.4	788182.9*	788384.0	788380.6	786965.0	786764.4	785831.9
7	793152.0	790398.5	790600.5	788131.7	788328.4	788332.8	786345.8	786146.2	784641.7
9	794217.3	790897.3	791100.8	788064.0*	788257.9	788268.0	785706.4	785512.8	783440.5
11	795267.0	791379.7	791585.5	787979.9*	788172.3*	788186.3*	785055.4	784862.9	782221.1
13	796299.4	791844.6	792053.4	787880.2	788071.8*	788087.7*	784387.8	784198.9	780989.1
15	797313.9	792293.2	792503.4	787765.4	787954.5	787974.0*	783705.9	783517.4	
17	798312.0	792722.8	792937.0	787631.9	787818.3	787846.5	783008.4	—	
19		793139.4	793355.0	787483.5	787666.3	—	782295.6	782113.8	
21			793754.7	787318.8	787502.4	787538.7	781566.7	781382.9	
23				787137.5		787353.6	780824.3		
25						787164.1			
27						786949.0			

†Numbers that bear asterisks pertain to overlapping lines the wavenumbers of which could not be measured as accurately as for the isolated lines.

Table 2. Experimental linestrengths $S/10^{-28}$ m of some lines in the band
$a^1\Delta_g(v'=0)-X^3\Sigma_g^-(v''=0)$ of $^{16}O_2$ at 296 K.†

R	^sR	^rR	^rQ	^qQ	^qP	^qR	^pP	^pQ	^oP
1	0.93	1.53	0.60						
3	1.36	1.94	1.29	1.46	0.37*	1.00*	0.33	0.78	
5	1.51	3.33	1.45	2.20*	0.47	0.70	0.42	1.32	
7	1.30	2.80	1.87	2.47	0.69	1.04	0.31	1.63	0.38
9	1.19	2.42	2.15	3.25*	0.56	1.21	0.95	1.77	1.15
11	1.36	2.32	1.22	3.41*	0.93*	1.87*	0.59	2.04	0.81
13	1.06	1.89	1.43	2.98	0.15*	0.62*	0.65	1.52	0.48
15	0.57	1.06	1.17	1.78	0.38*	0.20	0.43	0.60	
17	0.44	1.63	0.66	1.92	0.10	0.09		0.87	
19		0.51	0.23	0.91		0.18	0.37	0.47	
21			0.29	0.55	0.31	0.20	0.36	0.52	
23				0.40				0.34	
25				0.69					
total	9.71	18.4	12.4	22.0	3.96	9.74	4.41	11.9	2.82

†Numbers that bear asterisks indicate overlapping lines; the
entries in the table reflect the estimated contribution to
the total intensity of overlapping lines.

The rotational, spin-rotational and orbital-rotational coupling parameters of the $a(v'=0)$ and $X(v''=0)$ states are all known with great precision from the pure rotational[7] and far infrared[8] spectra; the applicable data are listed in Table 3. The wavenumbers of the lines in the absorption band were calculated by means of these parameters, through the following formulae:[7,9,10]

$$X^3\Sigma_g^- : F_1''(R) = B_0'' R(R+1) - D_0''[R(R+1)]^2 + \gamma_0/2 - \lambda_0 + B_0''(2R+3)$$
$$- [(2R+3)^2(B_0'' - \gamma_0/2)^2 + \lambda_0^2$$
$$- 2\lambda_0(B_0'' - \gamma_0/2)]^{1/2},$$

$$F_2''(R) = B_0'' R(R+1) - D_0''[R(R+1)]^2,$$

$$F_3''(R) = B_0'' R(R+1) - D_0''[R(R+1)]^2 - \gamma_0/2 - \lambda_0 - B_0''(2R-1)$$
$$+ [(2R-1)^2(B_0'' - \gamma_0/2)^2 + \lambda_0^2$$
$$- 2\lambda_0(B_0'' - \gamma_0/2)]^{1/2};$$

$$a^1\Delta_g : F'(J) = B_0'[J(J+1) - \Lambda^2] - D_0'[J(J+1) - \Lambda^2]^2$$
$$+ \tfrac{1}{2}(-1)^J q_0 J(J+1)[J(J+1) - \Lambda].$$

Hence, R denotes the quantum number for rotational angular momentum in the X state and the other symbols follow traditional usage; the use of these parameters indicated that the measured wavenumbers could be used neither to improve the accuracy of these parameters nor to generate significant values of further parameters such as H_0' or H_0''. Thus, the only parameter that could

Table 3. Spectroscopic parameters/m^{-1} of the $a^1\Delta_g(v'=0)$ and $X^3\Sigma_g^-(v''=0)$ states of $^{16}O_2$.

a $^1\Delta_g$ (v'=0) [†]	X $^3\Sigma_g^-$ (v''=0) [‡]
$B'_0 = 141.7798186$	$B''_0 = 143.7675594$
$D'_0 = 5.10209 \times 10^{-4}$	$D''_0 = 4.790 \times 10^{-4}$
$q_0 = -1.80 \times 10^{-8}$	$\lambda_0 = 198.475136$
	$\gamma_0 = 0.8425412$
	$\lambda_D = 1.94497 \times 10^{-4}$
	$\lambda_{DD} = 1.114 \times 10^{-8}$
	$\gamma_D = -8.18219 \times 10^{-7}$
	$\gamma_{DD} = -4.803 \times 10^{-12}$

†Ref. 7; ‡Ref. 8.

be given an improved value by means of a fit of the measured wavenumbers was the band origin $v_0 = 788,809.53 \pm 0.82 \text{ m}^{-1}$.

The intensity measurements lead to a bandstrength, the sum of the measured linestrengths, $S_{00} \sim (9.4 \pm 2.4) \times 10^{-27} \text{ m}$. This value is consistent with values of the Einstein coefficients for absorption $B \sim 5.4 \times 10^9 \text{ m kg}^{-1}$ and emission $A \sim 1.3 \times 10^{-4} \text{ s}^{-1}$, with the statistical degeneracy factors $g' = 1$ and $g'' = 3$. The oscillator strength thus has the value $f \sim 1.1 \times 10^{-12}$. If one assumes that the electronic transition is mostly of magnetic dipole character,[2] then the magnitude of the magnetic dipole transition moment may be estimated to be $1.7 \times 10^{-26} \text{ J T}^{-1}$.

DISCUSSION AND CONCLUSION

Our results are mostly consistent with existing published data. Separate sets of lines have now been identified for all the nine rotational branches with different values of ΔJ and ΔN, as listed in Table 1, and the numbers of lines in some branches have been increased. The present weak absorption of the spectral lines cannot be taken to exclude the possibility of the existence of still weaker lines due to electric quadrupole transitions, although their absence during the search procedure permits one to estimate an upper limit of $2 \times 10^{-29} \text{ m}$ for their linestrengths. The fundamental vibration–rotational band has been proved to have electric quadrupole character.[11] If the measured band of the electronic spectrum had only an electric quadrupole transition moment, then the value of this transition moment, calculated from the measured bandstrength, would be $4.2 \times 10^{-41} \text{ C m}^2$, comparable with the value of the observed transition moment of the fundamental vibration–rotational band.[11] For comparison, the magnetic dipole transition moment is much smaller than the permanent magnetic dipole moment of O_2 in the $X^3\Sigma_g^-$ electronic state, $2.62 \times 10^{-23} \text{ J T}^{-1}$ but, because of the multiplicity change in the electronic transition, a smaller transition moment is to be expected. Brault has detected some weak lines of electric quadrupole character in the electronic transition $b(v' = 0)-X(v'' = 0)$ of O_2; in that case the electric quadrupole lines were only 3×10^{-6} as intense as the main magnetic dipole transitions.[12] The origin of the band $a(v' = 0)-X(v'' = 0)$ differs from the value obtained from the previous measurements, $788,239 \text{ m}^{-1}$ from the absorption spectrum[2] and $788,376.18 \text{ m}^{-1}$ from the emission spectrum[4] only as a consequence of our incorporation of the quantity $-B'_0\Lambda^2$ in the rotational term for the $a^1\Delta_g$ state. The accuracy of the present result reflects the accuracy of the interferometric method for wavenumber measurements, traceable to the stabilized He–Ne laser, the accurate calibration standards,[6] and the accurate spectroscopic parameters of the two states.[7,8] The bandstrength measurement must also be regarded as confirming earlier results, because our value $A/10^{-4} \text{ s}^{-1}$

~ 1.3 lies near the value 1.5 determined in a study of the excitation mechanism of the twilight airglow.[13] However, spectra of greater resolution for samples at smaller densities in greatly increased absorbing paths are still required in order that quantitative wavenumber and intensity data of desirable accuracy may be derived; specifically, on the basis of the present results one can estimate that a path of length at least 100 m through samples at number densities $\leqslant 10^{25}$ m^{-3} with spectral resolution better than 1 m^{-1} would be required to obtain definitive data. The dependence of the results on density and resolution should also be tested at that time. The present values of the linestrengths may nevertheless be useful in the preparation of tables of atmospheric transmission coefficients in the infrared region; because the measured linewidths were greater than the instrumental resolution, the values of the linestrengths should have at least semiquantitative accuracy, within the estimated error range, despite the small extent of absorption in these experiments. The agreement between the relative measured linestrengths and the ratios from the Hönl–London factors is roughly as expected in accordance with the error estimates given above;[14] for this reason, there is no evidence of a strong vibration–rotational or electron–rotational interaction that would distort the relative intensities of the branches.

The question of the possibility of perturbations between the state $v'' = 5$ of the $X^3\Sigma_g^-$ state and the $v' = 0$ state of the $a^1\Delta_g$ electronic state might arise, because of the similar energies of the rotational manifolds connected with these vibrational states. Apart from the nature of the operator that might give rise to an observable irregularity of either line wavenumbers or intensities, a calculation of the vibration–rotational energies (above the $v'' = 0$ state) shows that up to values of J at least equal to 35 the energies of the two sets of rotational states with the same value of J are separated by at least 20,000 m^{-1}. Therefore the observation of any perturbations is not expected within this range of J.

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