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The γ-band of $^{16}O_2$, $^{16}O^{17}O$, $^{17}O_2$ and $^{18}O_2$

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Abstract

The $b^1\Sigma_g^+ - X^3\Sigma_g^-$ (2,0) band of the $^{16}O_2$, $^{16}O^{17}O$, $^{17}O_2$ and $^{18}O_2$ oxygen isotopomers was investigated by means of cavity-ring-down laser spectroscopy. Line positions of the four branches in each band were determined with an accuracy of 0.01 cm^{-1}. Improved or new molecular constants are derived for the $b^1\Sigma_g^+$, $v=2$ excited state of the four isotopomers. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: γ-Band; Cavity-ring-down laser spectroscopy; Isotopomers

1. Introduction

The oxygen 'γ-band' is a very weak absorption feature, corresponding to the (2,0) band of the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ electronic system of the O_2 molecule. This γ-band is a highly forbidden transition, since it is a gerade–gerade, $\Sigma^+ - \Sigma^-$ and a singlet–triplet transition, while also the Franck–Condon factor for the (2,0) band is very small (0.00264) [1]. This magnetic-dipole-allowed transition has an oscillator strength of only 0.63×10^{-12}, but is despite its weakness (375 times weaker than the oxygen 'A-band'), a pronounced absorption feature readily observed in the Earth's atmosphere. In fact the first spectroscopic study of this γ-band was performed through absorption in a large air mass in the Earth's atmosphere at sunset [2].

From spectroscopic measurements on atmospheric ozone isotopic ratios in O_3 were found to deviate from the terrestrial abundance of oxygen isotopes [3,4]. This phenomenon was ascribed to dynamical processes occurring in the atmosphere. To gain deeper understanding of these processes it is of importance to identify transitions by which the isotopic constitution of oxygen bearing molecules can be determined. The $b^1\Sigma_g^+ - X^3\Sigma_g^-$ electronic system is such a tool to probe O_2-isotopomers in the Earth's atmosphere, as was demonstrated by Osterbrock et al. [5] and by Slanger et al. [6].

In the present work we report on a high resolution spectroscopic study of the oxygen γ-band, using the experimental technique of cavity-ring-down spectroscopy (CDRS) [7]. This technique was previously used in an investigation of the oxygen Herzberg bands in the ultraviolet [8] and, in our laboratory, for an investigation of the A-band for all isotopomers of O_2 [9] as well as for

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the B-band [10]. We present results for $^{16}O_2$, $^{16}O^{17}O$, $^{18}O_2$ and $^{17}O_2$. For $^{16}O_2$ the presently obtained accuracy is similar to that of the old work of Babcock and Herzberg [2], although the conditions in our laboratory experiment are better controlled, allowing for an improved assessment of pressure shifts. The γ-band of $^{16}O_2$ was investigated by Wheeler et al. [11], also using CDRS, however without focusing on accurate calibration of the oxygen resonance lines. For $^{18}O_2$ the γ-band was previously studied by Hill and Schawlow [12] and by Engeln et al. [13] with a slightly lower accuracy. For $^{16}O^{17}O$ and $^{17}O_2$ no results exist in the literature. New spectroscopic constants for the $b^1\Sigma_g^+$, $v=2$ state of the various O_2-isotopomers are derived, while in case of $^{17}O_2$ also improved rotational constants for the $X^3\Sigma_g^-$, $v=0$ ground state are derived. These data allow for improved predictions of the positions of various bands, such as $b^1\Sigma_g^+ - X^3\Sigma_g^-$ $(2,v'')$, which may be useful for future analysis of atmospheric emission phenomena.

2. Spectroscopic results on $^{16}O_2$, $^{16}O^{17}O$, $^{18}O_2$ and $^{17}O_2$

The experimental method used in the present study is similar to the one applied previously for the investigation of the oxygen A and B-bands [9,10]. Pulsed laser radiation of 5 ns duration is obtained from a Nd-YAG pumped dye laser system (Quanta-Ray PDL-3) running on DCM dye, allowing for tunability in the relevant wavelength range 625–640 nm. For the general principles of CDRS we refer to Refs. [7,11]. Specifics for the present investigation are mirrors with reflectivities of 99.98% and radii of curvature of 1 m forming a stable cavity at a mirror separation of 45 cm. Spectral recordings of the O_2-isotopomers were obtained by averaging five decay transients and on-line evaluation of the cavity decay time as a function of wavelength.

The spectrum of $^{16}O_2$ was obtained from a natural gas sample, while spectral recordings of $^{16}O^{17}O$ and $^{17}O_2$ were obtained from a 50% ^{17}O-

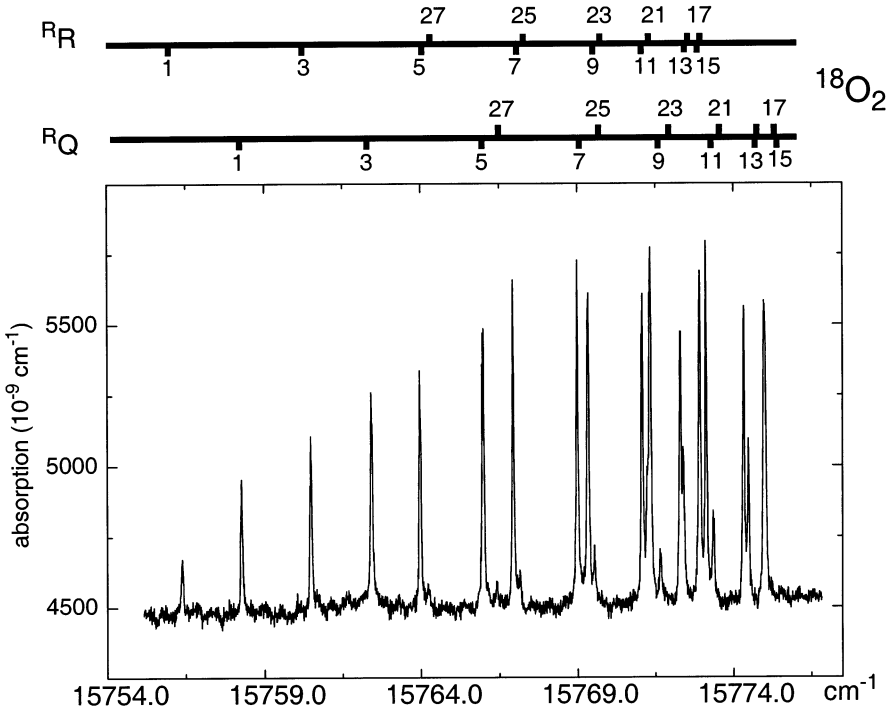

Fig. 1. Cavity-ring-down spectral recording of the R-bandhead of $^{18}O_2$ obtained from an enriched sample.

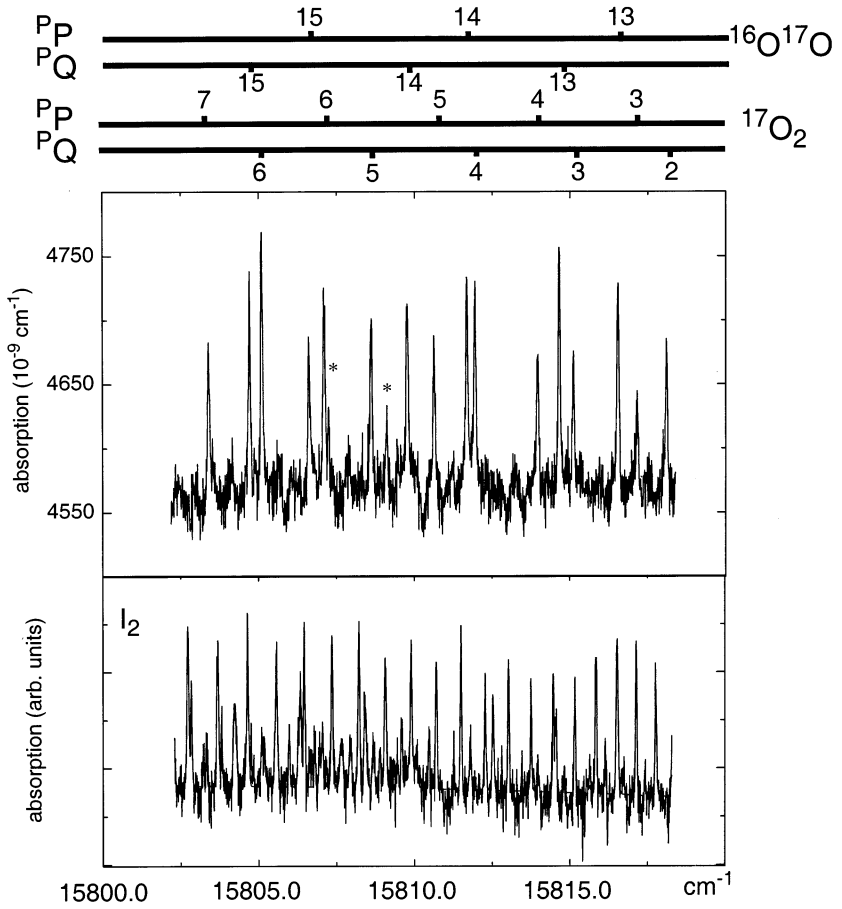

Fig. 2. Observed spectrum from a ^{17}O (50% atom) enriched sample showing resonances pertaining to $^{16}O^{17}O$ and $^{17}O_2$. Resonances indicated with (*) belong to $^{16}O_2$. The spectrum in the lower panel is the simultaneously recorded I_2-absorption spectrum.

enriched oxygen sample (Campro Scientific) and $^{18}O_2$ from a 95% enriched sample (Eurisotop). The spectra of $^{16}O_2$ were recorded using typical pressures of 60 Torr in the cell, while in case of the enriched samples pressures of 200 Torr were applied. Signals of $^{16}O^{18}O$ and $^{17}O^{18}O$, observed for the A and B-bands [9,10], were in case of the γ-band too weak to be reliably detected. Since the available mirrors at 630 nm have a lower reflectivity than the set available at 760 nm, the noise-equivalent detection limit at 630 nm is a factor of 10 higher at 1×10^{-8} cm^{-1}, thus prohibiting observation of weaker features. We note that the γ-band is a factor of 375 weaker than the A-band [1]. Fig. 1 shows a spectrum of part of the R-bandhead of $^{18}O_2$. In Fig. 2 a spectrum measured from the ^{17}O enriched sample is presented, showing $^{16}O^{17}O$ and $^{17}O_2$ resonances. Here also an on-line measured I_2-calibration spectrum is displayed.

Wavelength calibration of the oxygen lines is the central issue of this paper. For this purpose I_2-absorption spectra were recorded simultaneously with the oxygen spectra. To obtain a good signal-to-noise ratio on the I_2-spectra, the I_2-sample in a glass cell was heated to 30°C, thus reaching a vapour pressure of 1 Torr. Three passes through the 40 cm long cell, with normalization to a power spectrum of the laser output and averaging over five laser pulses, was sufficient to record typical I_2-absorption spectra at 630 nm, as displayed in the lower panel of Fig. 2. Gaussian curves were fitted to the I_2-resonances and after

assignment with the I_2-reference atlas [14] a spline interpolation between the fitted I_2-lines provides an accurate frequency scale for the simultaneously recorded oxygen spectrum. The O_2 resonances were then fitted to Voigt profiles. With linewidths in the I_2 and O_2-spectra of 0.06 cm^{-1}, predominantly caused by the laser bandwidth, this results in an absolute accuracy for strong and non-overlapped O_2-lines of 0.01 cm^{-1}. In the I_2-atlas the energy range 15 789–15 806 cm^{-1} is missing due to interference with the HeNe-laser line during the production of the atlas. Therefore an interpolation over that range had to be made during the present measurements without being able to correct for nonlinearities in the scan. This explains the offset of the $^{P}Q(23)$ and $^{P}P(23)$ lines of $^{16}O_2$ by 0.06 cm^{-1}.

Table 1
The γ-band of $^{16}O_2$

N	^{P}Q		^{P}P		^{R}R		^{R}Q	
	Observed	Δ_{o-c}	Observed	Δ_{o-c}	Observed	Δ_{o-c}	Observed	Δ_{o-c}
1	*	*	15899.534	−0.007	15907.660	−0.009	15909.549	0.004
3	15895.372	−0.005	15893.311	0.019	15912.259	0.004	15914.206	0.001
5	15888.392	0.000	15886.376	−0.005	15916.179	0.004	15918.167	0.004
7	15880.784	0.004	15878.814	0.008	15919.432	0.005	15921.446	0.004
9	15872.514	−0.001	15870.570	0.000	15922.005	−0.003	15924.037	−0.010
11	15863.601	0.009	15861.658	−0.012	15923.911	−0.005	15925.975	−0.003
13	15853.985	−0.023	15852.102	−0.006	15925.144	−0.006	15927.234	0.002
15	15843.768	0.005	15841.871	−0.012	15925.705	−0.001	15927.828	0.020
17	15832.853	−0.002	15831.011	0.017	15925.579	−0.003	15927.719	0.016
19	15821.282	0.000	15819.438	−0.002	15924.761	−0.014	15926.916	0.002
21	15809.036	−0.007	15807.218	−0.001	15923.282[b]	0.001	15925.442	0.004
23	15796.060[a]	−0.077	15794.279[a]	−0.052	15921.101	0.005	15923.282[b]	0.010
25	15782.560	−0.002	15780.785	0.011				
27	15768.324	0.009	15766.526	−0.019				

[a] Due to missing part in I_2-atlas, calibration inaccurate.
[b] Blended line.

Table 2
The γ-band of $^{18}O_2$

N	^{P}Q		^{P}P		^{R}R		^{R}Q	
	Observed	Δ_{o-c}	Observed	Δ_{o-c}	Observed	Δ_{o-c}	Observed	Δ_{o-c}
1	*	*	15749.142	−0.004	15756.377	−0.006	15758.292	0.000
3	15745.650	−0.006	15743.610	0.006	15760.490	0.002	15762.442	−0.011
5	15739.489	0.005	15737.477	−0.010	15764.017	0.001	15766.006	−0.005
7	15732.771	0.008	15730.797	0.001	15766.969	0.004	15768.986	0.002
9	15725.478	0.002	15723.536	0.004	15769.335	0.000	15771.377	0.003
11	15717.616	−0.003	15715.708	0.013	15771.133	0.009	15773.190	0.009
13	15709.190	0.001	15707.279	−0.005	15772.335	0.005	15774.408	0.004
15	15700.183	−0.004	15698.298	−0.001	15772.957	0.006	15775.035	−0.007
17	15690.604	−0.008	15688.727	−0.013	15772.990	0.006	15775.080	−0.012
19	15680.457	−0.004	15678.606	−0.001	15772.436	0.007	15774.555	0.002
21	15669.734	−0.001	15667.886	−0.011	15771.283	0.003	15773.432	0.011
23	15658.424	−0.009	15656.610	0.000	15769.551	0.014	15771.698	0.004
25	15646.569	0.017	15644.737	−0.008	15767.184	−0.013		
27	15634.086	−0.005	15632.290	−0.009	15764.265	0.010	15766.441	−0.002

Table 3
The γ-band of $^{17}O_2$

N	^{P}Q		^{P}P		^{R}R		^{R}Q	
	Observed	Δ_{o-c}	Observed	Δ_{o-c}	Observed	Δ_{o-c}	Observed	Δ_{o-c}
0	*	*	*	*	*	*	15827.999	−0.001
1	*	*	15820.928	−0.004			15830.491	0.011
2	15820.230	0.008	15818.068	−0.003	15830.848	0.018	15832.780	0.019
3	15817.132	−0.003	15815.065	0.008	15832.911	−0.007	15834.877[a]	0.002
4	15813.908	−0.011	15811.884	−0.005	15834.877[a]	0.026	15836.830	0.003
5	15810.575	0.003	15808.564	−0.003	15836.633	0.003	15838.623	0.002
6	15807.077	0.000	15805.100	0.009	15838.239	−0.014	15840.257	−0.001
7	15803.424	−0.008	15801.413[a]	−0.048	15839.711	−0.011	15841.726	−0.012
8	15799.608	−0.027	15797.665	−0.013	15841.033	−0.001	15843.083	0.021
9	15795.674	−0.012	15793.736	−0.005	15842.184	−0.008	15844.231[a]	0.001
10	15791.578	−0.006	15789.648	−0.002	15843.216	0.023	15845.245[a]	0.003
11	15787.323	−0.006	15785.410	0.004	15844.044	0.006	15846.093	−0.004
12	15783.958[a]	0.037	15781.013	0.006	15844.729	0.001	15846.814	0.018
13	15778.366	0.007	15776.475	0.019	15845.245[a]	−0.015	15847.342[a]	0.004
14	15773.659	0.015	15771.749	−0.001	15845.621	−0.015	15847.701[a]	−0.022
15	15768.771	−0.005	15766.886	−0.005	15845.840[a]	−0.015	15847.939[a]	−0.012
16	15763.756	0.002	15761.887	0.009	15845.916	−0.001	15848.012	−0.009
17	15758.564	−0.015	15756.706	−0.006	15845.840[a]	0.019	15847.939[a]	0.005
18	15753.276	0.027	15751.394	0.003	15845.536[a]	−0.032	15847.701[a]	0.011
19	15747.761	−0.005	15745.919	0.002	15845.126[a]	−0.030	15847.342[a]	0.055
20	15742.128	−0.001	15740.271	−0.018	15844.571	−0.015	15846.730	0.005
21	15736.352	0.013			15843.860	0.002		
22								
23					15841.926	0.003		

[a] Blended line.

3. Data analysis

Line positions obtained from the computerized fitting and interpolation procedures are listed in Tables 1–4 for $^{16}O_2$, $^{16}O^{17}O$, $^{18}O_2$ and $^{17}O_2$, respectively. The data were, for each isotopomer separately, included in a least-squares fit, to deduce molecular constants. Here the values were weighted with the estimated errors. For blended lines the uncertainties were taken higher than the nominal uncertainty of 0.01 cm^{-1}. The effective Hamiltonian of Rouillé et al. [15] was used to describe the $X^3\Sigma_g^-$, $v=0$ ground state. As in our previous studies the ground state constants were kept fixed at the accurate values derived from microwave and far-infrared spectroscopy [9]. For the $b^1\Sigma_g^+$, $v=2$ excited state we use the representation:

$$E(N) = v_{20} + B'N(N+1) - D'N^2(N+1)^2 \qquad (1)$$

The fitting routines then yield values and uncertainties (1σ) for the v_{20}, B' and D' molecular constants, which are listed in Table 5. The least-squares fits converge with standard deviations ranging from 0.007 to 0.010 cm^{-1} (listed in Table 5). We note that the value of v_{20} is taken with respect to the zero energy as represented by the equations of Rouillé et al. This zero-level does not coincide with a particular quantum state, hence the band origins deviate by a certain amount from other studies. For $^{17}O_2$ no accurate ground state constants are available form microwave or far-infrared spectroscopy. Therefore the present data on the γ-band are included in a combined fit with data pertaining to the A and B-bands [9,10] of our previous studies. In the fit to 266 points the

rotational constants of the ground state as well as three constants for each vibrational level in $b^1\Sigma_g^+$ were varied resulting in updated values for the electronic ground state of $^{17}O_2$: $B_0 = 1.35300\ (2)\ cm^{-1}$ and $D_0 = 4.272\ (16) \times 10^{-6}\ cm^{-1}$. This procedure results in the constants for the excited state as listed in Table 5.

In principle the method of CDRS is suitable for determining absolute values of absorption strengths. The intensity-scales of Figs. 1 and 2 indeed represent absorption strengths in cm^{-1}, while the background level represents the (slightly wavelength-dependent) reflectivity of the mirrors. However the data have to be cautiously treated before an interpretation in terms of an absolute cross-section is valid. In cases where the bandwidth of the laser exceeds the Doppler or collision broadened linewidth the absolute intensities in CDRS are systematically underestimated, as was discussed by Jongma et al. [16] and by Hodges et al. [17].

4. Discussion and conclusion

From this CRDS-study, accurate line positions for the γ-band of four molecular oxygen isotopomers ($^{16}O_2$, $^{16}O^{17}O$, $^{18}O_2$ and $^{17}O_2$) and molecular constants for the $b^1\Sigma_g^+$, $v = 2$ excited state result.

These recordings were taken in a laboratory environment at well-defined pressures, that were constant over the absorption path. Phillips and Hamilton [18] have determined pressure shifts, amounting to $-0.011\ cm^{-1}\ atm^{-1}$ for the A-band and $-0.014\ cm^{-1}\ atm^{-1}$ for the B-band.

Table 4
The γ-band of $^{16}O^{17}O$

N	^{P}Q Observed	Δ_{o-c}	^{P}P Observed	Δ_{o-c}	^{R}R Observed	Δ_{o-c}	^{R}Q Observed	Δ_{o-c}
1	*	*	15860.545	−0.015	15868.443	−0.008	15870.348	0.013
2	15859.762	−0.012	15857.628	0.019	15870.762[a]	0.002	15872.693	0.006
3	15856.602	0.027	15854.480	−0.018	15872.942	0.033	15874.870[a]	0.007
4	15853.262	0.000	15851.211	−0.017	15874.870[a]	−0.028	15876.871	0.000
5	15849.798	−0.007	15847.798	0.001	15876.726	0.001	15878.720	0.005
6	15846.187	−0.008	15844.214	0.007	15878.393	0.001	15880.401	0.006
7	15842.425	−0.004	15840.454	−0.003	15879.903	0.007	15881.908	−0.005
8	15838.496	−0.010	15836.542	−0.006	15881.241	0.001	15883.254	−0.014
9	15834.427	0.003	15832.481	0.002	15882.425	0.003	15884.466	0.005
10	15830.185	0.002	15828.247	−0.003	15883.423	−0.018	15885.508[a]	0.017
11	15825.781	−0.003	15823.860	−0.001	15884.293	−0.006	15886.371[a]	0.012
12	15821.232	0.007	15819.309	−0.004	15884.999	0.005	15887.067	0.003
13	15816.504	−0.003	15814.611	0.006	15885.508[a]	−0.018	15887.602	−0.003
14	15811.624	−0.006	15809.738	0.000	15885.893	−0.002	15887.974	−0.010
15	15806.589	−0.004	15804.712	0.002	15886.114[a]	0.014	15888.230[a]	0.031
16	15801.413	0.017	15799.527	0.004	15886.114[a]	−0.028	15888.230[a]	−0.020
17	15796.033[a]	−0.006	15794.168	−0.008	15886.022	0.002	15888.143	0.006
18	15790.521	−0.002	15788.651[a]	−0.017	15885.734	0.001	15887.858	−0.001
19	15784.843	−0.003	15783.003	0.002	15885.302	0.020	15887.426	0.009
20	15779.013	0.003	15777.173	0.000	15884.678	0.013	15886.818	0.009
21	15773.041[b]	0.028	15771.211	0.026			15886.022[a]	−0.014
22	15766.886[a]	0.031	15765.021	−0.015	15882.939	0.003	15885.084	−0.013
23	15760.527	−0.010			15881.812	−0.009		
24					15880.540	0.000		

[a] Blended line.
[b] Calibration problem due to extrapolation.

Table 5
Molecular constants for the $b^1\Sigma_g^+$, $v=2$ excited state of molecular oxygen[a]

	$^{16}O_2$	$^{16}O^{17}O$	$^{18}O_2$	$^{17}O_2$
ν_{20}	15903.748 (3)	15864.681 (2)	15753.033 (2)	15824.969 (3)
B	1.35463 (2)	1.31523 (2)	1.20614 (2)	1.27587 (3)
D	5.49 (3) 10^{-6}	5.16 (4) 10^{-6}	4.32 (2) 10^{-6}	4.69 (5) 10^{-6}
σ	0.009	0.010	0.007	0.010

[a] The values for ν_{20} are not corrected for possible pressure shifts (see text). σ represents the standard deviation of the fit. All values in cm^{-1}.

In a simple extrapolation a pressure shift of -0.017 cm^{-1} atm^{-1} would follow for the γ-band. For the present measurements conducted at pressures of 60 Torr (for $^{16}O_2$) this implies a pressure shift of -0.0013 cm^{-1}, while for the $^{16}O^{17}O$, and $^{17}O_2$ and $^{18}O_2$ spectra a pressure shift of -0.005 cm^{-1} may be expected assuming that the pressure shift is isotope independent. The values for ν_{20} in Table 5 are not corrected for these pressure shifts.

For $^{16}O^{17}O$ and $^{17}O_2$ the present data are the first reported for the γ-band. For $^{18}O_2$ the γ-band was previously studied by Hill and Schawlow [12], however without an absolute calibration. Relative frequency measurements yielded rotational constants $B=1.2067$ (5) cm^{-1} and $D=4.7$ (5) $\times 10^{-6}$ cm^{-1}, in agreement with the present findings. Engeln et al. [13] did not perform a rotational analysis on their data for the γ-band of $^{18}O_2$. The old data of Babcock and Herzberg [2] are still considered the most accurate for the γ-band of $^{16}O_2$. It should be noted that the value for ν_{20} given in Ref. [2] relates to the lowest $N=1$, $J=0$ level which is offset by 1.3316 cm^{-1} from the zero-level contained in the Hamiltonian of Rouillé et al. [15]. When corrected for this offset a value of 15903.747 cm^{-1} results for the band origin in the work of Babcock and Herzberg exactly coinciding with the present value. Since the data of Ref. [2] were obtained from atmospheric observations where most absorption occurs in a high density region, a corrected value for the band origin would be slightly blue-shifted form the present value.

In a recent study of the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ (3,0) band of $^{16}O_2$ [19] a discrepancy was found with the data of Ref. [2]. The value for the band origin of Ref. [2] was found to be red-shifted with respect to the value of Ref. [19]. This was attributed to a systematic error in Ref. [2]. The present results do not support the conclusion of a red-shift in the old data of Ref. [2].

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