Cavity-Ring-Down Spectroscopy on the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ (1,0) Band of Oxygen Isotopomers

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The $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ (1,0) band of ${}^{16}O^{17}O$, ${}^{16}O^{18}O$, ${}^{18}O_2$, ${}^{17}O^{18}O$, and ${}^{17}O_2$ isotopomers was investigated employing the technique of cavity-ring-down spectroscopy. More than 400 transition frequencies of magnetic dipole lines were determined with a typical uncertainty of 0.01 cm⁻¹. This work results in new or improved accurate molecular constants for the excited $b^1 \Sigma_g^+$, v = 1 state of all isotopomers and for the $X^3 \Sigma_g^-$, v = 0 ground state of ${}^{17}O_2$. © 1998 Academic Press

1. INTRODUCTION

The oxygen A and B bands, corresponding to the (0,0) and (1,0) bands of the $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ system are prominent features in the absorption spectrum of the terrestrial atmosphere. Nevertheless these bands are very weak due to the strongly forbidden character of gerade-gerade and $\Sigma^+ - \Sigma^-$ transitions, and they can only be observed via a magnetic dipole transition moment. The atmospheric B band, the subject of the present investigation, has an experimentally determined radiative rate A(1,0) ranging from 0.0069 s⁻¹ (1) to 0.00724 s⁻¹ (2, 3). Recent *ab initio* calculations yield a rate of 0.00954 s⁻¹ (4). These values correspond to an oscillator strength of f_{10} = 1.6×10^{-11} . Hence the oxygen B band is 10 orders of magnitude weaker than ordinary electric dipole-allowed transitions. Spectroscopically the b-X(1,0) band was studied by Babcock and Herzberg (5). Their data were reanalyzed by computer fitting procedures to yield accurate and consistent molecular constants for ground and excited electronic states (6). Later the (1,0) band was reinvestigated by Fourier-transform methods resulting in accurate constants and pressure shift parameters (7, 8). These latter studies concentrated on the ${}^{16}O_2$ molecule, while Babcock and Herzberg also observed the ¹⁶O¹⁸O and ¹⁶O¹⁷O isotopomers.

The technique of cavity-ring-down (CRD) laser spectroscopy, invented by O'Keefe and Deacon (9), has in recent years been developed into a tool for quantitative measurement of very weak absorptions (10–12). It has been applied to study some weak systems in oxygen, the *A* band in the near infrared (13, 14), as well as the Herzberg systems in the ultraviolet (15). In this work the CRD technique is employed for a spectroscopic study of the *B* band for all oxygen isotopomers other than ${}^{16}O_2$ resulting in new or improved molecular constants for the $b^1\Sigma_g^+$, v = 1 state.

2. EXPERIMENTAL PROCEDURES

The experimental setup, schematically shown in Fig. 1, is similar to the setup previously used for a study of the A band (14) with the exception of the wavelength calibration part. Tunable radiation near 688 nm, in pulses of 5-ns duration and a repetition rate of 10 Hz, is obtained from a Nd:YAG pumped pulsed dye laser running on Pyridine-1 dye. For the principles of converting the ring-down transients into an absorption spectrum we refer to Refs. (9-13). With highly reflecting mirrors ($R \approx 99.998\%$, Research Electro Optics) transients with decay times of $50-60 \ \mu s$ were established, corresponding to an effective absorption path of 50 km (3τ) . The CRD-spectra of ¹⁶O¹⁸O and ¹⁷O¹⁸O isotopomers were recorded in static gas of ≈ 30 Torr from a ¹⁸O-enriched sample (Euristop, $95\%^{-18}O_2$), in which the signals on $^{18}O_2$ lines were saturated (see Fig. 2), i.e., deviate from the linear approximation of Beer's law. The ¹⁸O₂-linepositions were



FIG. 1. Experimental setup. PD, photodiodes; PMT, photomultiplier; f, optical bandpass filter.



FIG. 2. CRD spectrum from a (95%) ${}^{18}O_2$ -enriched sample at 31.6 Torr (top) and a simultaneously recorded I₂-absorption spectrum after intensity normalization (bottom). ${}^{18}O_2$ lines, as indicated, are saturated. This spectrum was used to determine linepositions of ${}^{17}O{}^{18}O$. Some weak ${}^{16}O{}^{18}O$ lines are visible (not marked).

measured from a sample at 1 Torr. A ¹⁷O-enriched sample (Campro Scientific, 50% ¹⁷O atom) was used to record spectra of ¹⁷O₂ and ¹⁶O¹⁷O isotopomers, which appeared to have equal intensity.

The O_2 spectra are somewhat manipulated before being used for analysis. As often in recorded CRD spectra, an oscillation occurs on the absorption baseline, in our case having a period of 0.9 cm⁻¹. The exact origin of this phenomenon is not known, but from the evidences gathered we ascribe it to beating of high-order modes that undergo different decay times in the high-Q cavity. Via a computerized method the baseline oscillation was subtracted from the absorption spectrum. At O₂ pressures below 30 Torr the pressure-induced shift is $0.001-0.002 \text{ cm}^{-1}$ (7), so negligibly small in the present experiment. Doppler broadening, 0.03 cm^{-1} for the *b*-*X*(1,0) band at room temperature, contributes somewhat to the observed linewidth, which is dominated by the laser bandwidth of 0.06 cm^{-1} .



FIG. 3. CRD spectrum from a (50% atom) ¹⁷O-enriched sample at 16.5 Torr (top) and a simultaneously recorded I₂-absorption spectrum after intensity normalization (bottom). ¹⁶O¹⁷O and ¹⁷O₂ lines as indicated. Resonances marked with * are ¹⁷O¹⁸O. Additional resonances due to ¹⁶O¹⁸O are also visible (marked with +), while three intense resonances of ¹⁶O₂ are marked with an arrow.

TABLE 1 ¹⁶0¹⁷0

	P _{Q(N)}		P _{P(N)}		R _{R(N)}		R _{Q(N)}	
N	Obs.	0C.	Obs.	0C.	Obs.	0C.	Obs.	0C.
1	14500 707		14503.45	4008	14511.453	005	14513.337	006
2	14502.707	005	14500.52	6020 5 011	14513.873	.000	14515.793	007
3	14499.575	007	14497.49	0 001	14510.100	.003	14510.111	005
4	14490.309	006	14494.33	9001	14010.021	005	14520.309	.010
5	14493.037	001	14491.05	6 .000 6 .001	14520.302	002	14522.300	.007
7	14409.000	.009	14407.00	2 007	14522.275	001	14526.090	.002
/ Q	14400.007	- 007	14404.10	6 - 006	14525 707	004	14527 746	- 002
0 0	14402.505	000	14400.42	6 003	14527 238	014	14520 202	000
10	14474 674	010	14472 74	5 015	14528 653	- 006	14530 709	000
11	14470 623	008	14468 69	0 - 003	14529 948	011	14531 994	- 003
12	14466 444	.002	14464 53	7.006	14531.097	.009	14533.171	.013
13	14462 148	002	14460.24	8 .004	14532,112	.000	14534,193	.001
14	14457.733	.009	14455.84	3 .011	14533.023	.015	14535.095	002
15	14453.178	001	14451.30	9 .013	14533.774	001	14535.861	013
16	14448.506	003	14446.61	9017	14534.420	.006	14536.521	001
17	14443.717	.003	14441.85	4 .004	14534.930	.006	14537.032	009
18	14438.790	005	14436.93	2008	14535.286	019	14537.427	004
19	14433.764	.013	14431.91	7 .012	14535.540	017	14537.691	001
20	14428.586	.004	14426.73	7008	14535.672	007	14537.816*	007
21	14423.274	014	14421.44	5015			14537.816*	007
22	14417.878	.010	14416.06	1 .012				
23	14412.319	005	14410.49	8015				
24	14406.648	006	14404.84	8004				
25	14400.877	.019	14399.08	3 .018				
26	14394.944	.007	14393.15	4 .002				
27	14388.880	009	14387.10	4009				
28	14382.770*	.054	14380.95	6 .008				
29	14376.409	007	14374.66	3 .006				

* blended lines

For the purpose of wavelength calibration an absorption spectrum of molecular iodine was recorded simultaneously with the CRD spectrum of oxygen. Since in the wavelength range near 688 nm I₂ has strong transitions in the B-X system for (v', v' = 6) bands, the I₂-sample was heated in an oven to 430 K, to reach sufficient population of v'' = 6 levels. From the weight of solid iodine evaporated in the cell an operation pressure of 60 Torr I₂ gas is estimated at which the absorption measurements are performed. At these pressures collisional broadening of I₂ lines does occur, but not in the amount to affect the width of the observed resonances (0.07 cm^{-1}). Pressureinduced shifts at 60 Torr in I2 are on the order of 0.002 cm^{-1} . Three passes through the heated I₂ cell creates a total absorption length of 1.4 m. The signal-to-noise ratio of the thus observed I_2 absorption spectrum is improved by normalizing to the laser power, measured for each pulse on a separate photodiode.

With computerized fitting the peak positions were determined in the I₂ spectra. Subsequently, after identification of the I₂ lines, the frequencies of the I₂ atlas (*16*) were used to create a linearized frequency scale, which, in turn, was employed to calibrate the frequencies of the O₂ resonances. For the intense lines this produces results in an uncertainty of 0.01 cm⁻¹. In the experimental procedures wavelength steps of 0.01 cm⁻¹ were taken. So 15 data points contribute to the line profile of 0.07 cm⁻¹ width (FWHM).

In principle the CRD spectra can provide information on the absolute absorption strengths of the resonance lines. In our case such information could be derived from the calibrated vertical scales in Figs. 2 and 3. However, if CRD transients are induced by a light source, which is broader than the Doppler- and collisionally broadened spectral lines, intricate corrections have to be implemented to deduce reliable linestrengths (11, 13), and this was not pursued in the present study.

	PQ(N) PP(N)		R _{R(N)}		R _{Q(N)}			
N	Obs.	0. - C.	Obs.	0C.	Obs.	0C.	Obs.	0C.
0	• • • • • • • • • • • • • • • •						14493.211	.000
1			14486.104	.005	14493.857	025	14495.758	016
2	14485.410	004	14483.263	.001	14496.241	.007	14498.149	016
3	14482.376	.002			14498.453	011	14500.385	036
4			14477.233	.007	14500.535	038	14502.518	030
5	14476.042	.011	14474.026	.000	14502.518*	042	14504.543	008
6			14470.704	002	14504.411	013	14506.429	.000
7			14467.267	.002	14506.166	001	14508.195	.011
8	14465.670	.009	14463.716	.013	14507.794	.007	14509.833	.018
9	14461.976	.010	14460.018	003	14509.294	.010	14511.336	.013
10	14458.156	.004	14456.234	.016	14510.660	.001	14512.711	.003
11	14454.238	.020	14452.290	005	14511.902	008	14513.958	011
12	14450.152	2011			14513.040	.001	14515.094	013
13	14445.982	2006	14444.082	003	14514.031	012	14516.117	004
14	14441.690)003	14439.799	.000	14514.916	008	14516.996	015
15	14437.267	'010	14435.394	.001	14515.661	019	14517.786	.010
16	14432.759	.018	14430.877	.012	14516.310	002	14518.426	.008
17	14428.093	.010	14426.217	.000	14516.814	006	14518.940	.006
18	14423.299	9006			14517.193	009	14519.352	.027
19					14517.458*	001	14519.625	.035
20	14413.369	016	14411.542	003	14517.595*	.005	14519.758	.028
21	14408.246	6003			14517.595*	.000	14519.758'	*006

* blended lines

3. RESULTS AND ANALYSIS

In Figs. 2 and 3 simultaneous recordings are shown of CRD spectra of O_2 , for ¹⁸O- and ¹⁷O-enriched samples, respectively, and I_2 -calibration spectra. Via the computerized calibration and interpolation procedure, described above, frequency positions of all isotopomer lines except ¹⁶O₂ were determined. The transition frequencies, presented in Tables 1–5 for the various isotopomers, were included on the input deck of a least squares fitting routine for each isotopomer, in which the excited state is represented by

$$E(N) = \nu_{10} + BN(N+1) - DN^2(N+1)^2,$$

while the $X^3 \Sigma_g^-$, v = 0 ground state energies were represented by an effective Hamiltonian as given by Rouillé *et al.* (17). Except for ${}^{17}O_2$ the molecular constants for the ground state, rotational as well as spin-coupling constants, were kept fixed at the accurate values from far-infrared and microwave spectroscopy from Steinbach and Gordy (18) and Cazolli *et al.* (19). In our previous paper (14) a detailed listing of all relevant ground state constants was given.

In the weighted least squares fits the data were included with uncertainty of 0.01 cm^{-1} for the intense lines and 0.02

or 0.03 cm^{-1} for the weaker or partially overlapped lines. In that case the resulting χ^2 equals the number of data points, demonstrating that 0.01 cm^{-1} indeed represents the experimental uncertainty of the spectroscopic method. For each resonance line the deviation between measured transition frequency and calculated value is given in Tables 1-5. Molecular constants, resulting from the fitting procedures, for the $b^{1}\Sigma_{g}^{+}$, v = 1 excited state are presented in Table 6, with the errors representing one standard deviation. For comparison the most recent values for ${}^{16}O_2$ (8) are included in Table 6. The listed value of the band origin ν_{10} is dependent on the definition of the zero energy level. Usually the lowest energy state is chosen at zero energy, but in the case of ${}^{16}O_2$ and ${}^{18}O_2$ the N = 0, J = 1 level does not exist for symmetry reasons. Here we define zero at the energy given by the Rouillé Hamiltonian without spin and rotation, i.e., not at a specific level. With this definition the level N =0, J = 1 is about 0.45 cm⁻¹ below zero, slightly dependent on isotopomer. For clarity the values for the offset between N = 0, J = 1 levels and the trace of the Hamiltonian are given for each isotopomer in Table 6.

For the $X^{3}\Sigma_{g}^{-}$, v = 0 ground state of ${}^{17}O_{2}$ no accurate molecular constants are available, except from our previous study on the electronic A band (14). In a combined fit

TABLE 3 ¹⁷0¹⁸0

	P _Q (N)		PP(N)		R _{R(N)}		R _{Q(N)}	
N	Obs.	0C.	Obs.	0C.	Obs.	0. - C.	Obs.	0. - C.
1			14466.203	.019			14475.620	007
2	14465.588	.015	14463.422	015				
3	14462.633	.000	14460.567	006				
4	14459.629	.013					14482.194	.000
5	14456.496	.001	14454.512	.018	14482.141	003	14484.133	004
6	14453.272	.008	14451.275	006	14483.952	003	14485.967	.007
7	14449.909	010	14447.943	008	14485.644	003	14487.668	.004
8	14446.442	017	14444.500	004	14487.208	014	14489.253	.003
9			14440.948	.007	14488.669	009	14490.716	.000
10	14439.201	.006	14437.267	.006	14490.008	007	14492.054	009
11	14435.394	.006	14433.469	.004	14491.238	.005	14493.290	001
12	14431.473	.007	14429.571	.018	14492.329	004	14494.395	004
13	14427.439	.012	14425.514	009	14493.290*	022	14495.365	023
14	14423.299*	.027	14421.391	.014	14494.170	002	14496.241	016
15	14419.012	.012	14417.130	.016	14494.900	012	14496.985	020
16	14414.640	.029	14412.739	.005	14495.520	011	14497.624	009
17	14410.102	004	14408.246	.009	14496.036	.007	14498.149	.010
18	14405.482	001	14403.622	001	14496.409	.003	14498.520	005
19	14400.781*	.038	14398.882	009	14496.671	.010	14498.780	008
20					14496.807*	.013	14498.933'	.003
21					14496.807*	.003	14498.933	015

* blended lines

TABLE 4

	PQ(N)	i	PP(N)		R _{R(N)}		R _{Q(N)}	
N	Obs.	0C.	Obs.	0. - C.	Obs.	0C.	Obs.	0. - C.
1			14448.277	.000	14455.607	.001	14457.515	.000
3	14444.865	014	14442.828	.002	14459.928	.002	14461.893	.002
5	14438.930	.008	14436.922	003	14463.786	006	14465.788	.001
7	14432.550	.011	14430.581	.009	14467.204	.002	14469.218	002
9	14425.708	005	14423.760	009	14470.143	013	14472.188	006
11	14418.443	.004	14416.514	001	14472.650	002	14474.697	·012
13	14410.713	004	14408.806	006	14474.697	.009	14476.770	.008
15	14402.559	.014	14400.655	002	14476.259	003	14478.350	003
17	14393.924	.001	14392.054	.003	14477.376	.004	14479.488	.008
19	14384.844	005	14382.975	019	14478.017	.001	14480.137	003
21	14375.339	.016	14373.526	.042	14478.190	002	14480.330	002
23	14365.328	016	14363.524	.003	14477.897	.001	14480.051	002
25	14354.891	020	14353.089	014	14477.132	.005	14479.313	.014
27	14344.012	009	14342.227	003	14475.893	.012		
29	14332.665	010	14330.888	011	14474.169	.014		
31	14320.868	003	14319.119	.009	14471.934	014		
33	14308.607	.000	14306.863	.002				
35			14294.160	.011				

* blended lines

TABLE	5
¹⁷ 0,	

	PQ(N)		PP(N)		R _{R(N)}		R _{Q(N)}	
N	Obs.	0C.	Obs.	0C.	Obs.	0C.	Obs.	0C.
0					• • • • • • • • • •		14490.945	5 .021
1			14483.824	4 .003	14491.583	.005	14493.462	2009
2	14483.144	002	14481.009	9 .014	14493.917	005	14495.858	.004
3	14480.109	008	14478.07	2.024	14496.148	.003	14498.103	.001
4	14477.022	.011	14474.98	2 .001	14498.249	.002	14500.203	3020
5	14473.797	001	14471.79	2002	14500.203	025	14502.212	2007
6	14470.477	.005	14468.48	7 .001	14502.074	013	14504.090)001
7	14467.035	.006	14465.05	3006	14503.816	009	14505.848	.007
8	14463.461	007	14461.51	3 .002	14505.436	004	14507.467	7001
9	14459.795	.007	14457.85	1 .008	14506.942	.008	14508.963	3010
10	14455.994	.005	14454.05	5 .000	14508.302	003	14510.342	2012
11	14452.079	.008	14450.15	1.004	14509.558	.004	14511.612	2001
12	14448.035	.003	14446.114	4005	14510.674	006	14512.744	004
13	14443.875	.001	14441.97	1.000	14511.673	010	14513.751	009
14	14439.579	017	14437.69	4008	14512.555	007	14514.659	.011
15	14435.192	006	14433.31	3 .000	14513.325	.008	14515.412	2001
16	14430.692	.013	14428.80	2001	14513.938	011	14516.063	.010
17	14426.035	005	14424.17	0003	14514.465	.010	14516.580	.011
18	14421.270	010	14419.42	6 .004	14514.848	.011	14516.965	.006
19	14416.387	012	14414.55	2 .002	14515.104	* .010	14517.239	9* .014
20	14411.377	021	14409.54	9008	14515.225	* .000	14517.374	1* .010
21	14406.276	.001	14404.44	6 .003	14515.225	*005	14517.374	1 *004
22	14401.040	.009	14399.21	9 .012	14515.104	*005	14517.239	9*026
23	14395.689	.023	14393.85	6 .006				
24	14390.157	022	14388.35	6016				
25	14384.593	.023	14382.77	0001				
26	14378.828	011	14377.07	2 .024				
27	14372.989	.004	14371.18	7015				
28	14367.007	001	14365.23	5 .001				

including the data of both the (1,0) and (0,0) band, a more accurate set of rotational constants for the ${}^{17}O_2$ ground state was derived and listed in Table 7; in this procedure the spin

coupling constants were estimated from the other isotopomers (λ'_0 and μ_0 scaled proportional to *B* and μ'_0 scaled proportional to B^2) and kept fixed in the fit.

TABLE 6Molecular Constants for the $b^1 \Sigma_g^+$, v = 1 Excited State of Molecular Oxygen Isotopomers

			0			
	16 ₀₂ (a)	16 _O 17 _O	160180	18 ₀₂	17 ₀ 18 ₀	17 ₀₂
В	1.372951 (18)	1.332761 (15)	1.29727 (3)	1.221495 (15)	1.25710 (3)	1.292776 (14)
D	5.397 (50) 10 ⁻⁶	5.11 (2) 10 ⁻⁶	4.80 (8) 10 ⁻⁶	4.28 (2) 10 ⁻⁶	4.77 (8) 10 ⁻⁶	4.95 (2) 10 ⁻⁶
v10	14526.9976 (12)	14507.583 (2)	14490.145 (3)	14452.164 (2)	14470.146 (3)	14487.858 (3)
$\Delta_{\rm off}$	-0.450	-0.4645	-0.478	-0.509	-0.494	-0.480

Note. Δ_{off} refers to the calculated offset of the N = 0, J = 1 level to the trace of the Hamiltonian, chosen as the zero energy. All values in cm⁻¹.

 $^{\rm a}$ Values for $^{16}{\rm O}_2$ taken from Ref. (8).

TA	BI	Æ	1

Molecular Constants for the $X^3\Sigma_g^-$, v = 0 Ground State of ${}^{17}O_2$ as Obtained from a Combined Fit to the *B-X* (1,0) and (0,0) Bands

1.353038 (7)
4.349 (10) x 10 ⁻⁶
1.9846762 ^(a)
1.8 x 10 ^{-6 (a)}
7.9 x 10 ^{-3 (a)}
8.0 x 10 ⁻⁹ (a)

^a Constants estimated from values for other isotopomers (18, 19).

4. CONCLUSION

Transition frequencies of the $b^{1}\Sigma_{g}^{+}-X^{3}\Sigma_{g}^{-}(1,0)$ band were measured for ${}^{16}O^{17}O$, ${}^{16}O^{18}O$, ${}^{18}O_{2}$, ${}^{17}O^{18}O$, and ${}^{17}O_{2}$ isotopomers, with an accuracy of 0.01 cm⁻¹, under pressure conditions, where pressure shifts are negligibe. Combined with previous work (5, 8, 14) spectral positions of the atmospheric A and B bands are now known with high accuracy for all isotopomers of oxygen.

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