TOWARD THE EVALUATION OF THE OSCILLATOR STRENGTH OF THE $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ TRANSITION OF MOLECULAR OXYGEN

Thesis by

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ABSTRACT

The oscillator strength of the oxygen $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition is evaluated in two ways: from the equivalent width of an individual line of the 0-0 band; and from the collective equivalent width of the Q-lines around the 0-0 band head.

These two methods give values for B/c, the Einstein coefficient for spontaneous absorption, of about .027 (erg-sec-molecule)$^{-1}$ and .05 (erg-sec-molecule)$^{-1}$, respectively.

INTRODUCTION

The $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition of molecular oxygen occurs as a twilight emission at an altitude of about 70 km., and with a lifetime of about ½ hr. The 0-0 band, located at 1.27 microns, is the most intense, and was the subject of the work described here.

Since the mechanism by which the $^1\Delta_g$ state is excited has not yet been fully understood, it was thought desirable to measure the intensity of the transition under laboratory conditions; accurate values for the Einstein coefficients would permit more critical appraisal of the various mechanisms which have been proposed[1], and would also permit the formation of a somewhat clearer picture of high altitude chemical processes.

EXPERIMENTAL

Instumentation was a recording IR spectrometer with a White cell attached to permit examination of gas spectra at large path lengths (up to 32 meters), and moderately elevated pressures (up to about 4 atmospheres absolute). The instrument employs a grating monochromator, a semiconductor detector, and an interrupted light source and lock in amplifier at the same frequency. Glass filters and a thin layer of water are employed to cut out undesired orders from the grating.

While many spectra were run, tracings of six were photographically enlarged and all measurments were made on them.

Spectra A and D were made with a path length of 32 m., and at a pressure of 49 psig; X_1 and X_2 at 32 m., 17 psig; Y_1 and Y_2 at 16 m., 49 psig. In all cases the sample was commercial compressed oxygen.

Measurements were made on tracings of the enlargements onto graph paper with 1 mm. squares; the traced line was kept in the middle of the recorder line to eliminate uncertainties due to the finite width of the recorder line. The absorption of the individual lines was measured by counting squares on the tracing. This gave an area in $mm.^2$, which was converted to energy terms by multiplication by the factor 3.39×10^{-4} cm^{-1} per $mm.^2$. This figure combines the conversion from the linear wavelength scale in mm. to wavenumbers (effectively constant over the small range of the spectra), and the conversion of the height of a line in mm. to fractional transmittance. A hypothetical line 10mm. wide and 10mm. high would thus have an absorption of 3.39×10^{-2} cm^{-1}.

To correct for the non-coincidence of the recorder's 100% transmittance line with those of the individual lines, the absorption figures were then divided by the fractional transmittance at their bases, giving the equivalent widths. If our hypothetical line had its base at 10% transmittance, then this would give an equivalent width of 3.39×10^{-1} cm^{-1}.

Table I presents the absorption values (equivalent widths) for 13 lines, calculated by the above method. A second tracing of spectrum A was made to give an idea of the variability of these numbers, and the equivalent widths derived from this tracing are included.

TABLE I

LINE EQUIVALENT WIDTHS
in cm^{-1}

branch	J-value	wavenumber	A	D	X_1	X_2	Y_1	Y_2	A
R_R	1	7888.02	.0164	.0185	.0199	.0140	.0079	.0128	.0191
R_R	3	7893.50	.0177	.0163	.0126	.0122	.0112	.0110	.0189
R_Q	3	7895.47	.0069	.0073	.0075	.0076	.0066	.0057	.0069
R_R	5	7898.79	.0286	.0248	.0179	.0172	.0151	.0134	.0236
R_Q	5	7900.78	.0058	.0124	.0103	.0069	.0045	.0041	.0070
R_R	7	7903.93	.0163	.0171	.0146	.0169	.0106	.0064	.0167
R_Q	7	7905.98	.0105	.0101	.0073	.0089	.0045	.0099	.0124
R_R	9	7909.63	.0245	.0299	.0215	.0182	.0110	.0160	.0244
R_R	11	7913.78	.0190	.0152	.0165	.0100	.0125	.0137	.0200
R_Q	11	7915.84	.0117	.0133	.0162	.0074	.0114	.0054	.0136
R_R	13	7918.43	.0167	.0182	.0162	.0132	.0089	.0069	.0177
*R_Q	13	7920.54	.0218	.0241	.0155	.0197	.0146	.0081	.0230
R_R	19	7931.40	.0153	.0208	.0129	.0086	.0107	.0116	.0145
S_R	9	7942.15	.	.	.	.	.0050	.0074	.

*probably includes line S_R 5.

The value B/c was calculated from the equivalent width of the line R_2 7, using the formula:

$$B/c = Q/(S_J \cdot e^{-E/kT}) \cdot (\int K_\nu d\nu) \cdot (1/h\nu)$$

where Q is the rotational partition function

= 215 at T= 298° K

S_J is a weighting factor corresponding to the theoretical intensity of the line under consideration.[2]

= 8.75

$K_\nu d\nu$ is the equivalent width (evaluated earlier) divided by the number of molecules in a path 1 cm^2 in cross section under the conditions of the spectrum.

= 3.89×10^{-26} cm^{-1} molecule^{-1}

E is the rotational energy of the lower state
= $\tilde{\nu}hc$

= 80 cm^{-1} x hc (value taken from a table of solar spectrum lines)(4)

Using these values, we find that B/c = 2.70×10^{-2} (erg-sec-mole)$^{-1}$

Consideration of the solar spectrum, combined with reasonable assumptions about the atmosphere, suggested that this value was low by about a factor of 2. The deficit occurs because of the inseparability of the line structure of the spectrum from a pressure induced continuous absorption that underlies the line structure. This inseparability is due to overlap of the lines from pressure broadening and from the finite resolution of the instrument.

Figure 1 shows a part of the spectrum with two alternative lines dividing the line structure from the continuous absorption.

Line I assumes that the line absorption is zero between line pairs, a patently false assumption; line II is a possible actual division line; its exact placement is not deduceable

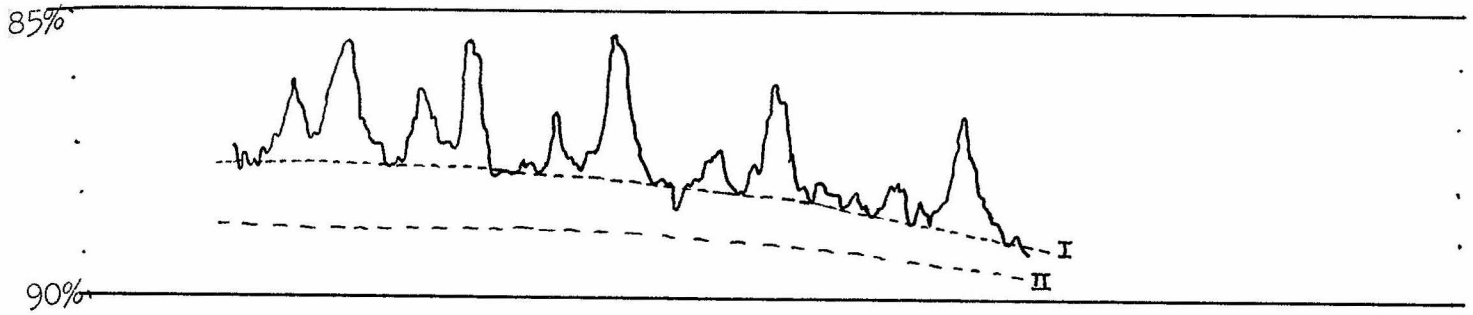

FIGURE 1

from the spectrum alone, but may be guessed.

The area between I and II represents the error in the final answer for B/c.

Since the large clump of Q-branch lines around the band head is fairly well isolated (i.e., no other lines are near it), the absorption due to the line structure of the spectrum goes more nearly to zero on each side. Thus, by taking the large mass of lines together, a better value for B/c may be calculated. Figure 2 shows the band head configuration.

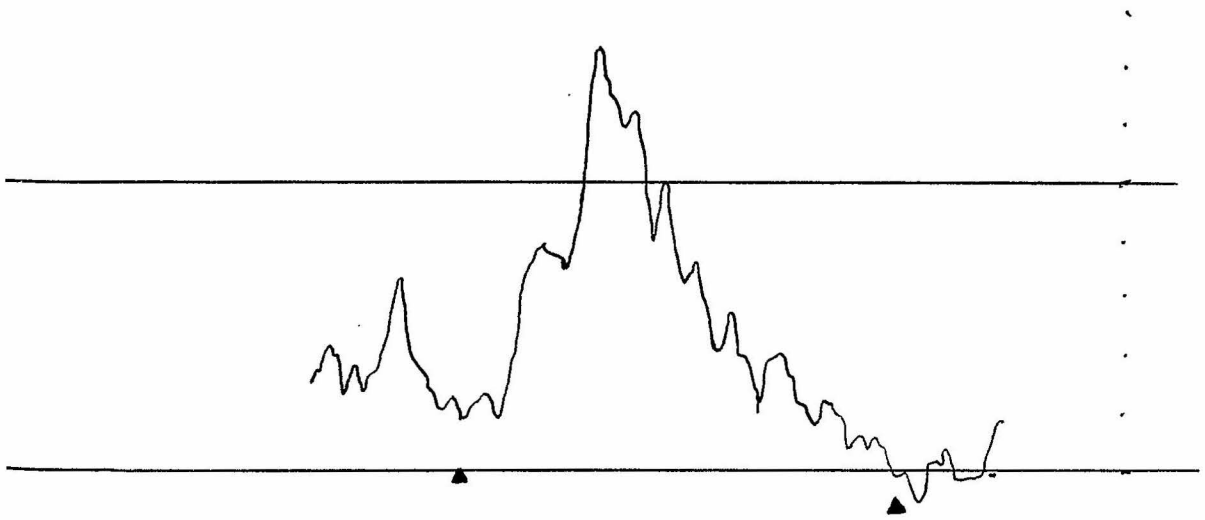

FIGURE 2

The photographic spectrum in Herzberg[3] shows more clearly just how isolated the band head is. Taking the area and converting it to equivalent width, the different spectra measured give:

$\underline{A}$: .350 cm^{-1} $\quad \underline{X}_1$: .235 cm^{-1} $\quad \underline{Y}_1$: .195 cm^{-1}

$\underline{D}$: .360 cm^{-1} $\quad \underline{X}_2$: .169 cm^{-1} $\quad \underline{Y}_2$: .227 cm^{-1}

The calculation of B/c from these figures employs the formula used before, except that the term $S_J \cdot e^{-E/kT}$ is replaced by the summation of this quantity over all the lines included in the band head structure. The lines included are:

^qR 3-21, perhaps 23

^qQ 3-19. perhaps 21

^qP 3-23

P_Q 3

P_P 3

By taking the pairwise averages of the equivalent widths, and the included lines both with and without the uncertain lines, six values are derived. These are given in Table II.

TABLE II

	B/c VALUES IN $(erg\text{-}sec\text{-}molecule)^{-1}$		
	a	b	c
I	.0448	.0511	.0534
II	.0438	.0501	.0522

I: not including ^qR 23 & ^qQ 21

II: including ^qR 23 & ^qQ 21

a: spectrum taken with 32 m. path length, 49 psig O_2

b: 32 m, 17 psig.

c: 16 m, 49 psig.

CALCULATIONS

I. $e^{-E/kT}$ $E = h\tilde{\nu}c/kT$, where $\tilde{\nu}$ is the rotational energy in cm^{-1}. This was evaluated at T= 298° by calculating $10^{-(\tilde{\nu} \times 2.10 \times 10^{-3})}$

II. S_J Calculated according to the following, taken from reference 2:

^{Q}P: $(J-2)(J-1)(J+1)/J(2J+1)$

^{P}P: $(J-2)(J-1)/J$

^{O}P: $(J-2)(J-1)/(2J+1)$

R_Q: $(J+2)(J-1)/J$

^{Q}Q: $(J+2)(J-1)(2J+1)/J(J+1)$

P_Q: $(J+2)(J-1)/(J+1)$

^{S}R: $(J+2)(J+3)/(2J+1)$

^{R}R: $(J+2)(J+3)/(J+1)$

^{Q}R: $J(J+2)(J+3)/(J+1)(2J+1)$

Calculated values of both of these quantities are presented in Table III.

TABLE III

a		b	c	d	e	f
Q_R	3	2.67	16	.0336	.9255	2.47
	5	3.73	42	.0881	.8164	3.05
	7	4.74	80	.168	.6792	3.22
	9	5.75	128	.269	.5383	3.09
	11	6.75	189	.397	.4009	2.70
	13	7.75	261	.548	.2831	2.19
	15	8.75	344	.721	.1901	1.66
	17	9.75	439	.920	.1202	1.17
	19	10.75	545	1.143	.0719	o.77
	21	11.75	662	1.390	.04064	o.48
Q_Q	3	5.83	18	.0378	.9166	5.34
	5	10.27	44	.0924	.8083	8.32
	7	14.46	82	.172	.6730	9.72
	9	18.58	130	.273	.5333	9.90
	11	22.7	191	.401	.3972	9.01
	13	26.7	263*	.552	.2805	7.49
	15	30.7	346	.726	.1879	5.77
	17	34.8	441	.925	.1189	4.14
	19	38.8	547	1.150	.0708	2.75
Q_P	3	.833	16	.0336	.9255	.77
	5	1.795	42	.0881	.8164	1.47
	7	2.78	80	.168	.6792	1.89
	9	3.77	128	.269	.5383	2.07
	11	4.76	189	.397	.4009	1.90

TABLE III cont.

a	b	c	d	e	f
13	5.76	261.	.548	.2831	1.63
15	6.76	344	.721	.1901	1.28
17	7.76	438	.920	.1202	0.94
19	8.76	544	1.141	.0723	0.63
21	9.76	662	1.390	.04064	0.39
23	10.76	791	1.660	.0219	0.24
P_Q 3	1.33	16	.0336	.9255	1.23
P_P 3	.67	18	.0378	.9166	0.62
Q_Q 21	42.8	664	1.392	.0406	1.74
Q_R 23	12.75	791	1.660	.0219	.28

a: line identification

b: S_J

c: $\tilde{\nu}$ taken from solar spectrum table[4] in cm^{-1}

d: $\tilde{\nu} \times 2.10 \times 10^{-3}$

e: $10^{-(\tilde{\nu} \times 2.10 \times 10^{-3})} = e^{-E/kT}$ $\quad T = 298° K$

f: $S_J \cdot e^{-(E/kT)}$

*- value in solar spectrum table is in error here; this is an extrapolated value

1. Chamberlain, Physics of the Airglow and the Aurora, pp. 480-482

2. Van Vleck, Astrophysical Journal, 80 161 (1934)

3. Herzberg, Astrophysical Journal, 105 355 (1947)

4. Orren C. Mohler, Photometric Atlas of Near Infrared Solar Spectrum, University of Michigan Press, 1950

For a general discussion of the structure of the O-O band, see

G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand, 1950