The atmospheric oxygen bands

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THE ATMOSPHERIC OXYGEN BANDS

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SUMMARY. — *In continuation of a theoretical investigation, observational data are discussed, gathered* a) *from the photometric atlas of the solar spectrum and* b) *from other authors. The method of deriving the temperature, damping constant and transition-probabilities is described in section* 2. *The results are shown in tables* 4, 5 *and* 6 *respectively. Great discrepancies are found between measurements by various authors. The underlying mistake, made plausible in section* 3, *is a systematically erroneous height of the continuous back-ground.*

In conclusion the relative transition-probabilities are computed by quantum mechanics. The agreement with observations is satisfactory.

The relevant literature is tabulated and a list of references is given.

1. FORMER RESEARCHES.

From the moment absorption lines were discovered in the solar spectrum, the red B band and infra-red A band have been interesting phenomena. When in the years about 1930 the large scale attack on all band-spectra was launched, these too were taken hold of. MULLIKEN interpreted them as a $^1\Sigma \leftarrow {}^3\Sigma$ transition of the O_2 molecule. This was wholly confirmed by a detailed term analysis by BADGER and MECKE [1] (1), who also found the doublet distances to be in accordance with the formula deduced by KRAMERS [6].

Meanwhile investigators became interested in the width of the single lines. By observing at various zenith distances, the number of absorbing molecules could be varied in a known way. UNSÔLD arrived at the result that the width should increase proportionally to the square root of this number. The discrepancies initially found [7] [8] could be explained as a result of insufficient resolving power. Since then this difficulty was eliminated by using the invariant *equivalent widths.*

The relative intensities are theoretically equal to $i \cdot e^{-E/kT}$, where E is the energy of the initial state. The factors i should be linear functions of the rotatonal quantum number J, but were unknown for this intercombination transition. By interesting measuring-experiments en the laboratory CHILDS and MECKE [10] obtained

(1) The numbers between brackets are the same as those used in table 8 at the end of this paper, where all relevant literature is systematically arranged.

the values given in table 1. Afterwards SCHLAPP [14] computed theoretical values, but most measurements of equivalent widths agree better with the first-mentioned values. Though a decisive conclusion cannot be drawn, we shall use CHILDS and MECKE's values throughout this paper.

TABLE I

LINE	MECKE & CHILDS	SCHLAPP	LINE	MECKE & CHILDS	SCHLAPP
—	—	—	—	—	—
$R_1(J)$	$J + \frac{1}{2}$	$J + 1$	$P_3(J)$	$J + \frac{1}{2}$	J
$R_2(J)$	$J - 1$	$J - 1$	$P_2(J)$	$J + 2$	$J + 2$

The experiment of MECKE and CHILDS also furnished the first estimate of the absolute *transition probability* of the A band. This was for VAN VLECK [15] the decisive argument for interpreting these bands as the effect of a magnetic dipole transition. CHILDS [11] determined the transition probabilities of the A band and B band also in the solar spectrum and found them to be in accordance with the laboratory values. In computing the *damping constant,* however, he had to be satisfied with the kinetic collision diameter. ALLEN [13] improved on this by measuring also such weak lines, as were needed for deriving the damping constant from the observations themselves. At the end of this article the literature concerning the atmospheric oxygen bands is systematically arranged and numbered in table 8, and a list of the references, thus numbered, is added. The *isotope bands* are not discussed in the present article.

The present investigation was started in 1940, just after the completion of the *Photometric atlas of the solar spectrum* [20]. The oxygen bands were considered to be a suitable object for testing the accuracy of the atlas. When, however, we had obtained the equivalent widths, the theory turned out to fail. Afterwards, stimulated by investigations into allied subjects, we developed an improved theory, which is published separately [21]. Finally we made a fresh start in working up the observational material, including all data available. As will be shown, the agreement is now in broad lines satisfactory ; but still we badly felt a want for more complete and accurate data. In particular : *a*) The wings of the strong lines are likely to be taken insufficiently into account in our own measurements as well as in those published formerly. *b*) Stubborn efforts — for which I owe thanks to C. DE JAGER — at measuring the A band in the spectrum of a terrestrial light source were frustrated by the bad war-time photographic material. *c*) No temperatures and other meteorological data for the Mt. Wilson plates were available ; moreover the sec z given is not very accurate. In view of these deficiencies all values found must be regarded as *preliminary values.*

2. A method of deriving simultaneously the temperature, damping constant and transition probability.

In a homogeneous atmosphere the equivalent width W would be given by (1)

$$(37) \qquad W = 2iC_{\rm I} \sec z \, e^{-E/kT} \quad \text{for very weak lines,}$$

$$W^2 = 2iC_{\rm II} \sec z \, e^{-E/kT} \quad \text{for very strong lines.}$$

In this case by plotting $\log W - \log 2i$ or $2 \log W - \log 2i$ against E we should obtain a straight line. The slope of this line yields the *temperature* and from its position follow the constants $C_{\rm I}$ or $C_{\rm II}$ respectively. The constant $C_{\rm I}$ contains the *transition probability*, while $C_{\rm II}$ contains the product of transition probability and *damping constant.* By this graphical method we might, therefore, derive the three unknowns simultaneously.

This simple scheme, however, is crossed by two complications. 1° The atmosphere is not homogeneous and 2° not all lines are very weak or very strong. First we consider the first complication only. The local number of oxygen molecules pro cm³ in a particulat state n is

$$(38) \qquad N_n = \beta N 2i \, e^{-E/kT} / \Sigma,$$

where N = number of air-molecules pro cm³, β = volume fraction of oxygen, $2i$ = statistical weight, $E = E_{\rm el} + E_{\rm vib} + E_{\rm rot}$ = energy of the state. When we put $E = 0$ on the lowest level, the partition function (Zustandssumme) F is to a high approximation equal to

$$(39) \qquad \Sigma = \Sigma_{\rm rot} \; \Sigma_{\rm vib} \; \Sigma_{\rm el} = 1{,}03 \frac{kT}{Bhc} \times 1{,}00 \times 1{,}00,$$

where B = the rotational constant and the factors 1,03, 1,00 and 1,00 are computed for atmospheric temperatures. On substituting $\beta = 0{,}21$, $B = 1{,}44$ cm^{-1}, and putting

$$(40) \qquad C = \frac{\beta}{1{,}03} \frac{Bhc}{k} = 0{,}42 \text{ degrees},$$

the expression for the local strength of the transition is found to be identical with formula (26). The exact values of the equivalent width according to the two asymptotic laws now follow from (28) and (30) :

$$(41) \qquad W_{\rm I} / 2if_{\rm I} = C_{\rm I} \sec z \, e^{-E/kT_{\rm I}},$$

$$W_{\rm II}^2 / 2if_{\rm II} = C_{\rm II} \sec z \, e^{-E/kT_{\rm II}},$$

(1) For more convenient reference the formulae are numbered consecutively with the formulae of the preceding article.

where

$$C_{I} = CKI_{I}{}^{0}N_{0}/T_{0}, \qquad (42)$$
$$C_{II} = CKI_{II}{}^{0}N_{0}/T_{0} \times \gamma_{0}/\pi$$

and the meaning of the other symbols is clear from the preceding article.

The other complication can be taken into account by writing the true value of the equivalent width as

$$W = g_{I}W_{I} = g_{II}W_{II}, \qquad (43)$$

where g_{I} and g_{II} are correction factors tangent to 1 for very weak lines and for very strong lines respectively. Their values depend on the exact form of the curve of growth of a particular line. Now, however, we simplify the problem by supposing that all *curves of growth* have the *same form*, though their positions differ, depending on the effective damping constant. On this suitable approximation g_{I} and g_{II} are functions of $W/W_{I\,II}$; we read them from ALLEN's curve, which is hardly distinct from a curve for damping only.

Summarizing the above, our procedure of deriving the temperature, damping constant and transition probability from equivalent widths is the following. First plot $2 \log W - \log 2i - \log f_{II}$ against E. The strongest lines show a straight graph, from which we read T_{II} and C_{II}. If the graph is not perfectly straight, plot the residuals against $\log W$. Comparing this graph with the theoretical graph of $\log g_{II}$ against $\log (W/W_{I\,II})$, we obtain an estimate of $W^{0}_{I\,II}$ and an improved value of C_{II}. Then plot $\log W - \log 2i - \log f_{I}$ against E and repeat the process m.m. for the asymptotic law I. Resulting values are T_{I}, C_{I} and another estimate of $W^{0}_{I\,II}$. Finally compute $W^{0}_{I\,II} = C_{II}/C_{I}$ and make a further improvement, if necessary. Now T_{0} follows from (34), K and γ_{0} from (42), (40) and (33). The procedure seems somewhat cumbrous, but is indeed straightforward, since f_{I}, f_{II}, g_{I} and g_{II} appear as slight corrections only. We omit a numerical example for lack of space and of perfectly reliable data.

3. Observational material.

The greater part of the observational material was gathered from the *Photometric atlas of the solar spectrum.* Our experience with the atmospheric lines and independent tests of the solar lines made by W. J. CLAAS, showed its intensity scale to be quite reliable. Moreover we checked the accuracy by photometry of some lines in the B band on first order plates photographed by MULDERS, but not used for the *atlas.* Taking all this into account we can state that *no errors larger than a few per cent will occur in the intensity scale of the atlas.* The other authors mentioned may have attained a similar accuracy.

For all this reliability, however, the resulting constants show discrepancies up to a factor 2 ! In view of this rather unexpected check we summarize the method of obtaining equivalent widths from the relative intensity curves recorded in the *atlas.* First the intensity curve is smoothed excluding other visible lines. Then the continuous background is drawn on the face of it. Finally the area is counted or measured and divided by the height of the continuum and by the dispersion, so as to give the equivalent width W expressed in Ångström units. Lines down to 5 or 1 mÅ can be measured. An abstract of our measurements is given in table 2.

TABLE 2

Equivalent widths from the photometric atlas (abstract).

BAND	LINE	λ	CONTINUUM	W
—	—	—	—	—
(A) 0 — 0	P_2 (0)	7 621,0	100,0	920 mÅ *
	P_3 (6)	7 631,0	100,0	1 133
	P_2 (6)	7 632,2	100,0	1 351
	P_3 (34)	7 709,9	101,0	12
	P_2 (34)	7 710,9	101,0	13
(B) 0 — 1	P_3 (6)	6 892,4	100,5	198
	P_2 (6)	6 893,3	100,5	215 *
	P_3 (18)	6 918,1	99,0	87
	P_2 (18)	6 919,0	99,0	91
(α) 0 — 2	P_3 (6)	6 295,2	102,5	21,8
	P_2 (6)	6 296,0	102,5	25,2
	P_3 (22)	6 328,9	99,5	2,0
	P_2 (22)	6 329,6	99,5	1,7
(α') 0 — 3	P_3 (6)	5 802,7	—	1,3
	P_2 (6)	5 803,3	—	1,3
	P_2 (14)	5 816,8	—	1,1
(A) 1 — 1	P_3 (6)	7 720,3	—	4,2
	P_2 (6)	7 721,5	—	5,2
	P_3 (14)	7 738,9	—	1,2
* with corrected continuum.				
(A) 0 — 0	P_2 (0)	7 621,0	102,5	1 110 mÅ
(B) 0 — 1	P_2 (6)	6 893,3	101,6	250

The weakest link in this scheme is known to be the second one. However, not until large discrepancies were found in the final constants, did we recognize how large an error could result from a continuus back-ground drawn at a wrong height. Lines having entended wings, such as the strong atmospheric lines are particularly sensitive to this error. Let us regard for example the line 7 621,0 of the A band. Its left wing is not blended by strong lines and can be traced as far as 4 cm from the centre. On the face of it we drew the continuum at height 100, not surmising any large error. Since the depression in the far wings is, theoretically, proportional to the inverse square of the distance from the centre, we can deduce the correct continuum. MINNAERT's method [29] unmistakebly gave the height 102,5. On integrating the far wings (cf. figure 1) we find that the cut-off parts 1 and 4 are equal to the rectangles 2

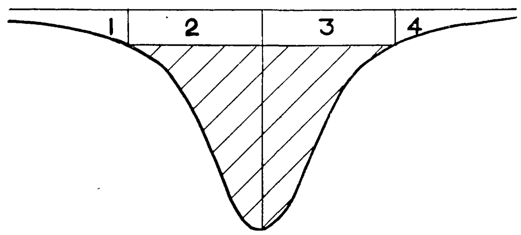

FIG. 1. — Large error in equivalent width.

and 3. The total ares must therefore be augmented by 4 × 42 × 2,5 = 420 mm i. e. 23 % of its provisional value. Accordingly the equivalent width increases from 920 mÅ to 1 110 mÅ, log W increases with 0,08 and 2 log W with 0,16.

Table 2 contains another example of such a correction : 2 log W of a strong line in the B band increases with 0,13.

Now we consider that *a*) the above examples are favoured by a free wing, by a moderate strength and by a rather high sun, *b*) in provisionally fixing the continuum the far wings had been taken into account already to a certain extent, *c*) other authors may not have evaded the same trap. These considerations warrant the conclusion that *discrepancies up to a factor* 2 *in the resulting constants may arise from a continuous back-ground drawn at a wrong height.*

Unfortunately we cannot correct each line in this way, because most wings are strongly blended. Moreover, the consistent procedure would be to analyse not only the far wings, but the total profile, including a discussion of instrumental distortion, etc. Viewed from this side *the theoretical invariancy of the equivalent width loses much of its working value when applied to strong atmospheric lines.*

For the time being we gave up the search for a more accurate position of the continuum and used the original measurements only. Eventually we may tentatively apply the following corrections to the value of log C_{II} :

A band + 0,20, B band + 0,12, α band + 0,05.

The uncorrected data from the atlas and from other sources are compiled in table 3.

TABLE 3

Compilation of observational results

Observer		MULDERS	WOOLLEY	ALLEN	CHILDS	VON KLÜBER
reference		[20] = *Atlas*	[7] 1)	[13]	[11] 2)	priv. comm. 4)
place		Mt. Wilson	Mt. Wilson	Pasadena	Bonn	Potsdam
altitude (km)		1,74	1,74	0,2	0,0	0,1
date		'36 Oct./Nov.	1930 Dec. ?	1936 ...	1936 June	1931 June
ground temperature		?	?	301	297 3)	290
		2. *Values of* $^{10}\log \sec z$ 5)				
band = vibrational transition	0 — 0	0,23 to 0,33		0,08	0,83	0,14 to 0,69
	0 — 1	0,10 to 0,22	0,24 to 0,99	0,46	0,76	
	0 — 2	0,09 to 0,10		0,70		
	0 — 3	0,22 to 0,30				
	1 — 1	0,23 to 0,33				
		3. *Effective temperatures*				
from strong lines T_{II}		264 ± 4 6)	240 ± 15	259 ± 3	276 ± 7	270 ± 7
from weak lines T_{I}		uncertain		uncertain		
		4. *Constants read from graphs* (unit = 1 sec^{-1})				
$^{10}\log C_{\mathrm{II}}$	0 — 0	20,78 ± 0,01		20,67 ± 0,02	20,45 ± 0,03	20,59 ± 0,04
	0 — 1	19,49 ± 0,01	19,35 ± 0,10	19,55 ± 0,01	19,28 ± 0,02	
	0 — 2	17,94 ± 0,08		18,18 ± 0,04		
$^{10}\log C_{\mathrm{I}}$	0 — 0	11,58 ± 0,03		11,27 ± 0,04		
	0 — 1	10,31 ± 0,02		10,05 ± 0,04		
	0 — 2	8,71 ± 0,03		8,67 ± 0,01		
	0 — 3	7,29 ± 0,05				
	1 — 1	11,41 ± 0,02				
$^{10}\log (C_{\mathrm{II}}/C_{\mathrm{I}})$	0 — 0	9,20 ± 0,03		9,40 ± 0,04		
	0 — 1	9,18 ± 0,02		9,50 ± 0,04		
	0 — 2	9,23 ± 0,08		9,51 ± 0,04		
		5. *For reducing to a normal atmosphere add* 7)				
correction for altitude	II	0,16	0,16	0,02	0,00	0,01
	I	0,08		0,01		
	II/I	0,08		0,01		
correction for temperature	II	— 0,04	— 0,04	0,04	0,04	0,02
	I	— 0,03		0,03		
	II/I	— 0,01		0,01		
total correction	II	0,12	0,12	0,06	0,04	0,03
	I	0,05		0,04		
	II/I	0,07		0,02		
		6. *Constants in a normal atmosphere* (unit = 1 sec^{-1})				
$^{10}\log C_{\mathrm{II}}$	0 — 0	20,90		20,73	20,49	20,62
	0 — 1	19,61	19,47	19,61	19,32	
	0 — 2	18,06		18,24		
$^{10}\log C_{\mathrm{I}}$	0 — 0	11,63		11,31		
	0 — 1	10,36		10,09		
	0 — 2	8,76		8,71		
	0 — 3	7,34				
	1 — 1	11,46				
$^{10}\log (C_{\mathrm{II}}/C_{\mathrm{I}})$	0 — 0	9,27		9,42		
	0 — 1	9,25		9,52		
	0 — 2	9,30		9,53		

COMMENTS ON TABLE 3. — 1) WOOLLEY gives widths of the lines at intensities 75 % and 90 % of the continuum. By comparing the empirical relation between both widths with a similar graph theoretically computed, we derived *a*) the half width of the apparatus function, tallying with the atlas value (70 mÅ near λ 6 900 in the second order); *b*) the equivalent width of each line. Neither result has a high accuracy.

2) CHILDS recorded the A band at such a low sun that both lines of a doublet have strong overlapping wings. We deduced the quotient

$$\frac{\text{sum of equivalent widths of both single lines}}{\text{equivalent widths of the doublet}}$$

from graphs of the theoretical profiles. Then we computed the numerator from the denominator measured by CHILDS. For example, from CHILDS' value $W_{\text{doublet}} = 3{,}20$ Å we find $2 \times W_{\text{single line}} = 1{,}15 \times 3{,}20 = 3{,}68$ Å. The correction rapidly vanishes for weaker doublets.

3) This value was implicity given by CHILDS' formulae.

4) Professor VON KLÜBER kindly sent us some equivalent widths of lines in the A-band underlying his paper [9].

5) When several plates of one band have been used, the extreme values of log sec z are given. All resulting constants apply to the zenith value sec $z = 1$.

6) Probable errors of all constants are roughly estimated from the spreading of the plotted points.

7) For comparison the values obtained at different observatories had to be reduced to a single " normal atmosphere ". Two corrections are needed. *a*) *Correction for altitude* : C_{I} and $C_{\mathrm{I}}/C_{\mathrm{II}}$ must be increased proportionally to N_0, the number of air-molecules at the altitude of the observatory; C_{II} is proportional to the square of this number. *b*) *Correction for temperature.* When we assume a constant pressure, a high T_0 implies a low N_0. The corrections are then :

in C_{II} proportional to $N_0^2 T_0^{-1/2} \sim T_0^{-5/2}$
in C_{I} " " $N_0 T_0^{-1} \sim T_0^{-2}$
in $C_{\mathrm{II}}/C_{\mathrm{I}}$ " " $N_0 T_0^{1/2} \sim T_0^{-1/2}$

4. RESULTS OF TEMPERATURE DETERMINATION.

The effective temperature T_{II} is deduced from the strong lines obeying the square root law. Theoretically it is related to the temperature T_0 at the observing station by

$$T_0 = 1{,}09\ T_{\mathrm{II}}. \tag{34}$$

This relation permits of a computation of T_0 from the observed equivalent widths and thus provides a check on both theory and observations. Table 4 shows an excellent agreement.

TABLE 4

Temperature determination.

OBSERVER	T_{II}	$T_0 = 1{,}09\ T_{\mathrm{II}}$	TRUE T_0
—	—	—	—
Mulders	246 ± 4	268	near freezing
Woolley	240 ± 15	262	near freezing
Allen	259 ± 3	282	301
Childs	276 ± 7	301	297
Von Klüber	270 ± 7	294	290

The difference between summer and winter observations is evident. The agreement is the more remarkable in view of the large errors presumably present in the underlying equivalent widths.

A similar determination of T_0 from weak lines obeying the linear law is far more uncertain, because of random errors. Another determination would follow from the relative intensities of the 0–0 band and the 1–1 band, once their transition probabilities are known. But the relative intensities of the bands 0–0, 0–1, 0–2 have nothing to do with temperature since they arise from the same molecular state. For that reason SEVERNY's discussion [28] of the subject is entirely erroneous.

5. RESULTING DAMPING CONSTANTS.

We notice two empirical facts. *a*) The damping constant does not sensibly vary with the rotational quantum number J. This supposition, underlying our theoretical treatment, is confirmed by the agreement between theory and observations as regards the effective temperature T_{II}. *b*) The damping constant does not sensibly vary with the vibrational bands. This is inferred at once from the values C_{II}/C_I in table 3. For these reasons, pressure and temperature being given, *a single damping constant applies to all atmospheric oxygen lines.*

As to the local variation there is no such evidence. From table 3, part 4 we read the mean values log (C_{II}/C_I) = 9,19 from the atlas and 9,47 from ALLEN's measurements. Only part of the discrepancy is accounted for by the different positions of the observatories. A difference 9,49 — 9,27 = 0,22 is left after reduction to a normal atmosphere. Taking the atmospheric conditions into account in more detail, for example a steeper temperature gradient of the summer air, might give a further improvement, but a discrepancy of this amount cannot be explained. Evidently observational errors are the chief cause. This is no wonder since C_{II}/C_I is the quotient of two empirical constants, both of which are susceptible of large errors. When tentative corrections are applied to C_{II} (cf. section 3), the mean atlas value increases 9,40, which at the same time may be the most probable value. It yields the local damping constant on Mt. Wilson level b_0 = 2,32 micro wave lengths near λ 6 300 ; we assumed this value in deducing the apparatus function of the atlas [22].

The definition of C_{II}/C_I is : $1/\pi \times$ effective damping constant of lines starting from low states, observed from sea level in a normal atmosphere. By adding 0,32 to its logarithm we find the local value of $1/\pi \times$ damping constant. We compute then the *optical collision diameter* σ by substituting (c. g. s. units)

$$\log N_0 = 19{,}41 \qquad \log T_0 = 2{,}46 \qquad (44)$$
$$\log \mu_1 = \log \mu_2 = 1{,}50$$

into (17). Table 5 summarizes the results. The resulting probable value σ = 4,1 Å exceeds the kinetic collision diameter decidedly.

A *direct* determination of the effective damping constant from the profile of a weak line is hampered — but not frustrated — by instrumental distortion. We doubt whether PANOFSKY's interferometer measurement [12] is sufficiently free from this error. The apparatus function of a grating spectrograph is too broad for a correct determination of the damping constant ; the obvious line of research there rather points the other way. But *differential measurements* of lines starting from high and low molecular states might show the differences in damping constant. We gave this possibility a test by measuring in the atlas : *a*) the halfwidths of some high lines in the main A band ; and *b*) the halfwidths of some free lines in the isotope A band. When extrapolated towards a central depression 0, a small but definite difference $a - b = 2{,}26 - 2{,}18 = 0{,}08$ mm results. This tallies with our theoretical statement that higher lines must have a greater effective damping constant.

TABLE 5

Effective damping constant and collision diameter.

	$\log (C_{II}/C_I)$	$\log \sigma$
	—	—
from atlas uncorrected	9,27	0,54 — 8
from atlas corrected	9,40	0,61 — 8
from ALLEN's equivalent widths	9,49	0,66 — 8
derived by ALLEN	—	0,62 — 8
direct determination by PANOFSKY	—	0,71 — 8
probable value	9,40	0,61 — 8
kinetic collision diameter		0,43 — 8

6. RESULTING TRANSITION PROBABILITIES.

The transition probabilities can be deduced from C_I and, if the damping constant is known, from C_{II} as well. The values in all entries of table 3 part 6 should be identical. They show, however, quite irregular variations. Every attempt to explain these as real variations, for example arising from deviating conditions in the atmosphere or from a deviating behaviour of the damping constant, is disproved by two arguments. *a*) The discrepancies are too great ; and *b*) From his daily measurements of the intensity of the A band in prismatic dispersion LEJAY [23] found no distinct seasonal variations. There remain only observational errors to account for these discrepancies. As to the values of C_I this is not unlikely, though the differences are on the high side. The C_I of the A band and B band in particular is based on a few weak lines only. In section 3 we have shown besides, that the troublesome wings involve the possibility of strongly underestimating C_{II}. The low values found at low sun (CHILDS and VON KLÜBER) tally with this explanation. No definite conclusions can be drawn, however, without a new extensive analysis of accurate measurements. For the time being we assume log $(C_{II}/C_{I}) = 9{,}40$ and drop all measurements by other authors. The atlas values of C_{II} and C_{I} in a normal atmosphere give the mean values of log C_{I} presented in table 6.

TABLE 6

Empirical values of molecular absorption coefficient K and absolute transition probability B_{nm}.

BAND $n - m$		log C_{I}	log K	log B_{nm}
(A)	0 — 0	11,66	9,11 — 20	11,17
(B)	0 — 1	10,34	7,79 — 20	9,81
(α)	0 — 2	8,74	6,19 — 20	8,17
(α')	0 — 3	7,34	4,79 — 20	6,73
(A)	1 — 1	11,46	8,91 — 20	10,98

Finally by substituting these values and (33), (40), (44), in (42) we deduce the molecular absorption cœfficient K and by (2) the EINSTEIN transition probability B_{nm}.

Slightly different methods of deriving the transition probabilities have been applied by several authors.

1. PANOFSKY finds log $K = 6{,}20 - 20$ from interferometer measurements of some lines in the α band. This value is in fair agreement both with ALLEN's and with the atlas values. 2. MECKE & CHILDS measured the transition probability of the A band in the laboratory. Their result log $B_{00} = 11{,}02$ is not reliable, since they did not measure equivalent widths. Yet this method promises well for future investigations. 3. BAUMANN & MECKE deduced the relative transition probability log B_{11} — log $B_{00} = -0{,}10$ from estimates of equality. This method has the advantage of giving results free from systematic errors. 4. In a similar way BABCOCK's note on the 1 — 2 band led us to the estimate log B_{12} — log $B_{01} = +0{,}03$ to $+0{,}08$. It is to be noted that this difference has the opposite sign, just as we expect from the quantum mechanical computation now to be discussed.

7. QUANTUM MECHANICAL CALCULATION OF RELATIVE TRANSITION PROBABILITIES.

A theory of transition probabilities in diatomic molecules has been given by HUTCHISSON [24] and discussed by DUNHAM [26]. We applied this theory to the oxygen molecule. Our lack of knowledge of the electron wave functions is the reason why only rough estimates of the absolute transition probability can be made. The relative values, however, are dependent on the radial wave functions of the nuclear movement only, if some interaction terms are neglected. The matrix elements are (1)

(45) $$q_{nm} = \int R'_n(r) R''_m(r) \mathrm{d}r.$$

Their squares are proportional to the EINSTEIN transition probabilities B_{nm}. R' and R'' denote the radial wave functions of lower and higher states respectively. For these, HUTCHISSON takes the wave functions of two harmonic oscillators, the frequency and zero of which are different. This is expressed by the parameters α and δ. In the case of the atmospheric oxygen bands these parameters are

(46) $$\alpha = (\omega''/\omega')^{1/2} = 0{,}95,$$

$$\delta = (\omega''/2)^{1/2}(B''^{-1/2} - B'^{-1/2}) = 0{,}356,$$

found by substituting $B' = 1{,}446$, $B'' = 1{,}401$, $\omega' = 1\,580{,}3$, $\omega'' = 1\,432{,}6$ (cm^{-1}). The last columm of table 7 contains the values $2 \log |q_{nm}|$.

In comparing these with the observed values taken from table 6 we should consider the following points.

1. Formula (45) is deduced under supposition of an electric dipole transition, for which the matrix elements of the place vector $\vec{r}$ are needed. For a *magnetic dipole* transition we need matrix elements of the operator

$$\frac{\hbar}{2im}\left(\overrightarrow{\mathrm{grad}} - \overleftarrow{\mathrm{grad}}\right).$$

The difference, however, affects only the absolute value ; the relative value (45) is the same in both cases.

2. The oscillators are not strictly harmonic, nor may the interaction terms be neglected completely. The first variance might be taken into account by a very complicated calculation [26]. The second one is considerable as appears from the fact that the relative weights $2i$ of the rotational lines deviate from their theoretical values.

3. If the oscillators were identical, q_{mn} would be 1 for $n = m$ and 0 for $n \neq m$. The nearer the real values approach to 0, the more sensitive they become to the above objections.

(1) SEVERNY [28] wrongly refers to the matrix elements $\int R_n(r) r R_m(r) \mathrm{d}r$, computed by SCHOLTZ [27], which apply to purely vibrational bands.

TABLE 7

Relative transition probabilities.

BAND $n - m$	log (B_{nm}/B_{00}) OBSERVED	COMPUTED
—	—	—
0 — 0	0	0
0 — 1	— 1,36	— 1,16
0 — 2	— 3,00	— 3,84
0 — 3	— 4,44	— 4,0
0 — 4	—	— 5,4
1 — 1	— 0,19	— 0,06
1 — 2	(— 0,8)	— 0,86

In view of these considerations and the observational uncertainties, the agreement shown by table 7 is quite satisfactory. In particular the ratios between the first and second A and B bands are well confirmed.

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TABLE 8

Literature on the atmospheric oxygen bands.

VIBRATIONAL TRANSITION		λ	$O_{16}O_{16}$ FREQUENCIES	$O_{16}O_{16}$ INTENSITIES	λ	$O_{16}O_{18}$ FREQUENCIES	INTENSITIES
—		—	—	—	—	—	—
(A)	0 — 0	7 621	1	7 — 10	7 620	16,17	19
(B)	0 — 1	6 884		11	6 901	18	18
(α)	0 — 2	6 288	2 3	12 13	6 317	(18)	
(α′)	0 — 3	5 796					
(αê)	0 — 4	5 384					
(A)	1 — 1	7 710	4	4			
(B)	1 — 2	6 975	5				
Theory			6	14, 15		18	19

REFERENCES TO TABLE 8.

[1] R. M. Badger & R. Mecke, *Z. Phys.*, **60**, 59, 1930.
[2] G. H. Dieke & H. D. Babcock, *Proc. Nat. Ac. Sci*, **13**, 670, 1927.
[3] W. Ossenbrüggen, *Z. Phys.*, **49**, 167, 1928.
[4] R. Mecke & W. Baumann, *Z. Phys.*, **73**, 139, 1932.
[5] H. D. Babcock, *Phys. Rev.*, **51**, 148, 1937.
[6] H. A. Kramers, *Z. Phys.*, **53**, 422, 1929.
[7] R. v. d. Riet Woolley, *Ap. J.*, **73**, 185, 1931.
[8] D. Eropkin, *Poulkowo Obs. Circ.*, **2**, 16, 1932.
[9] H. von Klüber, *Z. Ap.*, **6**, 161, 1933.
[10] W. H. J. Childs & R. Mecke, *Z. Phys.*, **68**, 344, 1931.
[11] W. H. J. Childs, *Phil. Mag.*, **14**, 1049, 1932 and *Ap. J.*, **77**, 212, 1933.
[12] H. A. Panofski, *Publ. Asvr. Soc. Pac.*, **53**, 239, 1941 (abstract) ; only recently we received the full paper *Ap. J.*, **97**, 180, 1943.
[13] C. W. Allen, *Ap. J.*, **85**, 156, 1937.
[14] R. Schlapp, *Phys. Rev.*, **39**, 806, 1932.
[15] J. H. van Vleck, *Ap. J.*, **80**, 161, 1934.
[16] R. Mecke & W. Wurm, *Z. Phys.*, **61**, 37, 1930.
[17] H. D. Babcock, *Proc. Nat. Ac. Sci.*, **15**, 471, 1929.
[18] D. Eropkin & V. Kondratjew, Acad. Sci. U. R. S. S. *Bulletin de la commission du soleil*, **8**, 1934.
[19] R. Mecke & W. H. J. Childs, *Z. Phys.*, **68**, 362, 1931.

FURTHER REFERENCES

[20] M. Minnaert, J. Houtgast & G. Mulders, *Photometric atlas of the soalr spectrum*, Amsterdam, 1940.
[21] H. C. v. d. Hulst (preceding article).
[22] H. C. v. d. Hulst, *B. A. N.*, **10**, 71, 1945.
[23] P. Lejay, *C. R.*, Paris, **205**, 585, 1937.
[24] E. Hutchisson, *Phys. Rev.*, **36**, 410, 1930.
[25] E. Hutchisson, *Phys. Rev.*, **37**, 45, 1931.
[26] J. L. Dunham, *Phys. Rev.*, **36**, 1553, 1930.
[27] K. Schöltz, *Z. Phys.*, **78**, 751, 1932.
[28] A. B. Severny, *Astr. J. Sovjet Union*, **15**, 350, 1938.
[29] M. Minnaert, *Z. f. Astrophys.*, **10**, 40, 1935.