

The Continuous Absorption of Oxygen Between 1750 and 1300A and Its Bearing Upon the Dispersion

R. LADENBURG AND C. C. VAN VOORHIS, *Palmer Physical Laboratory, Princeton University*

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In connection with recent measurements of the dispersion of oxygen down to 1920A, the continuous absorption of oxygen between 1750 and 1300A has been investigated quantitatively with a small fluorite spectrograph by the photographic-photometric method. The results are given in a graph, which shows that the absorption coefficient α as function of the wave number ν has a relatively sharp maximum at $6.8 \times 10^4 \text{ cm}^{-1}$ ($\lambda = 1450\text{A}$) and falls off rather symmetrically on both sides. The maximum absorption coefficient reduced to N.P.T. is about 490 cm^{-1} . The absorption in this region of the spectrum is so strong that during a few minutes exposure a great part of the oxy-

gen disappears, being dissociated and probably absorbed by the metal walls of the tube. By integration of the absorption curve one gets the corresponding f -value according to the equation $\int \alpha(\nu) d\nu = \pi N f e^2 / mc^2 = (2.38 \times 10^7) f$. The f -value calculated from this expression is 0.193 compared with 0.202 calculated from the dispersion measurements. The corresponding resonance wave-length from the dispersion measurements is 1468 in fairly good agreement with the observed position of the maximum of absorption. A dispersion formula which takes into account the distribution of absorption in a continuous band is given, and is applied to the dispersion of oxygen.

IN a recent paper, Ladenburg and Wolfsohn have shown,¹ that the dispersion of oxygen between the visible and 1920A can be described quantitatively by three resonance wave-lengths $\lambda_1 = 1899\text{A}$, $\lambda_2 = 1468\text{A}$ and $\lambda_3 = 544\text{A}$, with the three corresponding "strengths" (number of oscillators per atom) $f_1 = 4.0 \times 10^{-5}$, $f_2 = 0.202$ and $f_3 = 5.93$.

λ_1 can be ascribed to the Schumann-Runge band $\nu'' = 0 \rightarrow \nu' = 5$ the head of which lies at 1903A, and has according to its very small f value only a slight influence upon the dispersion and only in the region up to 1960A. The influence of the even weaker bands² (0.4), (0.3) \dots at 1923, 1945 \dots seems to be negligible. The resonance wave-length λ_2 has obviously to be attributed to the continuous absorption on the short wave-length side of the Schumann-Runge bands which sets in at 1750A. In order to learn more about this absorption as well as about the even stronger absorption at lower wave-lengths $-\lambda_3$ being $= 544\text{A}$ and $f_3 = 5.93$, i.e., approximately 30 times as large as f_2 , we have investigated the absorption of oxygen by means of vacuum spectrographs, partly in collaboration

with J. C. Boyce. A preliminary account of these investigations was published some months ago.³ The qualitative experiments carried through by means of the 2 meter vacuum grating spectrograph, designed by Drs. K. T. Compton and J. C. Boyce, showed strong absorption of oxygen from 1100A down and still quite strong at 300A, the estimated maximum of which is in fair agreement with the resonance wave-length.

A more complete account of our experiments on the continuous absorption spectrum of oxygen between 1750 and 1300A and of its bearing upon the dispersion is the subject of this paper.

APPARATUS AND EXPERIMENTAL PROCEDURE

Spectrograms recording the O_2 absorption were obtained by the use of a hydrogen discharge tube, which gives many strong lines in the spectral region investigated, an absorption cell with suitable diaphragms, and a Cario and Schmidt-Ott fluorite spectrograph,⁴ all connected together with white wax as shown in Fig. 1. The H_2 discharge tube was constructed of Pyrex glass and had a water-cooled capillary about 5 mm inside diameter and 17.5 cm long, coated inside

¹ R. Ladenburg and G. Wolfsohn, *Zeits. f. Physik* **79**, 42 (1932).

² Cp. W. Weizel, *Handb. Experimental-Physik, Ergänzungsband I*, 366 (1931).

³ R. Ladenburg, C. C. Van Voorhis and J. C. Boyce, *Phys. Rev.* **40**, 1018 (1932) (Letter to the Editor).

⁴ G. Cario and H. D. Schmidt-Ott, *Zeits. f. Physik* **69**, 719 (1931).

with a layer of silver so thin that it conducted practically none of the electric current. Electrolytic hydrogen dried over P_2O_5 was used in the discharge tube at about 1 mm pressure, a 5 liter flask serving as a stabilizing reservoir during a run.⁵ The electrodes were aluminum hollow

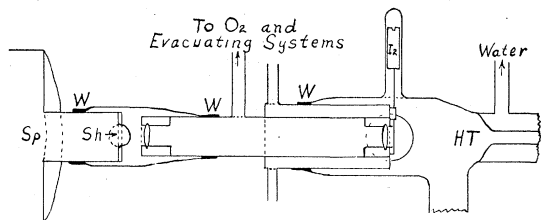


FIG. 1. Connections between hydrogen tube *HT*, absorption tube and spectrograph *Sp*.

cylinders 8 cm long and 4 cm in diameter and the direct current of from 15 to 100 milliamperes was supplied by a 3000 volt motor-generator set run on a large storage battery to ensure constant current.⁶ Beakers of water surrounding the electrode chambers prevented overheating of the electrodes. To allow for the use of a quartz mercury lamp in adjusting the optical system a quartz plate was sealed to one end of the discharge tube. The other end of the discharge tube was provided with the necessary openings and side tubes for waxing in the absorption chamber and mounting the set of diaphragms and its controls. Fig. 2 shows in detail the construction of the absorption chamber and diaphragm system. The absorption chamber whose length between lenses was 12.3 cm was made of brass and all parts were nickel-plated after being fabricated. The fluorite lenses *F* were waxed into the ends of the chamber with white wax. The caps *C*₁ and *C*₂ and lead washers *L* serve to hold the lenses in place, thus relieving any strains on the wax when there is high pressure in the absorption chamber and low pressure in the discharge tube and spectrograph. The cap *C*₂ was fastened with set screws to allow for the proper orientation of the diaphragm carrier which it also supports. To prevent possible heating to

⁵ As there are no strong hydrogen lines above $\lambda = 1645\text{\AA}$ we used the CO lines obtained by adding a slight amount of CO_2 to the hydrogen for investigating the longer wavelengths.

⁶ Direct current is important for photographic-photometric measurements.

the softening point of the wax in the end sealed into the H_2 discharge tube this end was surrounded by a water jacket constructed as shown in Fig. 2. Though this end enters the discharge tube the resistance of about 10 meters of tap water flowing through rubber tubing was enough to prevent any appreciable discharge to the absorption tube when the nearest electrode was grounded.

The set of diaphragms consisted of five with relative open spaces for *a*, *b*, *c*, *d* and *e* of 1.000, 0.494, 0.244, 0.131 and 0.062 (accuracy within 2 percent) respectively, as determined with a projector lamp, thermopile and galvanometer. The diaphragms were mounted in a carrier with the openings symmetrical about the vertical axis as shown in Fig. 2. The diaphragm carrier slid in grooves in cap *C*₂ thus allowing each diaphragm to be brought into position in front of the lens and very close to it, by means of a solenoid acting on the soft iron rod *I*₁ which slid in a horizontal glass side tube of the discharge tube. The spring *S* in an opposite horizontal side tube and the ratchet *R* catching in the notches *N* served to locate the diaphragms exactly in front of the lens, the ratchet being lifted at will by another solenoid around *I*₂ in a third side tube rising vertically.

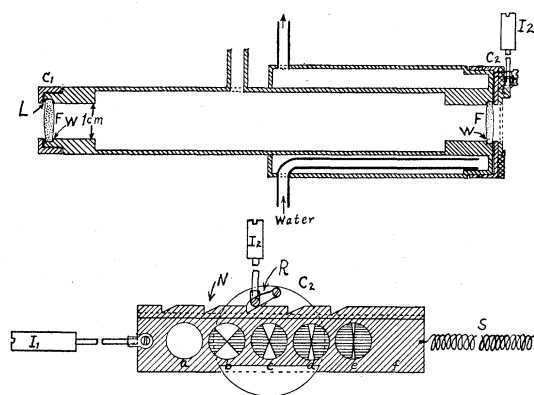


FIG. 2. Absorption tube and diaphragms.

The end of the discharge tube receiving the one end of the absorption tube and the diaphragm system was so dimensioned as to locate the lens about 5.5 cm from the near end of the discharge tube capillary. The spectrograph was so placed that the slit was about 6.0 cm from the

second lens of the absorption tube, 6.0 cm being the focal length of each lens for $\lambda = 1450$.

The O_2 used in the absorption chamber was prepared by the electrolysis of dilute H_2SO_4 and dried over P_2O_5 ; the pressure of the O_2 giving suitable results was between 1.86 mm and 0.079 mm (Hg).

Eastman Type 3-0 Ultra Violet Sensitive Plates⁷ were used in the spectrograph because though the grain was coarser than in Nujol-sensitized Cramer Contrast Plates the former were likely to be more uniform over the whole area of the plate than the latter. After exposure the plates were rinsed in acetone to remove the sensitizing dye and were then developed for three minutes in 1 to 20 Rodinal solution. Seven spectrograms could be made on each plate.

The following is the procedure used in making the spectrograms. After running the H_2 discharge tube for a half-hour or more to obtain constant conditions, four or five exposures were made for a given length of time, each with a different diaphragm in front of the absorption chamber. Then the three (or two) remaining exposures were made for the same length of time with the fully open diaphragm *a* in position and suitable pressures of O_2 in the absorption chamber. Thus under proper conditions two or three independent sets of results could be obtained from each plate. The times of exposure for different plates varied in our work from 20 to 120 seconds with a possible timing error of less than 0.4 second, a magnetically-operated sliding shutter *Sh* (Fig. 1) serving to open and close the spectrograph.

Rather large discrepancies appeared in the earlier results, some of which were obtained with the volume of O_2 in communication with the absorption tube small (about 30 cc) because of a nearby stopcock being closed, and others with the much larger volume of the McLeod gauges, liquid air trap and connecting tubing, i.e., about 425 cc, in communication. These discrepancies were found to be due to a very large "clean up" action in O_2 produced by light in this region of the spectrum. This disappearance of O_2 molecules is attributed to their optical dissociation by the short wave-lengths and presumably to consequent adsorption or chemical action on the metal surface of the absorption chamber or to the

formation of O_3 . The spectrograms whose positives are reproduced in Fig. 3 illustrate this clean up effect. Spectrograms 1, 2, 3 and 4 were taken with diaphragms *a*, *b*, *c* and *d*, respectively, then 5 was made, with diaphragm *a* in place, immediately after the 425 cc volume had been filled with O_2 at 0.27 mm pressure, and 6 and 7 were made 3 and 20 minutes, respectively, after the stopcock had been closed, limiting the volume to about 30

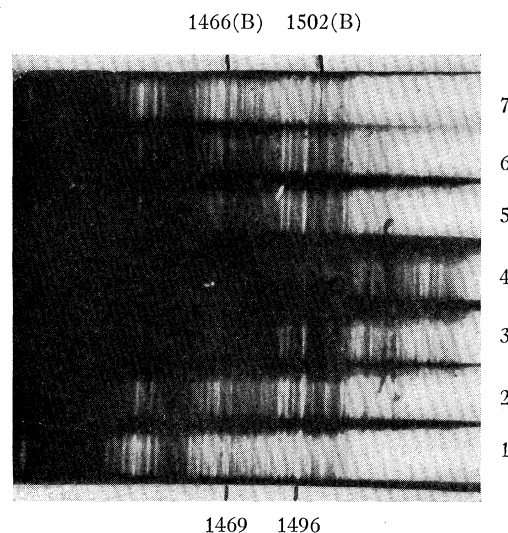


FIG. 3. Positives of spectrograms. Six and seven show the effect of clean up.

cc. At the end of the 20 minutes the light absorption of the O_2 was only 20 to 25 percent of its value at the beginning, i.e., from 75 to 80 percent of the O_2 molecules apparently had been "cleaned up." The discharge tube current for this run was 70 milliamperes, and plate exposure time 20 seconds for all seven spectrograms. To minimize the error resulting from the "photo-cleanup" effect on the O_2 pressure, the light was completely cut off from the absorption tube until just before an exposure was to be made, by drawing the solid end *f* (Fig. 2) of the diaphragm carrier in front of the lens, the larger volume (425 cc) of O_2 being always connected with the absorption chamber.

MEASUREMENT OF THE PLATES AND CALCULATION OF RESULTS

The absorption of O_2 was measured between 1670 and 1334A. The relative densities of the

⁷ Cf. C. E. Kenneth Mees, J.O.S.A. 21, 754 (1931).

lines (and of the continuous background⁸) of the several spectrograms on a plate were found by means of a photoelectric densitometer whose readings were rather accurately proportional to the transparency of the plate (which is of course not indispensable for the method used but rather useful) the reciprocals of the densitometer readings giving the relative densities.

For the calculations from the experimental data the absorption coefficient β was defined by the equation

$$I = I_0 e^{-\beta p l} \quad (1)$$

where I_0 is the intensity of the light passing through the absorption tube when evacuated, I the light intensity after passing through a column of O_2 (in the absorption tube) of length l in cm and pressure p in cm (of Hg) at temperature 20° . For most of the spectrograms l was = 12.3 cm though some measurements were made with the spectrograph filled with O_2 , so that the light path for the wave-lengths investigated was nearly 3 times as large (34.5 cm). The β values calculated from these latter spectrograms agreed with the others within the errors of measurement. In order to correct for the effect of the part of continuous background on our plates because of scattered and fluorescence light in the spectrograph, the following graphical method was used to calculate the values of β for the different prominent hydrogen lines. For each line, logarithms of one thousand times (to make all logs positive in sign) the reciprocal of the densitometer scale readings in mm of the spectrograms taken with the absorption tube evacuated and the several diaphragms successively in position, were plotted as ordinates against the logarithms of the actual light intensities in percent, determined by the diaphragms, as abscissas. Then smooth curves were drawn through these points as shown in Fig. 4 for the examples $\lambda 1469$ and $\lambda 1496$ of the plate shown in Fig. 3, these lines having been chosen as illustrations, because the former is on this plate near the limit in weakness with which it was possible to make calculations

⁸ In order to get good measurements the slit of the spectrograph had to be moderately wide, and on account of this, that part of the background which was produced by stray light of other wave-lengths was rather disturbing. This disturbance would be less if a spectrograph of wider dispersion were used.

while the latter is one of the very strongest lines. A small extrapolation of the curves when necessary can be done fairly accurately, because they must approach asymptotically the level marked "Clear Plate" in Fig. 4 which is determined by the densitometer readings in the dimmest parts of the spectrograms. From these plate-calibration curves the intensities of the light of these same wave-lengths after passing through some O_2 in the absorption chamber are found in the usual way. Also the apparent intensities of the light producing the continuous background of the plate is found in the same way from these curves and the densitometer readings of the clearer spaces between the lines of the plate. Thus, as shown in Fig. 4, with the absorption tube evacuated the intensity of the background, $\lambda 1466$ (B) is 53.8 percent of the total intensity of $\lambda 1469$ plus background, hence the true inten-

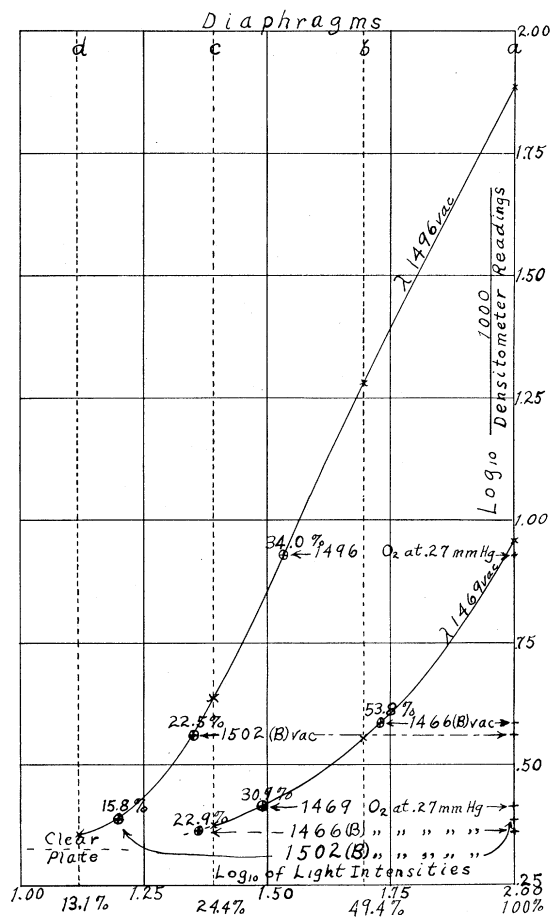


FIG. 4.

sity of $\lambda 1469$ alone is 46.2 percent of its apparent intensity. Likewise with 0.27 mm O_2 in the absorption tube, the apparent intensity of $\lambda 1469$ is 30.9 percent of the apparent intensity without O_2 , of which 22.9 percent is due to the background (the intensity of the light producing the background not being diminished by the same proportion as $\lambda 1469$), hence the true value of the unabsorbed $\lambda 1469$ is $30.9 - 22.9$ or 8.0 percent, consequently $I = 8.0/46.2 = 0.173$ or 17.3 percent of I_0 , and therefore, for $\lambda 1469A$

$$\beta = \left(\frac{2.30}{12.3}\right) \left(\frac{2 - \log 17.3}{0.027}\right) = 5.28.$$

For line 1496

$$I = (34.0 - 15.8)/(100 - 22.5) = 0.235$$

or 23.5 percent of I_0 , and

$$\beta = 0.187(2 - \log 23.5)/0.027 = 4.36.$$

Because of the disturbing influence of the background and the uncertainty of photographic-photometric measurements in this region of the spectrum we estimate that the error of the β values obtained may be as much as 5–10 percent.

RESULTS AND DISCUSSION

The results are shown in the graph of Fig. 5 where we have drawn a smooth curve, although the measured values in the region of 6.6×10^4 seem to indicate a slight bend in the curve. Abscissas are wave numbers and the ordinates are absorption coefficients α which have been obtained by reducing the mean values of β mentioned in the last paragraph to N.P.T. of oxygen.

The absorption curve resembles a nearly symmetrically broadened spectral line with its maximum at $\nu = 69,000$, $\lambda = 1450A$, where the absorption is so strong that a layer of 0.0014 cm of O_2 at N.P.T. would reduce light of this wave-length to about one-half of its intensity. The absorbed light produces dissociation of the oxygen molecule into the atoms one of which is excited to the 1D level. This action of the light is the cause for the clean up effect described above.

For $\lambda > 1700$ and $< 1350A$ the absorption becomes very low—as a matter of fact our above-mentioned measurements with a large two meter

grating spectrograph made in collaboration with Dr. J. C. Boyce have shown that between $\lambda 1300$ and 1100 oxygen of 0.25 mm pressure is practically transparent in a layer of 4 m length. Above 1750A the line spectrum of the Schumann-Runge bands sets in, and we learn from our results that the absorption in these band lines is very much smaller than in the continuous part below 1700. This is just what one should expect from the application of the Franck-Condon principle to the potential energy curves of O_2 calculated by Morse⁹ and Stueckelberg.¹⁰ Recently Stueckelberg has shown¹¹ that it is even possible to calculate the distribution of the continuous absorption of O_2 from these potential energy curves following the way shown by Condon.¹² The thus calculated absorption curve is in fairly good agreement with our measurements.¹³

Finally we can compute the f value from the graph of the absorption coefficient by assuming

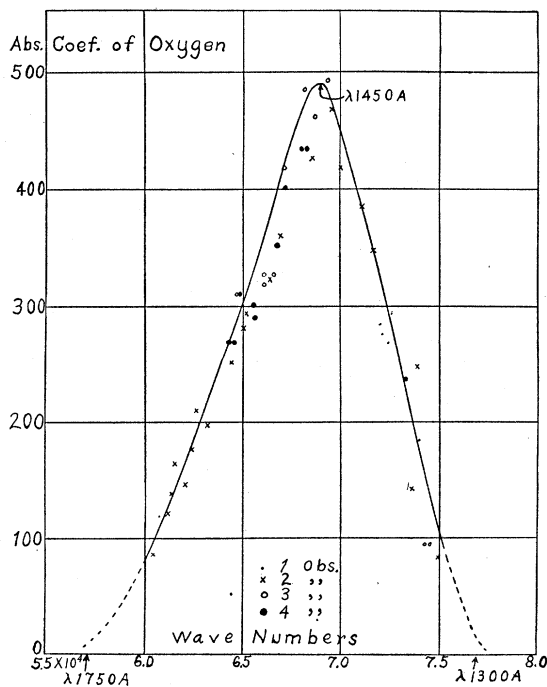


FIG. 5. Absorption coefficients of oxygen between 1750A and 1300A.

⁹ P. M. Morse, Phys. Rev. **34**, 57 (1929).

¹⁰ E. C. G. Stueckelberg, Phys. Rev. **34**, 65 (1929).

¹¹ E. C. G. Stueckelberg, Phys. Rev. **42**, 518 (1932).

¹² E. U. Condon, Phys. Rev. **32**, 858 (1932).

¹³ Compare Fig. 4 of Stueckelberg's second paper.

the classical relation between absorption and dispersion¹⁴

$$\int \alpha d\nu = \pi N f e^2 / mc^2 = f \times 2.38 \cdot 10^7 \quad (2)$$

where N means the number of molecules at N.P.T.¹⁵ Thus we get for the absorption of oxygen in the Schumann region the value $f=0.193$ and $\lambda_{\max}=1450\text{\AA}$ in very good agreement with the conclusions drawn from the dispersion curve.¹⁶

Added in proof

On the other hand, since we know now the real distribution of absorption in the continuous part on the short wave-length side of the Schumann-Runge bands it seems worth while to calculate the influence of this continuous absorption upon the dispersion. For such calculations the following formula for the refractive index seems reasonable.

$$n(\nu) - 1 = C \left[\sum_s \frac{f_s}{\nu_s^2 - \nu^2} + \int \frac{\varphi(\omega) d\omega}{\omega^2 - \nu^2} \right] \quad (3)$$

where $C = Ne^2/2\pi mc^2$, the ν_s are resonance frequencies and f_s the corresponding "strengths." Now in analogy to the relation

$$\int \alpha d\omega = (\pi Ne^2/mc^2) f \quad (\text{compare Eq. (2)})$$

we may write

$$\alpha(\omega) = (\pi Ne^2/mc^2) \varphi(\omega),$$

so that Eq. (3) goes over into the equation¹⁷

$$n(\nu) - 1 = C \sum_s \frac{f_s}{\nu_s^2 - \nu^2} + \frac{1}{2\pi^2} \int \frac{\alpha(\omega) d\omega}{\omega^2 - \nu^2}. \quad (4)$$

This formula is obviously the reasonable generalization of a dispersion formula for a gas (outside its region of absorption) which shows a continuous absorption band besides its absorption lines—as every gas does.

¹⁴ R. Ladenburg, Verh. d. D. Phys. Ges. **16**, 769 (1914); Zeits. f. Physik **4**, 451 (1921).

¹⁵ The values used are: $N = 2.706 \times 10^{19}$, $e = 4.770 \times 10^{-10}$, $e/mc = 1.76 \times 10^7$ and $c = 2.998 \times 10^{10}$.

¹⁶ It should be mentioned that from his measurements of the dispersion of air, J. Koch in 1912, had already deduced a resonance frequency of 1421\AA which he attributed to oxygen (Archiv. f. Math. Astr. och Fysik **8**, No. 20 (1912)). This paper was overlooked in the work of Ladenburg and Wolfsohn.¹

¹⁷ Compare the formula for the dispersion of Roentgen rays (H. Kallmann and H. Mark, Ann. d. Physik [4] **82**, 587 (1927) and other authors).

The integral

$$G(\nu) \equiv \frac{1}{2\pi^2} \int_a^b \frac{\alpha(\omega) d\omega}{\omega^2 - \nu^2}$$

between the limits $a=56,000$ and $b=78,000$ by using our values of α for oxygen given in the graph of Fig. 5 was kindly calculated for us by Mr. F. Seitz.¹⁸ In the following Table I the

TABLE I. Influence of the continuous absorption between 1750 and 1300\AA upon the dispersion of oxygen.

ν	λ	$G(\nu)$ $\times 10^7$	$(n(\nu)-1)$ $\times 10^7$	$H(\nu)$ $\times 10^7$	$I(\nu)$ $\times 10^7$
55,000	1818\AA	1612			
52,084	1920	1277	3589	2312	2330
51,020	1960	1193	3508	2315	2323
50,000	2000	1125	3441	2316	2317
45,000	2222	907	3195	2288	2288
40,000	2500	768	3036	2268	2262
35,000	2860	680	2921	2241	2240
30,000	3333	618	2838	2220	2222
25,000	4000	573	2775	2202	2206

results for different values of ν between 55,000 and 25,000 ($\lambda=1818$ and 4000\AA) are given to as many places as the values of the dispersion of oxygen $(n(\nu)-1)$ measured by Ladenburg-Wolfsohn (L-W) which are also given in the table. The possible error of the G -values is at least ten times that of the dispersion values which are accurate to within one unit. If we try to represent the differences $n(\nu)-1-G(\nu) \equiv H(\nu)$ by one term $C \cdot f_s / \nu_s^2 - \nu^2 \equiv I(\nu)$ (comp. Eq. (4)) we get the values $f_s = 7.143$ and $\lambda_s = 1/\nu_s = 501.3\text{\AA}$ instead of $f_s = 5.928$ and $\lambda_s = 544.4\text{\AA}$ as was originally found by L-W who fitted the dispersion measurements by the usual formula with single resonance frequencies (compare p. 315). The agreement between the values $I(\nu)$ calculated in this way and the observed values $H(\nu)$ is quite good, considering the inaccuracy of the G -values and the fact that only two arbitrary constants f_s and ν_s are now used instead of four. The apparent systematic deviation at the highest frequencies ($\lambda = 1960-1920\text{\AA}$, compare the table) can be explained by a slight change in the α -values within the errors of the absorption measurements.

¹⁸ We want to thank Mr. Seitz as well as Professor E. U. Condon for their valuable help in this matter.

This comparison shows further that not much weight can be put on the meaning of the resonance frequency ν_1 ($\lambda_1=1899\text{\AA}$) and the corresponding f -value $4.04 \cdot 10^{-5}$ as originally calculated from the dispersion measurements (compare p. 315). It is necessary to introduce this frequency as long as the dispersion measurements down to 1920\AA are represented by single resonance frequencies. But by taking into account the continuous absorption band it appears quite possible that the single weak lines of the Schumann-Runge bands have no appreciable influence upon the dispersion down to 1920\AA . But the absorption measurements are not accurate enough to decide this question.

The result of these considerations is that on the whole it is quite a good approximation to represent the dispersion measurements of molecular gases as oxygen by the usual dispersion formula using isolated resonance frequencies instead of taking care of the distribution of absorption in the absorption band, and when the dispersion measurements go near enough to the absorption band one gets in this way the position of the center of gravity of the absorption band and the value of $\int \alpha(\nu) d\nu$.

However a rigorous dispersion formula must be of the type of Eq. (4) which takes into account also the distribution of absorption in the continuous band.

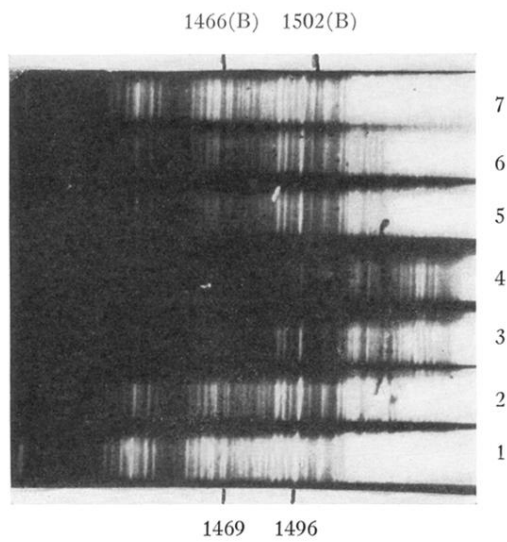


FIG. 3. Positives of spectrograms. Six and seven show the effect of clean up.