OXYGEN BANDS IN THE ULTRA-VIOLET

By Vivian M. Ellsworth and J. J. Hopfield

Abstract

The formula calculated by Birge for the first negative group of oxygen is

$$\nu = \frac{38308}{38108} + (887n' - 13.4n'^2) - (1859.9n'' - 16.53n''^2)$$

This is based upon data published by Johnson. The only transition to zero final state indicated by those data is the 6-0 and consequently there has been some doubt as to whether the first constant of the formula is correct. New photographs of this system show additional pairs of bands degraded to the red. Some of the new bands have been measured and found to represent the 7-0, 8-0, 9-0, 10-0, 9-1, 10-1 transitions as given by the formula above. The existence of the lowest final state represented by this formula is therefore established. The 0-9 band, not previously observed, is also present. Other new bands appear further to the ultra-violet. They have the appearance of belonging to the system, but are too faint to measure. It seems probable that these bands will be found to constitute from one to three progressions to still lower final states.

Introduction

FOUR systems of electronic bands of oxygen are known, two of which are due to the normal molecule and two to the ionized. A "system" includes all the bands representing a common electronic transition. Occurring simultaneously with this are transitions from a series of initial vibrational states to a series of final vibrational states, producing as a consequence the individual bands of the system.

Of the two systems due to normal oxygen, one is known in the solar spectrum[1] where it is produced by oxygen absorption in the earth's atmosphere. The other is the system which includes the absorption bands first observed by Schumann,[2] later extended and measured by Hopfield and Leifson[3] and interpreted by Birge.[4] This system lies in the region $\lambda\lambda 1950-1750$. Füchtbauer and Holm,[5] in high temperature absorption, found other bands which they have interpreted as representing higher final states (initial in absorption) in the same system and Mulliken[6] has recently shown that the seven Runge[7] bands which appear in emission

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[1] Heurlinger, Diss. Lund, S. 42 (1918); Kratzer, Ann. d. Physik **67**, 134 (1922).

[2] Schumann, Smithsonian Contributions to Knowledge (1903).

[3] Hopfield and Leifson, Phys. Rev. **25**, 716 (1925); Leifson, Astrophys. J. **63**, 73 (1926).

[4] Birge and Sponer, Phys. Rev. **28**, 259 (1926); Birge, Nat. Res. Coun., Report on Molecular Spectra, Ch. 4, Sec. 7.

[5] Füchtbauer and Holm, Phys. Zeit. **26**, 345 (1925).

[6] Mulliken, private communication.

[7] Runge, Physica **1**, 254 (1921).

in the near ultra-violet ($\lambda\lambda$3850–2980), are also a part of this system. Since the Schumann bands and the atmospheric bands are both produced by absorption in cold gas, the initial state (final in emission), must be the same for both and must be the normal state of the oxygen molecule.

The two band systems due to the ionized oxygen molecule are the first negative group, in the region $\lambda\lambda$4400–2000, and the second negative group, or Schuster bands, in the visible. The latter are commonly observed in the greenish-yellow glow about the electrode of an oxygen discharge tube.

The first negative group has the peculiar intensity distribution which is not known in any other band systems except those of the β bands of nitrogen, due to NO, and the iodine bands. In these systems, all the bands having low quantum numbers in both the initial and final states are missing in emission. (See Table II.) The position of the 0–0 band can be located therefore only by extrapolation. It is the position of this band which determines the normal level of the ionized oxygen molecule. Bands of this system were observed and measured by Stark[8] and later by Johnson.[9] The latter arranged them in Deslandres progressions. We have photographed the same system and find additional members which are of importance in locating the position of the 0–0 band.

Apparatus

The discharge tube, constructed of 1 cm Pyrex glass tubing, was of the π-shaped end-on type, the total length being about one meter. The oxygen was generated by electrolysis and passed through a phosphorus pentoxide drying tube. It entered the discharge tube through a valve at one electrode and was exhausted by the necessary pumps at the other. This valve was of the torsion capillary type recently developed by Hopfield[10] for providing a continuous flow of gas. By means of it, unusual control of the gas flow into the discharge tube was possible and the pressure in the tube could be maintained constant at any desired value. Excitation was produced by an alternating current from an 11,500 volt, 10 kw transformer.

Two different spectrographs were used for photographing the spectrum. The first was a one meter concave grating. The slit, grating, and camera box containing the plate-holder were set up on an optical bench and properly adjusted for photographing the first order spectrum. The discharge tube when used with this apparatus, was provided with a quartz

[8] Stark, Ann. d. Physik **43**, 319 (1914).

[9] Johnson, Proc. Roy. Soc. **A105**, 683 (1924).

[10] Hopfield, J.O.S.A. **12**, 391 (1926).

window. Later the discharge tube, without the quartz window, was connected directly to a vacuum grating spectrograph of 50 cm focal length. The receiver of the spectrograph and the discharge tube were exhausted by separate pumping systems. The advantage of this arrangement of pumps was that the pressure in the spectrograph could be reduced to practically zero, while that in the tube, although low, was high enough for the discharge to pass. In this way oxygen absorption in the receiver was eliminated.

Commercial films were used. They were lightly coated with a transparent mineral oil in order to increase their sensitivity toward the ultra-violet end of the spectrum.

EXPERIMENTAL

Spectrograms were made with currents varying from 0.008 to 0.6 amps. No difference in the number or intensity distribution of the bands was observed as a result of this wide variation in the current. The spectrogram A on Plate 1 was made with a current of 115 milliamps. and an exposure of 13 hours. The pressure was almost as low as possible for a discharge to pass, about 0.02–0.03 mm of mercury. The spectrograms B and D were made with approximately the same current and pressure and exposures of 24 and 50 hours respectively.

THE SPECTROGRAMS

Fig. 1, A, B, and D show some of the new photographs. A was taken with the meter grating in air. It shows the portion toward the ultra-violet of the first negative group of oxygen and includes practically the same bands as those measured by Johnson[9] in this region. The system consists of pairs of bands degraded to the red. The pairs, whose members are separated by a constant frequency difference of 200 units, are indicated on the plate. The last band which was measured by Johnson at this end of the spectrum is $\lambda2318$. On each side of it on our spectrogram, there is a faint band for which Johnson published no measurement. Each of these faint bands have been found to differ from $\lambda2318$ by 200 frequency units. Photograph B is one taken with the vacuum grating spectrograph. This photograph shows definitely eight new pairs of bands further to the ultra-violet. There is probably a ninth pair partially overlapping the last of these and on a similar photograph, D, two more pairs show. Accurate measurements of the new bands on these spectrograms could not be obtained because the oiled film warped during the long exposure so that the sharp focus was destroyed. On comparing these plates, however, with earlier ones taken by Hopfield, some of the new bands were found on them also and in good focus. One of these

earlier plates is shown in Fig. 1, C. The presence in the second order of the nitrogen triplets at λ1134 and λ1200[11] indicates that there was nitrogen impurity in the discharge tube when this spectrogram was made, whereas the new spectrograms are entirely free from nitrogen lines. The new oxygen bands identified on the earlier spectrogram are indicated by lines connecting B and C on the plate. Accurate wave-lengths of these bands were obtained from C. Both spectrograms show the second order of the strong ultra-violet triplet series of oxygen and the singlets λ999.4 and λ1152.0 also due to oxygen.[12] These lines were the standards used in measuring the bands. The wave-lengths and frequencies in vacuum,
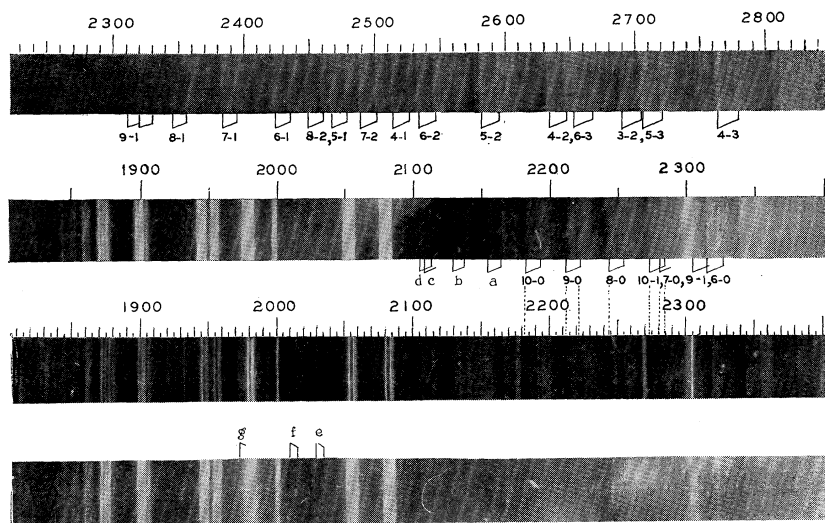

Fig. 1. Photograph of the first negative group of oxygen.

observed and calculated, are given in Table I. The difference between the calculated and observed values is constantly positive for the bands

TABLE I

Oxygen bands. Wave-lengths and frequencies in vacuum, observed and calculated

λ	ν(obs.)	ν(calc.)	Δν	λ	ν(obs.)	ν(calc.)	Δν
4399.4	22723	22708	−15	2285.79	43753	43794	+41
4363.1	22912	22908	− 4	2275.34	43950	43994	+44
						44346	—
2328.7	42929	42947	+18	2246.93	44506	44546	+40
2317.9	43129	43147	+18	2224.35	44958	45005	+47
2307.2	43329	43361	+32	2213.78	45174	45205	+31
2291.83	43634	43660	+26			45638	—
2281.26	43837	43860	+23	2183.91	45789	45838	+49

[11] Hopfield, Phys. Rev. 27, 801 (1926).
[12] Hopfield, Astrophys. J. 49, 114 (1924).

toward the violet and can be accounted for by the method of using the comparator. The difference corresponds to a shift of the comparator setting toward the red by 0.04–0.06 mm.

THEORETICAL

The bands of this system are arranged diagramatically in Table II in the usual manner. Only the short wave-length members of the pairs are given. The arrangement is substantially the same as that published by Johnson.[9] The new bands are included and are indicated by stars. The vibrational quantum number of the initial state is indicated by n' and that of the final state by n''. The lowest known state in either case is termed zero and other states are numbered in order. Progressions of initial states, or bands representing transitions from a series of initial states to a single final state, appear in columns in the table and pro-

TABLE II

Oxygen.—1st negative group

$$\nu = \frac{38308}{38108} + (887n' - 13.4n'^2) - (1859.9n'' - 16.53n''^2)$$

n'	$n''=0$	1	2	3	4	5	6	7	8	9
0					OH	29427	27757	26104	29490	22912*
1					OH	OH	28611	26976		
2				OH	32853	OH	29466	27821		
3			37188	OH	33670	OH	OH			
4		39785	37978	36202	OH	OH	OH			
5		40551	38739	36953						
6	43126	41281	39474	37701						
7	43837*	41991	40181							
8	44506*	42668	40859							
9	45174*	43326*								
10	45789*	43950*								

*New bands.

gressions of final states in lines across the table. The frequency differences in both initial and final states are determined by the spacing of the respective vibrational energy levels. This spacing decreases as the quantum numbers increase, but the relative spacing in one state is different from that in another because of the difference in electronic configuration. For this reason, bands representing the same change in vibrational quantum number, as 0–1, 1–2 and 2–3, etc., are not superposed, but lie in a sequence in the spectrum.

The frequencies of a system of vibrational bands are expressed by the formula

$$\nu = \nu_e + (\omega'n' - x'\omega'n'^2) - (\omega''n'' - x''\omega''n''^2)$$

Birge[13] and Mecke[14] each computed the constants of this formula from

[13] Birge, Phys. Rev. **25**, 240 (1925).
[14] Mecke, Phys. Zeits. **26**, 217 (1925).

the data published by Johnson.[9] But Mecke omitted λ2318 whose frequency is ν43126 and for that reason his quantum assignment and formula differ from those of Birge. The new work proves that this band should be included in the system. Its companion, although faint, appears, as well as four more pairs of bands to the same final state. These five pairs constitute a progression to a lower final state than the one designated as zero by Mecke.[14] If there are no more progressions of this system further to the ultra-violet, the formula

$$\nu = \frac{38308}{38108} + (887n' - 13.4n'^2) - (1859.9n'' - 16.53n''^2)$$

calculated by Birge[13], represents the system.

Bands appear, however, on *B* and *D* taken with the vacuum grating spectrograph, which cannot be identified on *C* because of the presence of impurity on the latter, and therefore cannot be measured accurately. Their positions are indicated by small letters. It seems probable from the appearance of these bands that they belong to the system and represent from one to three final states lower than those whose existence is already established. Further evidence for this conclusion is furnished by the result obtained by Birge and Sponer[4] for the ionization potential of molecular oxygen from spectroscopic data. This value, based upon data which include the heat of dissociation of ionized oxygen calculated from the first negative group, is 14.1 volts. The experimental value obtained by Hogness and Lunn[15] from positive ray analysis is 13 ± 1 volts. If the normal level of ionized oxygen is lower than that given by the formula above, the value of the heat of dissociation based upon the present data is too low. Each new progression to a lower final state, the presence of which is suggested by the dim bands on the new photographs, increases the value of the heat of dissociation of the ionized molecule by approximately 0.23 volts and consequently decreases the calculated value of the ionization potential of the neutral molecule by the same amount.[16] The presence of two or three more progressions toward the ultra-violet in the spectrum of the first negative group would therefore result in better agreement between the experimental and calculated value for the ionization potential of molecular oxygen. The dim bands on the new photographs indicate that these progressions probably exist.

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[15] Hogness and Lunn, Phys. Rev. **27**, 642(A), 732 (1926).
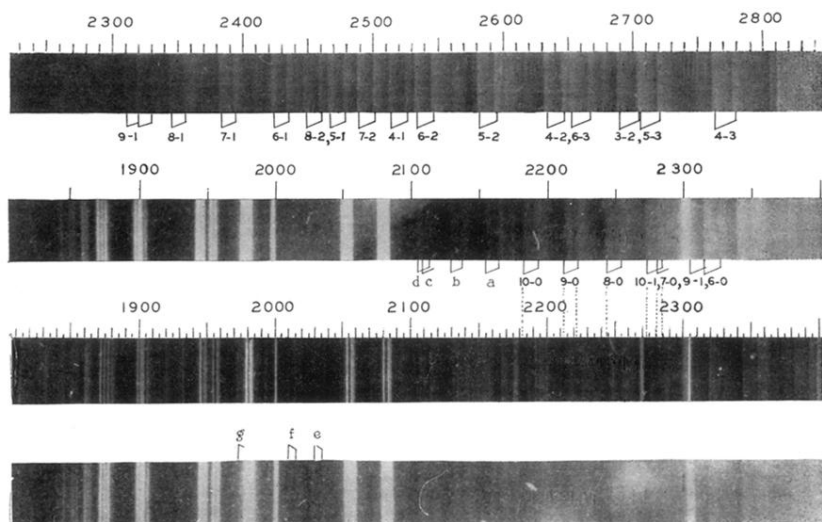[16] See Birge and Sponer (loc. cit.) for details.

Fig. 1. Photograph of the first negative group of oxygen.