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XXX. *The Absorption-spectrum, Luminous and Ultra-violet, of large masses of Oxygen.* By Professors LIVEING and DEWAR*.

IN the course of experiments on the spectra of gases at high pressures, we have made observations on the absorption-spectrum of oxygen which confirm and extend the observations of Egoroff and Jansen. The interest of this spectrum is so great, on account of the important part which oxygen plays in our world, and its free condition in our atmosphere, and, as we therefore conclude, in the interplanetary space, that it deserves a separate notice.

In order to include the ultra-violet rays in our observations we have had to contrive windows of quartz to the apparatus containing the gases. A strong steel tube, 165 centim. long

Section through one end of the tube.

and 5 centim. wide, was fitted with gun-metal ends, bearing by curved surfaces upon the conical openings of the tube, and forced home by powerful screw-caps. Each gun-metal end was pierced centrally by a conical opening fitted with a quartz stopper, 2.1 centim. thick and of the same diameter, with plane polished ends. A small amount of wax was interposed between the stopper and the gun-metal for the purpose of ensuring a uniform bearing for the quartz, which is very brittle. Trial proved that the tube thus fitted would sustain, without leakage, a pressure of upwards of 260 atmospheres. The tube had, besides, near each end a screw-plug valve for admitting the gases. About the centre of the tube was placed a quartz lens, rather less in diameter than the tube, held in place by three springs which pressed against the walls of the tube. This lens had a focal length of about 46 centim.; so that when a source of light was placed about 10 centim. from one end of the tube, an image of it was formed on the slit of the spectroscope at about the same distance from the other end

* Communicated by the Authors.

of the tube, and thereby loss of light, so far as it was due to the distance of the source, was reduced to a minimum.

Ordinary oxygen was let into the tube from an iron bottle until the pressure reached 85 atmospheres, and on viewing an arc light through the tube the following absorptions were visible:—

(1) A very dark band sharply defined on its more refrangible side, gradually fading out on its less refrangible side, and divided into two parts by a streak of light, occupying the position of A of the solar spectrum.

(2) A much weaker but precisely similar band in the position of B of the solar spectrum.

(3) A dark band very diffuse on both edges, extending from about $\lambda 6360$ to $\lambda 6225$, with a maximum intensity at about $\lambda 6305$.

(4) A still darker band a little above D, beginning with a diffuse edge at about $\lambda 5810$, rapidly coming to a maximum intensity at about $\lambda 5785$, and then gradually fading on the more refrangible side, and disappearing at about $\lambda 5675$.

(5) A faint narrow band in the green at about $\lambda 5350$.

(6) A strong band in the blue, diffuse on both sides, extending from about $\lambda 4795$ to $\lambda 4750$.

When photographs were taken of the ultra-violet part of the spectrum of the arc, and of the iron spark, the gas appeared to be quite transparent for violet and ultra-violet rays up to about $\lambda 2745$. From that point the light gradually diminished, and beyond $\lambda 2664$ appeared to be wholly absorbed.

The pressure of the oxygen in the tube was then increased to 140 atmospheres. This had the effect of increasing sensibly the darkness of all the bands above described; but brought out no new bands, except a faint band in the indigo at about $\lambda 4470$. In the ultra-violet the absorption appeared to be complete for all rays beyond about $\lambda 2704$.

The foregoing observations were made with a spectroscope of small dispersion. We next brought to bear on the spectrum a large instrument with one of Rowland's gratings. Even with the high dispersion of this instrument the bands at A could not be resolved into lines; they remained two diffuse bands; though the red potassium-lines, which were produced by sprinkling the electrode of the arc with a potassium-salt, were sharply defined and widely separated. None of the other bands were resolvable into lines. This we attribute to the density of the gas, by which the lines are expanded so as to obliterate the interspaces; and this supposition is confirmed by the observation of Ångström, that the band in the solar spectrum which appears to be identical with that observed by

us a little above D was resolved into fine lines when the sun was high, but appeared as a continuous band when the sun was near the horizon.

On letting down the pressure the bands were all weakened; A, though weaker, became more sharply defined at the more refrangible edge. The faint band in the indigo $\lambda 4470$ remained just visible until the pressure fell below 110 atmospheres. At 90 atmospheres A and B were still well seen and sharp, but all the other bands weaker. B remained visible until the pressure fell to 40 atmospheres. A was then still well seen, the band just above D very faint, and the others almost gone. At 30 atmospheres A was still easily seen, and there was a trace of the band above D. At 25 atmospheres this band had gone, but A remained visible until the pressure fell to less than 20 atmospheres. Hence an amount of oxygen not greater than that contained in a column of air 150 metres long at ordinary pressure is sufficient to produce a visible absorption at A. The quantity of oxygen in the tube at the highest pressure we used falls, however, far short of the quantity traversed by the solar rays in passing through the atmosphere when the sun is vertical.

It will be noted that the bands, if we except the faint two in the green and indigo respectively, appear to be identical with those terrestrial bands in the solar spectrum which Ångström found to be as strong when the air was dried by intense frost as at other times. At least the positions of the maxima agree closely, and that near D shows the same peculiarity in having its maximum near the less refrangible end. We did not, however, observe α , which would be fainter than B, and if, like A and B, unresolvable, would be lost in the diffuse band which covers that region. The bands above numbered 3, 4, 5, 6 agree also with those observed by Olszewski (*Wied. Ann.* xxxiii. p. 570) to be produced by a layer of liquid oxygen 7 millim. thick. The point also at which the absorption of the ultra-violet rays begins agrees with that at which the absorption by ozone begins, as observed by Hartley (*Journ. Chem. Soc.* xxxix. p. 57); but the oxygen, as we used it, did not appear to transmit the more refrangible rays beyond 2320 which seem to pass through ozone. Egoroff (*Comptes Rendus*, ci. p. 1144) found that A remained visible when he looked through 80 metres of atmosphere, but 3 kilog. of atmosphere failed to produce α .

When the pressure in our tube was reduced, a cloud was always formed which rendered the contents of the tube nearly opaque; the faint light which was then transmitted had always a green tinge.

It is remarkable that the compounds of oxygen do not show any similar absorptions. Ångström thought it improbable that oxygen should have a spectrum of such a character, since he failed to obtain an emission spectrum resembling it; and suggested that the absorptions might be due to carbonic-acid gas or to ozone, or possibly to oxygen in the state in which it becomes fluorescent (*Spect. Norm.* p. 41). Neither carbonic-acid gas nor nitrous oxide, at a pressure of 50 atmospheres in our tube, show any sensible absorption in the visible spectrum; and the absorption of the ultra-violet rays by the latter gas begins at a higher point, namely about λ 2450, than that of uncombined oxygen. In fact we see the anomalies of the selective absorption by compounds as compared with that of their elements when we take the case of water, which has a remarkable transparency for those ultra-violet rays for which oxygen is opaque.

These observations show that all stellar spectra observed in our atmosphere, irrespective of the specific ultra-violet radiation of each star, must be limited to wave-lengths not less than λ 2700, unless we can devise means to eliminate the atmospheric absorption by observations at exceedingly high altitudes.

Postscript.—Since the foregoing paper was written we have extended our observations to much longer columns of oxygen. A steel tube 18 metres long was fitted with the same quartz ends as had been used with the shorter tube, and with two quartz lenses symmetrically placed inside the tube, one near each end, so that when an arc-lamp was placed about 14 centim. from one end of the tube the image of it was formed on the slit of the spectroscope at the same distance from the other end.

When the tube was filled with air only at ordinary pressure no absorptions could be detected, but when the air was replaced by oxygen at the pressure of the atmosphere the absorption of A was just visible, though neither B nor any other absorption-band could be traced. As the pressure of the oxygen was increased A became much darker and more distinct, and B came out sharply defined. The absorption-band about λ 5785 was next seen, and the dark bands about λ 6300 and λ 4770 were just visible when the pressure reached 20 atmospheres.

At a pressure of 30 atmospheres A was very black, B also strong and sharply defined, and the forementioned bands were all quite strong and had the same general characters as when seen through the shorter tube; the band about λ 5350 also could be seen, but there was only a bare trace of that in the indigo about λ 4470. At 60 atmospheres these last two absorptions could be well seen, all the other bands were very strong,

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B still quite sharp, but A somewhat obscured by a general absorption at the red end. At 90 atmospheres this general absorption at the red end seemed to extend to about one third of the distance between A and B; but A could still be seen, when the slit was wide, as a still darker band on a dark red background; B was still sharp, and the other absorptions all strengthened and somewhat expanded. The diffuse edges of the several bands now extended from about—(1) λ 6410 to 6190, (2) λ 5865 to 5635, (3) λ 5350 to 5280, (4) λ 4820 to 4710, (5) λ 4480 to 4455.

Photographs taken when the pressure of the oxygen was 90 atmospheres show a faint absorption-band about L of the solar spectrum, a stronger band extending from about λ 3600 to 3640, a broad diffuse band about the place of the solar line O, and complete absorption above P.

The absorbent column in the tube at the highest pressure used contained a mass of oxygen about equal to that in a vertical column of the earth's atmosphere of the same section as the tube; but the intensity of the bands produced by the compressed gas was far greater than that of the corresponding bands in the solar spectrum with a low sun. When the arc-light was replaced by a piece of white paper reflecting light from the sky through the tube, it appeared to the naked eye to have a faint blue tint, similar to that of liquid oxygen, which, comparing our observation with Olszewski's, seems to have the same absorptive powers as the dense gas, if we except A. This exception is probably only apparent, and due to the difficulty of observing A under the circumstances of Olszewski's experiment.

The greatly increased intensity of the absorption-bands at high pressures bears out Jansen's observation, that in this group the absorption is proportional to the product of the thickness of the absorbent stratum into the square of its density, while the absorptions to which A and B belong vary directly as the density.

The appearance, on looking through the tube when gas at high pressure is streaming into it, is very much like that of a black and a colourless liquid, which do not mix, being stirred together, and the tube soon ceases to transmit any light. Transparency returns as the density becomes uniform. Currents produced by heating the tube at one or two points produce a similar effect, and show that such currents in the atmosphere of a star may stop all rays coming from its interior.

We hope before long to get the tube fitted with rock-salt ends and lenses, and to determine the total absorption of radiation by similar masses of oxygen, nitrogen, and hydrogen.

Cambridge, August 18, 1888.