

XVII.—*On the Constitution of the Lines forming the Low-Temperature Spectrum of Oxygen.* By PIAZZI SMYTH, Astronomer Royal for Scotland.

(Read 30th January 1882.)—Ordered by the Council to be issued with Professor SMYTH's paper on "Gaseous Spectra."

I had added (at p. 140 of my paper on "Gaseous Spectra") to the "small dispersion" account therein given of the above mentioned spectrum of luminous oxygen gas,—that two, if not four, of its very few and scanty lines appeared, when viewed with much higher dispersion, to be double; but that I hoped to give a more exact account of them, after completing some arrangements then in progress for increasing both the dispersion and magnifying power of my spectroscope.

These improvements, together with a great advance in definition, were finished last November, and almost the first result they yielded was, to much more than confirm what I had only suspected before; and to do so, moreover, with such vigour and certainty, as to make me inquire right and left for several weeks to ascertain if what I then saw, was really a new discovery, or had perhaps been known long before to older and better spectroscopists.

So far as I have been able to gather, the thing is new, and promises to be important to theorists in molecular vibrations, on account of what it fulfils. To explain this, let me refer to Dr. ARTHUR SCHUSTER's valuable paper in the "Transactions of the Royal Society," London, for 1879, "On the Spectra of the Metalloids; Spectrum of Oxygen." Beginning his exposition of the low-temperature spectrum—after having treated very fully of the exceedingly different high-temperature spectrum, of oxygen,—with the late Prof. PLUCKER's account of it, and concluding with his own confirmatory observations, Dr. SCHUSTER shows that the low spectrum had always been found to consist of only four single, wide-apart lines,—viz., one in the orange, one in the citron, another in the green, and another still in the indigo-violet; and to that spectrum, containing only four such solitary, single, simple lines, the learned Doctor gave the second or *alias* name of "the compound-line" spectrum of oxygen.

The reason for such an apparent misnomer, or *lucus à non lucendo*, was, that at the very moderate temperature of electric illumination at which this trifling lined spectrum of oxygen appears, most other gases do give forth very compound-line spectra indeed; spectra with hundreds or even thousands of lines, arranged in peculiar bands or parcels, and known generally as "fluted spectra." Hence Dr. SCHUSTER's name for what he saw in oxygen, while prin-

cipally intended to show the physical circumstances under, or temperature level on, which it is produced,—might perhaps privately have been intended to indicate that he had somehow an idea that if the lines were not compound, they ought to have been, and would one day be found so to be.

That, so far as I can ascertain, is the furthest point the subject has even yet reached elsewhere ; and it was at that point that I had taken it up in 1879 and 1880, in the paper already printed by this Society. In the regular course of that paper, going through many gases, with single prism power only, I abundantly confirmed Messrs. PLUCKER's and SCHUSTER's four wide apart lines, as constituting in themselves alone, almost the whole and entire low-temperature spectrum of oxygen ; I did indeed also find a strong line in the scarlet-red, besides two in the red or ultra-red, and two in the citron-green, of extreme faintness, and only probably belonging to the same spectrum. But they did not in any way alter the apparent anomaly of the Doctor's name ; for each of these new lines was also solitary : and what are after all nine, or to keep within more certain bounds five, simple lines standing separate, and along a length where 10,000 such could take their places without interfering with each other !

But when I looked last November with the improved apparatus, what a change was there ! for, of the five certain lines, no less than four were found to be triple ; after a fluted fashion too. These four truly compound lines then were,—mine in the scarlet-red, and PLUCKER and SCHUSTER's three lines in the orange, the citron and the green respectively ; but their last line in the indigo-violet remained persistently and positively single. Still, with four-fifths of this most scanty spectrum, now proved to consist of triplets instead of single lines, Dr. SCHUSTER's original and really most happy name for it, of “the compound-line spectrum” of oxygen was fully justified, at the same time that the miniature scale of the triplets seemed to make the physical nature of oxygen more markedly different than ever, from all other known gases ; for they, at the same temperature level, generally make their bands or compound line arrangements, on a comparatively enormous scale, and in multitudinous groupings.

To those who are engaged in chemical spectroscopy it will at once convey an idea of the small-sized triplicity of these oxygen lines to be told, that from the first to the second of each triplet the distance is one-fifth that of the well-known salt-line double ; and from the second to the third is between one-eighth and one-ninth of the same space ; while the salt-line double itself is only one-eighth of the average distance apart of the stronger flutings of the citron-band of the carbo-hydrogen blow-pipe flame, which band has some six or seven of such flutings within its easily perceivable breadth.

Or, again, if we should on the black board represent the separation of the first and second of any oxygen triplet by a tenth of an inch, and from the second

to the third by six-hundredths of an inch (when it will require a good eye from the other side of the table to separate them), that would indicate a scale for the whole spectrum, or from red to violet, of 25 feet; and that is rather more than three times as long as the late Professor ANGSTRÖM's grand and almost universally followed "Normal Solar Spectrum."

For bright line, chemical, spectroscopy, and especially with the faint light of incandescent gas in a low temperature electric spark, it is by no means usual or easy to separate lines so very close together as the members of one of the oxygen triplets. A few words of explanation may, therefore, be demanded of me in proof that the resolution was real, and not an optical deception. The propriety of the demand, too, I am quite ready to allow, knowing only too well that there are prisms which will fringe every bright line with diffraction repetitions; or, when out of the best focus, will double or treble any line, and others again that make them so broad and hazy that clear separation of very close lines would be utterly impossible.

As my gas-vacuum tube spectroscope admits only of a deviation range up to 45° , or that of a single white-flint prism of 52° refracting angle, I was compelled to have recourse to compound prisms to get up the necessary dispersion for crucial cases, say that of seven or eight such prisms. Now, although some beautiful compounds were made for me both in France and this country, they invariably failed in the item of perfect definition. I then tried a large fluid bisulphide-of-carbon prism made in Paris, but that failed in several ways. So lately I entered into a contract with an exceedingly skilful as well as persevering optician in London, viz., Mr. ADAM HILGER, to make two large bisulphide prisms, having a clear circular aperture of 2.1 inches in diameter, a refracting angle of 104° , anti-prisms of crown glass square at the ends, and a central angular bored block of the same material to hold the fluid.

The troubles poor Mr. HILGER had to go through were almost overwhelming. He bored through block after block of crown glass only to find after an hour, or a day, or a week that it fell in pieces of its own accord, until he had a heap of tunnelled fragments large enough to make a cautionary photograph of. And when he had at last succeeded by his unconquerable perseverance in securing two blocks that stood, and the anti-prisms were to be fastened on their faces, he tried almost every patented and unpatented cement before he found one, or rather a particular method of using it, which could withstand the action of the bisulphide for more than a day or two.

At last, however, though long after the contracted time, he brought the two prisms here complete, and they passed successfully through the severest trial I had prepared for them, viz., that when a hydrogen line was at its brightest, shining like a ray of sunlight in a dark field, its light must be entirely and

sharply confined to the width of opening of the slit for the time being. Not, however, until some months after, when the telescope power was also improved, and a new class of difficulties with the prisms had been overcome, could the desired trial on oxygen be made. Now, whereas I had, as mentioned already, on previous occasions with the best compound glass prisms I could procure, seen only an uncertain idea that some of the oxygen lines might be double, I now saw the real triplicity of four of the lines, and measured them micrometrically with a degree of certainty and satisfaction that I had never dreamt of with the older apparatus; and this triplicity of these lines never came out more remarkably than when the singularity of really single lines, such as those of hydrogen impurities in the same gas tube, was rendered most distinctly. I will, therefore, now only seek to conclude with a few words on the bearing of this tripleness of the oxygen lines,—first, on the disputed question of the existence of oxygen in the atmosphere of the sun; and, second, on the absence of hitherto recognised oxygen manifestations, though oxygen is so well known to exist as a large part of the earth's atmosphere, in the telluric rays that become visible in the solar spectrum at sunrise or sunset.

Oxygen in the Sun.

For many years it was a sort of crying wonder that the spectroscope showed no traces in the sun of so necessary a gas to combustion as oxygen. The expected test being, that we should see there as dark lines all the lines which are seen bright, when oxygen gas, on being rendered incandescent in a *high*-electric temperature, then shows what is called its “elemental-line spectrum.” But not one of those lines could be detected by its dark counterpart in the sun. At length Professor HENRY DRAPER, of New York, from a series of experiments made with extraordinary skill and power, announced that oxygen appears in the solar spectrum not in its dark but in its bright lines, outshining where they come the brightness of the sun's continuous spectrum background. Yet though he gallantly made a voyage from New York to London especially to describe his experiments, and was honourably received and attentively heard, there are some persons there who are not convinced yet.

Now Dr. SCHUSTER had already compared his four lines, though of the low-temperature oxygen spectrum, with ÅNGSTRÖM'S normal solar spectrum map, under the idea apparently that, though the solar oxygen might have been rendered incandescent in the very hottest central regions of the sun, it might have its Fraunhofer dark correspondences checked off by cooler oxygen vapour outside. But as his then knowledge of oxygen low temperature lines made them only four single, simple, thin lines, the comparison was not attended

with any very certain result; for there are so many of such lines, unclaimed for any element, strewn all along the solar spectrum. But now that I had found four out of five lines to be triplets of an accurate kind, could anything further in the way of identification be ascertained?

In apparently the very place of the three fainter of the above-described triplets there is a close double of peculiarly thin Fraunhofer lines depicted by Professor ANGSTRÖM in his normal solar spectrum map; and in the place of the brightest of them, viz., SCHUSTER's orange line, there is a triple* of the same kind of *ultra* thin lines; and not one member of all those four groups has been claimed for any known element by the great Swedish physicist. Yet I am by no means satisfied that the degree of correspondence is conclusive; and can only hope that those who have the means will positively confront the new oxygen triples with the sun itself, and inform us what they find.

Oxygen of the Earth's Atmosphere in the Telluric Solar Spectrum.

If the long silence of the spectroscopist touching oxygen in the sun was a wonder, and perhaps something the reverse of praise to those who used the supposed all-powerful instrument, what shall be said for its continued silence as to the presence of any free oxygen in the earth's atmosphere, when *some* gases that are therein do make themselves most signally conspicuous on the solar spectrum, in the shape of dark lines or bands, growing as the sun descends in altitude, until they become at last more grandly thick and black than all the truly solar markings put together.

Amongst these gigantic cases of Fraunhofer lines of some kind of telluric gaseous origin, we do indeed know, by a sort of inductive process rather than by any positive proof, that the band too hastily called "little a" and other bands and lines near C, and near D, are the spectroscopic proofs of *watery vapour*, as an invisible but potent gas in our atmosphere. But what makes the far greater A, or great B, and the α (alpha) band, no one pretends to know.

At first sight it might well be suggested that they must be formed by one or other or both of the two grand constituents of the earth's atmosphere as established by the chemists, viz., oxygen and nitrogen. But there we are instantly met by ANGSTRÖM's inflexible law, promulgated by him in 1853, and repeated at page 39 of the description of his Normal Solar Spectrum in 1868; viz., that "a gas in the state of incandescence emits luminous rays of the same refrangibility as those which it can absorb." Or, conversely, when it acts by

* That triplicity is indeed there broken in upon by a far stronger line, which ANGSTRÖM traces to sodium, (Na); but such cases of mere optical *juxta*-position are frequent in the crowds of lines in much of the solar spectrum, without any physical connection being supposed to be implied thereby.

absorption, it produces dark, in all the spectrum places where, when in a state of incandescence, it produced bright, lines.

Now we know by laboratory experiments what bright lines are given out by both oxygen and nitrogen in various states of incandescence ; and not one of those lines is in the place, and at the same time endowed with the physiognomy, of great A or great B, or of the α (alpha) band of the sunset solar spectrum.

To get over this astonishing difficulty, ANGSTRÖM, who held that all these three bands are of a similar visible constitution, viz., a thick line and then a band of thin lines stretching out towards the red end of the spectrum—suggested that they might be produced by “carbonic acid.” But over and above the difficulty, that carbonic acid is an almost insensible impurity in the open air, and could hardly be expected to extinguish every sign of the existence of the atmosphere’s two great constituents,—we do know the spectrum given by incandescent carbonic acid in the laboratory, and it cannot claim to having a band in the place of either A or B or α (alpha), besides its series being turned in the opposite direction, or every band vanishing towards the violet, in place of the red, end of the spectrum.

Evidently then, in despair, this sorely tried and now departed philosopher of Upsala, but who is still our chief authority in this line, on page 41 of his Memoir already cited, after acknowledging that he had, in another place, suggested “carbonic acid,” says further, perhaps it is ozone which produces these bands. No reason is given, but the prudent caution is inserted,—if there is free ozone in the earth’s atmosphere. Or, again, he adds as a third supposition, perhaps they are produced by “fluorescence of oxygen,” a gas which he there states gives forth “a faint phosphorescence in a Geissler gas-vacuum tube when an electric current is caused to pass through it.” But this is just as far from presenting us with the very definite lines constituting the bands of great A, great B, and α (alpha) of the sun-set telluric solar spectrum, as before.

Now I have not, any more than all the rest of the world at this moment, any positive and proved means of raising Professor ANGSTRÖM out of the difficulties he eventually sunk under. But the minute triplicity of the greater part of the low temperature lines of the oxygen spectrum described in the beginning of this paper, may perhaps let in a chink of light upon the difficulty, when combined with the true constituent features of these grand telluric lines A, B, and α (alpha) as set forth in my Lisbon solar spectrum, so recently honoured by the Royal Society, Edinburgh, with their Makdougall-Brisbane Prize.

ANGSTRÖM, observing these three bands when they were thick and clumsy at sunset, pronounced their constitution as being exactly similar in every case. I, on the contrary, observing them in a high sun, when they were divested of the rotundity of flesh, and only their thin, linear, bones appeared, found the

ultimate constitution of the α (alpha), to be perfectly different from that of A and B; for in place of many regular and symmetrically arranged powerful lines, it was made up of little doublets and triplets of both inconceivable minuteness and of very irregular occurrence (see the said Lisbon spectrum as printed in Vol. XXIX. of the Society's Transactions). These Lilliputian foundation stones of the α (alpha) band appeared to me at the time almost ridiculous in their smallness;—but now I recognise them as having a close family resemblance to the triplicity of the low-temperature oxygen lines which I have been trying hereinbefore to describe. They are not indeed the very same, for they are in different spectrum places; but they do give the idea (suggested also by some points in both the aurora spectrum and cometary spectra not yet reproduced in any laboratory electrical experiments) that there is a temperature-level in Nature for the incandescence of gases, much lower than the low-temperature oxygen spectrum of these pages. Wherefore, if we could artificially produce that kind of ultra low-temperature illumination, electric probably, we might find that the α (alpha) band in the solar sunset spectrum represented the oxygen, while the A and B bands showed us the nitrogen gas thereof; they two being the mighty gas constituents known so well to everyone, *except telluric-line solar spectroscopists*, to exist in the earth's atmosphere; and in such overpowering quantity as to practically exclude everything else except watery vapour.