ART. XXIV.—*On the Aqueous Lines of the Solar Spectrum*,¹ by
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A CAREFUL examination of the solar spectrum continued during several months with the spectroscope described in a recent article² in this Journal has led me to the conclusion that a very large number of the more faint dark lines of the solar spectrum hitherto known simply as *air lines*, are due solely to the *aqueous vapor* of our air, and hence that the absorption of the luminous solar rays by the atmosphere is chiefly at least owing to the aqueous vapor which it contains.

The appearance of the Fraunhofer's line D, seen under precisely the same conditions, but with increasing quantities of aqueous vapor in the atmosphere, is shown in figures 1, 2, 3, and 4. The D line is selected because being a favorite test-object for the spectroscope its general appearance is well known to all observers. But even more marked changes than those here illustrated have been noticed in others, but chiefly in contiguous, portions of the solar spectrum.

These changes attracted my attention from my earliest observations with the spectroscope; but with my first instrument, and the bisulphid of carbon prisms then employed, it was almost impossible to eliminate the effects which might be caused by the variations in the condition of the instrument itself; and, as these were known to be very great, it was possible that they might account for all the variations observed. With the improved instrument, however, just referred to, absolute constancy of action is obtained, and all merely instrumental variations avoided.

A peculiar condition of the atmosphere gave the first clue as to the cause of the changes under consideration. The weather on the 17th of November, 1865, at Cambridge, Massachusetts, was very unusual, even for that peculiar season known in New England as the Indian Summer. At noon the temperature on the

¹ Communicated to the American Academy of Arts and Sciences, Jan. 9, 1866.

² Vol. xl, Nov., 1865.

east side of my laboratory was 70° F., while the wet bulb thermometer indicated 66°, showing an amount of moisture in the atmosphere equal to 6·57 grains per cubic foot. At the same time the atmosphere was beautifully clear and the sun shone with its full splendor. I have never seen the aqueous lines of the spectrum more strongly defined than they were on this day, and the total number of lines visible in the yellow portion of the spectrum was at least ten times as great as are ordinarily seen.

The appearance of the D line on that day is shown in fig. 4. Between the two familiar broad lines D₁ and D₂ there were eight sharply defined lines of unequal intensity, which is only very imperfectly represented by the wood-cut. In addition to these on the more refrangible side of the space between the two D lines there was a faint but broad nebulous band, barely re-

solvable into lines of still lower magnitude.* It is impossible to represent this band accurately with a wood-cut, and the shaded broad band marked $\ast$, on the right hand side of fig. 4, only serves to indicate its position and approximate breadth.

The 26th of December was also a warm day for the season, with a brilliant sun. At 1 P. M. the dry bulb thermometer marked 55° , the wet bulb 50° , and hence the amount of moisture in the atmosphere was 3.76 grains per cubic foot. The appearance of the D line at this time is shown in fig. 3. Two of the lines, η and θ , and the nebulous band $\ast$, seen on the 17th of November were invisible, and moreover, the group of three lines δ ϵ ζ , on the left hand side of the figure, were only just within the limits of visibility.

On the 25th of December only two lines were visible within the D lines marked α and β in fig. 2, and the last of these was quite faint. The temperature at the time of observation was 46° ; the wet bulb thermometer indicated 40° , and the amount of moisture in the air was 2.42 grains per cubic foot. The sky was clear and the sun brilliant. Lastly, on January 5, 1866, one of the clear cold days which are so common in our climate during the winter, only the single line α was visible within the D line, as is shown in fig. 1. At the time of observation near noon the dry bulb thermometer marked 10° , the wet bulb 9° , and hence the amount of moisture in the atmosphere was only 0.81 of a grain per cubic foot. The sun, however, was as brilliant as in either of the previous cases. The D line also appeared as in fig. 1, on the 8th of January, 1866, when the thermometer at noon stood at 10° below zero Fahrenheit, and when the barometer attained the unusual height of 31 inches.

The above figures have been drawn so as to show as nearly as possible the relative intensity of the different lines under different atmospheric conditions. As no accurate means of making the comparison are yet known, I was obliged to depend upon my eye alone, and small differences at different times of observation may easily have escaped my notice. Indeed I should have been liable to great error were it not for the fact that one of the lines within the D lines, marked α in all the figures does not vary in intensity, and served as a constant standard in making the observations. This is the only line which is given by Kirchhoff in his chart of the solar spectrum between the two D lines, and it is referred by him to the nickel vapor as the D lines themselves are to the sodium vapor in the sun's atmosphere. It is an undoubted solar line and has been drawn with the same strength in all the figures in order to show that it is invariable.

* We use this word in the same sense in which it is used by astronomers in reference to the fixed stars.

With a very dry atmosphere the line α is the only one which appears within the D lines, as shown in fig. 1. As the amount of vapor increases the line β makes its appearance. At first it is barely visible, but as the amount of vapor increases still further it becomes more and more prominent, until at last, as shown in fig. 4, it is even more intense than the line α . A careful comparison of these two lines might indeed serve as an approximate measure of the amount of vapor in the atmosphere, and a series of comparison, made under the same conditions at different heights would give data for determining the law according to which the amount of vapor decreases with the elevation above the sea level.

All the aqueous lines change in intensity like the line β . They first appear very faintly when the amount of vapor in the air reaches a definite point, varying for the different lines, and gradually gain in intensity as the amount of vapor increases. Thus the group of three lines δ, ϵ, ζ do not appear in fig. 2, are barely visible in fig. 3, but become very marked in fig. 4.* The lines η and θ and the nebulous band $\ast$ do not appear until the air is very moist and even when it contains 6.57 grains of vapor per cubic foot they are still very faint. Under still more unusual atmospheric conditions they will undoubtedly become more intense, and we shall then probably be able to completely resolve the nebulous band and count the lines of which it consists.

It is hardly necessary to repeat that the examples here given are selected from a large number of observations. During the cold dry weather of winter the appearance of the D line is uniformly as shown in fig. 1, the line β only occasionally appearing when the atmosphere becomes more moist. During the warm weather of summer, when the absolute amount of moisture in the air is in almost all cases greater than in winter, the appearance of the D line is as uniformly that shown in fig. 3. It is only very rarely in the dry climate of New England, even during the summer, that all the lines shown in fig. 4 are visible, and, as already stated, I never saw them before so sharply defined as on the 17th of November last. Several conditions must evidently concur in order that the aqueous lines should be developed in their greatest intensity. In the first place the air must be charged with vapor not only near the surface of the earth, but also through a great height of the atmosphere. Local causes might greatly increase the amount of moisture in the lower strata of the atmosphere and affect powerfully the hygrometer, which would not, to the same extent at least, influence the indications of the spectroscope. In the second place, other

* With an increasing quantity of vapor in the atmosphere the line γ of fig. 3 is seen before the group of lines δ, ϵ, ζ , and an intermediate figure between 3 and 4 might be given showing only the lines $D_1, \alpha, \gamma, \beta, D_2$.

things being equal the intensity of the aqueous lines must be strengthened by increasing the length of the path of the sun's rays through the atmosphere, and this is the longer the lower the altitude of the sun. But then again the intensity of the light has such an important influence on the definition of the lines, and the slightest haze in the atmosphere so greatly impairs the distinctness, that I have generally found that the aqueous lines are seen best when the sun is near the meridian. Hence with an equal amount of moisture in the atmosphere the late autumn may be a more favorable season for seeing the aqueous lines than the summer; for not only must the solar rays, when most brilliant at noon, traverse a greater extent of air, but moreover, the atmosphere at this time is usually clearer, and the reflected beam of light, which enters the spectroscope, is at times even more brilliant than when the sun attains a higher elevation and the light is reflected under less favorable conditions.

In the examples cited above the comparisons were made under as nearly as possible the same conditions so as to eliminate all causes of variation except the one under consideration. Days were selected when the atmosphere was perfectly clear and the sun's light, so far as I could judge, equally brilliant. Moreover, the position of the spectroscope and mirror remained unchanged during the whole time. This mirror which is used for reflecting the sun's light upon the slit of the spectroscope is so arranged that it can be turned into any position by the observer while his eye is at the eye-piece of the spectroscope, and it was always carefully adjusted to the position of best definition at each observation. The manipulation of the mirror is fully as important in the use of the spectroscope as it is in microscopy.

It will be of course understood that the power of developing these faint aqueous lines depends very greatly on the optical capabilities of the spectroscope, and that the figures here given are relative to the instrument used in the observations. This instrument has been fully described in the article already cited. It is sufficient for the present purpose to state that it is provided with nine flint glass prisms of 45° refracting angle, which bend the rays of light corresponding to the D line through an angle of $267^\circ 37' 50''$, and that corresponding to the H₁ line through an angle of $260^\circ 42' 20''$, when each passes through the prisms at the angle of minimum of deviation. The dispersive power, therefore, of the instrument for these two rays is equal to $18^\circ 4' 30''$, and the rays corresponding to the two D lines are separated $1' 10''$. The object glasses of the two telescopes of this spectroscope are $2\frac{1}{2}$ inches in diameter and have a focal length of $15\frac{1}{2}$ inches, and lastly the size of the prisms and of the various parts of the instrument is adapted to these dimen-

sions. With a more powerful instrument a larger number of aqueous lines would be seen under the same atmospheric conditions. My own instrument has a set of sulphid of carbon prisms which disperse the light nearly twice as much as the flint prisms. These sulphid of carbon prisms are very variable in their action; but, under the best conditions, they might show the D line as in fig. 3, when with the flint prisms it would appear as in fig. 2.

The facts stated in this paper fully account for the discrepancies in the representations which different observers have given of the D line. Some time since Mr. Gassiot of London gave in the *Chemical News* a representation of the D line as seen with his instrument, showing several lines in addition to those seen by myself and other observers. On visiting the Kew Observatory, in the summer of 1864, I was surprised to find that this instrument was less powerful than the one I was then using, and I also learned that these lines were only seen on a single occasion. The moist climate of England is the evident explanation of the additional lines.

As I stated at the first of this paper the D line has been selected simply to illustrate a general truth. The development of aqueous lines in contiguous portions of the spectrum is even more marked than in the exceedingly limited portion here represented. Indeed, as has been already intimated, the number of these lines seen in the yellow region of the spectrum on the 17th of November was at least ten times as great as that of the true solar lines. That part of the yellow of the spectrum which lies on the more refrangible side of the D line, and in which during dry weather only a comparatively few lines can be distinguished, was then as thickly crowded with lines as the blue or the violet, but the lines were of course far less intense.

Professor Tyndall of London has shown by a remarkable series of experiments with the thermo-multiplier not only that aqueous vapor powerfully absorbs the obscure thermal rays; but also that the elementary gases of the atmosphere exert little or no action upon them. I have endeavored to establish in this paper, from direct observations with the spectroscope, a similar truth in regard to the luminous rays. It has been estimated by Pouillet and others that about one-third of the solar rays intercepted by the earth are absorbed in passing through the atmosphere, and it now appears that aqueous vapor is the most important if not the chief agent in producing this result. It is impossible, however, from any data we yet possess, to determine how great a power of absorption is exerted by the oxygen and nitrogen gases which constitute the great mass of our atmosphere. I have shown that a very great many, and I have no doubt that almost all the lines, hitherto distinguished as air lines,

are simply aqueous lines, but it is very difficult to distinguish atmospheric lines from the true solar lines, and our knowledge of the first is as yet very incomplete. It still remains to make careful comparisons throughout the whole extent of the spectrum before we can determine absolutely the relative absorbing power of the different constituents of our atmosphere.

One other inference from the facts here developed is worthy of notice before closing this paper. It has been for some time suspected that the blue color of the sky was in some way connected with the vapor in the atmosphere, and it is a fact of common observation that this color is more intense during the moist weather of summer than during the dryer weather of winter. The distribution of the aqueous lines through the solar spectrum not only confirms the opinion previously entertained, but also points to the cause of the color. So far as my observations have extended the aqueous lines are almost wholly, if not completely, confined to the more refrangible portions of the spectrum. Here they are found in vast numbers, and I am not positive that they exist anywhere else. If, then, the aqueous vapor absorbs most powerfully the yellow and red rays of the spectrum, the blue color of the sky is the necessary result. The color is therefore due to simple absorption and not to repeated reflections from the surface of drops of water, as some physicists have supposed.

As can readily be seen the aqueous lines of the solar spectrum present a very wide field for investigation, but one which can only be cultivated under peculiar atmospheric conditions. This paper is only intended to open the subject. I hope to be able to continue the study on every favorable opportunity, and shall take pleasure in communicating through the pages of this Journal any future results.

Cambridge, Jan. 9, 1866.