Johann Jacob Balmer (1825-1898)

Note on the Spectral Lines of Hydrogen

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Using measurements by H. W. Vogel and by Huggins of the ultraviolet lines of the hydrogen spectrum I have tried to derive a formula which will represent the wavelengths of the different lines in a satisfactory manner. I was encouraged to take up this work by Professor E. Hagenbach. Ångström's very exact measurements of the four hydrogen lines enable one to determine a common factor for their wavelengths which is in as simple a numerical relation as possible to these wavelengths. I gradually arrived at a formula which, at least for these four lines, expresses a law by which their wavelengths can be represented with striking precision. The common factor in this formula, as it has been deduced from Ångström's measurements, is h = 3645.6(mm /10^7).

We may call this number the fundamental number of hydrogen; and if corresponding fundamental numbers can be found for the spectral lines of other elements, we may accept the hypothesis that relations which can be expressed by some function exist between these fundamental numbers and the corresponding atomic weights.

The wavelengths of the first four hydrogen lines are obtained by multiplying the fundamental number h = 3645.6 in succession by the coefficients 9/5; 4/3; 25/21; and 9/8. At first it appears that these four coefficients do not form a regular series; but if we multiply the numerators in the second and the fourth terms by 4 a consistent regularity is evident and the coefficients have for numerators the numbers 3^2, 4^2, 5^2, 6^2 and for denominators a number that is less by 4.

For several reasons it seems to me probable that the four coefficients which have just been given belong to two series, so that the second series includes the terms of the first series; hence I have finally arrived at the present formula for the coefficients in the more general form: $m^2/(m^2-n^2)$ in which m and n are whole numbers.

For n = 1 we obtain the series 4/3, 9/8, 16/15, 25/24, and so on, for n = 2 the series 9/5, 16/12, 25/21, 36/32, 49/45, 64/60, 81/77, 100/96, and so on. In this second series the second term is already in the first series but in a reduced form.

If we carry out the calculation of the wavelengths with these coefficients and the fundamental number 3645.6, we obtain the following numbers in 10^{-7} mm.

According to the formula	Ångström gives	Difference
Hα (C-line) = 9/5 h = 6562.08	6562.10	+0.02
Hβ (F-line) = 4/3 h = 4860.8	4860.74	-0.06
Hγ (near G) = 25/21 h = 4340	4340.1	+0.1
Hδ (h-line) = 9/8 h = 4101.3	4101.2	-0.1

The deviations of the formula from Ångström's measurements amount in the most unfavorable case to not more than 1/40000 of a wavelength, a deviation which very likely is within the limits of the possible errors of observation and is really striking evidence for the great scientific skill and care with which Ångström must have worked.

From the formula we obtained for a fifth hydrogen line $49/45 \cdot 3645.6 = 3969.65 \cdot 10^{-7}$ mm. I knew nothing of such a fifth line, which must lie within the visible part of the spectrum just before H_I (which according to Ångström has a wavelength 3968.1); and I had to assume that either the temperature relations were not favorable for the emission of this line or that the formula was not generally applicable.

On communicating this to Professor Hagenbach he informed me that many more hydrogen lines are known, which have been measured by Vogel and by Huggins in the violet and the ultraviolet parts of the hydrogen spectrum and in the spectrum of the white stars; he was kind enough himself to compare the wavelengths thus determined with my formula and to send me the result.

While the formula in general gives somewhat larger numbers than those contained in the published lists of Vogel and of Huggins, the difference between the calculated and the observed wavelengths is so small that the agreement is striking in the highest degree. Comparisons of wavelengths measured by different investigators show in general no exact agreement; and yet the observations of one man may be made to agree with those of another by a slight reduction in an entirely satisfactory way.

These measurements are all arranged together in the accompanying table, and the resulting wavelengths according to the formula compared with them. The figures of Vogel and Huggins lie close to the formula but always a bit lower, as though the fundamental number for hydrogen were reduced to $3645 \cdot 10^{-7}$ mm.[1]

Table of Wavelengths for Hydrogen lines in 10^{-7} mm.

						Ultraviolet				
Fraunhofer's symbol	Hα = 9/5 h, C	Hβ = 4/3 h, F	Hγ = 25/21 h, near G	Hδ = 9/8 h, h	Hε = 49/45 h, near H_I	Hζ = 16/15 h	Hη = 81/77 h	Hθ = 25/24 h	Hι = 121/117 h	Average value of the fundamental number h
Observer:										
Van d. Willigen[2]	6565.6	4863.94	4342.80	4103.8	(H_I = 3971.3)	--	--	--	--	h = 3647.821
Ångström	6562.10	4860.74	4340.10	4101.2	(H_I = 3968.1)	--	--	--	--	h = 3645.589
Mendenhall	6561.62	4860.16	--	--	--	--	--	--	--	h = 3645.232
Mascart	6560.7	4859.8	--	--	(H_I = 3967.2)	--	--	--	--	h = 3644.842
Ditscheiner	6559.5	4859.74	4338.60	4100.0	(H_I = 3966.8)	--	--	--	--	h = 3644.460
Huggins	--	for the ultraviolet H-lines white stars				3887.5	3834	3795	3767.5	h = 3643.846
Vogel	--	--	--	--	3969	3887	3834	3795	6769[3]	h = 3644.379
Formula: $H = m^2/(m^2 - 2^2)\ h$	m = 3	m = 4	m = 5	m = 6	m = 7	m = 8	m = 9	m = 10	m = 11	
h = 3645.6	6562.08	4860.8	4340	4101.3	3969.65	3888.64	3834.98	3797.5	3770.2	
h = 3645	6561	4860	4339.283	4100.625	3969	3888	3834.35	3796.875	3769.615	

These comparisons show that the formula also holds for the fifth hydrogen line, which lies just before the first Fraunhofer H-line (which belongs to calcium). It also appears that Vogel's hydrogen lines and the corresponding Huggins lines of the white stars can be represented by the formula very satisfactorily. We may almost certainly assume that the other lines of the white stars which Huggins found farther on in the ultraviolet part of the spectrum will be expressed by the formula. I lack knowledge of the wavelengths. Using the fundamental number 3645.6, we obtain according to the formula for the ninth and following hydrogen lines up to the fifteenth:

121/117 h = 3770.24

36/35 h = 3749.76

169/165 h = 3733.98

49/48 h = 3721.55

225/221 h = 3711.58

64/63 h = 3703.46

289/285 h = 3696.76

Whether the hydrogen lines of the white stars agree with the formula to this point or whether other numerical relations gradually replace it can only be determined by observation.

I add to what I have said a few questions and conclusions.

Does the above formula hold only for the single chemical element hydrogen, and will not other fundamental numbers in the spectral lines of other elements be found which are peculiar to those elements? If not, we may perhaps assume that the formula that holds for hydrogen is a special case of a more general formula which under certain conditions goes over into the formula for the hydrogen lines.

None of the hydrogen lines which correspond to the formula when n = 3, 4, and so on, and which may be called lines of the third or fourth order, is found in any spectrum as yet known; they must be emitted under entirely new relations of temperature and pressure if they are to become perceptible.

If the formula holds for all the principal lines of the hydrogen spectrum with n = 2, it follows that these spectral lines on the ultraviolet sides approach the wavelength 3645.6 in a more closely packed series, but they can never pass this limiting value, while the C-line also is the extreme line on the red side. Only if lines of higher orders are present can lines be found on the infrared side.

The formula has no relation, so far as can be shown, with the very numerous lines of the second hydrogen spectrum which Hasselberg has published in the *Mémoires de l'Academie des Sciences de St. Petersbourg*, 1882. For certain values of pressure and temperature hydrogen may easily change in such a way that the law of formation of its spectral lines becomes entirely different.

There are great difficulties in the way of finding the fundamental numbers for other chemical elements, such as oxygen or carbon, by means of which their principal spectral lines can be determined from the formula. Only extremely exact determinations of wavelengths of the most prominent lines of an element can give a common base for these wavelengths, and without such a base it seems as if all trials and guesses will be in vain. Perhaps by using a different graphical construction of the spectrum a way will be found to make progress in such investigations.

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[1]I translated and reinserted this paragraph and the following table, omitted by Boorse & Motz. --CJG

[2]If one assigns to these values, which stand about 1/1500 higher on average, a weight only 1/3 as great as the remaining observations, one still preserves the same average for h: 3645. [original note]

[3]Sic. Obviously a typo for 3769. --CJG