trum of phosphoretted hydrogen. If a little phosphorus is intro­duced into an apparatus generating hydrogen, the flame will show a series of bands chiefly in the green. The spectrum gets more brilliant if the flame is cooled. This can be done, according to Salet,@@1 by pressing the flame against a surface kept cool by means of a stream of water or by surrounding the tube, at the orifice of which the gas is lighted, by a wider tube through which cold air is blown. The process of cooling the flame, according to Lecoq,@@2 changes the relative intensity of the bands in a perfectly regular manner. The almost invisible least refrangible band becomes strong, and the second band, which was weaker than the fourth, now becomes stronger. Another example of a similar change is the spectrum shown by a Bunsen burner. By charging the burner with an indifferent gas@@3 (N, HC1, CO2) the flame takes a greenish colour, and, though the spectrum is not altered, the least refran­gible of the bands are increased in intensity. While in these in­stances the changes are perfectly regular, the more refrangible rays gaining in relative intensity as the temperature is increased, there are other cases, some of which have already been mentioned, in which the changes are very irregular ; such are those which take place in the spectra of tin, lithium, and magnesium. In the case of zinc the less refrangible of the group of blue rays gains in relative intensity. We cannot, therefore, formulate any general law.

*Numerical Relations between the Wave-lengths of Lines belonging to the Spectrum of a Body.*

It seems *a priori* probable that there is a numerical relation be­tween the different periods of the same vibrating system. In certain sounding systems, as an organ-pipe or a stretched string, the relation is a simple one, these periods being a submultiple of one which is called the fundamental period. The harmony of a com­pound sound depends on the fact that the different times of vibra­tion are in the ratio of small integer numbers, and hence two vibrations are said to be in harmonic relation when their periods are in the ratio of integers. We may with advantage extend the expression “harmonic relation” to the case of light, although the so- called harmony of colours has nothing to do with such connexions. We shall therefore define an “ harmonic relation ” between different lines of a spectrum to be a relation such that the wave-lengths or wave-numbers are in the ratio of integers, the integers being suffi­ciently small to suggest a real connexion. Some writers use the word in a wider sense and call a group of lines harmonics when they show a certain regularity in their disposition, giving evidence of some law, that law not being in general the harmonic law. We shall here use the expression in its stricter sense only. We begin by discussing the question whether there are any well-ascertained cases of harmonic relationship between the different vibrations of the same molecule. The most important set of lines exhibiting such a relationship are three of the hydrogen lines which, when pro­perly corrected for atmospheric refraction, are, as pointed out by Johnstone Stoney, very accurately in the ratio of 20:27:32 (*Phil. Mag.,* xli. p. 291, 1871). Other elements also show such ratios; but when a spectrum has many lines pure accident will cause several to exhibit whatever numerical relations we may wish to impose on them. If we calculate the number of harmonic ratios which, with an assumed limit of accuracy, we may expect in a spectrum like that of iron, we find that there are in reality fewer than we should have if they were distributed quite at random (*Proc. Roy. Soc.,* xxxi. p. 337, 1881). With fractious having a denominator smaller than seventy the excess of the calculated over the observed values is very marked, while there are rather more coincidences than we should expect on the theory of probability if we take fractions having a denominator between seventy and a hundred. The cause of this, probably, is to be sought in the fact that the lines of an element are liable to form groups and are not spread over the whole spectrum, as they would be if they were distributed at random. This increases the probability of coincidence with fractions between high numbers, and diminishes the probability of coincidence with fractions between lower numbers. There is one point which deserves renewed investigation. When the limits of agreement between which a coincidence is assumed to exist are taken narrower, there is an increased number of observed as compared with calculated coincidences in the iron spectrum ; and this would seem to point to the existence of some true harmonic ratios. With the solar maps and gratings put at our disposal by Professor Rowland, we may hope to obtain more accurate measurements, and therefore more definite information. Even if the wave-lengths of two lines are found to be occasionally in the ratio of small integer numbers, it does not follow that the vibrations of molecules are regulated by the same laws as those of an organ-pipe or of a stretched string. E. J. Balmer@@4 has indeed lately suggested a law which differs in an important manner from the laws of vibration of the organ-

pipe and which still leaves the ratios of the periods of vibration integer numbers. According to him, the hydrogen spectrum can be represented by the equation

-π∖>=λ, wr - 4

where *λ*0 is some wave-length and *m* an integer number greater than 2. The following table (I.) shows the agreement between the calculated and observed hydrogen lines. And the agreement is a very remarkable one, for the whole of the hydrogen spectrum is re­presented by giving to *m* successive integer values up to sixteen.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| λ0 = 3645. | | Observed  Hydrogen  Spectrum. | λ0=3645. | | Observed  Hydrogen  Spectrum. |
| *m*. | *m*2*λ*0/(*m*2-4). | *m.* | *m*2*λ*0/(*m*2-4). |
| 3 | 6561·0 | 6562∙1 | 10 | 3796∙9 | 3795∙0 |
| 4 | 4860·0 | 4860∙7 | ll | 3769∙6 | 3767·5 |
| 5 | 4339∙3 | 4340∙l | 12 | 3749·1 | 3745∙5 |
| 6 | 4100∙6 | 4101∙2 | 13 | 3733∙3 | 3730·0 |
| 7 | 3969∙0 | 3968∙1 | 14 | 3720∙9 | 3717∙5 |
| 8 | 3888∙0 | 3887∙5 | 15 | 3711·0 | 3707∙5 |
| 9 | 3S34∙3 | 3834·0 | 16 | 3702∙9 | 3699∙0 |

The differences between the observed and the calculated numbers show a regular increase towards the ultra-violet. It might be thought that a better agreement could be obtained by taking a number slightly different from four in the denominator ; but this is not the case. On the contrary, the agreement in the visible part is at once destroyed if we make the ultra-violet lines fit better. The agreement is not improved but rendered slightly worse if we take account of atmospheric refraction.

As a first approximation Balmer’s expression gives a very good account of the hydrogen spectrum. If the law was general we should find that in the iron spectrum, for instance, which is the only spectrum carefully examined, those fractions would occur more frequently than others which can be put into the form *m*2*∕(m*2*-n*2), that is to say, 3/4 and 8/9 for fractions made up of numbers smaller than 10. A reference to the table in *Proc. Roy. Soc.,* vol. xxxi. p. 337, shows that these fractions do not occur more frequently than others. But, if we change the sign of *n*2 in the denominator, we find 4/5 and 9/10 as the only fractions falling within the range of spectrum examined, and these two fractions are indeed those which occur more frequently than any others made up of numbers smaller than 10.

It might be worth trying to see whether the wave-lengths of lines making up a fluted band can be put into the form ~~w~~~~∙Γ-fc,~~~~t~~~~⅞~~∖; accord­ing to the sign chosen in the denominator, the band would shade off' towards the blue or red. The form of expression seems at first sight well adapted, for it shows how by giving *m* gradually in­creasing numbers the lines come closer and closer together towards what appears in the spectrum as the sharp edge of the band. If we take periods of vibration instead of wave-lengths Balmer’s expression would reduce to

T=T0[1-(*n*/*m*)2]

where T0 is a fixed period of vibration, *n* a constant integer, and *m* an integer to which successive values are given from *n* upwards.

It is often observed, and has already been mentioned, that the spectrum of some elements contains in close proximity two or three lines forming a characteristic group. Such doublets or triplets are often repeated, and if the harmonic law was a general one we should expect the wave-lengths of these groups to be ruled by it ; but such is not the case. The sodium lines which lie in the visible part of the spectrum are all double, the components being the closer to­gether the more refrangible the group. But neither are the lines themselves in any simple ratios of integers, nor do the distances between the lines show much regularity. The ultra-violet lines of sodium as photographed by Liveing and Dewar are single, with the exception of the least refrangible of them (3301). But this line is a very close double, and it may be that the others will ultimately be resolved. Some elements, such as magnesium, calcium, zinc, cadmium, show remarkable series of triplets ; and the relative dis­tances of the three lines seem well maintained in each of them. Even the distances when mapped on the wave-number scale are so nearly the same for each element that it would be a matter of great importance to settle definitively whether the slight variations which are found to exist are real or due to errors of measurement. In the following table (II.) we give the position of the least refrangible line of each triplet together with the distances between the first and second (column B) and between the second and third line of each triplet (column C). The figures in column *A* represent the number of waves in one millimetre. For the zinc and calcium triplets the measurements of Liveing and Dewar are given; the magnesium triplets are put down as measured by Cornu as well as by Hartley and Adeney. The differences in these measιιrements will give an idea of the degree of uncertainty. The triplets of cadmium are farther apart and are mixed up with a greater number of single lines.

@@@1 *Ann*. *Chim. Phys.,* xxviii. p. 57 (1873). @@@2 *Spectre Lumineux,* p. 188 (1874).

@@@3 *Op. cit.,* p. 43 (1S74).

@@@4 *Wied Ann., xxv.* p. 80 (1S85).