Report of the Committee, consisting of Professor DEWAR, Dr. WILLIAMSON, Dr. MARSHALL WATTS, Captain ABNEY, Mr. STONEY, Professor HARTLEY, Professor MCLEOD, Professor CAREY FOSTER, Professor A. K. HUNTINGTON, Professor EMERSON REYNOLDS, Professor REINOLD, Professor LIVEING, Lord RAYLEIGH, Dr. SCHUSTER, *and* Professor W. CHANDLER ROBERTS (*Secretary*), *appointed for the purpose of reporting upon the present state of our Knowledge of Spectrum Analysis.*

THE GENESIS OF SPECTRA. *By* DR. SCHUSTER.

IT is the ambitious object of Spectroscopy to study the vibrations of atoms and molecules in order to obtain what information we can on the nature of the forces which bind them together. The vibrations we know must be of a very complicated nature, yet it is natural that not many years after Spectrum Analysis was raised to the rank of a science by the labours of Kirchhoff and Bunsen attempts were made to discover a law in the apparent irregularity with which different lines of the same element are distributed over the spectrum. If an atom can vibrate in more ways than one, it is certain that some connection must exist between the different periods, and this connection we may attempt to find out by trial. Or we may speculate on the causes which produce such vast differences in the chemical properties of some of the elements, while other elements have properties which resemble each other to an equally marked degree. We may be led on by such speculations to try whether we can trace any similarity in the periods of vibration of molecules which have similar chemical properties, or we may endeavour to classify the elements according to their spectra, and see whether such a classification would divide the elements into groups agreeing with those into which they have been divided by means of their chemical and physical behaviour.

When different elements combine together the vibrations of the compound molecule are not obtained by the simple addition of the periods of the elements. The spectrum of a molecule is entirely distinct from that of its elements, and we may well ask the question whether we can trace in the spectrum of the compound the influence of the different atoms composing it. Thus, for instance, we might trace some relationship between the spectra of the oxides, bromides, chlorides, or iodides of a metal and that of the metal itself, or we may in the absorption spectrum of a salt trace one part to the influence of the base, the other to the influence of the acid. Such and similar questions have been raised and have been partially answered. But we must not too soon expect the discovery of any grand and very general law, for the constitution of what we call a molecule is no doubt a very complicated one, and the difficulty of the problem is so great that were it not for the primary importance of the result which we may finally hope to obtain, all but the most sanguine might well be discouraged to engage in an inquiry which, even after many years of work, may turn out to have been fruitless. We know a great deal more about the forces which produce the vibrations of sound than about those which produce the vibrations of light. To find out the different tunes sent out by a vibrating system is a problem which may or may not be solvable in certain special cases, but it would baffle the most skilful mathematician to solve the inverse problem and to find out the shape of a bell by means of the sounds which it is capable of sending out. And this is the problem which ultimately spectroscopy hopes to solve in the case of light. In the meantime we must welcome with delight even the smallest step in the desired direction.

It is the object of the present report to bring together the various attempts which have been made to trace a connection either between the vibrations of the same body, between those of different compounds of the same body, or finally between the vibrations of similarly constituted bodies.

I. *Connection between the different periods of Vibration of one Molecule.*

In some acoustical systems the different periods of vibration are connected together by means of a very simple law, and it was a natural idea to trace the same law if possible in the luminous vibrations of molecules. If the law holds good the periods of vibrations or the lengths of the waves of light sent out by molecules ought to be in the ratio of small integer numbers. The first published attempt to trace such a connection is due to Lecoq de Boisbaudran, who investigated the spectrum of nitrogen[1] with special reference to this point. The spectrum in question, which is the one appearing at low temperatures, is made up of two sets of bands, one reaching from the red into the green, and one reaching from the green into the violet. Lecoq de Boisbaudran tried to show that each band of the second set had a wave-length which was in the ratio of three to four, with a corresponding band of the first set. The author had, however, only a one prism spectroscope at his disposal, and the wave-lengths as determined by him could not possibly possess that accuracy which is necessary for an investigation of this nature. The more accurate measurements of Thalèn do not bear out Lecoq's result. Thus, for instance, two bands, 5064 and 6752, according to Lecoq, are nearly in the required ratio; if the agreement was perfect the latter number ought to be 6748; but Thalèn, though giving to the green band a number agreeing fairly well with Lecoq's, puts the red band at 6786, differing very considerably from 6754, the required value, if Thalèn's measurement for the green band is used. The other coincidences pointed out by Lecoq are similarly disproved by more exact measurements. Inquiries such as those attempted by Lecoq can only be conducted with advantage when we have measured to the highest degree of accuracy which we can obtain in our best instruments, and many of the apparent harmonic ratios which at one time were thought to hold good had to give way when subjected to a severer test. Mr. Johnstone Stoney,[2] realising this fact, has, however, pointed out one set of harmonic ratios which seems to hold good to a high degree of accuracy. We know of four hydrogen lines in the visible part of the spectrum, and three of these are found to be in the ratios of 20 : 27 : 32. The wave-lengths of these lines are amongst those best determined by Ångström, and they were corrected by Mr. Stoney for atmospheric refraction. The following table exhibits the very remarkable coincidence.

TABLE I.

Observed Wave-length		Calculated Values		Differences
h = 4102·37	.	$\frac{1}{32} \times 131277{\cdot}14 = 4102{\cdot}41$	.	+ 0·04
F = 4862·11	.	$\frac{1}{27} \times 131277{\cdot}14 = 4862{\cdot}12$	.	+ 0·01
C = 6563·93	.	$\frac{1}{20} \times 131277{\cdot}14 = 6563{\cdot}86$		– ·0

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[1] *C. R.* lxix. p. 694 (1869).

[2] *Phil. Mag.* xli. p. 291 (1871).