

The Quantum Theory of Band Spectra.

OPTICAL spectra present two main types of regularity, line series and band series. The two are very different in appearance: the line series is seldom recognisable by inspection, for it comprises as a rule comparatively few lines, the strongest of which are widely separated and usually confused with other lines; whilst band series are among the most striking and beautiful of spectral phenomena, containing large numbers of lines crowding together to so-called "heads" in the most obviously orderly manner. Their arrangement may be described by associating successive integers m with successive lines, when their wave-numbers are found to be given, to a near approximation, by an expression of the form $A + Bm + Cm^2$, where A, B, C are constants. Moreover, a law of the same general type was found by Deslandres to connect the wave-numbers of heads of associated bands when these occur in groups, as is commonly the case. Finally, there may be a number of these groups of heads constituting what may be called a system of bands, and these again are distributed in much the same way as the heads within a group or the lines associated with a head.

A system of bands is thus a very complex affair,

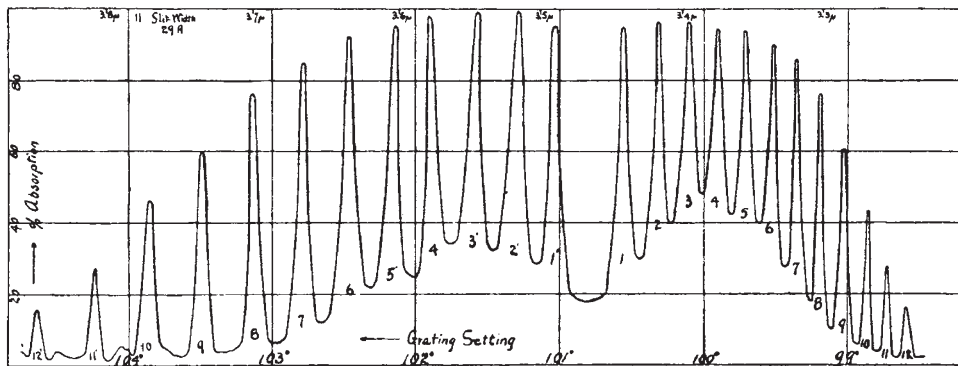


FIG. 1.—The hydrogen chloride band at 3.46μ , mapped with 7500-line grating; hydrogen chloride at atmospheric pressure.

containing, it may be, some thousands of lines and requiring much labour and powerful instrumental means for its complete analysis. Nevertheless, fairly comprehensive data have now been accumulated for the more intense band systems lying in the visible and near ultra-violet regions of the spectrum, and these offer a rich field of investigation to the theoretical physicist. It is proposed in this article to indicate in the broadest outline the present position with regard to the theoretical interpretation of band spectra.

A historical survey cannot be attempted; suffice it to say that the failure of the classical electromagnetic theory was just as complete here as in the case of line series, and the success of the quantum theory no less remarkable. The principles introduced by Bohr and extended by Wilson and Sommerfeld have been applied to the problem and have again proved extraordinarily fruitful. But the radiating systems here involved are molecules instead of atoms, and complications ensue—complications which are reflected in the complex structure of a band series as compared with that of a line series. For whereas an atom can only radiate energy associated with its constituent electrons, a molecule may possess, in addition to this type of energy, two other types, namely, those due to rotation of the molecule as a whole and to vibration of the constituent atomic nuclei. But it appears that each of the three types of motion is separately subject to the rules of generalised quantum mechanics, whilst the fre-

quency of the radiation emitted in consequence of a change in the condition of the molecule is given by dividing the *total* decrease of energy by Planck's constant h .

The simplest case arises when the initial and final states of the molecule differ only in respect of rotation; that is to say, when the emission is solely due to a decrease of one unit in the angular momentum of the molecule. The energy change, and therefore the frequency of the radiation emitted, will depend upon the initial state, and the spectrum should consist of a number of nearly equally spaced lines. Calculations based on known molecular data lead us to expect that these lines will occur in the far infra-red region, and such series have in fact been observed; but work in this region is difficult, and the experimental data are as yet too fragmentary to permit of a conclusive test of the theory.

Passing next to the case in which the rotation change is accompanied by a change in the vibrational energy of the nuclei, the theory predicts a set of bands each of which should consist of two series of lines. One of these arises from an increase of rotational energy and the other from a decrease, and they

should occur respectively on the low- and high-frequency sides of the "fundamental" frequency associated with the nuclear vibration. Bands of this character have been observed in a number of absorption spectra lying in the near infra-red, notably in that of hydrogen chloride, which has been studied by several workers under relatively high dispersion.

In Fig. 1, which represents results obtained by Imes, it will be noted that the lines are not quite equally spaced, but close up gradually in the direction of increasing wave-number. The theory provides an immediate interpretation of this feature; it is due to a difference between the moments of inertia of the molecule in its initial and final states, a difference which is to be expected when it is remembered that the nuclei occupy different mean positions in the two cases. Here also, although the theory in its main outlines is firmly established, much more extensive experimental data are wanted. Those available at present mostly relate to absorption only, and few of them are on a sufficiently large scale of dispersion to permit of the band structure being studied.

The third class of band is that in which the rotation change is accompanied by a change in the electron configuration, or, it may be, by a modification in the nuclear vibration as well. The energy liberated is here much larger in amount than in the previous cases, and the resulting emission is consequently of higher frequency, usually lying in the visible or

ultra-violet regions. The theoretical problem is now one of great complexity, owing to the interactions between the various types of motion co-existing. For example, the configuration of the molecule, and hence its moment of inertia and rotational energy, may be considerably modified by the electron transition; again, the moment of inertia will be a function of the rotational velocity (owing to distortion by centrifugal force), and the latter may also affect the energy of vibration of the nuclei. At present, therefore, only conclusions of a somewhat general character are possible.

Nevertheless, important progress is being made, notably by Kratzer, who has succeeded, for example, in accounting for the well-known cyanogen band heads (the more refrangible group) in terms of various nuclear vibrational states. Thus the group of heads ranging from $\lambda 4606$ to 4515 is attributed to a quantum change of -2 units, that between 4216 and 4153 to one of -1 unit, and so on, whilst in each group the individual heads originate in different absolute values of the quantum numbers concerned. The individual lines associated with each head arise, as before, from transitions between successive states of rotational motion.

Now the correspondence principle leads us to expect the occurrence of the changes ± 1 (and, in special cases, 0) in the rotational quantum number, each of which would give rise to a separate series, so that each band should consist of two (or at most three) branches, the arrangement of which can readily be calculated. A structure of this nature was in fact discovered in a number of bands by Heurlinger in 1918, before the development of the theory; yet detailed study of these and other bands reveals some very important features the theoretical significance of which is at present obscure. For example, there may be many more than three branches constituting one band—as many as twelve sometimes exist; and even in cases where this unexpected multiplicity is not encountered other discrepancies become apparent.

It is safe to say that no band is yet known for which a complete theoretical explanation is available. Even the comparatively simple infra-red absorption bands (hydrogen chloride, etc.) present one important peculiarity of a very puzzling nature, namely, the absence of one line, and only one, in the centre of the band. This presumably corresponds to one of the two rotational changes $0 \rightarrow 1$ and $1 \rightarrow 0$, and its absence would naturally be interpreted as due to the non-occurrence, or, more strictly, the non-participation, of the rotationless state of the molecule in one of these two processes (there is as yet no means of distinguishing one from the other). But why, if one may occur, the other should be prohibited, has not up to the present received a satisfactory explanation.

A similar difficulty occurs in bands in the optical region of the spectrum, but here many other complications usually exist. The simplest case yet found, and one therefore of particular interest, is that of the band spectrum of helium. This is due to a highly unstable molecule which can only be formed by the union of "excited" atoms of helium, but persists long enough to emit a characteristic spectrum containing numerous bands. The constituent lines are in this case all single instead of double, as is often

the case in other spectra, and each branch consists of relatively few lines (never more than about ten), so that there is little difficulty, such as usually occurs, due to overlapping of two or more branches. Further, the lines are much more widely spaced than in any other known bands, and their arrangement can thus be studied more conveniently, only moderate dispersion being necessary. The analysis of the spectrum is not yet complete, but the structure of one of the bands is illustrated in Fig. 2. It will be seen to consist of three branches, designated as P, Q, and R, in accordance with the nomenclature introduced by Heurlinger.

The theory in its original form indicated that these resulted from the rotational quantum changes $m \rightarrow (m+1)$, $m \rightarrow m$, and $(m+1) \rightarrow m$ respectively, but exact measurements show at once that some modification of this view is necessary. For example, if it were correct, the P and R branches should extrapolate over into one another, thus virtually forming one series, but for the suppression of some lines in the centre. In point of fact, their failure to do so could not be more pronounced, for the extrapolated lines

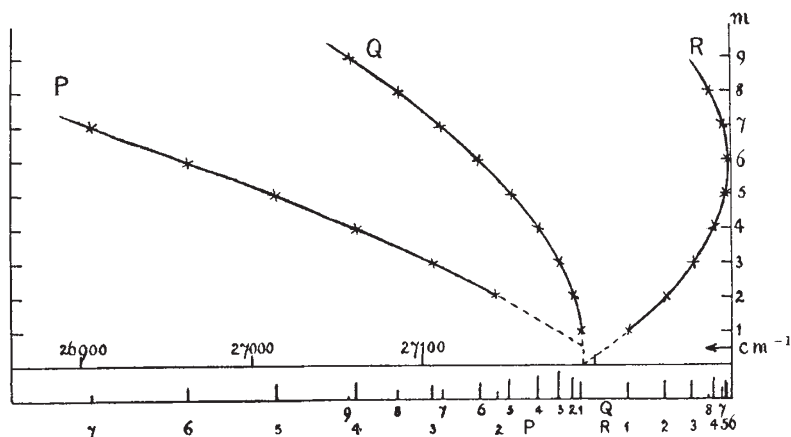


FIG. 2.—The helium band near $\lambda 3680$. Wave numbers plotted against ordinal numbers. Intensity represented by vertical height of line. Note that P and Q curves intersect at $m = \frac{1}{2}$, and Q and R at $m = 0$.

of one fall just midway between the lines of the other, and this behaviour is characteristic of every band in the spectrum which has been analysed up to the present. The conclusion from this seems irresistible. We must suppose that instead of one set of molecular states, as hitherto postulated, here exist two, their characteristic quantum numbers differing by about one-half. Thus, for example, the P branch might arise from the changes $1 \rightarrow 2$, $2 \rightarrow 3$, etc., whilst the R branch would then be due to the changes $1\frac{1}{2} \rightarrow \frac{1}{2}$, $2\frac{1}{2} \rightarrow 1\frac{1}{2}$, etc. It may also be remarked that the same kind of modification suffices to remove the difficulty mentioned above in connexion with the infra-red absorption bands. The necessity for it is probably connected with the effect of the structure of the molecule. In dealing with the rotation of the latter it is not permissible to treat it as rigid and structureless; the motion of the constituent electrons should be taken into account.

The problem is a difficult one, for exact knowledge of the structure of even the simplest molecule is entirely lacking, and apart from this it is even possible that the quantum theory in its present somewhat restricted form is not capable of furnishing a solution. However that may be, it is clear that we may look to work on band spectra to provide data of the greatest value in the investigation of the problems of molecular structure.