SOME ASPECTS OF GROSS INTENSITIES IN ELECTRONIC BANDS WITH SPECIAL REFERENCE TO C_2 (SWAN) AND N_2 (SECOND POSITIVE) SYSTEMS.

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1. *Introduction.*

The subject of spectral intensities is one of the most difficult in modern spectroscopy and one which has received very little attention at the hands of experimental physicist. However, with the researches of Dorgelo[1] in the field of atomic spectra in the years 1923 and 1924, the study of relative intensities of spectral lines entered on a new stage of development. After the enunciation by Burger and Dorgelo[2], in 1924, of the sum rule for intensities in a line multiplet, the interest in the subject has grown very rapidly and it has been actively investigated among others by Ornstein and Burger and their colleagues in the University of Utrecht.

As the experimental results advanced, it was found that the sum rule which followed closely upon the modern concepts of quantum mechanics, was found to agree better in some atomic series, but in others it was merely an approximation. But on the whole it served as a useful guide. In other fields also, *viz.*, the X-rays and the Zeeman patterns, the intensities follow closely the theoretical formulæ developed for optical line spectra.

In the sphere of molecular spectra the sum rule was found to be applicable to intensities with the retention of exponential Boltzmann factor. The intensity factors for heavy symmetric molecules derived theoretically by Hönl and London[9], by using the matrix and wave-mechanics were found to agree with the sum rule. With the quantitative estimation of intensities for different series in helium bands, Johnson and Turner[6] have recently succeeded in verifying Bonger's formula of Balmer series with certain modifications. The knowledge of intensities within the structure of a band enables us to assign certain "effective temperatures" to emitting gas as evidenced from the results of Ornstein and Van Wijk[3] on the negative nitrogen (N_2^+) bands and of Kapuscinski and Eymers[4] on the mercury hydride bands. These methods have also been extended by Richardson[5] (R.S.) to stellar bodies to know their "effective temperatures". It may therefore be said that as far as

the structure lines of an individual band are concerned, the results are in many cases in accordance with the predictions of theory.

When it is a question of gross intensities of several bands in a system, the problem becomes different. On account of the large spectral ranges involved in this branch, the experimental work is often very difficult. Theoretical ideas in this connection began to be advanced in the year 1925, with the explanation by Franck[7], of the mechanism of dissociation of molecules by light absorption. Condon[8] extended the ideas to electronic bands and by means of his theory, now known as Franck-Condon principle, predicted certain general characteristics of intensity distribution in a system. Quantitative work on vibrational intensities is very little. Confirmation of Franck-Condon theory was a sort of semi-quantitative data mostly obtained as eye-estimates. With a view to get, therefore, accurate data, a programme of intensity measurements was undertaken by us at London with the latest and improved experimental technique. From experimental standpoint, this problem of vibrational intensities appears more promising, on account of the ease with which the band heads could be photographed in preference to rotational structure lines. The investigation of even an empirical relation between temperature and gross intensities, might lead to the application of band spectroscopic methods to problems in astro-physics.

2. *The Problem.*

Quantitative investigations into gross intensities in band systems were undertaken in Utrecht in 1930, by Elliott[10] who made accurate measurements on bands of β-system of boron oxide (BO) and latterly on the α-system.[11] Ornstein and Brinkman[12] have measured the intensities of violet CN-system with a view to determine the temperature of carbon arc. Wurm[13] in Potsdam has also determined the intensity distribution in the absorption bands of CN and C_2 (Swan) systems as obtained in R- and N-type stars. In our programme of work we undertook the measurements in C_2 (Swan)[15] and N_2 (Second positive)[16] systems, both produced under a variety of experimental conditions, and the results of which have since been published. Herzberg[14] has also made an attempt to measure the intensities of 2nd positive and negative bands of N_2, but his results do not appear to have been obtained with the rigorous technique of heterochromatic photometry.

It is known that conditions of excitation play a prominent part in producing or isolating certain spectra. It is from this standpoint that some aspects, not hitherto touched, of our results on C_2 and N_2 bands will be studied in the present paper. Reference will also be made to certain relevant features of CN-violet system[17], the improved results on which are awaiting publication.

3. *Experimental.*

The methods and technique of intensity measurement have been sufficiently dealt with in a paper by Read and L. W. Johnson[18] and in a subsequent paper by Johnson and author.[15] It is therefore deemed unnecessary to enter here into any of those details. It is believed, however, that the results of intensity measurements on which interpretations have been based in the present paper are accurate enough to justify the conclusions drawn. By way of illustration discrepancy between eye-estimates and accurate microphotometric results in N_2 (Second positive) system can be judged from the following figure (Fig. 1). Similar results have been obtained for Swan

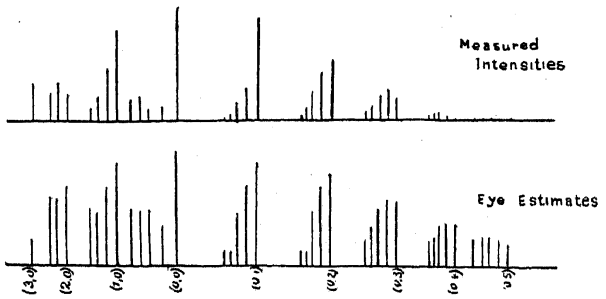

FIG. 1. Comparison of eye-estimates with measured intensities (N_2 second positive).

system. Comparison shows that our visual results are generally over-estimated by several hundred per cents.

4. *Results and Discussion.*

For a normal distribution of intensity in a band system, the 0—0 band is the strongest, the intensity falling rapidly for other bands in that sequence. For bands of other sequences, the intensities gradually diminish, the point of maximum intensity shifting from the first band to bands of higher v' v'' values. The band systems under study are said to have normal distribution and this has been verified by our experimental results. In Figs. 2 and 3 are drawn the slopes of relative intensity fall or rise in sequences of both systems. One point, however, that requires special mention, is in regard to 0—0 sequence of N_2. In this the intensity falls rapidly at first upto (2, 2) and then rises suddenly at (3, 3) in all the sources except the spark where the rise is found at (4, 4) band. It is difficult to understand this unless we assume two Condon parabolas of distribution with their apex at (0, 0) and (3, 3) respectively. But in the absence of bands having values above $v'=4$, this is impossible to study.

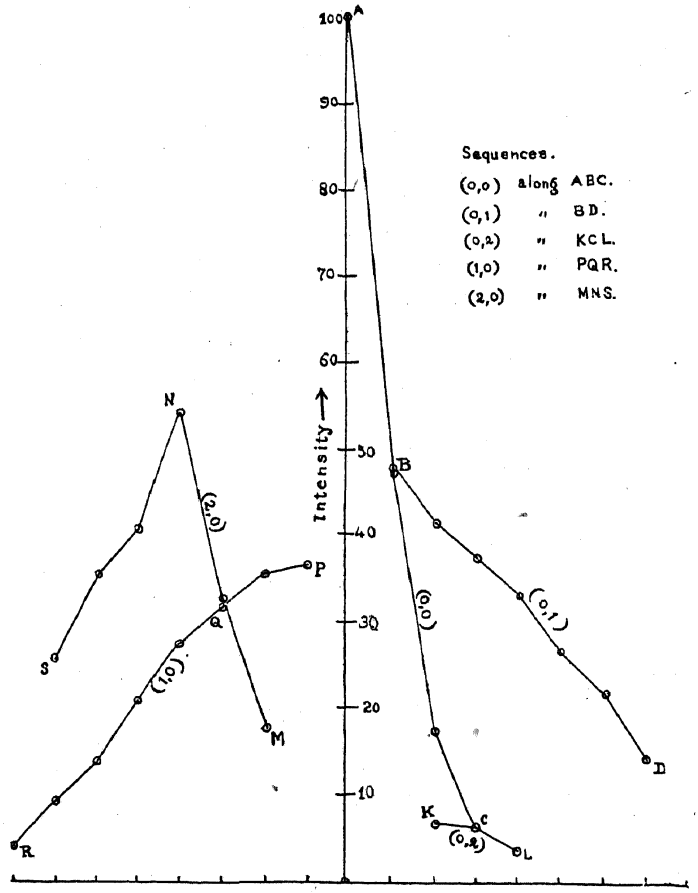

FIG. 2. Relative intensity slopes in sequences of C_2 (Swan) system.

According to equation

$$I/\nu^4 = A.p_{v'v''}.e^{-\frac{E_{v'}}{kT}}$$

the function $\sum_{v'} I/_{\nu^4}$ for the initial levels should diminish as we go to higher v' values if the temperature equilibrium holds. This appears to be true in both C_2 and N_2, for all conditions except the argon discharge, where the Swan bands are excited in about 30 mms. pressure of the inert gas. Here the log $\Sigma I/_{\nu^4}$ is shown as a function of $E_{v'}$, the vibrational energy of initial levels (Fig. 4). The graph is quite unusual giving a parabolic shape with apex at about $v'=2$. This distribution is obscure in its origin and if genuine, will have to be explained, apart from temperature, probably as a specific effect of the inert gas resulting from unknown collision processes.

In each sequence, if the log of band intensity divided by ν^4 is proportional to $E_{v'}$, we should expect statistical equilibrium of molecules with their surroundings at a particular temperature. Whether this holds in the case of arc

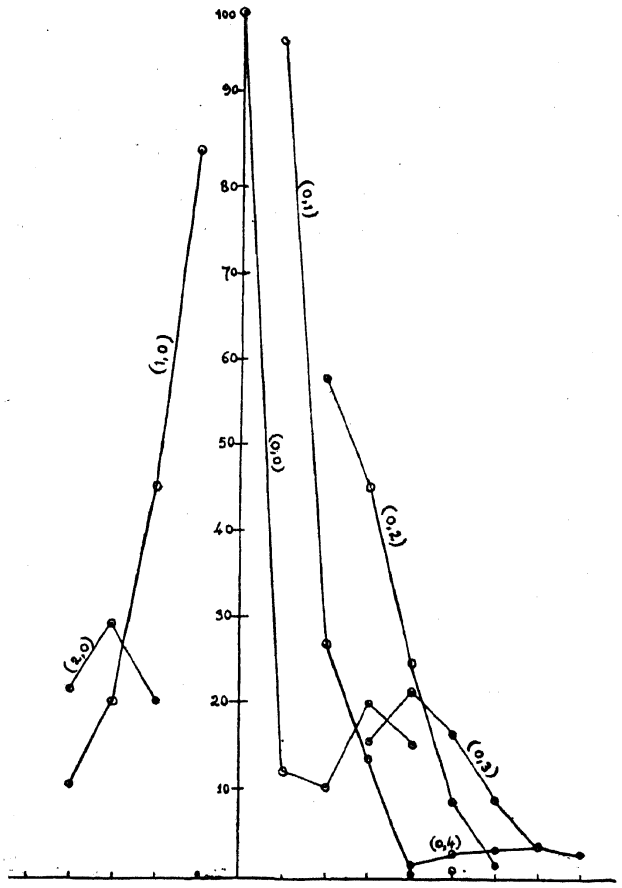

FIG. 3. Relative intensity slopes in sequences of N_2.

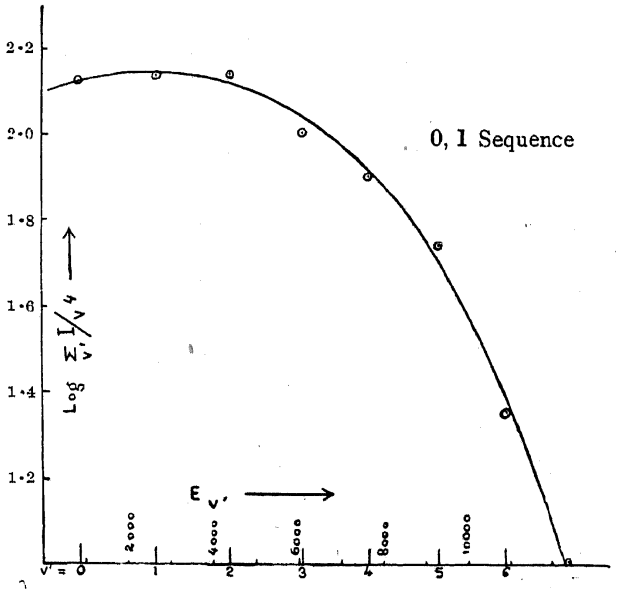

FIG. 4. Log $\sum_{v'} I/_{\nu^4}$ as a function of $E_{v'}$ for Swan bands in argon,

which is generally classed with flames, we have drawn graphs showing log $I/_{\nu^4}$ of each band of sequence against $E_{v'}$ of the Swan and CN violet systems both produced in carbon arc, the former in presence of hydrogen. Similar figures have also been constructed for oxy-coal-gas flame excitation. (See Figs. 5 to 9.) One is led to conclude from these figures that a thermal distribution nearly prevails for cyanogen in arc, as is the case with oxy-coal-gas flame

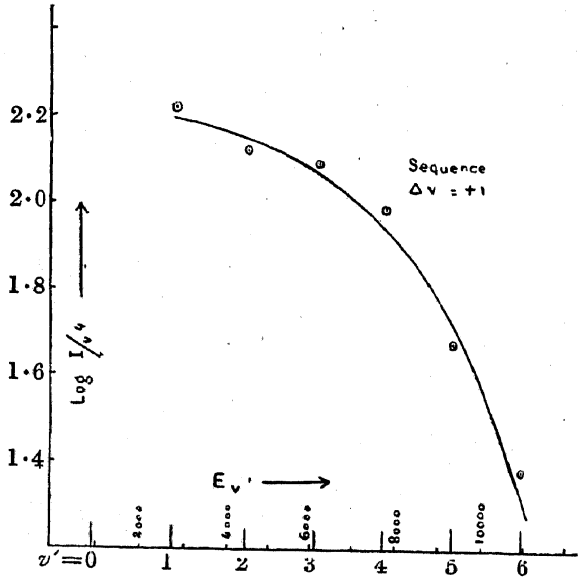

FIG. 5. Log $I/_{\nu^4}$ as a function of $E_{v'}$ in sequences of Swan bands in arc.

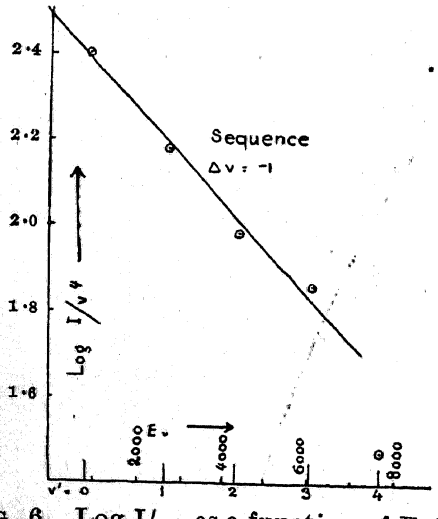

FIG. 6. Log $I/_{\nu^4}$ as a function of $E_{v'}$ in sequences of Swan bands in arc.

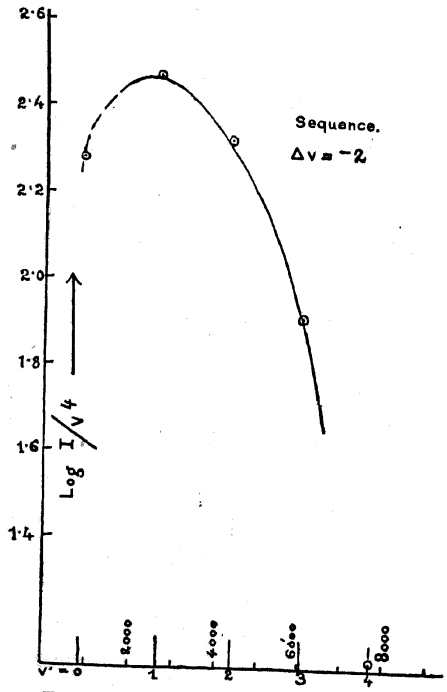

FIG. 7. Log $I/_{\nu^4}$ as a function of $E_{v'}$ in sequences of Swan bands in arc.

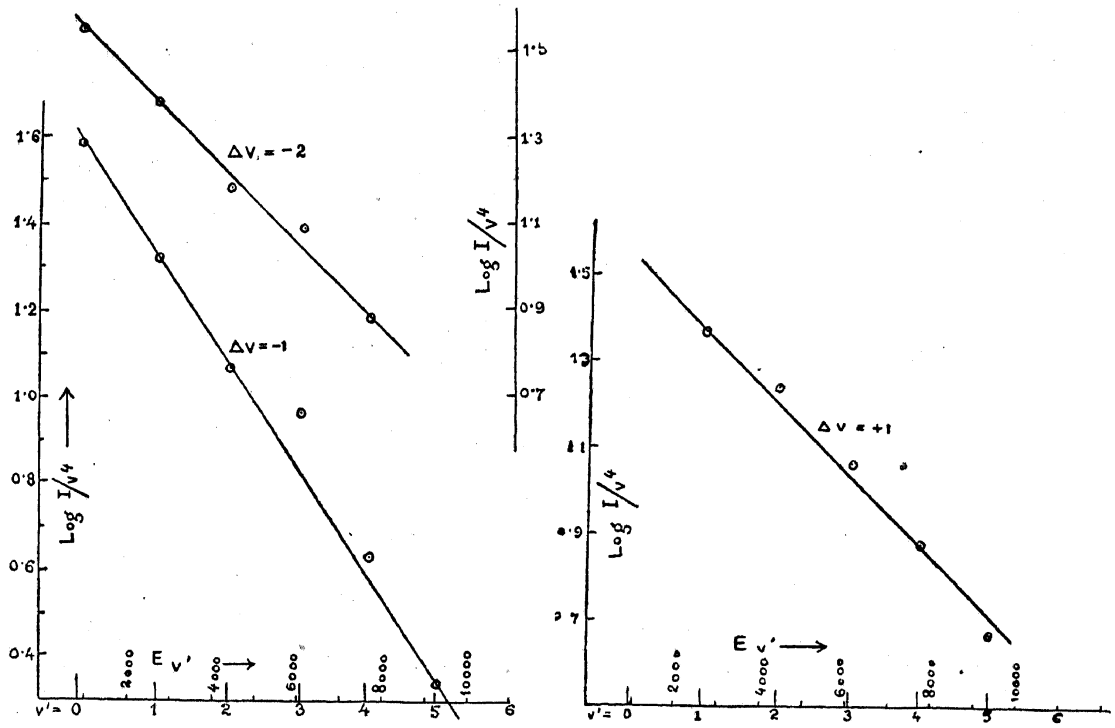

FIG. 8. Log I/ν^4 in sequences of C_2 (Swan) in oxy-coal-gas flame.

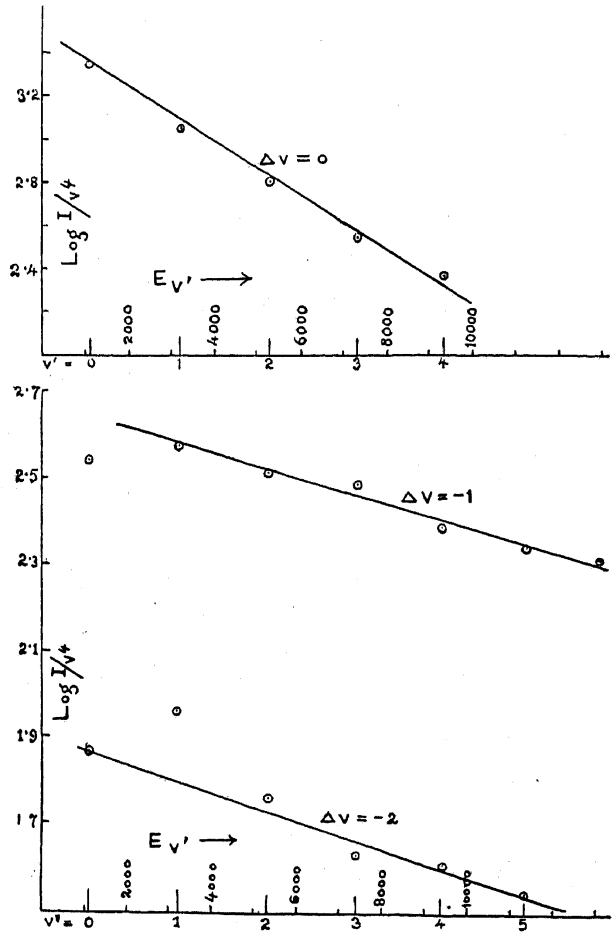

FIG. 9. Log I/ν^4 in sequences of CN-system in arc.

though the values of temperatures derived on this basis give no clear evidence of it. Its absence in Swan bands in arc, which can be deduced by the nature of graph, may be attributed to the formation of C_2 molecule from more complex molecular groupings, energy changes in which are not understood. Consequently the excitation of Swan bands in arc may be non-thermal in origin. Its presence in CN-system is a likely consequence of the greater affinity of carbon to atmospheric nitrogen at high temperatures. In discharge tubes where low temperature conditions prevail, the CN bands are only obtained in presence of active nitrogen. The discharge in low pressure air with carbon electrodes or with carbon as impurity generally gives bands of CO molecule (Ångstrom bands).

5. *Intensity Centres.*

In the next treatment, the Swan bands have been particularly chosen to discuss the positions of maxima of intensities. In various sequences from the observed values of band intensity and wavelength, we could form the quantity

$$=\bar{\lambda}\frac{\Sigma I\lambda}{\Sigma I}$$

according to procedure adopted by Johnson.[19] $\bar{\lambda}$ may be described as the "optical centre of gravity" or the "centre of intensity" of the sequence. Such results are given below in Table I.

TABLE I.

Positions of "Intensity Centres".

C_2 (Swan System).

Sequence	Spark	Arc	Bunsen flame	Oxyflame	Argon
2, 0 ..	4370·3	4370·2	4370·8	4373·2	4374
1, 0 ..	4715	4709·7	4712·6	4713·1	4706
0, 0 ..	5155·6	5154·5	5155·3	5157	5147·5
0, 1 ..	5580·3	5582·0	5586·3	5585	5557·4
0, 2 ..	6044	6105·7	6100·9	6099·3	6035

With the extension of the same reasoning, we have also calculated the "Intensity Centre" of the Swan system in the different sources.

The values are tabulated below in Table II.

TABLE II.

Condition of excitation	Intensity centre $\bar{\lambda}$
Spark under glycerine ..	5075
Arc in H_2 ..	5190
Bunsen flame ..	5252
Oxy-coal-gas flame ..	5252
Argon discharge ..	5355

Fig. 10 shows how the "intensity centre" shifts from one condition to the other in sequences as well as in the whole system. Assuming the approximate temperatures as follows, *viz.*, Argon discharge 600° K, flame 2200° K, arc 4000° K, and spark 6500° K, some of which have been determined by different

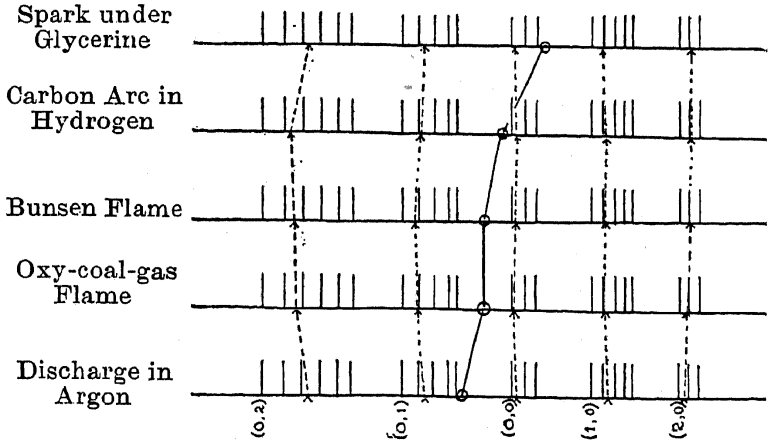

FIG. 10. "Intensity Centres" in sequences and in the system (Swan Bands of C_2).

N.B.—Dotted line passing through "Centres" in sequences. Full line across for "Centres" in the system.

authors by spectroscopic or other methods, a graph is drawn showing these against wavelength of the "intensity centre" ($\bar{\lambda}$) of the whole system. This is given in Fig. 11. It appears from this that $\bar{\lambda}$ of the "intensity centre" is some function of temperature within the sources, the exact form of which cannot be clearly defined.

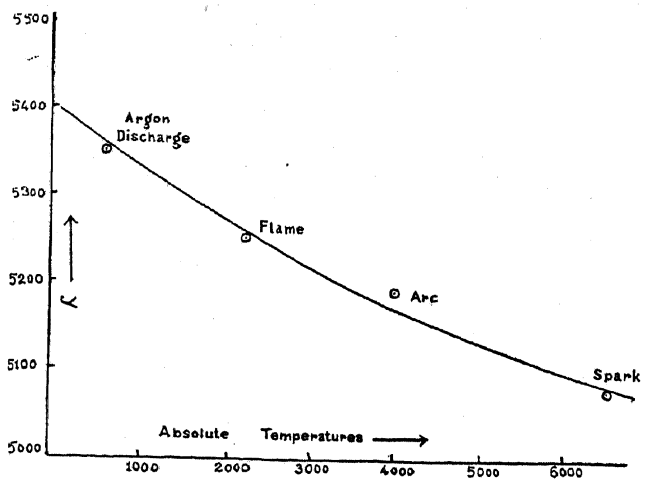

FIG. 11. Wavelength of "Intensity Centres" and temperatures of sources. (C_2 Swan system.)

Taking the two thermally excited sources, *i.e.*, bunsen and the oxy-coal-gas flames, we get the same $\bar{\lambda}$ for both. If the temperature difference between these be of the order of $\pm 500°$, we may not expect an appreciable redistribution of intensity, and this may account for the same "centre" found for both. It may be noted in this connection that the temperatures derived for these by Johnson and Tawde[15] on the assumption of Boltzmann distribution of vibrational energy in the excited state, also give a common value for both, *viz.*, 4700°K. although this cannot be the real temperature in either of these two sources.

Another point which may be mentioned is the relative total "weights" of levels in the different sources, derived by taking the sum of $\sum_{v'} I/_{\nu^4}$ of all the levels. These are found in the ratios,

Bunsen flame,	Arc,	Spark,	Oxy-flame,	Argon
1	: 1·052	: 1·073 :	1·205	: 2·341

which can be taken as those of radiating molecules in the different sources. Argon again offers here a point of special interest.

6. *Transition Probabilities.*

Irrespective of the conditions of excitations, the *maximum* transition probabilities generally obey the Franck-Condon principle. Such a result is to be expected as Condon's theory does not take into account the distribution of molecules in the initial states. Any discrepancy between theory and experimental results is to be sought in the degree of accuracy of the nuclear potential energy function defining the potential curves. The values of maximum transitions derived by the use of Morse function[20]

$$U(r) = D_e (e^{-2ax} - 2e^{-ax})$$

closely agree with experimental values as may be seen from the following Table:

TABLE III.

Most Probable Transitions in C_2 (Swan).

$r_{max} \rightarrow r_{max}$		$r_{min} \rightarrow r_{min}$	
Theoretical	Experimental	Theoretical	Experimental
1, 0	1, 0	0, 2	0, 1
2, 1	2, 1	1, 3	1, 3
3, 2	3, 2	2, 4	2, 4
..	4, 3	3, 6	3, 5
5, 4	5, 4	4, 7	4, 6
6, 5	6, 5	5, 8	5, 7
7, 6	7, 6		

But this function does not satisfy the transitions observed in BeO by Johnson and Dunston[24] and N_2 (Second positive) bands by Tawde.[23] They approximate to theoretical values derived from Rydberg function,[21]

$$U(r) = D_e (ax+1)e^{-ax}.$$

Nothing in favour of one or the other can be said at present unless we are in possession of more experimental material.

Leaving aside the maximum probabilities, we shall now discuss the effect of conditions of excitation on the relative probabilities of transition in various v''-progressions. In Figs. 12 to 15 are plotted these results for C_2 (Swan) system.

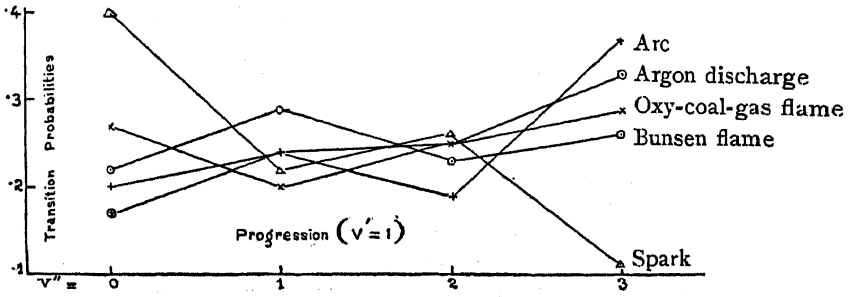

FIG. 12. Transition probabilities in v''-progressions (C_2).

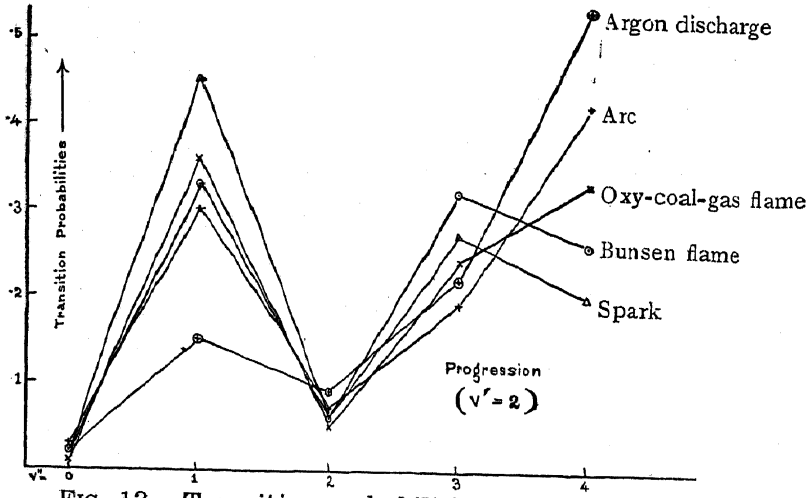

FIG. 13. Transition probabilities in v''-progressions (C_2).

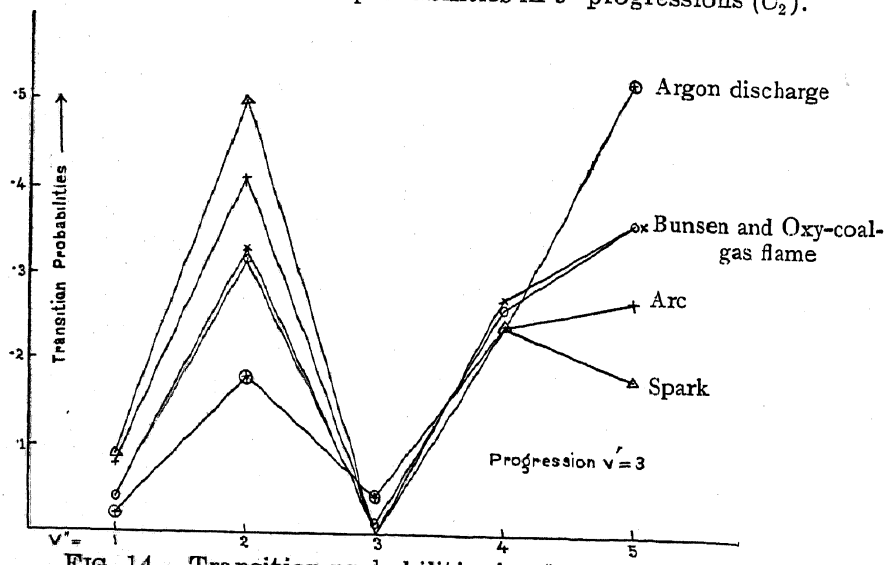

FIG. 14. Transition probabilities in v''-progressions (C_2).

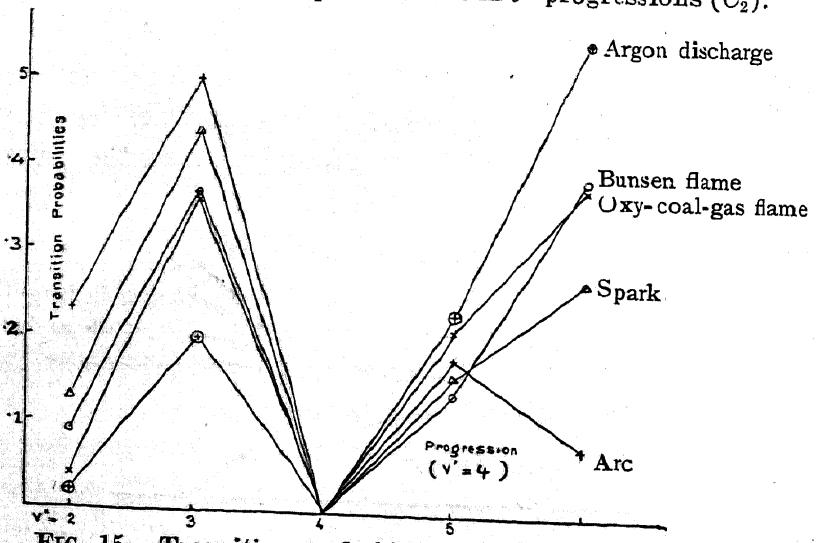

FIG. 15. Transition probabilities in v''-progressions (C_2).

From a study of these figures, it may be concluded that the radiating C_2 molecules in argon tend to favour levels above $v''=4$. The transitions in the spark, on the other hand, are more or less of opposite nature, the molecules in this case preferring levels below $v''=4$. This is particularly noticeable upto progression $v'=3$. But above this, the arc conditions begin to predominate and we get in the latter case, the bands (4, 2), (5, 4) and (6, 5) to have very high probabilities. The corresponding highly probable transitions in argon are $5\rightarrow 7$ and $6\rightarrow 8$.

Purely thermal conditions such as the bunsen flame or the oxy-coal-gas flame do not show such selective behaviour probably on account of the steady nature of excitation as against the violent one of electrical conditions like spark.

In the case of spark under glycerine, the transitions $0\rightarrow 0$, $1\rightarrow 0$, $2\rightarrow 1$, $3\rightarrow 2$, are very high in comparison to others. The fact is that C_2 molecule is formed here from a more complex hydro-carbon molecule like glycerine. It is believed that in the dissociative process which goes on in the spark, the radiating C_2 molecules find themselves in the intense electrical fields of neighbouring charged atoms especially of hydrogen and these may cause their early dissociation giving more probable transitions for the above bands.

To come again to argon, it offers a special problem for study. Here the levels $v''=4, 5, 6, 7, 8$ are favoured more than others, as pointed out already, giving higher probabilities for bands (2, 4), (3, 5), (4, 6), etc. It may be remarked that the production of these bands in preference to others is characteristic of argon which brings out spectra of low energy conditions. Johnson and Cameron[22] have investigated the effect of argon and other inert gases on certain molecular spectra and they classify this effect under three heads: (i) isolation of spectra difficult to obtain otherwise; (ii) redistribution of spectral energy, usually towards the red; and (iii) reduction of broadening of lines. Out of these, the effect observed in Swan bands under study may be classed under (ii). This can be verified from the position of "intensity centre" at longer λ 5355 relative to others. We shall revert to this subject of argon in the following paragraph when dealing with nitrogen.

In the case of nitrogen, the most probable transitions which follow from Condon's theory are verified to nearer approximation, only by the use of Rydberg function as said elsewhere. With regard to relative values of these in v''-progressions two of which are given in Figs. 16 and 17, the high probability for $2\rightarrow 1$ transition in argon has been suggested by the author in a recent paper[16] as a consequence of Heitler and London level in its neighbourhood, being not favoured by N_2 molecules in presence of the inert gas.

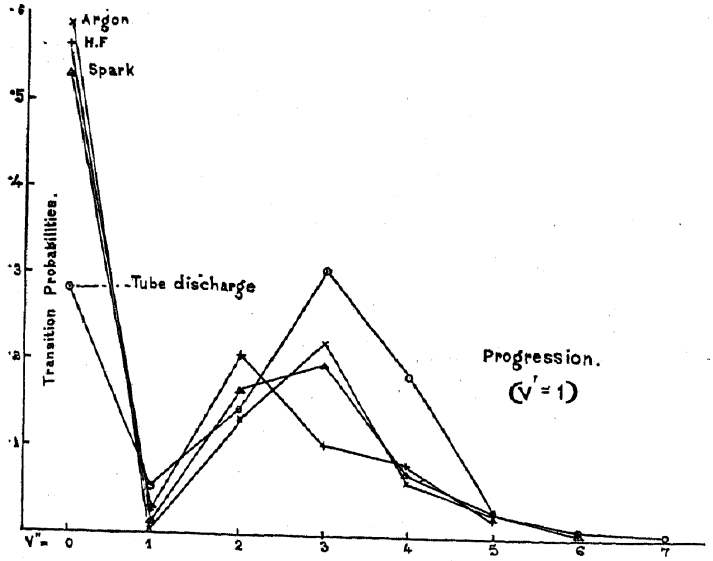

FIG. 16. Transition probabilities in v''-progressions (N_2).

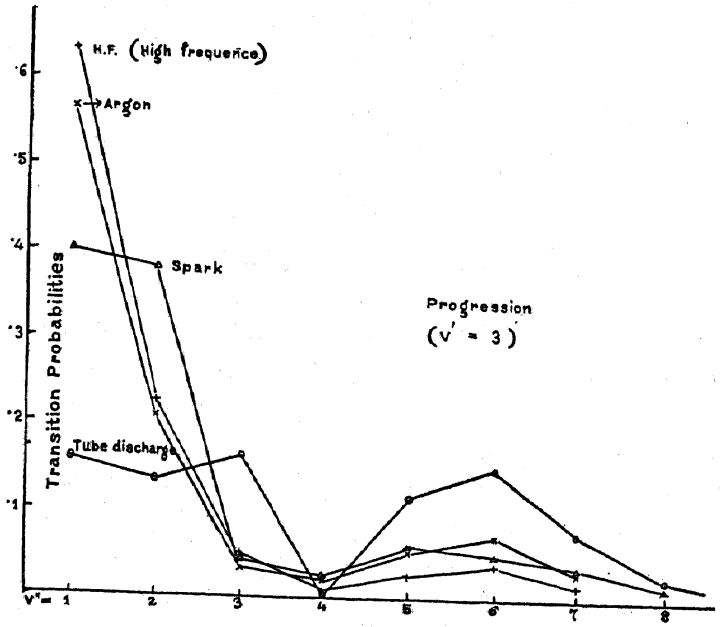

FIG. 17. Transition probabilities in v''-progressions (N_2).

Another point which requires to be noted here is the absence of transition $4 \rightarrow 3$ in argon in spite of its high value in other sources. The same source also gives a very high probability for transition $(4 \rightarrow 2)$. According to quantum theory, the action of inert gas may be described as increasing the probability of those orbits which correspond to smaller energy quanta. With argon present in such large proportions (99% to 0·7% N_2) at a pressure of about 40 mms., we may expect this to happen under the present conditions. But it is surprising to note that unlike Swan bands in argon, we get here

some evidence of energy displacement towards the violet end instead of towards the longer wavelengths. This can be seen from high values of probabilities obtained for transitions $1 \rightarrow 0$, $2 \rightarrow 1$, $3 \rightarrow 1$ and $4 \rightarrow 2$. The effect might be analogous to one observed by Johnson[19] in the first positive system of this molecule, where for a trace of nitrogen in argon, the energy displacement towards the more refrangible end is of the order of 30 to 40 A.U. Determination of the "centres of intensity" in various sources will furnish some additional material for interpretation, but it has been found impossible to complete it within the scope of this paper.

Summary.

(1) The development of the subject of spectral intensities to gross intensities of bands has been reviewed.

(2) The Swan system of C_2 and N_2 (second positive) systems have been chosen to treat some aspects relating to the conditions of excitation.

(3) The probabilities of transition, the temperatures, and the "centres of intensity" have been discussed in relation to each other where possible.

(4) Attempt has been made to explain some unusual intensity features of bands excited in different sources especially in argon.

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