

Physics. — *The Excitation of Band Systems.* I. By L. S. ORNSTEIN and G. O. LANGSTROTH. (Communication from the Physical Institute of the University of Utrecht.)

(Communicated at the meeting of April 29, 1933).

The relative transition probabilities for bands having the same electronic transition can be determined from the FRANK-CONDON theory, and the results are in semi-quantitative agreement with experiment in many cases. Such calculations are made possible by the fact that the wave functions for a molecule can be approximately written as the product of two functions, one depending on the electronic coordinates, and the other on the nuclear coordinates¹⁾. Therefore it is possible to separate the electric moment for any transition into a part dealing with the electronic transition and one dealing with the nuclear vibrations²⁾. Hence in discussing the relative transition probabilities of bands of this type it is sufficient to consider only the nuclear motions, since the electronic transition is the same for all.

For a complete theory of the relative *intensities*, however, it is necessary to know the details of the accompanying phenomenon of excitation. The excitation probabilities for bands from different electronic levels is, of course, extremely complicated, but the excitation analogue of the FRANK-CONDON principle presents an obvious simplification. A beginning of the study of this problem is made in the present paper. Its final object is to make possible the formulation of a theory of excitation for band systems, starting with assumptions similar to those of the FRANK-CONDON theory for emission.

The fundamental point in the FRANK-CONDON classical picture³⁾, which is upheld in its essentials by wave mechanics, is that during an electron transition the nuclear motions are unaffected, i.e. the Hamiltonian for the oscillating system at the end of the transition can be obtained from that at the beginning of the transition simply by replacing the initial nuclear potential function by the appropriate potential function for the final state. This applies equally well to the transition probabilities in absorption spectra. In this case also the nuclear momenta and position may be considered as unchanged⁴⁾ during the electronic transition, presumably

¹⁾ BORN and OPPENHEIMER. *Ann. Phys.* **84**, 457, 1927.

²⁾ CONDON. *Phys. Rev.* **32**, 858, 1928; also HUTCHINSON. *Phys. Rev.* **36**, 410, 1930.

³⁾ CONDON. *Phys. Rev.* **28**, 1182, 1926.

⁴⁾ The classical picture is over-precise in this point since it violates the uncertainty principle.

because of the extremely small momentum of the light quantum, and of the extremely short transition time.

The question now arises, "How will the nuclear motions be affected in similar transitions which are due to electron impact?". FRANK and JORDAN¹⁾ suggested that the same considerations should hold here also. In the case of nitrogen for example, each nucleus is about ten thousand times as massive as the exciting electron, and it is perhaps to be expected that the direct effect on the nuclear motions should be very small. If this is so the relative intensities of bands having the same electronic transition but different initial vibrational quantum numbers in emission, should be independent of the velocity of the exciting electrons²⁾.

The relative intensities of the bands $0 \rightarrow 2$ (λ 3805), $1 \rightarrow 3$ (λ 3755), and $2 \rightarrow 4$ (λ 3710) of the second positive group of Nitrogen were determined at various electron voltages from 14 to 25 volts. Measurements were taken so that the 'total' excitation curves (i.e. curves dependent on the probability of electronic transition as well) were also obtained, but we are chiefly interested in the relative intensities of the bands. They were found to be strongly dependent on the velocity of the exciting electrons for voltages below 20 volts, but above this value they became constant³⁾. On the other hand, the development of the rotational structure did not differ appreciably over the voltage range examined.

It is not our purpose in this preliminary paper to attempt a detailed explanation of this behaviour but merely to present some experimental facts which will be discussed in a later publication.

Experimental.

The type of tube used in this research has been fully described elsewhere⁴⁾. It consisted of hot filament from which electrons fell through a known accelerating potential and passed through a 'grid' into the field free observation space. It was filled with purified nitrogen to one tenth of a millimetre of mercury pressure. In general, the tube current used was 0.30 milliamperes.

The spectrograph was a standard quartz HILGER E 1, with a dispersion of about $10 \text{ \AA}^\circ/\text{mm.}$ at λ 3800. It was used with a very wide slit (about 0.5 mm.) in order to blend the rotational structure completely. Quartz optics were used. The exposure time was 30 minutes.

Several exposures were taken on each plate with the same tube current

¹⁾ "Anregung von Quantensprüngen durch Stösse". Springer, (Berlin), 1926.

²⁾ Provided of course that the nuclear and electronic functions can still be treated as independent factors. As a matter of fact, HERZBERG (Zeit. Physik. **49**, 761, 1928) has shown that the relative intensities of the bands can be varied in electrodeless ring discharge, but the processes involved are so complicated that it is difficult to say anything definite concerning their nature.

³⁾ Data since obtained show that they remain constant for considerably higher voltages.

⁴⁾ LINDH, Zeit. Physik. **67**, 67, 1930.

and exposure time, but with different accelerating potentials. In this way each plate had one exposure at least within the voltage range of some other plate, so that the determination of the total excitation curve, as well as the relative intensities of the bands at each voltage, was possible.

The intensity-blackening scale was put on each plate by means of a standard quartz band lamp and step-slit. In order that the exposure times for the bands and for the intensity marks should be equal, it was necessary to use the diffuse reflection from a 'white' plane smoked with magnesium oxide. The diffuse reflection coefficient for this substance changes by only a very small fraction of one percent over the range $\lambda 3700$ to $\lambda 3800$ ¹⁾. Accordingly no appreciable error was made in using the energy distribution calculated for direct radiation from the lamp itself.

A MOLL microphotometer was used to obtain the relative intensities of the bands from their maximum blackenings in the usual way ²⁾. The use of the maximum blackening values is not in itself objection free for bands, since they may differ in the spacing or development of the rotational structure, in which case such measurements lead to erroneous results for the total band energies. Accordingly the intensity curves for the bands were determined for several plates by means of the analysing apparatus ³⁾ designed by WOUDE, and the areas under them were measured with a planimeter. Each area was then taken as a measure of the total band intensity. This method must give objection free results, and in the present case the values so found agreed with those found from the maximum blackening measurements within the experimental error.

There were no interfering bands or lines, and the bands under consideration were so far separated that the tail of one did not reach the head of the next. There was no background. The measured intensities are good to about 8 percent for a single determination.

Results.

The results for the total excitation functions are given in table I. The intensity of $0 \rightarrow 2$ at 18.0 volts has been set arbitrarily at 100, and the other values follow from this. No ν^4 corrections have been made since they are unnecessary for our purpose in the present paper.

The ratios of the band intensities at various voltages are given in table II.

The results of both these tables have been plotted in figures 1 and 2. The average values for the maximum blackening and integration determinations have been used. The approximate excitation curve for the negative band $\lambda 3914$ included in figure 1, has been taken from LINDH's paper (loc. cit.).

¹⁾ TAYLOR, Jour. Opt. Soc. Am., 21, 776, 1931.

²⁾ ORNSTEIN, MOLL, and BURGER, "Objektive Spektralphotometrie" (Vieweg) 1932.

³⁾ Zeit. Physik., 79, 511, 1932.

TABLE I.
Relative Intensities of the Bands at Various Voltages.

| Accelerating Voltage | 0 \rightarrow 2 | | 1 \rightarrow 3 | | 2 \rightarrow 4 | |
|----------------------|-------------------|------|-------------------|------|-------------------|------|
| | M.B. | Area | M.B. | Area | M.B. | Area |
| 12.0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 14.0 | 23 | 24 | 13 | 15 | — | — |
| 14.0 | 26 | 26 | 14 | 14 | 3.4 | 3.6 |
| 15.0 | 65 | 67 | 39 | 43 | 10.2 | 9.9 |
| 15.0 | 63 | 60 | 36 | 36 | 8.3 | 9.5 |
| 15.9* | 74 | — | 58 | — | 15.0 | — |
| 16.0 | 95 | 95 | 70 | 74 | 19.0 | 19.0 |
| 16.0 | 95 | 95 | 68 | 66 | 19.0 | 19.0 |
| 18.0 | 100 | 95 | 79 | 83 | 26.0 | 25.0 |
| 18.1 | 97 | — | 83 | — | 25.0 | — |
| 20.0 | 84 | 84 | 70 | 73 | 22.0 | 24.0 |
| 20.0 | 80 | — | 76 | — | 23.0 | — |
| 20.0 | 85 | — | 77 | — | 24.0 | — |
| 22.2 | 79 | — | 69 | — | 19.0 | — |
| 25.3 | 70 | — | 65 | — | 20.0 | — |

M.B. and Area refer to the values of the intensities calculated from maximum blackening and integration measurements.

* This value lies somewhat far off the curve drawn through the other values. The discrepancy is probably due to a change in tube current or accelerating voltage for this exposure, but since such was not noted at the time the value has been included in the results.

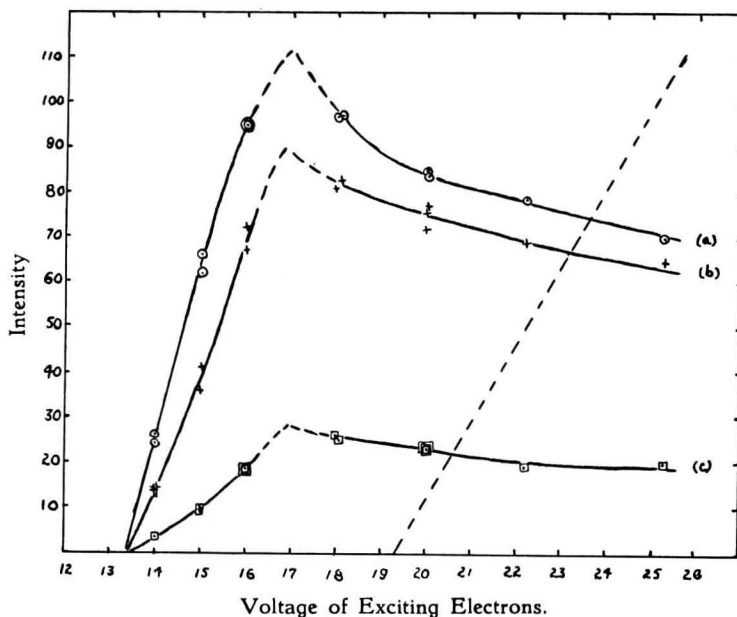


Fig. 1. Total excitation curves for three bands of the second positive group of Nitrogen. They are, in the order (a), (b), (c), 0 \rightarrow 2, 1 \rightarrow 3, and 2 \rightarrow 4. The broken line represents approximately the excitation function for the negative band λ 3914.

TABLE II.
Band Ratios at Various Voltages.

| Accelerating Voltage | 1 \rightarrow 3 / 0 \rightarrow 2 | | 2 \rightarrow 4 / 0 \rightarrow 2 | | 2 \rightarrow 4 / 1 \rightarrow 3 | |
|-------------------------|---------------------------------------|------|---------------------------------------|------|---------------------------------------|------|
| | M. B. | Area | M. B. | Area | M. B. | Area |
| 14.0 | 0.57 | 0.62 | — | — | — | — |
| 14.0 | 0.53 | 0.57 | 0.13 | 0.14 | 0.24 | 0.26 |
| 15.0 | 0.60 | 0.65 | 0.16 | 0.15 | 0.26 | 0.23 |
| 15.0 | 0.57 | 0.61 | 0.13 | 0.16 | 0.23 | 0.26 |
| 15.9 | 0.78 | — | 0.20 | — | 0.26 | — |
| 16.0 | 0.74 | 0.78 | 0.20 | 0.20 | 0.27 | 0.26 |
| 16.0 | 0.72 | 0.70 | 0.21 | 0.20 | 0.28 | 0.29 |
| 18.0 | 0.79 | 0.88 | 0.26 | 0.27 | 0.33 | 0.30 |
| 18.1 | 0.86 | — | 0.26 | — | 0.30 | — |
| 20.0 | 0.84 | 0.88 | 0.26 | 0.29 | 0.31 | 0.33 |
| 20.0 | 0.94 | — | 0.28 | — | 0.30 | — |
| 20.0 | 0.91 | — | 0.28 | — | 0.31 | — |
| 22.2 | 0.87 | — | 0.24 | — | 0.28 | — |
| 25.1† | 0.88 | — | 0.27 | — | 0.30 | — |
| 25.3† | 0.87 | — | 0.26 | — | 0.30 | — |
| 25.3 | 0.93 | — | 0.28 | — | 0.31 | — |

† Values marked thus are not suitable for the determination of the "total" excitation curves (table I) because of slight variations in the tube current during an exposure. They may however be used in this table, since the ratios of the bands intensities at a particular voltage are independent of the current (within certain limits) for the magnitude of tube current used in this experiment.

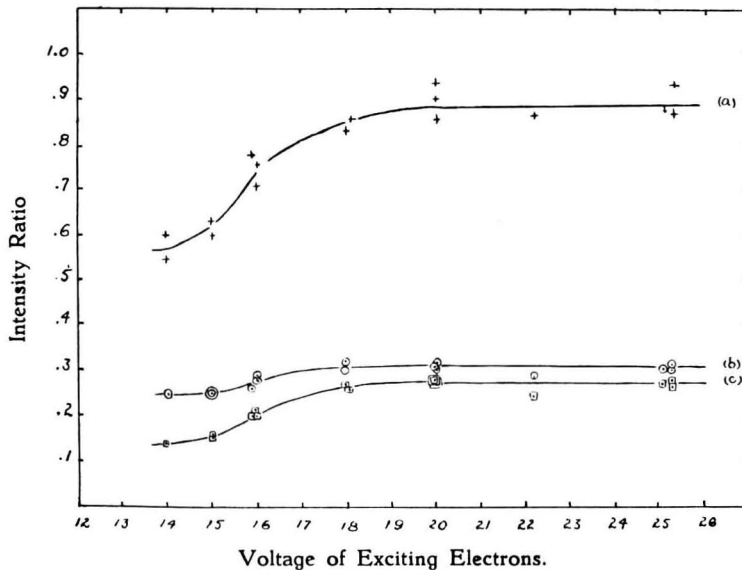


Fig. 2. Variation of the band ratios with the energy of the existing electrons. They are, in the order (a), (b), (c), 1 \rightarrow 3 / 0 \rightarrow 2, 2 \rightarrow 4 / 1 \rightarrow 3, and 1 \rightarrow 3 / 0 \rightarrow 2.

Discussion.

Inspection of figure 1 shows that the 'total' ¹⁾ excitation curves have the usual form for triplet transitions. Extrapolation of the curves to zero intensity gives a value for the excitation potential of the second positive bands (13.4 volts) in good agreement with the value found by SPONER ²⁾ ($13.0 \pm .3$ volts).

The curves for the variation of the intensity ratio of the bands with the energy of the exciting electrons (figure 2) show decided departures, below 20 volts, from straight lines parallel to the x axis. Above 20 volts however the intensity ratios are constant ³⁾. The fact that this constancy first appears near the point at which ionization sets in (16.5 volts) might be taken to indicate that it is due to the filling of the initial (emission) levels by the recombination of the molecular ion with an electron. This process would be, insofar as the relative populations of the initial levels are concerned, independent of the velocity of the exciting electrons. That this cannot be the explanation is shown by the following consideration.

If the constancy of the ratios is a result of recombination, it follows that above the voltage at which the constancy first occurs recombination must predominate in filling the initial levels. Now it is known from the excitation function for the negative band $\lambda 3914$ ⁴⁾ and from other sources, that the number of molecular ions and ions increases strongly with the voltage of the exciting electrons (cf. figure 1). We should then expect the intensities of the positive bands to increase proportionately. This is not the case as shown by figure 1, and therefore we must attribute the character of the curves in figure 2 to an excitation effect.

The relative excitation functions for these bands are therefore not independent of the velocity of the exciting electrons below 20 volts energy, and it is necessary to consider factors which are unimportant in the analogous theory for radiation. Above 20 volts, however, these factors probably become unimportant in excitation also (at least for the particular case examined). Further experimental data are being obtained, and will be presented along with a discussion of the problem in a later publication.

Examination of table I shows that there is no similar effect of electron impact on the molecular rotation, for if this were so it would cause a difference in the relative development of the rotational structure of the bands, which would result in different values for the relative intensities as calculated from maximum blackening and from integration measurements.

¹⁾ We use the term "total" to indicate that the probability of excitation of the electronic part of the molecule is included.

²⁾ Zeit. Physik., **34**, 622, 1925.

³⁾ Results obtained since this paper was composed show that they are constant to considerably higher voltages, and that the intensities of the bands continue to decrease.

⁴⁾ LINDH, loc. cit.

Our thanks are due to Mr. H. BRINKMAN for discussions on the subject, and to Mr. G. G. ZAALBERG for assistance in carrying out the experimental work. One of us (G. O. L.) is indebted to the Royal Commission for the Exhibition of 1851, whose award made his stay in Utrecht possible.

Hydrodynamics. — *On the application of statistical mechanics to the theory of turbulent fluid motion.* V.¹⁾ By J. M. BURGERS. (Mededeeling N^o. 26 uit het Laboratorium voor Aero- en Hydrodynamica der Technische Hoogeschool te Delft).

(Communicated at the meeting of April 29, 1933).

4. *Application of the normal functions obtained from equation (19) to the reduction of the exponent occurring in the distribution function (12).*

We proceed with the investigation of the statistical distribution of the relative motion and shall introduce the development of the stream function ψ of an arbitrary mode of relative motion (which satisfies the boundary conditions) according to the system of normal functions deduced from eq. (19).

It must be borne in mind that with the normalizing conditions assumed in § 3 the characteristic values of the parameter A all will be positive, provided that α is positive. It is convenient to adhere to the restriction of α to positive values, and to the type of functions obtained in § 3, but in the development of the stream function also terms will occur in which the sign of α is reversed (that is to say terms representing functions which are the symmetrical ones — with respect to the line $x=0$ — of those obtained before). As moreover both types of terms may have arbitrary phases with respect to x , we must expect that any stream function ψ will be built up from an aggregate of terms of the form:

$$\begin{aligned} & a(\chi_I \cos \alpha x + \chi_{II} \sin \alpha x) + b(-\chi_I \sin \alpha x + \chi_{II} \cos \alpha x) + \left\{ \begin{array}{l} \\ \\ \end{array} \right. \quad . \quad . \quad . \quad (25) \\ & + c(\chi_I \cos \alpha x - \chi_{II} \sin \alpha x) + d(\chi_I \sin \alpha x + \chi_{II} \cos \alpha x) \end{aligned}$$

It is convenient to introduce complex quantities, and so we assume that the stream function ψ_m of the mode of relative motion numbered m can be represented by the expression:

$$\psi_m = \frac{1}{2} \sum_{\alpha k} \{ e^{-i\alpha x} (A_{\alpha k} \chi_{\alpha k} + B_{\alpha k} \bar{\chi}_{\alpha k}) + e^{i\alpha x} (\bar{A}_{\alpha k} \bar{\chi}_{\alpha k} + \bar{B}_{\alpha k} \chi_{\alpha k}) \} \quad . \quad . \quad (26)$$

where $A_{\alpha k} = A_{\alpha k}^I + i A_{\alpha k}^{II}$, $\bar{A}_{\alpha k} = A_{\alpha k}^I - i A_{\alpha k}^{II}$, etc. Any mode of relative motion is now specified by the values of the A 's and B 's, and in calculating statistical mean values the summation with respect to the number m (i.e. the summation over the "ξ-space") can be replaced by an inte-

¹⁾ Part IV has appeared in these Proceedings, 36, p. 276, 1933.