

INTENSITY VARIATIONS IN ~~THE~~ SPECTRA OF
ATMOSPHERIC GASES AT LOW TEMPERATURES

by

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Abstract.

This thesis describes experiments in which the intensities of bands of the nitrogen first positive system were measured. The system was excited by a low temperature discharge through both pure nitrogen and mixtures of nitrogen and helium at various pressures and currents.

Several arrays of Franck Condon factors have recently been calculated for the system, both analytically and numerically. The experimental results were used to assess the reliability of each array and it was found that those calculated numerically were more reliable. The various arrays were used to investigate the effect of different q values on the calculated variation of the electron transition moment. A table of relative band strengths has been presented. The experimental results were also used to estimate the applicability, over a wide range of conditions, of the theory behind the calculation of the band strengths. There were indications that the theory does not hold for all conditions.

Possible excitation processes have been examined and intensity distributions predicted theoretically. These, together with the experimental distributions, enabled the importance of the various processes to be assessed. The experimental and theoretical distributions were compared with auroral distributions.

A series of computer programmes was written to facilitate the systematic processing of the experimental results and several more programmes were written to perform all the necessary theoretical calculations.

Some new bands in the oxygen second negative system were observed and measured, and other bands have been reclassified. The variation of intensity of the bands with changing conditions was observed.

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CHAPTER I.
INTRODUCTION.

1. General.

The intensity distributions in the spectra of upper atmospheric radiations, e.g. Aurorae, night sky, have for a long time been used in an attempt to explain the processes responsible for their occurrence. A greater understanding of these processes may be obtained from laboratory measurements of the intensity distribution in a band system and a determination of the way in which this distribution is dependent on source conditions.

The interpretation of spectral intensities is greatly dependent on the relevant theoretical data being accurate. In recent years, with the advent and increasing availability of large capacity computers, several arrays of Franck Condon factors have been calculated numerically. From these it is possible to make predictions as to the intensity distribution. Comparison of predicted and observed intensities will then give an indication as to the reliability of the published arrays. By investigating

the intensities for a wide range of source conditions, their reliability can be checked further. The general applicability of the theory on which the predictions are based may be tested by observing whether the relationship between observed and theoretical data varies systematically with the conditions.

2. Choice of Problem.

In choosing a problem on which to work, it was desired to maintain a link between this and previous work carried out in this laboratory as part of the same programme. This consisted of the following experiments.

Steers (1957) investigated both rotational and vibrational intensity distributions in the nitrogen second positive system. He used several sources, both cooled and uncooled, and compared the results from each source.

Sharma (1959) investigated the effect of helium on the intensity distribution of various band systems, one of which was the N_2 second positive. Both vibrational and rotational intensities were measured.

Tyte (1962 a,b,c), using a single liquid oxygen cooled discharge, investigated the intensities of the N_2 second positive system in pure nitrogen and nitrogen-helium mixtures for a large number of different conditions. From this he was able to obtain information on excitation processes and also to assess the reliability of the Franck Condon factors he used.

The nitrogen second positive system was an obvious choice for the above investigations for several reasons. The nitrogen spectrum is of great astrophysical interest and is very well known. The second positive system lies in a very convenient spectral range (2800 Å-5000 Å) for intensity measurements and consists of several sequences of well separated bands.

It was felt that further investigation into the nitrogen spectrum would be of use, but that there was little more to be gained by measuring the second positive system. In order to understand the processes taking place in a source, investigations of the intensity distributions of a band system for a wide range of conditions are

useful, but in order to obtain a clearer picture, it is necessary to compare the distributions of several systems. By making this comparison as the conditions vary it should be possible to obtain an idea of how the various states of the molecule affect the excitation and deactivation processes. As a start towards this type of investigation, the first positive system of nitrogen was investigated using the same discharge tube and conditions as those in Tyte's experiments. In this way it was possible to investigate the intensity distribution of the system over a wide range of conditions and to compare directly with the results obtained by Tyte for the second positive system. This would also enable a check to be made on the Franck Condon factors for the first positive system.

Oxygen is also an important gas of astrophysical interest and it was hoped to perform an investigation, similar to the above, on one of its band systems. The easiest systems to excite in the discharge tube are the first and

second negative systems, but neither of these systems lends itself readily to accurate intensity measurements. It was decided therefore to investigate qualitatively the effect of changing conditions on the second negative system, noting at the same time the behaviour of the first negative bands.

3. The Nitrogen First Positive System.

There were several reasons for the choice of the first positive system.

- i) It is a very well known band system and has been thoroughly analysed.
- ii) It is emitted strongly in a discharge tube.
- iii) It is emitted strongly in the Aurora, especially the type B red Aurora (Chamberlain 1961), and is thought to be largely responsible for the red colouration of this type of aurora.
- iv) Several sets of Franck Condon factors for this system, calculated using different methods, are available and their accuracy could be tested.
- v) The upper state of the system ($B^3\Pi$) is also the lower state of the second positive system. It should therefore be possible to investigate quantitatively the dependence of one system on the other.

vi) Intensity measurements, both laboratory and Auroral, have been made by many workers. The results serve as a useful guide for comparison purposes.

vii) The system is the main system emitted in the active nitrogen afterglow where the intensity distribution is distinctly abnormal. Because of this, intensity investigations on this system are of interest.

The system is not as convenient for measurement as the second positive as it is very extensive, starting at about 5500 Å and extending well into the infra-red region. This means that only a small portion of the system can be observed photographically, but even this will provide enough information to make an investigation worthwhile.

4. Previous Work on the N₂ First Positive System.

Many workers have performed investigations into the intensity distribution of the first positive system and the way in which it is affected by the presence of rare gases.

Intensity measurements have been performed by Elliott and Cameron (1934), Tawde and Patankar (1944, 1947) and Turner and Nicholls (1954a).

The measurements of Tawde and Patankar were part of an investigation into the relative changes in the intensities of the first and second positive systems as the discharge gas was changed from pure nitrogen to air. Further details of the above experiments are given in Chapter VI.

There have also been numerous investigations on the appearance and intensities of the first positive system in the aurora. These include intensity investigations by Petrie and Small (1953), Hunter (1955) and Omholt (1961).

Rare gases are known to produce some anomalous intensities in the bands of the system. Johnson (1924a) found that in argon containing a trace of nitrogen, only bands from three upper levels appeared. From his photographs it would appear that the enhanced levels were $v' = 7, 8$ and 9 . Bernard (1940), using a controlled electron excitation source, found that a trace of nitrogen in Xenon produced enhancement of $v' = 5$, a fact which he explained on the basis of energy exchange between a metastable $\text{Xe}(^3\text{P})$ atom and a ground state nitrogen molecule. Herman and Rakotoarijimy (1960) have also observed this phenomenon.

Some work on the intensity distribution in pure nitrogen and nitrogen-neon mixtures has been performed by Grenat, Herman and Hepner (1961).

Theoretical calculations of Franck Condon factors for the first positive system are numerous. Arrays have been calculated, using various methods, by Pillow (1954), Montgomery and Nicholls (1951), Jarman, Fraser and Nicholls (1953), Jarman and Nicholls (1954), Nicholls (1961), Zare, ~~Lazerson~~ and Berg (1965), Joshi, Parthasarathi and Sastri (1966) and Benesch, Vanderslice, Tilford and Wilkinson (1966b).

5. The Oxygen first and second Negative Systems.

The O_2^+ first negative system arises from the transition $b^4\Sigma^-g \longrightarrow a^4\Pi_u$. It is grouped in sequences in the wavelength region $5000 \text{ \AA} - 8000 \text{ \AA}$. The structure of the bands is very complex and there is a great deal of overlapping of bands within a sequence which makes accurate intensity measurement impossible. At the dispersion used, it was difficult to pick out even the heads of the bands in each sequence.

The second negative system arises from the transition $A^2\Pi_u \longrightarrow X^2\Pi_g$. It is a very extensive

system of double headed bands ranging from 1950 Å⁰ to 6500 Å⁰. The bands have an open rotational structure and there is a considerable amount of overlapping which makes intensity measurement difficult though not as difficult as for the first negative system.

There have not been many attempts at quantitative intensity measurements on the two systems. Rao (1963) measured peak intensities of bands in the first negative system for 4 different sources and compared the results. The accuracy obtained cannot have been very good. It was sufficient for the comparison to be made, but it is doubtful whether it would be good enough for a reliable quantitative determination of the population distribution to be performed. Robinson and Nicholls (1958) have measured integrated intensities of bands in the second negative system.

Not nearly as much work has been done on calculating Franck Condon factors for these systems as for the nitrogen band systems. No numerical calculations have been performed using large computers. The most extensive tables for both systems have been published by Nicholls (1965a).

CHAPTER 2.

EXPERIMENTAL TECHNIQUES.

1. Apparatus.

As this work was an extension of the investigation started by Tyte (1962a) it was decided to use the same apparatus. In this way it was possible to reproduce the conditions of his experiments and correlate his results with those obtained in the present experiment.

The details of the apparatus are given in Tyte's thesis and only a brief description will be given here.

a. Glassware.

The discharge tube (fig.1.) was designed so that the incoming gases should have reached a low temperature by the time they entered the main discharge column. The coil round the tube was filled with brass turnings and the tube immersed in liquid oxygen. Before entering the discharge, the incoming gas had to pass over 150 cms. length of cold metal, and by the time it reached the discharge column its temperature should have been reduced to that of the outside walls. The electrodes were dural cylinders and, as liquid oxygen is a good insulator, there was no need to insulate the wires leading to the electrodes.

Before reaching the discharge tube, the incoming gases were passed through the purification system (fig.2.). The helium was passed through a charcoal trap immersed in liquid oxygen after which the nitrogen or oxygen entered the system and the mixture was passed through two liquid air traps. This helped to cool the gases down and also removed higher

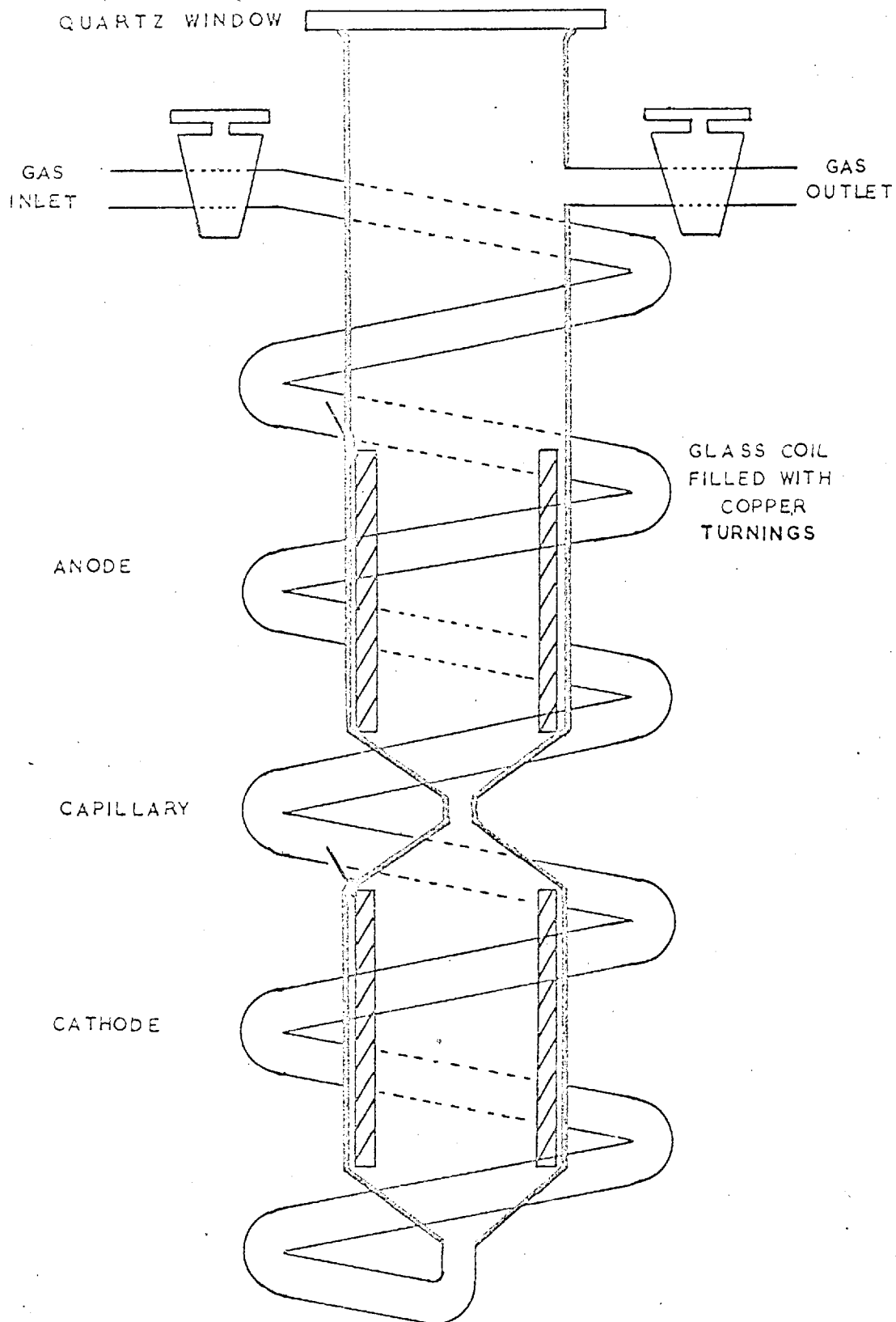


FIG. 1. THE DISCHARGE TUBE

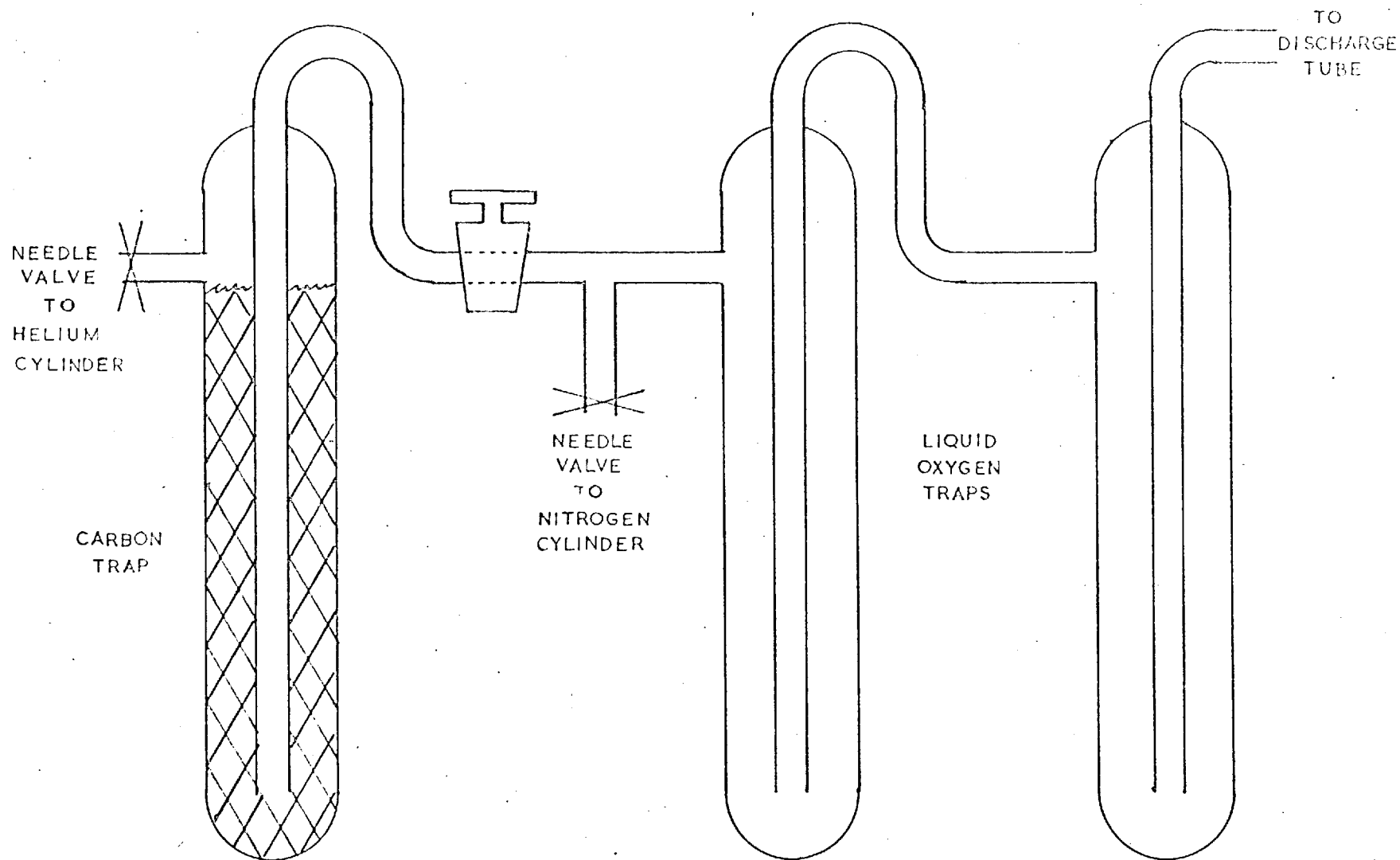


FIG 2. GAS PURIFICATION SYSTEM

boiling point impurities such as water vapour. The gases came from ordinary gas cylinders. No impurities were observed with nitrogen or helium. When oxygen was used there was a trace of nitrogen impurity but, as accurate intensity measurements were not attempted on the oxygen bands, this caused no inconvenience.

The gases were let into the system through needle valves which enabled a fine control to be kept on the pressure.

b. Pressure Measurement.

When the pressure of both the gases in the system was over 0.1 mm.Hg, an oil and mercury manometer was used for pressure measurement. The method of regulating the pressure was the same as that described by Tyte in his thesis. This method, however, was not very accurate for pressures below 0.1 mm. so an Edwards B5 Pirani gauge was placed in the system next to the manometer. The scale of this gauge was accurate between pressures of 0.01 mm. and 0.1 mm. and it was used when the required pressure of either gas fell in this range. Usually it was only the oxygen or nitrogen pressure which was set in this region and the following procedure was adopted.

The tap between the charcoal and the liquid air traps was closed and that between the two arms of the oil manometer was left open. The oxygen or nitrogen was let in to the system through the needle valve which was adjusted until the required pressure registered on the Pirani gauge. The manometer tap was then closed, helium let into the charcoal trap, the tap between the traps opened, and the needle valve at the helium inlet adjusted until the required pressure was registered on the manometer.

As it was usually only the helium pressure that was varied during the course of an experiment, this proved a very satisfactory method of pressure measurement. In cases where the total pressure was kept constant, the manometer tap was closed before either gas was admitted to the system and it then registered the total pressure. The system was pumped down with an Edwards 1SC150 rotary pump.

c. Optical Arrangement.

The discharge tube, sealed with a quartz window, was run vertically, immersed in a dewar of liquid oxygen. A plane, surface aluminised, mirror was placed 20 cms. above the constriction of the tube and was tilted at an angle of 45° to the tube axis. A surface aluminised concave mirror of focal length 60 cms. was used for collimation and was placed at the same height as the plane mirror and 100 cms. from it. The light from the tube was reflected from the two mirrors and was focussed on to the spectrograph slit 120 cms. away from the concave mirror, i.e. 20 cms. behind the plane mirror. The system was arranged so that the spectrograph slit & the two mirrors were all at the same height. The tube and plane mirror were placed a little to one side of the slit so that the collimating mirror was used only slightly off axis. Mirror collimation was used in order to avoid chromatic aberration. A diagram of the optical arrangement is shown in fig.3.

d. Electrical Arrangement.

The current for the discharge was taken from a smoothed D.C. power supply capable of providing a maximum current of 200 ma. at 1500 V. A 1000 ohm resistor and an ammeter were placed in series with the discharge tube and a voltmeter was connected across the terminals of the tube.

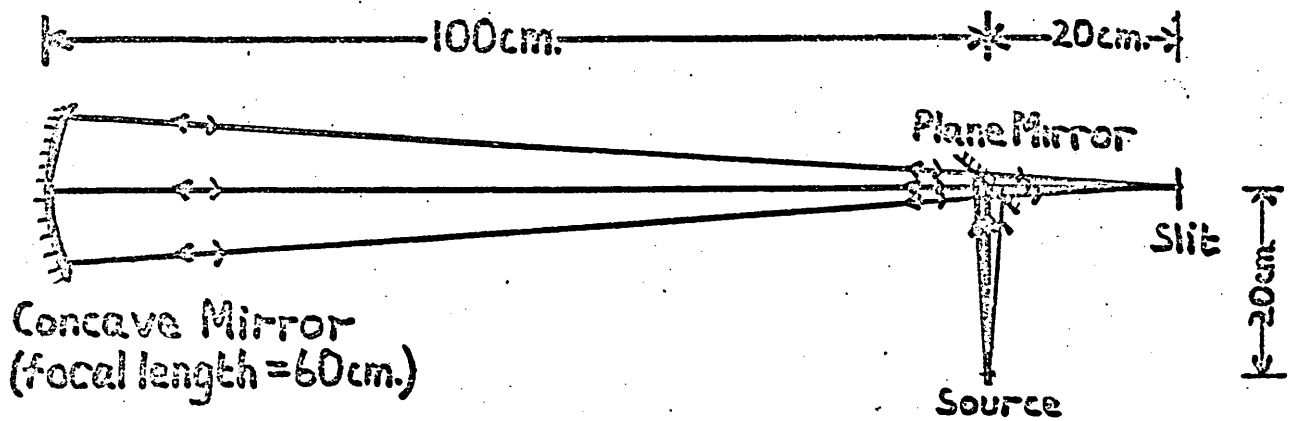


Fig.3 Optical Arrangement

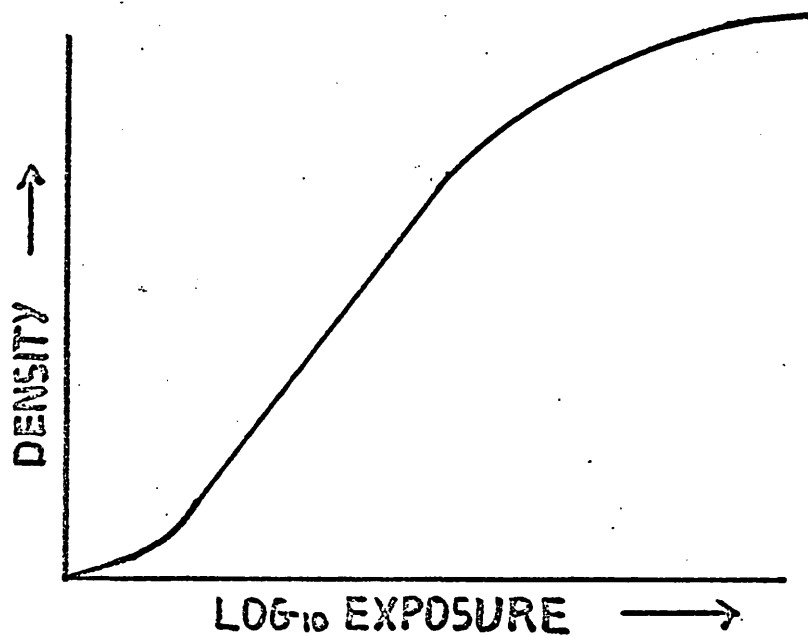


Fig.4 Typical Plate Characteristic Curve

The resistor was needed to stabilise the discharge. Tyte (1962a) found that, without it, the discharge was steady only within a limited range of pressures and currents.

2. Choice of Spectrograph.

In deciding on the most suitable spectrograph for use in the experiment, the following points had to be taken into consideration.

- 1) Both the band systems investigated are very extensive, the total range covering the region from the near ultraviolet to the infra-red.
- 2) The second negative system of oxygen is heavily overlapped and a spectrograph was needed that would separate the bands reasonably well.
- 3) Integrated band intensities were required (see section 5b) which means that the rotational structure should, if possible, be blended.
- 4) It was hoped to make some observations on rotational structure and this required an instrument with a fairly high dispersion.

Tyte, in his experiments, used a medium quartz spectrograph which was ideal for the second positive system of nitrogen. For the present experiments however, a higher dispersion instrument was required as the overlapping of the oxygen bands made them very hard to distinguish on the medium quartz. Also, the nitrogen first positive bands were beginning to blend together as the dispersion of the instrument in the red was extremely low.

There was one instrument available in the laboratory on which it was possible to fulfil all the above requirements. This was the Hilger large Littrow spectrograph with interchangeable glass and quartz optics. The main disadvantages were that not as much of the band systems could

be obtained on one exposure as on the medium quartz. There was also no photoelectric scanning attachment available and it was therefore necessary to use photographic photometry. Using the quartz optics, one could cover the range $2700 \text{ \AA} - 4100 \text{ \AA}$ on one exposure and this included a large enough section of the oxygen 2nd negative system for examination. For the nitrogen first positive system, the quartz optics were also used, The range used covered from $5500 \text{ \AA}$ where the system starts to about $8500 \text{ \AA}$ which is about the cut off point for the photographic emulsion. This meant that bands with $v' = 0$ and could not be measured but, as bands with $v' = 2-12$ fall in this region, a fairly useful analysis could be performed.

In order to try and blend the rotational structure of the bands and facilitate integrated intensity measurements, a wide slit was used. This also allowed more light into the spectrograph and cut down the exposure times necessary.

The dispersion of the instrument using the quartz optics was about $3 \text{ \AA/mm.}$ ($40 \text{ cm}^{-1}/\text{mm.}$) at $2700 \text{ \AA}$, $10 \text{ \AA/mm}$ ($60 \text{ cm}^{-1}/\text{mm.}$) at $4000 \text{ \AA}$, $25 \text{ \AA/mm}$ ($80 \text{ cm}^{-1}/\text{mm}$) at $5500 \text{ \AA}$, $40 \text{ \AA/mm.}$ ($100 \text{ cm}^{-1}/\text{mm.}$) at $6500 \text{ \AA}$, and $60 \text{ \AA/mm.}$ ($100 \text{ cm}^{-1}/\text{mm}$) at $8000 \text{ \AA}$.

When the glass optics were used the dispersion at $4000 \text{ \AA}$ was about $4 \text{ \AA/mm.}$ ($25 \text{ cm}^{-1}/\text{mm.}$). This enabled the rotational structure of the O_2^+ 2nd negative system to be observed.

3. Intensity Measurement.

There are two techniques commonly used in the measurement of spectral intensities. These are the photoelectric and photographic methods, the principles of which are outlined below.

a) Photoelectric Method

The photomultiplier is a device for turning a light signal into electric current. It has a very high gain and the current produced varies linearly with the incident light intensity and this is its main advantage over a photographic emulsion. For use in spectral intensity measurements, the photomultiplier is placed behind a slit which scans across the focal plane of the spectrograph and the output is recorded on a pen recorder. The response of the photomultiplier is wavelength dependent and this is calibrated with a standard lamp whose intensity variation with wavelength is known. This is placed in the same position that the source occupied and the continuous spectrum it produces is scanned. As the variation of photomultiplier response with current is linear, this one calibration trace is all that is required to determine the intensities of the lines or bands recorded.

The main disadvantage of this method is that only one part of the spectrum can be recorded at a given instant so that the method may only be used with a steady source as any fluctuations will cause inaccuracies. Noise may also cause problems, especially with a weak source.

As was mentioned previously, the most suitable available spectrograph to use for the experiments was the Littrow and this had no photoelectric scanning attachment. The source was weak and it was thought advantageous to record the spectrum photographically with a reasonably long exposure time. This also overcame the difficulty caused by any slight fluctuations in the source, as the whole spectral region required was being recorded at once. It was therefore decided to use the photographic technique.

b) Photographic Photometry.

Unlike the photomultiplier, the photographic emulsion does not have a linear response to the intensity of a source. Its response also varies with wavelength. No two plates can reliably be expected to respond in exactly the same way so each plate has to be very carefully calibrated.

For a given exposure time, the variation of the density of plate blackening with the exposure of the source is shown in fig.4. Density of plate blackening is defined as $\log_{10} I_0/I$ where I_0 is the intensity of a light beam incident on the plate and I is the intensity of the light transmitted by the plate. Exposure is defined as intensity X exposure time.

It can be seen that when the exposure reaches a certain value, the blackening reaches a saturation value and no further exposure will have any effect on the blackening of the plate. It is therefore necessary to choose the exposure time such that as many as possible of the bands will fall on the linear part of the curve otherwise intensity measurements become extremely unreliable.

4. Experimental Procedure.

As each plate had to be calibrated, as many exposures as possible were taken on each plate, the exposure time for each being the same. The plates were calibrated using a standard tungsten lamp and a rotating step sector. The sector is a device which enables seven sections along the length of the spectrograph slit to be illuminated for different times during an exposure, the exposure time for each section being half that of the section above it. For the exposure times used in the present

experiments, the intensities could be said to be proportional to the exposure times for each section so that, on one plate, there was a series of continuous spectra representing source intensities of S , $S/2$, $S/4$, $S/8$, $S/16$, $S/32$ and $S/64$, where S is the intensity of the standard lamp. From these an intensity against blackening curve could be plotted from which it would be possible to read off the intensities of the bands. The density of blackening corresponding to the various bands and calibration traces was measured using a Jarrell Ash recording micro-photometer. In this instrument which is designed to detect fluctuations in plate blackening, the plate is traversed across a beam of light which passes through a slit to a photomultiplier. The photomultiplier current is amplified and recorded by a pen recorder. The trace on the recorder chart represents a plot of plate blackening against distance. Before measuring each plate the scale had to be set as follows. First the light beam was prevented from reaching the photomultiplier by placing a piece of dark material across the beam and the pen was set on zero. Then a clear portion of the plate was selected, placed in the path of the beam, and the pen was set on 100. This ensured that every set of measurements was performed on the same scale.

5. Calibration of Plates.

a. Experimental

Each plate was calibrated using a Phillips standard tungsten filament lamp. In order to calibrate a plate accurately the light from the lamp must traverse exactly the same path, through the same optics (i.e. quartz window, plane mirror and concave mirror), as the light from the original

source. One way of doing this would be to detach the quartz window from the discharge tube, leaving the window in the same position, and arrange the lamp so that the filament is in exactly the same position that the constriction in the tube had occupied. To do this would involve removing and replacing the window, hence destroying the vacuum, after each plate had been taken and this would be very inconvenient and time consuming. It would also involve running the standard lamp with the filament horizontal and, as the lamp had been calibrated with the filament vertical, this could introduce further errors. It was therefore decided to change the positions of the lamp and window without altering the optical path.

Before any experimental work was started several quartz windows were tested in the following manner. The lamp was placed in front of the spectrograph slit and a quartz window placed between the lamp and slit. The spectrum was then photographed for a few seconds. This procedure was repeated for several quartz windows, each being placed in the same position, with the filament current and exposure time the same for each window. Each trace was run through the microphotometer and the resulting chart traces compared. Two windows were found which gave identical traces and they were tested using several filament currents and in each case identical traces were obtained. The two windows therefore had the same transmission properties and were both used in the experiments, one on the discharge and the other for calibration. No errors could be detected due to a possible change in transmission of either of the windows during the course of the experiments. There were several cases in which the discharge spectrum was photographed at different times for the same

set of conditions. In each case the results obtained were the same within the experimental errors. This would not occur if there were errors in calibration.

For each plate the experiments with the discharge were performed first, the image of the constriction being focussed on the slit. The calibration traces were obtained as follows. The plane mirror was kept at the same height but was placed vertically i.e. parallel to the tube axis, and tilted at 45 degrees to the vertical plane between the spectrograph slit and the concave mirror. The window was placed with its face parallel to the above plane at the same distance in front of the plane mirror as the tube window was below it. The standard lamp was then placed in front of the window and arranged so that the filament was vertical, the distance between it and the window being equal to that between the constriction and window of the discharge tube. All the components were placed at the same height as the concave mirror and the spectrograph slit which had not been moved. The light was then travelling in a horizontal plane through the same optical path as the light from the discharge tube. The rotating step sector was placed directly in front of the spectrograph slit. The filament current was adjusted to the required value and the filament temperature read off the temperature versus current graph provided.

b) Treatment of Traces.

There are two main techniques used in estimating the intensities of spectral features after the chart traces have been obtained. These are the peak intensity and integrated intensity methods.

The peak intensities are by far the easiest to measure. It has

already been stated that the microphotometer traces are plots of blackening against distance. The peak intensity of a band is calculated by measuring the height (i.e. blackening) of the maximum on the trace representing the band and reading the intensity from a graph of blackening against intensity. This graph would previously have been plotted from the heights of the calibration traces at the same wavelength as the peak of the band. This method is relatively simple but takes no account of the band profile which may vary from band to band, and may also vary with source conditions.

The integrated intensity is far more accurate than the peak intensity. It is calculated by converting the blackening versus distance plot into one of intensity against wavelength. This involves measuring the intensities at several points along each band using the method outlined in the previous paragraph. In addition, the distances must be converted into wavelengths by plotting a dispersion curve and reading off the wavelength. The intensities must then be plotted against wavelength, a smooth curve drawn through the points, and the area under the curve measured. The resultant area is the integrated intensity. In the present experiments, in which intensity determinations on a band system were to be performed for a large number of source conditions, the measurement of integrated intensities photographically would be virtually impossible using the above method. Peak intensities are not accurate enough as they take no account of the profiles of the bands. The following method was therefore used to integrate the band profiles.

The areas under the bands on the charts were measured with a polar planimeter. The positions on the calibration traces corresponding to

the measured bands were found by measuring the distance of each band head from the chart position representing one end of the plate and then marking off these distances on each calibration trace. The width of each band was also measured. The area under the portion of each standard lamp trace corresponding to each band was then determined. As the calibration trace was very nearly linear over the small region representing each band, the areas were treated as trapezia and were calculated. This saved time and was proved accurate by comparing a few of the results with those obtained using the planimeter. A graph of intensity against area under the trace was then plotted for the standard lamp traces representing each band. The calibration intensities for each band were taken as 1,2,4,8, 16,32,64 with 64 representing the actual intensity of the light emitted by the standard lamp at a given wavelength. The intensities of the bands, I_0 , were read off these graphs.

The above method does not, strictly speaking, give true integrated intensities, but it does make allowances for the variations of the profiles of the bands. The intensities calculated will give a truer indication of the band intensity than the peak intensities.

c) Theory.

The integrated intensity of a band is given by the expression

$$I = \int_{\lambda_1}^{\lambda_2} I_{\lambda} d\lambda \quad 2.1.$$

where I_{λ} is the intensity at wavelength λ , and λ_1 and λ_2 are the wavelengths at the limits of the wavelength range considered.

As was stated above, each band has been measured on the same intensity scale with 64 as the maximum. This takes no account of the variation

of the standard lamp intensity with wavelength. For each band; the intensity of the standard lamp corresponding to the wavelength λ , at the centre of the range $\Delta\lambda$, was taken as 64.

We therefore have

$$I_{\text{band}} = I_0 \cdot \frac{I_{\text{Standard}}}{64} \quad 2.2.$$

where I_{band} is the intensity value corresponding to I_0 , but on the scale representing the actual intensity of the standard lamp. I_{standard} is the intensity of the standard lamp at wavelength λ , and is given by the expression

$$I_{\text{standard}} = \frac{2h c^2 \pi}{\lambda^5} \frac{D_{\lambda} e_{\lambda}}{\left(\exp \left| \frac{hc}{\lambda kT} \right| - 1 \right)} \quad 2.3.$$

T is the true temperature of the filament as given by the calibration curve of the lamp. D_{λ} is the transmission of the lamp window at wavelength λ , and this data was provided with the lamp. e_{λ} is the emissivity of the tungsten ribbon, a quantity which takes into account the departure of the filament from a perfect blackbody (de Vos, 1954).

I_{standard} above is the intensity at the centre of the wavelength range $\Delta\lambda$, covered by the band. It was stated previously that the intensity variation of the standard lamp over this small region was approximately linear, therefore the integrated intensity, I_s , of the standard lamp in the range $\Delta\lambda$ is given by

$$I_s = I_{\text{standard}} \cdot \Delta\lambda \quad 2.4.$$

We therefore have for the intensity of the band at wavelength λ ,

$$I_{\text{Band}} = C \cdot I_0 \cdot \frac{D_{\lambda} e_{\lambda}}{64 \lambda^5 \left(\exp \left| \frac{hc}{\lambda kT} \right| - 1 \right)} \cdot \Delta\lambda \quad 2.5.$$

CHAPTER 3.

THEORETICAL CONSIDERATIONS.

1. Franck Condon Principle.

The various electronic states of diatomic molecules may be represented on a potential energy versus internuclear distance plot. The distribution of intensity among the vibrational transitions between any two electronic states can be explained in an easily visualised manner by the Franck Condon principle. Franck's (1925) original idea was that the electron jump in the molecule takes place so rapidly in comparison with the vibrational motion that immediately afterwards the nuclei still have very nearly the same relative position and velocity as before the jump. The transition can therefore be represented by a vertical line on the potential diagram (fig. 5a). The position in the vibrational motion from which the transition is most likely to take place is that in which the molecule spends most of its time i.e. at the end of the oscillation or in other words, at points on the potential curve.

In fig. 5a, when the molecule is in the vibrational level A B of the upper state, transitions are most likely to take place while the molecule is at A or B. A transition from A would result in its going to C and it will then vibrate along C D. Similarly, and with equal probability, a transition could take place from B to F causing the molecule to vibrate along EF. From any level in the upper state transitions to two levels in the lower state are most likely and these will form the most intense bands of the system.

If the intensities of the bands in a system are plotted in a Deslandres

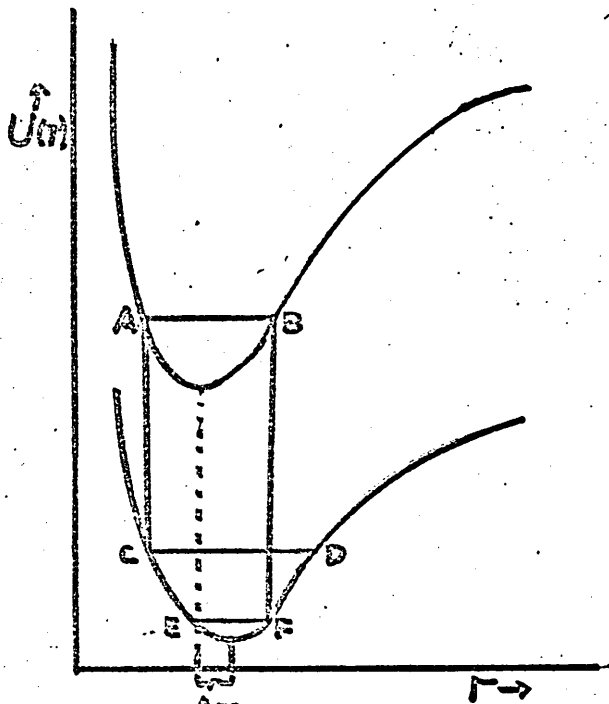


Fig 5a

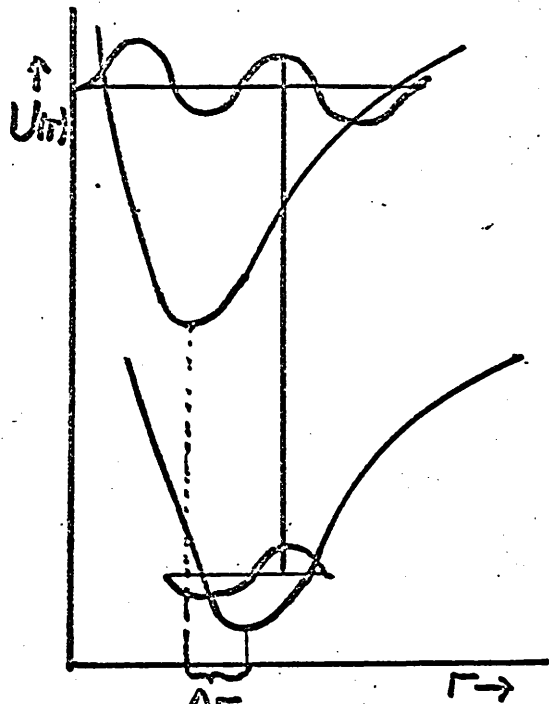


Fig 5b

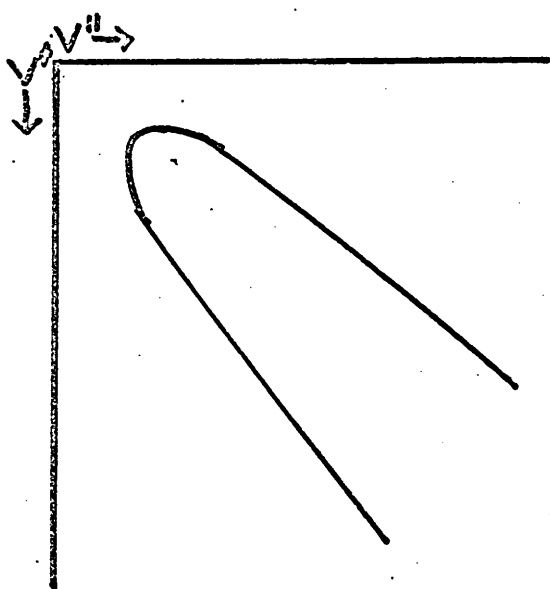


Fig 6a
 ΔE_e small

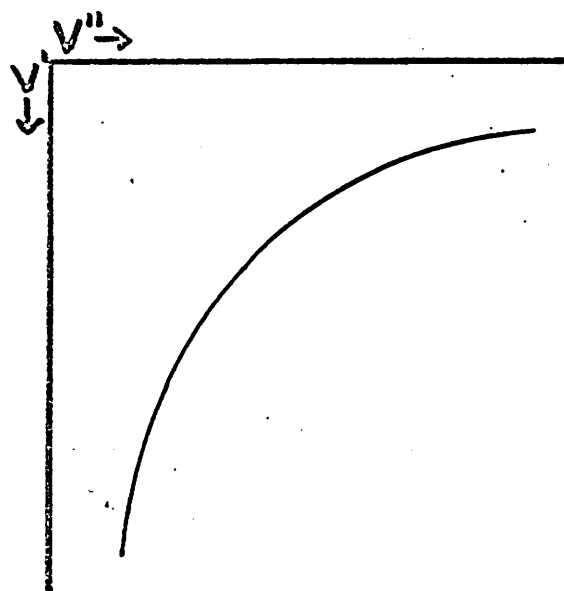


Fig 6b
 ΔE_e large

table, the locus of the bands of maximum intensity is approximately a parabola, known as a Condon parabola, whose width is determined by the shape of the potential curves and their relative positions. If Δr_e (fig. 5.) is small, the parabola will be narrow (fig. 6 a.) and if Δr_e is large, it will be wide (fig. 6 b.).

The principle was developed mathematically and given a wave mechanical basis by Condon (1926, 1928). In figure 5.b. the vibrational states are each represented by the appropriate wave functions. The probability of a transition between two states is determined by the degree of overlap of the wave functions. A transition would therefore be expected to occur when a maximum in the wave function of the upper state lies vertically above a maximum in the wave function of the lower state. For all the states except $v = 0$, the principal maxima lie near the potential curve and from these one obtains the classically expected transitions. However transitions will also occur when the principal maximum of a wave function in the upper state lies vertically above the inner maximum of a lower state wave function or vice versa. This is illustrated in fig. 5b, and leads to subsidiary Condon parabolae lying inside the main parabola. An example of this is the Oxygen 2nd negative system in which eight parabolae are obtained (Nicholls 1965 a).

The intensity of a spectral band $v' - v''$ in emission, $I_{v' v''}$, is defined as the energy emitted by the source per second into the wavelength region of the band. If there are $N_{v'}$ molecules in the upper excited state and $A_{v' v''}$ is the fraction of molecules in the initial state v' , undergoing the transition to v'' per second, then

$$I_{v' v''} = N_{v'} E_{v' v''} A_{v' v''} \quad 3.1.$$

where

$$E_{\nu', \nu''} = hc \nu_{\nu', \nu''} \quad 3.2.$$

is the energy of each light quantum of wavenumber $\nu_{\nu', \nu''}$ emitted in the transition.

The wave mechanics of dipole radiation gives (Herzberg 1950)

$$A_{\nu', \nu''} = \frac{64 \pi^4 \nu_{\nu', \nu''}^3}{3h} \left| R_{\nu', \nu''} \right|^2 \quad 3.3.$$

where $R_{\nu', \nu''}$ is the matrix element of the electric dipole moment.

Combining equations 3.1., 3.2., and 3.3. we obtain

$$I_{\nu', \nu''} \propto N_{\nu'} \nu_{\nu', \nu''}^4 \left| R_{\nu', \nu''} \right|^2 \quad 3.4.$$

The matrix element $R_{\nu', \nu''}$ is given by

$$R_{\nu', \nu''} = \int \psi_{\nu'}^* M \psi_{\nu''} d\tau \quad 3.5.$$

where $\psi_{\nu'}$ is the total eigenfunction of the upper state and $\psi_{\nu''}$ that of the lower state. M is the electric dipole moment.

After separation into electronic and vibrational components and allowance for the orthogonality of the electronic wavefunctions (Herzberg, 1950) the expression for $R_{\nu', \nu''}$ becomes

$$R_{\nu', \nu''} = \int \psi_{\nu'} \psi_{\nu''} dr \int M_e \psi_e'^* \psi_e'' d\tau_e \quad 3.6.$$

where $\psi_{\nu'}$ and $\psi_{\nu''}$ are the vibrational wave functions of the upper and lower states respectively, r is the internuclear distance, ψ_e' and ψ_e'' are the electronic wave functions and M_e is the electronic dipole moment.

We now define the electron transition moment R_e , by

$$R_e = \int M_e \psi_e'^* \psi_e'' d\tau_e \quad 3.7.$$

The wave mechanical formulation of the Franck Condon principle is based on the assumption that R_e varies slowly with the internuclear distance and that it may be replaced by an average value, $\bar{R}_e$, giving

$$R_{v', v''} = \bar{R}_e \int \psi_{v'} \psi_{v''} dr \quad 3.8.$$

Fraser (1954a) introduced the concept of an r-centroid, $\bar{r}$, of a band which he defined as

$$\bar{r}_{v', v''} = \frac{\int \psi_{v'} r \psi_{v''} dr}{\int \psi_{v'} \psi_{v''} dr} \quad 3.9.$$

and which varies from band to band in a system.

Fraser used this to refine equation 3.8. and obtained

$$R_{v', v''} = R_e (\bar{r}_{v', v''}) \int \psi_{v'} \psi_{v''} dr \quad 3.10.$$

Substituting into equation 3.4. we obtain

$$I_{v', v''} \propto N_{v'} \nu^4_{v', v''} \left| R_e (\bar{r}_{v', v''}) \right|^2 \left| \int \psi_{v'} \psi_{v''} dr \right|^2 \quad (3.11)$$

$\int \psi_{v'} \psi_{v''} dr$ is the overlap integral and is a measure of the overlapping of the wave functions.

$$q_{v', v''} = \left| \int \psi_{v'} \psi_{v''} dr \right|^2 \quad 3.12$$

is called the Franck-Condon factor for the $v' - v''$ transition

$$S_{v', v''} = \left| R_e (\bar{r}_{v', v''}) \right|^2 q_{v', v''} \quad 3.13.$$

is the band strength (often called the vibrational transition probability) of the transition.

We now have

$$I_{v', v''} = K N_{v'} S_{v', v''} \nu^4_{v', v''} \quad 3.14$$

where K is a constant depending to some extent upon the apparatus.

2. Potential Functions and Franck Condon Factors.

It can be seen from equations 3.14 and 3.13. that in order to be able to make good use of experimental intensity measurements it is necessary to have reliably accurate Franck-Condon factors. The wavefunctions, ψ_v , must therefore be accurately calculated and these are obtained from the Schrödinger equation

$$\nabla^2 \psi + \frac{8\pi^2\mu}{h^2} [E - U(r)] \psi = 0 \quad 3.15$$

μ is the reduced mass of the molecule, E is the energy and $U(r)$ is the potential function.

To solve the equation, a guess as to the form of $U(r)$ must be made and it is the accuracy of this potential function that determines the accuracy of the calculated Frank-Condon factors.

A wide variety of Franck-Condon factor calculations have been performed using the harmonic oscillator potential function.

$$U(r) = \frac{1}{2} k (r - r_e)^2 \quad 3.16$$

and the Morse function

$$U(r) = D \left[1 - \exp(-a(r - r_e)) \right]^2 \quad 3.17$$

Of these two functions, the Morse potential is a closer approximation to the shape of the true potential. Hutchisson (1930) used an analytic method to calculate the overlap integrals using a harmonic oscillator potential. He then improved on this method by allowing for the anharmonicity of the potential function (Hutchisson 1931). Gaydon and Pearse (1939) calculated wavefunctions by distorting the harmonic oscillator and used a numerical method to calculate the overlap integrals. Pillow (1951)

improved upon the method and calculated Franck Condon factors for a large number of band systems. Bates (1952) modified Hutchisson's formulae and produced a double entry table from which Franck Condon factors for any transition could be read for $0 \leq v \leq 2$ where v can represent either v' or v'' . The Morse potential has also been widely used in computing arrays of q values. Pillow (1951) used it as a basis for the distortion of the harmonic oscillator wavefunctions. Bates (1949) and Jarman and Nicholls (1954) carried out direct numerical integration on the Morse wavefunctions to produce arrays of Franck Condon factors. Fraser et.al. (Fraser and Jarman(1953), Jarman and Fraser (1953), Fraser (1954b)) developed a method by which overlap integrals of Morse wavefunctions could be calculated analytically and this has been applied to about 80 band systems.

The methods mentioned above were reasonably accurate only for low quantum numbers as the empirical potentials are not true representations of the physical situation and tend to become less accurate as v increases. Up till recently, when large capacity digital computers became more readily accessible, it was necessary to use approximate analytical methods in order to reduce the amount of work involved. The advent of large computers has made possible the accurate construction of potential curves, point by point, using data from the spectroscopic analysis of the band systems. It is also possible to solve the Schrodinger equation numerically using these 'realistic' potential functions and then to numerically compute the overlap integrals and hence the Franck Condon factors.

As an intermediate stage between the analytical calculations above

and accurate numerical evaluations, Nicholls (1961) devised a method for the calculation of Franck Condon factors up to high quantum numbers. He used a Morse potential, evaluated the wavefunctions at $0.01 \text{ \AA}$ intervals over the significant range of r , the internuclear distance, and performed numerical integrations to compute the Franck Condon factors. A slightly modified version of this method has been used by Felenbok (1963).

In the past few years several workers have written computer programmes to calculate accurate realistic potentials and have used them to numerically compute wavefunctions and Franck Condon factor arrays. Several workers have used an 'RKR' method further details of which may be found in papers by Spindler (1965), Zare, Larsson and Berg (1965) and Benesch, Vanderslice, Tilford and Wilkinson (1965, 1966 a,b). Because of the methods of calculation, these arrays should be more accurate than any previously calculated and it was part of the aim of this work to test experimentally whether this is, in fact, the case.

3. Treatment of Results.

a) Intensity Ratios.

Part of the aim of this work was to examine the simple theory that the band strength, $S_{v' v''}$, is a constant independent of conditions. The way in which this was done was to take the ratio of the intensities of two bands originating from the same upper vibrational level and to examine it over a wide range of conditions.

From equation 3.14 it can be seen that the ratio of intensities of the two bands coming from the transitions $v' - v_1''$ and $v' - v_2''$

$$\text{is } \frac{I_{v' v_1''}}{I_{v' v_2''}} = \frac{S_{v' v_1''} (\nu_{v' v_1''})^4}{S_{v' v_2''} (\nu_{v' v_2''})^4} \quad 3.18$$

If the simple theory is correct, and $S_{v', v''}$ is independent of conditions, then the intensity ratios should also remain constant under all conditions. Smallwood (1961) and Tyte (1962 a,b,c; 1965) examined these ratios for the nitrogen second positive system and found variations that could not be accounted for on the grounds of experimental error alone. In the present experiment this investigation has been extended to the nitrogen first positive system.

If several arrays of Franck Condon factors and hence band strengths are available, then their accuracy can be estimated by calculating theoretical intensity ratios from equation 3.18 and comparing with the experimentally obtained values. This has been done for the nitrogen first positive system.

b. Electron Transition Moment and Band Strengths.

A lot of intensity data has been processed assuming that the electron transition moment, $R_e(r)$, is constant over the wavelength region employed in which case the band strength is replaced by the Franck Condon factor for all transitions. The validity of this assumption was tested for the nitrogen first positive system by Turner and Nicholls (1954a). They did this by using the expression, obtained from equation 3.14.,

$$S_{v', v''} \propto I_{v', v''} \lambda_{v', v''}^4 \quad 3.19$$

Here, and in all further calculations, ν has been replaced by $1/\lambda$ as λ is a more convenient quantity to use and the error introduced is very small. By comparing $I_{v', v''} \lambda_{v', v''}^4$ with $q_{v', v''}$ along each v'' - progression, large differences were observed and this led to the belief that $R_e(r)$ was not constant for the band system.

In a second paper, Turner and Nicholls (1954b) used a method suggested

by Fraser (1954 a) by which their experimental intensities could be combined with theoretically calculated Franck Condon factors and $\bar{r}$ centroids to determine the way in which the transition moment varies over the band system.

From equations 3.13 and 3.14

$$R_e(\bar{r}_{v' v''}) \propto \frac{1}{\sqrt{N_{v'}}} \left(\frac{I_{v' v''} \lambda_{v' v''}^4}{q_{v' v''}} \right)^{\frac{1}{2}} \quad 3.20$$

For any two bands coming from the same v' , (v', v_1'') and (v', v_0'') , the following ratio is obtained

$$\frac{R_e(\bar{r}_{v' v_1''})}{R_e(\bar{r}_{v' v_0''})} = \frac{(I_{v' v_1''})^{\frac{1}{2}} (\lambda_{v' v_1''})^2}{(I_{v' v_0''})^{\frac{1}{2}} (\lambda_{v' v_0''})^2} \cdot \frac{(q_{v' v_0''})^{\frac{1}{2}}}{(q_{v' v_1''})^{\frac{1}{2}}} \quad 3.21$$

One band in each v'' - progression was chosen as the v', v_0'' band and the ratios calculated for the rest of the bands in the progression. The next step was to bring the values for each progression to the same scale i.e. remove the dependence on $N_{v'}$. For each v'' - progression a graph was plotted of $R_e(\bar{r}_{v' v''})/R_e(\bar{r}_{v' v_0''})$ against $\bar{r}_{v' v''}$ and the points were joined by straight lines. The ratios from two v'' progressions were brought to the same scale by normalising with respect to the areas under the graphs within the same range in $\bar{r}$. Details are given in Turner and Nicholls' (1954b) paper. The method was used to set the values for all progressions on the same scale as the progression corresponding to the lowest v' .

Now that all the values of $R_e(\bar{r}_{v' v''})$ were on the same scale a graph of R_e against $\bar{r}_{v' v''}$ was plotted and the least squares method was

used to fit a smooth curve to the scatter of points obtained. From the polynomial obtained to represent the curve, a smoothed value of R_e was obtained for each band and the band strength found from equation 3.13.

c. Populations of Excited States.

From equation 3.14

$$kN_{v'} = \frac{I_{v'v''} \lambda_{v'v''}^4}{S_{v'v''}} \quad 3.22$$

From the measured intensities and the smoothed band strengths calculated as above, a value of $kN_{v'}$ was found for each band. As k is a constant depending mainly on the apparatus, these values were a measure of the relative populations of the upper vibrational levels. The values for each band in a v'' - progression should be the same within the limits of experimental error. The final values of $N_{v'}$ were obtained by averaging the values for bands with a common v' .

A second way of calculating the populations was suggested by Pearse (1951) and used by Tyte (1962c) in his investigations on the nitrogen second positive system.

From 3.14

$$\text{Log } I\lambda^4/q = \text{Log } kN_{v'} R_e^2(\bar{r}) \quad 3.23$$

A graph of $\log I\lambda^4/q$ against wavelength should give a number of parallel straight lines or curves, one for each v'' progression. The shape of the curves will be dependent on the variation of $R_e^2(\bar{r})$ with wavelength and the spacing of the curves will be proportional to $\text{Log } N_{v'}$. In addition to obtaining values for the populations, the deviations of

the points for the individual bands from the curves can be used to detect systematic deviations due to extra emission or absorption or inaccurate Franck Condon factors.

In order to use this method it is necessary to measure a sufficient number of bands in each v'' - progression so that the general trend of a $\log I\lambda^4/q$ versus λ plot can be observed. Unfortunately this was not the case in the present experiments and the first method had to be used.

d) Effective Vibrational Temperature.

For a gas discharge in thermal equilibrium, the distribution of the molecules among the vibrational levels of the upper state is given by

$$N_{v'} = N_0 e^{-\frac{hcG'(v')}{kT}} \quad 3.24$$

where $G'(v')$ is the vibrational energy of the upper state and T the temperature of the discharge.

From equations 3.14 and 3.24

$$\left(\frac{I\lambda^4}{S}\right)_{v'v''} = KN_0 e^{-\frac{hcG'(v')}{kT}} \quad 3.25$$

$$\log_e \left(\frac{I\lambda^4}{S}\right)_{v'v''} = \text{Const.} - \frac{hc}{kT} G'(v') \quad 3.26$$

A graph of $\log_e \left(\frac{I\lambda^4}{S}\right)_{v'v''}$ against $G'(v')$ should therefore give a straight line from whose slope the temperature may be calculated. Even when, as in the present case, the excitation is not thermal, it is often possible to obtain a straight line from the above plot and obtain a temperature which is called the effective vibrational temperature.

e. Alternative Treatment.

Equation 3.8. is based on the assumption that the electron transition

moment remains constant over the range covered by a band system i.e. the band strength is assumed equal to the Franck Condon factor for each transition. This means that the populations and vibrational temperatures are calculated using $q_{v', v''}$ instead of $S_{v', v''}$. These calculations were also performed in the present experiment and compared with those using $S_{v', v''}$.

f. Examination of Franck Condon Factors.

It has been pointed out that the method used by Tyte to estimate the reliability of the Franck Condon factors he used could not be employed in the present experiment. It should however, be possible to find a similar method if two quantities could be found, one of which is dependent on q and would be expected to vary smoothly with the other.

The electron transition moment, which was calculated using q values, was expected to vary smoothly with the r -centroids and it was decided to combine the calculation of the transition moment with an assessment of the Franck Condon factors.

This is, in essence, the same method as that used by Tyte. The r -centroid is monotonically dependent on the wavelength (Nicholls 1965b) and $\log I/q\nu^4$ is proportional to $[R_e(\bar{r}_{v', v''})]^2$ for each v'' - progression. Tyte's plots of $\log I/q\nu^4$ against λ are therefore similar to plots of R_e^2 against $\bar{r}_{v', v''}$ for each progression. The main difference between the two methods is that, in this case, normalisation of the progression was necessary.

A preliminary examination was made using the tables of values of $R_e(\bar{r}_{v', v''})/R_e(\bar{r}_{v', v_0''})$. These tables were examined for each set of conditions and any value of $R_e(\bar{r}_{v', v''})/R_e(\bar{r}_{v', v_0''})$ which seemed ex-

cessively large or small was discarded to minimise errors in the normalisation routine. These discarded values were noted and examined to see if they were consistently large or small for all conditions indicating erroneous Franck Condon factors, or whether they varied systematically with the conditions indicating extra emission or absorption. It was necessary to take care that the band in each progression with respect to which the rest of the progression was normalised should be that which was most free from overlapping emissions. If there were some systematic error in this band, then it could be detected as it would lead to abnormal values for the rest of the bands in its progression.

The above method only served to remove those bands for which the errors were excessive. The values for the remainder of the bands were then fitted to a smooth curve as previously described, and the graphs obtained for all the conditions were examined. Points which continually lay above or below the curve were noted. If the deviations varied systematically with conditions then, as before, the errors were probably due to extraneous emission or absorption. If the deviation remained substantially constant for all conditions then the Franck Condon factor was probably in error.

The intensity ratios were also used to estimate the reliability of the q values (see section 3a).

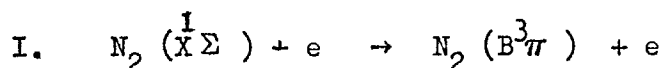
4. Theoretical Calculations of Populations.

a. Excitation Processes.

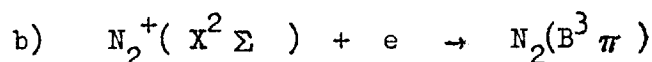
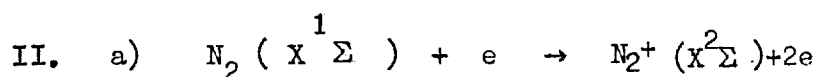
From the experimental measurements, the distribution of the molecules among the vibrational levels of the upper state of the first positive

system ($B^3\pi$) was determined from equation 3.22. It is of interest, in order to try and understand the processes occurring, to estimate the populations, N_v , of the $B^3\pi$ state expected for different excitation mechanisms.

The most likely processes are



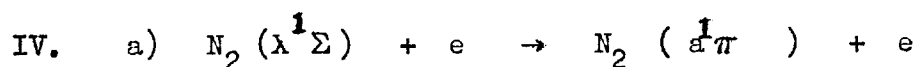
This represents excitation by electron collision with a ground state molecule.



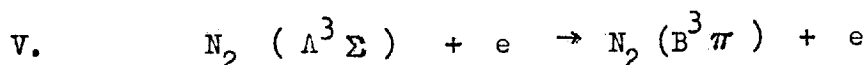
This represents ionisation followed by recombination.



This populates the B state by emission of the second positive system.



This process was suggested by Nicholls (1948). First the ground state molecule is excited to the metastable $a^1\pi$ state. A collision of the second kind with a slow electron then takes it down to the B state.



The $\Lambda^3\Sigma$ state is metastable with a lifetime ~ 0.1 secs. An appreciable population of this state is expected to be built up in

a discharge and collision with an electron is probable.

It was only possible to perform calculations for processes I, III and V as the necessary Franck Condon factors for calculations of processes II and IV were not available.

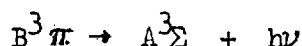
b. Theory.

A short time after switching on, the discharge will have settled down to a steady state condition. In this situation, the rate of population of a given state by all the processes exciting it is equal to the rate of depopulation.

All the above processes probably play some part in populating the B state, but each calculation was performed assuming just one process was occurring.

Process I.

Collisions of molecules with electrons were assumed to occur very quickly, the process thus obeying the Franck Condon principle. In this calculation it was assumed that process I was the only one populating the B state which was depopulated only by the process



resulting in emission of the first positive system.

If $N(v_x)$ is the population of the $v = v_x$ level of the $X^1\Sigma$ state then the rate at which this level populates the $v = v_B$ level of the $B^3\pi$ state, $g(v_x, v_B)$ is given by

$$g(v_x, v_B) = N(v_x) \cdot P(v_x, v_B) \quad 3.27$$

$P(v_x, v_B)$ is the transition probability, i.e. the fraction of the total population of the v_x level which is excited to the v_B level by collision

with electrons. Bates (1949) has shown that this transition probability is proportional to the band strength. This involves the assumption that the transition probability is independent of the electron energy. This may not be valid but will still give a useful estimate of the population distribution caused by this process.

Equation 3.27 now becomes.

$$g(v_x, v_B) = N(v_x) \cdot S(v_x, v_B) \quad 3.28$$

The total population rate, $g(v_B)$, of the v_B level is given by

$$g(v_B) = \sum_{v_x} N(v_x) \cdot S(v_x, v_B). \quad 3.29$$

The rate of depopulation $g^{\downarrow}(v_B, v_A)$ of the v_B level to the v_A level of the $A^3\Sigma$ state is given by

$$g^{\downarrow}(v_B, v_A) = N(v_B) \cdot A(v_B, v_A) \quad 3.30$$

where $N(v_B)$ is the population of the v_B level and $A(v_B, v_A)$ is the Einstein transition probability for emission of the (v_B, v_A) band.

$$\text{Now } A(v_B, v_A) \propto S(v_B, v_A) \left[\nu(v_B, v_A) \right]^3 \quad 3.31$$

where $\nu(v_B, v_A)$ is the frequency of the emitted radiation.

The total rate of depopulation by emission from the v_B level to all the levels of the $A^3\Sigma$ state is given by

$$g^{\downarrow}(v_B) = N(v_B) \sum_{v_A} S(v_B, v_A) \left[\nu(v_B, v_A) \right]^3 \quad 3.32.$$

The summation is only taken for the levels, v_A , lying below the level v_B .

Equating the two rates we obtain the steady state equation.

$$\sum_{v_x} N(v_x) \cdot S(v_x, v_B) = N(v_B) \sum_{v_A} S(v_B, v_A) \left[\nu(v_B, v_A) \right]^3 \quad 3.33$$

$$N(v_B) = \frac{\sum_{v_x} N(v_x) \cdot S(v_x, v_B)}{\sum_{v_A} S(v_B, v_A) [\nu(v_B, v_A)]^3} \quad 3.34$$

It is now necessary to make some assumptions about the distribution of the molecules among the vibrational levels of the ground state. The following three cases were considered.

i) All Molecules in $v_x = 0$ Level.

In this case $N(v_x) = 0$ except for $v_x = 0$ and there is no need for summation over v_x . Equation 3.34 becomes.

$$N(v_B) = \frac{S(v_x, v_B)}{\sum_{v_A} S(v_B, v_A) [\nu(v_B, v_A)]^3} \quad 3.35$$

ii) Equal Populations of all Levels.

In this situation all the values of $N(v_x)$ are the same. Equation 3.34 becomes

$$N(v_B) = \frac{\sum_{v_x} S(v_x, v_B)}{\sum_{v_A} S(v_B, v_A) [\nu(v_B, v_A)]^3} \quad 3.36$$

iii) Boltzmann Distribution of Temperature T.

The populations of the ground state levels in this case are given by

$$N(v_x) = N(0) \cdot \exp(-G(v_x)/kT) \quad 3.37$$

where $G(v_x)$ is the energy of the v_x level.

This leads to

$$N(v_B) = \frac{\sum_{v_x} S(v_x, v_B) \exp(-G(v_x)/kT)}{\sum_{v_A} S(v_B, v_A) [\nu(v_B, v_A)]^3} \quad 3.38$$

Process III.

Here we have $N(v_c)$ molecules in the v_c level of the $C^3\Pi$ state causing a population $N(v_B)$ in the v_B level of the $B^3\Pi$ state by emission of

radiation. The B state is depopulated by emission of the first positive system.

The rate of depopulation of the v_B level is given by equation 3.31.

By a similar argument, the rate of population of the v_B level by radiative transitions from all the levels of the $C^3\pi$ state is

$$\sum_{v_c} N(v_c) \cdot S(v_c, v_B) \cdot \left[\nu(v_c, v_B) \right]^3$$

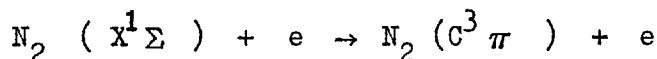
This leads to the steady state equation

$$N(v_B) = \frac{\sum_{v_c} N(v_c) \cdot S(v_c, v_B) \cdot [\nu(v_c, v_B)]^3}{\sum_{v_A} S(v_B, v_A) \cdot [\nu(v_B, v_A)]^3} \quad 3.39$$

This expression depends upon the population of the $C^3\pi$ state.

Two cases were considered.

a) One set of calculations was performed assuming electron excitation of the ground state to the C state.



where the same assumptions as before were made about the populations of the ground state levels. This would give equations 3.35, 3.36. and 3.38 with v_c substituted for v_B .

b) Tyte (1962a) has discussed the excitation mechanisms responsible for populating the $C^3\pi$ state on the basis of his experimental results. His experimentally determined values of $N(v_c)$ were used in equation 3.39 to determine $N(v_B)$ for all the conditions of his experiments. The same conditions were employed in the present experiments and the results compared with the theoretical quantities.

Process V.

The calculation was performed making the same assumptions about the population $N(v_A)$ of the $A^3\Sigma$ state levels as were made about the ground state levels for process I. The expressions are the same as equations 3.35, 3.36, and 3.38 with v_A replacing v_x .

In all the above expressions, proportionality constants have been omitted, but as relative populations were being calculated, this made no difference to the results.

CHAPTER 4.

FRANCK CONDON FACTOR ARRAYS AND ELECTRON TRANSITION MOMENTS.

1. Comparison of Franck Condon Factor Arrays.

Since Tyte (1962 a) performed his investigations, arrays of Franck Condon factors have been calculated using RKR potentials and numerical methods. These should be more accurate than those calculated from the Morse potential especially at high vibrational quantum numbers. Part of the aim of this work was to try and assess the reliability of the calculated arrays and, wherever possible, the results were analysed using Franck Condon factors calculated from both Morse and RKR potentials and the results compared. An investigation was also performed to see what difference, if any, a change of q values made to the functional dependence of the electron transition moment, R_e , on the r - centroid.

a) Nitrogen Second Positive System.

Tyte, using the Franck Condon factors calculated by Jarman, Fraser and Nicholls (1953) found, after thorough experimental investigations, that several values were probably inaccurate. Since these values were computed, Nicholls (1961) has extended the calculations which were based on a Morse potential, to higher quantum numbers and Zare, Larsson and Berg (1965) and Benesch, Vanderslice, Tilford and Wilkinson (1966b) have produced arrays calculated using an RKR potential. Table 1 lists the bands for which the q values were thought to be in error, the predicted direction of the error, and the four different sets of q values.

TABLE 1.Comparison of Franck Condon Factors for N₂ 2nd. Positive System.a) JFN q values estimated too low

Band	JFN	<u>q values</u>		
		N	ZLB	BVTW
1,2	0.196	0.204	0.212	0.203
2,1	0.312	0.322	0.335	0.341
2,3	0.049	0.0596	0.0691	0.0634
3,2	0.143	0.163	0.204	0.212
4,2	0.296	0.303	0.326	0.336
4,3		0.0475	0.113	0.126
4,6		0.0294	0.047	0.042

b) JFN q values estimated too high

1,6		0.0179	0.0152	0.0169
2,2	0.041	0.0330	0.0230	0.0238
3,8		0.0616	0.0526	0.0552
4,9		0.0802	0.0667	0.0658

JFN Jarmain, Fraser and Nicholls (1953) ZLB. Zare, Larsson and Berg, (1965)
 N Nicholls (1961) BVTW Benesch, Vanderslice, Tilford and
 Wilkinson (1966)

It can be seen from the table that, in each case, there is a marked difference between the Morse and RKR values, and the deviation is in the direction indicated by Tyte's experiments. For the bands for which Jarmain, Fraser and Nicholls did not calculate q values, it was assumed that Nicholls' values were used in Tyte's investigation.

2. Electron Transition Moment Calculations.a) Testing of the Computer Programme

In chapter 8 it is mentioned that the routine devised for the scaling procedure for the electron transition moments was tested using the data provided for the 1st positive system by Turner and Nicholls in tables I and II in their paper (1954 b). All the bands omitted by them were omitted in the present calculations so that the results obtained from the

programme ought to be the same as those in their table III. The two sets of results are listed in table 2. It can be seen that they agree for the progressions $v' = 0$ to $v' = 4$, but that for the $v' = 5$ progression onwards, there is a large discrepancy. Though all the values in the $v' = 5$ to $v' = 10$ progressions differed from those of Turner and Nicholls, the ratios by which the values in each progression were multiplied to bring them to the same scale as those in the previous progression were exactly the same for each set of values. This indicates that the error occurred in scaling the values of the $v' = 5$ progression to those of the $v' = 4$ progression. The fact that the programme worked for all the other progressions indicates that it was not the computational procedure that was at fault. The data cards were checked and found to be accurate. The graphs $(R_e(\bar{r}_{v', v''})/R_e(\bar{r}_{v', v''})_{v=0} \cdot \bar{r}_{v', v''})$ were then plotted by hand for the $v' = 4$ and 5 progressions, the areas corresponding to the range of $\bar{r}_{v', v''}$ common to both progressions were calculated, and the two sets of values brought to the same scale by multiplying the value for the 4,1 band by the ratio of the areas to give that for the 5,1 band. The result obtained corresponded exactly to that produced by the computer programme indicating that there was an error in Turner and Nicholls' calculation and that the computer programme was working satisfactorily.

b) Dependence of Transition Moment on r-centroid.

The errors found in Turner and Nicholls' calculations meant that their function for $R_e(\bar{r})$,

$$R_e(\bar{r}) = \exp(3.61 - 3.02 \bar{r}) \quad 4.1.$$

TABLE 2
 $\text{Re}(\bar{r}_{v',v''})/\text{Re}(\bar{r}_{00})$ For First Positive System
 Using Jarman and Nicholls (1954) $q_{v',v''}$

v'	v''	0	1	2	3	4	5	6	7
0	a	1.00	0.933	1.06					
	b	1.00	0.933	1.060					
1		0.653		1.05	0.920	1.14			
		0.656		1.06	0.925	1.14			
2		0.563	0.760	0.670		1.18	1.05		
		0.564	0.762	0.671		1.18	1.05		
3		0.495	0.604		0.757				
		0.496	0.605		0.758				
4			0.424	0.585		0.776			
			0.425	0.587		0.778			
5			0.414	0.463	0.653				
			0.358	0.401	0.566				
6			0.412	0.396	0.499		0.574		
			0.359	0.345	0.435		0.501		
7				0.380	0.376	0.500		0.601	
				0.330	0.327	0.435		0.523	
8					0.373	0.365	0.512		
					0.323	0.317	0.443		
9						0.311	0.364	0.531	
						0.271	0.318	0.464	
10							0.277	0.352	0.541
							0.242	0.307	0.473

a. Values from Turner and Nicholls (1954b) Table III
 b. Values computed in present work from same data.

was also probably in error.

The least squares polynomial fitting programme had already been written and thoroughly tested and was used to find a first degree polynomial for $\log_e R_e$ in terms of $\bar{r}$ and also a second degree polynomial for R_e in terms of $\bar{r}$. The deviations of the experimental values from those calculated from the polynomials were determined as a percentage of the calculated values and the root mean square standard deviation was found. The results obtained for the two fitted polynomials were

$$i) R_e(\bar{r}) = \exp(4.16 - 3.47 \bar{r}) = \text{Const} \times \exp(-3.47 \bar{r}) \quad 4.2.$$

$$\text{Standard deviation} = 11.4\%$$

$$ii) R_e(\bar{r}) = 12.49 - 15.31 \bar{r} + 4.81 \bar{r}^2 = \text{Const.}(1 - 1.23 \bar{r} + 0.39 \bar{r}^2)$$

$$\text{Standard deviation} = 10.3\%$$

$$4.3.$$

The constants are arbitrary because of the arbitrary scale chosen for R_e . It can be seen that the polynomial gives a slightly better fit than the exponential but the difference is not significant. These functions should only be used in the range $1.17 \text{ \AA} < \bar{r} < 1.59 \text{ \AA}$.

These smoothed curves, together with the experimental points, are shown in fig.7.

c) Influence of Franck Condon Factors on the Transition Moment.

As a preliminary investigation, the results of Turner and Nicholls (1954 b) were used. Their results covered a wider range of bands than the present experiments and thus the fitted curve for $R_e(\bar{r})$ would be more generally applicable than one using the present results.

In table I in their paper (1954 b), Turner and Nicholls listed quantities calculated from equation.3.21. and then used them to determine

the functional dependence of R_e on $\bar{r}_{v', v''}$. As these values are dependent on the q values used, it was thought that the function representing $R_e(\bar{r}_{v', v''})$ may also depend on the q values.

Turner and Nicholls used Morse potential q values calculated by Jarman and Nicholls (1954) and represented by $j^q_{v', v''}$. Values using an RKR potential were recently calculated by Zare, Larsson and Berg, (1965) and Benesch, Vanderslice, Tilford and Wilkinson (1966b) and will be represented by $z^q_{v', v''}$ and $b^q_{v', v''}$ respectively.

The quantities calculated by Turner and Nicholls from equation 3.21 were multiplied by

$$\left(\frac{j^q_{v', v''}}{j^q_{v', v_0''}} \right)^{\frac{1}{2}} \cdot \left(\frac{z^q_{v', v_0''}}{z^q_{v', v''}} \right)^{\frac{1}{2}} \text{ and } \left(\frac{j^q_{v', v''}}{j^q_{v', v_0''}} \right)^{\frac{1}{2}} \cdot \left(\frac{b^q_{v', v_0''}}{b^q_{v', v''}} \right)^{\frac{1}{2}}$$

This effectively replaced the Jarman and Nicholls q - values by those of Zare, Larsson and Berg, and Benesch, Vanderslice, Tilford and Wilkinson respectively. After normalisation as before, the functional dependence of R_e on $\bar{r}_{v', v''}$ was determined and compared for the three different sets of q values.

Table 3 shows the values of $R_e(\bar{r}_{v', v''})/R_e(\bar{r}_{v', v_0''})$ using the three sets of Franck-Condon factors. There were several values (marked *) in Turner and Nicholls' results which seemed excessively large and were omitted from their calculation of the function for $R_e(\bar{r}_{v', v''})$. These were explained on the grounds of erroneous q values or overlapping by other bands. Table 3 shows that, using q values from RKR potentials, most of these ratios fall into the expected range indicating that in most cases the q values were in error and that those calculated from the RKR potentials

TABLE 3

COMPARISON OF VALUES OF $\text{Re}(\bar{r}_{v'v''})/\text{Re}(\bar{r}_{v'v_0})$ Along v'' -Progressions.

$v' \backslash v''$	0	1	2	3	4	5	6	7
0	a 1.00 b 1.00 c 1.00	0.933 1.02 1.01	1.06 1.25 1.24					
1	1.00 1.00 1.00		1.61 1.29 1.28	1.41 1.35 1.33	1.74 1.83 1.81			
2	1.00 1.00 1.00	1.35 1.04 1.08	1.19 1.40 1.38	10.3* 2.13/ 2.18/ 2.18/	2.09 1.49 1.49	1.86 1.60 1.60		
3	1.00 1.00 1.00	1.22 1.01 1.05	2.60* 1.26 1.37	1.53 1.27 1.31	2.87* 6.00/ 5.96/	6.81* 2.55/ 2.60/		
4		1.00 1.00 1.00	1.38 1.09 1.14	8.27* 2.79/ 3.50/	1.83 1.32 1.37			
5		1.00 1.00 1.00	1.12 0.916 0.970	1.58 0.949 1.06		2.79* 1.31 1.45		
6		1.04 1.28 1.20	1.00 1.00 1.00	1.26 1.01 1.07	2.19* 1.12 1.28	1.45 1.55 1.55		
7			1.01 1.25 1.16	1.00 1.00 1.00	1.33 1.03 1.10	3.29* 1.15 1.37	1.60 1.41 1.45	
8				1.02 1.29 1.18	1.00 1.00 1.00	1.40 1.05 1.13		
9					0.854 1.10 1.00	1.00 1.00 1.00	1.46 1.03 1.12	
10						0.787 1.03 0.94	1.00 1.00 1.00	1.54 1.00 1.12

a. Calculated using Jarman and Nicholls (1953) $q_{v'v''}$.
b. Calculated using Zareet. al. (1965) $q_{v'v''}$.
c. Calculated using Benesch et. al. (1966.b) $q_{v'v''}$.

Bands marked* discarded by Turner and Nicholls. / discarded in present work.

TABLE 4Comparison of Values of $R_e(\bar{r}_{v'v''})/R_e(\bar{r}_{oo})$

$v' \backslash v''$	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
0	a) 1.00 b) 1.00	1.02 1.01	1.25 1.24					
1	0.828 0.828		1.07 1.06	1.11 1.10	1.52 1.50			
2	0.730 0.726	0.761 0.782	1.02 1.00		1.09 1.08	1.17 1.16		
3	0.658 0.623	0.663 0.654	0.827 0.852	0.832 0.814				
4		0.636 0.610	0.693 0.694		0.838 0.834			
5		0.679 0.611	0.622 0.592	0.644 0.645		0.889 0.884		
6		0.748 0.631	0.585 0.528	0.590 0.565	0.656 0.675	0.906 0.817		
7			0.731 0.599	0.583 0.517	0.601 0.569	0.672 0.709	0.821 0.748	
8				0.753 0.606	0.583 0.513	0.609 0.579		
9					0.682 0.538	0.619 0.537	0.638 0.603	
10						0.657 0.508	0.635 0.542	0.638 0.606

a Calculated using Zare et al (1965) $q_{v'v''}$ b Calculated using Benesch et al (1966) $q_{v'v''}$

$q_{VV''}$ from Morse Potential

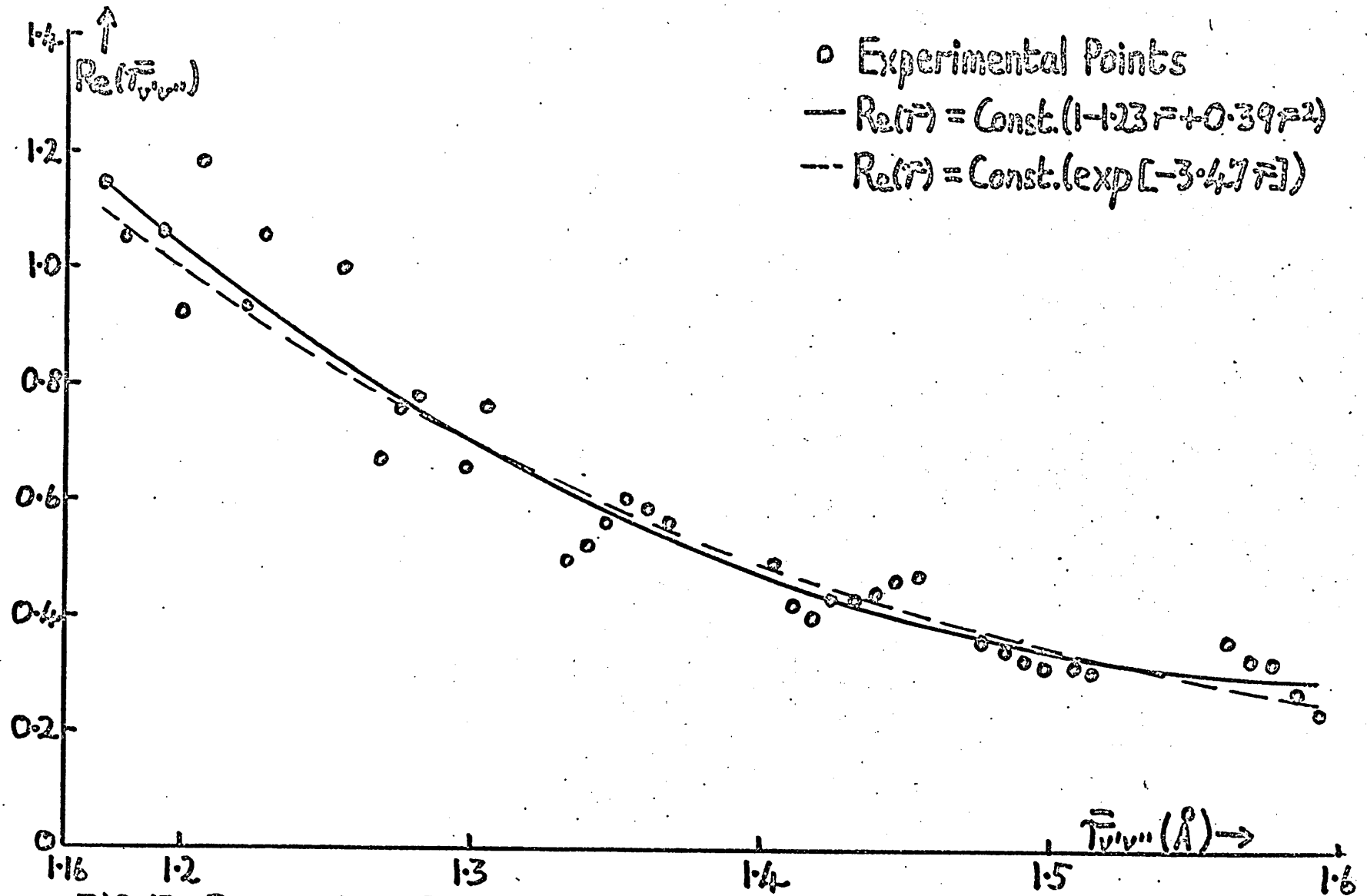


FIG.7 $Re(\bar{T}_{VV''})$ v. $\bar{T}_{VV''}$ TURNER & NICHOLLS' RESULTS

$q_{v'v''}$ from R.k.R. potential

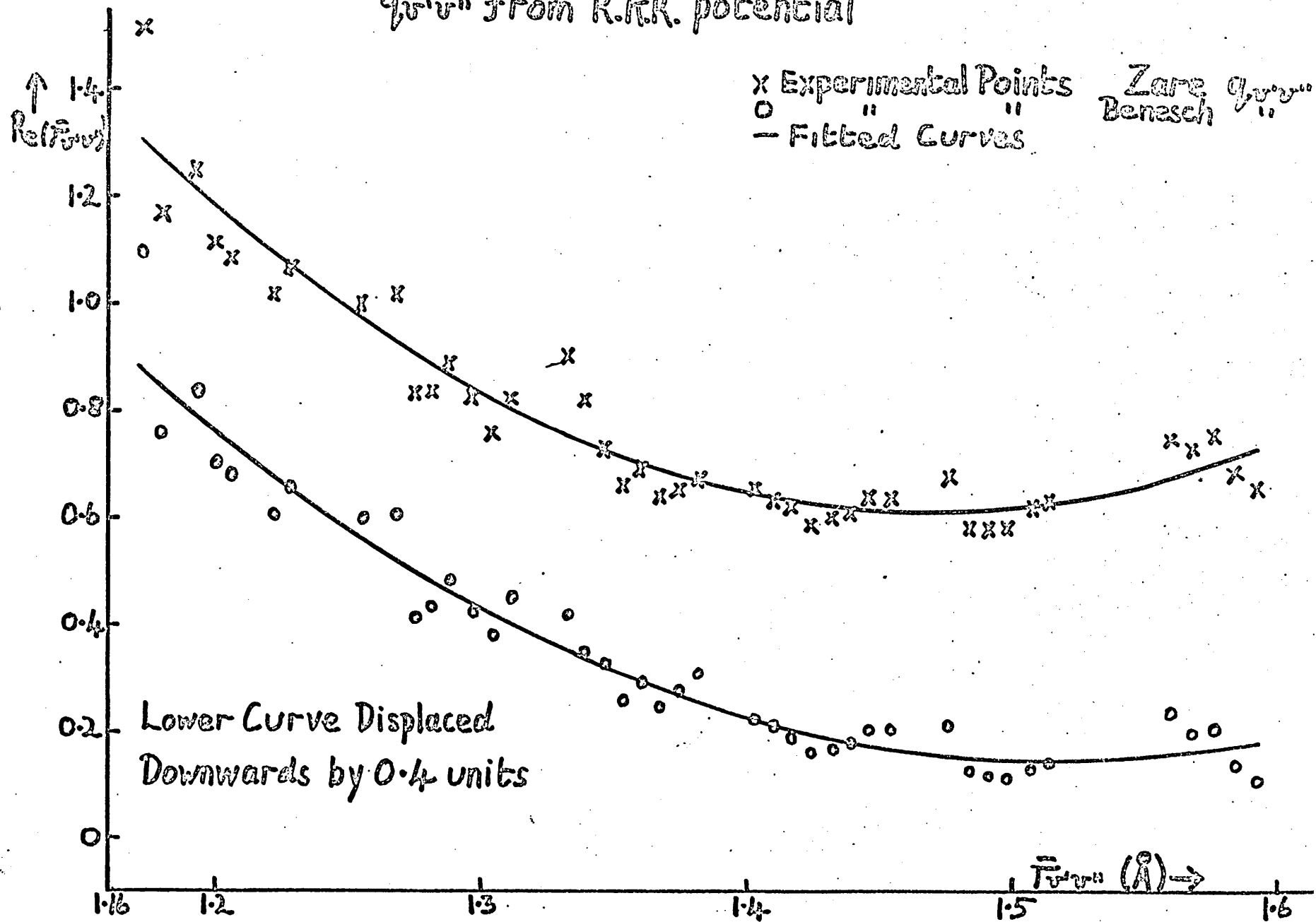


FIG.8

$Re(\bar{\Gamma}_{v'v''})$ v. $\bar{\Gamma}_{v'v''}$ USING TURNER & NICHOLLS' RESULTS

are, in fact, an improvement.

Normalisation was carried out as before and the ratios $R_e(\bar{r}_{v'v''})/R_e(\bar{r}_{00})$ are shown in table 4. As before, quadratic and exponential functions were fitted to the results and the standard deviations calculated. When Zare's q values were used, the exponential was a poor fit as the plot of the experimental points displayed a minimum (fig.8). The quadratic function, shown by the smooth curve in fig.8., fitted the points well. The function obtained was

$$\begin{aligned} R_e &= 17.95 - 23.64 \bar{r} + 8.06 \bar{r}^2 \\ &= \text{const.} \times (1 - 1.317 \bar{r} + 0.449 \bar{r}^2) \end{aligned} \quad 4.4.$$

Standard deviation = 6.8%

The points and curve obtained using Benesch's q values are also shown in fig.8., the relationship obtained being

$$\begin{aligned} R_e &= 15.26 - 19.48 \bar{r} + 6.44 \bar{r}^2 \\ &= \text{const.} \times (1 - 1.276 \bar{r} + 0.422 \bar{r}^2) \end{aligned} \quad 4.5.$$

Standard deviation = 6.5%

This curve does not show such a marked minimum as that produced by equation 4.4.

Comparing the standard deviations from equations 4.4. and 4.5. with those from equations 4.2. and 4.3. it can be seen that Zare's and Benesch's q values fit the experimental data equally well and considerably better than do those of Jarman and Nicholls. The differences between the two former arrays, both calculated from RKR potentials, arise from slight differences in the computational procedure. Benesch et.al.(1966b) mentioned that there may have been an error in vibrational numbering in Zare's calculations, which would lead to errors in the Franck Condon factors. Ex-

perimental methods are, however, not sensitive enough to detect this if it is the case, and it appears from equations 4.4. and 4.5. that either array of q_v, v'' may be used with equal accuracy in experimental investigations.

A glance at the tables and the curves shows that equation 4.3. produces a 4 fold variation of $R_e(\bar{r})$ in the region investigated whereas equations 4.4. and 4.5. produce a $2 - 2\frac{1}{2}$ fold variation. This shows that part of the variation obtained by Turner and Nicholls was not due to a real variation of the transition moment over the band system, but was just the result of the inaccuracy of the Franck Condon factors used. However, a two fold variation still remains even with more accurately computed q values, and this seems to be too large to discount on the grounds of experimental error. Both Zare et.al. (1965) and Joshi et.al. (1966) have expressed doubts as to the reality of the transition moment variation in this system and it is possible that the variation may have been caused by the overlapping of bands in the infra-red region. No definite conclusion can be reached until the techniques of intensity measurement are improved and measurements are made on this system further into the infrared in order to see if the observed trend continues.

Since Turner and Nicholls performed their experiments, Nicholls (1961) has calculated an array of q values to high quantum numbers using a Morse potential. These are very similar to those of Jarman and Nicholls and would be expected to give the same variation in R_e as equation 4.3.

It would appear from the results of this work that the Morse potential is an inadequate representation of the potential curve. It is well known

that it is not expected to be very accurate at high quantum numbers.

It was observed in the present case that Jarman and Nicholls took their values for the spectroscopic constants, necessary for a calculation of q - values, from Herzberg (1950) whereas both Zare et.al. and Benesch et.al. used later values listed by Lofthus (1960). Joshi et.al. (1966) have calculated q values from a Morse potential using the latter constants and the values agree better with Zare's than do those of Jarman and Nicholls, though there are still differences. Unfortunately those calculations only extended up to v' and $v'' = 5$ and this was insufficient for a test to be made of their effect on the transition moment variation. Nevertheless, their results show that the Morse potential is a better representation than the results of equation 4.3. suggest. However, now that large computers are available to perform rigorous numerical calculations, the usefulness of the Morse potential function in this field of research seems to be very limited.

3. Relative Band Strengths.

Nicholls (1955) and Jansson (1966) have both calculated smoothed arrays of relative band strengths using equations 4.1. and 3.13. Jansson has extended his table well outside the range of applicability of equation 4.1. Not much weight can therefore be attached to the accuracy of these values but they do serve as a useful guide in determining where strong bands are expected to exist.

An array of band strengths has been calculated using equations 4.4., 4.5. and 3.13 with the appropriate Franck Condon factors. The results obtained are displayed in table 5. The largest discrepancies between the two arrays occur for bands too weak to be observed. There are differences between values for some observed bands, but both arrays fit

TABLE 5

Relative Band Strengths of the N_2 First Positive System

$v' \backslash v''$	0	1	2	3	4	5	6	7	8	9
0 (a)	1000	1018	630							
(b)	1000	1036	634							
1	744 748	8.8 7.0	474 480	704 718	572 574					
2	219 223	505 492	148 157	64 63	426 437	586 598				
3	34 35	370 365	178 164	322 331	13 14	136 141	413 426			
4	3.4 3.3	97 96	395 379	18 12	315 316	127 133	6.4 7.0	196 208		
5	0.2 0.2	14 13	170 162	323 297	11 17	197 190	227 234	26 27	44 51	
6		1.3 1.2	34 31	232 215	213 183	76 88	76 67	242 246	112 113	0.2 0.0
7			4.1 3.6	63 57	270 241	109 84	143 152	9.0 5.5	184 183	181 184
8				9.8 8.6	101 88	282 239	36 22	175 176	4.7 8.4	99 95
9					20 17	146 122	268 215	3.2 0.2	165 158	40 48
10						36 30	193 156	233 173	4.2 10	125 112
11							59* 48*	240 186	184 126	28 38
12								90* 71*	283 205	132 62

a Using $q_{v',v''}$ from Zare et al.(1965)b Using $q_{v',v''}$ from Benesch et al.(1966b)

* extrapolated values.

the published experimental data equally well and both show some large deviations from Nicholls' and Jansson's values.

The r centroids used in these calculations are the ones listed by Turner and Nicholls (1954b). Strictly speaking, they should be calculated from the same data used for the Franck Condon factors but these r centroids have not been observed in the literature to date. It is not expected that they would greatly affect the results obtained as the r centroid is not expected to be as sensitive to small changes in the potential function as the wavefunctions and overlap integrals are.

CHAPTER 5.

RESULTS OF EXPERIMENTS WITH NITROGEN.

1. Experimental.

As one of the aims of this work was to investigate the relative variations with conditions of the intensities of the first and second positive systems, the experiments followed the same lines as those performed by Tyte (1962a). A wider range of conditions was used in order to identify the trends of the results with more certainty. These included those of Tyte's experiments so that a direct comparison could be made.

In all the experiments a spectrograph slit width of 0.08 mm. was used in order to blend the rotational structure and cut down the exposure time necessary. Several test plates were taken with the discharge tube and the standard lamp in order to determine the exposure time and standard lamp current which produced a satisfactory variation in the blackening of the plate.

There were two types of plate that could be used in the spectral region under investigation. These were Ilford Long Range Spectrum (LRS) and Astra III plates. The Astra III plate has a fairly constant response in the wavelength region required, but cuts off at about $6800 \text{ \AA}$ and therefore could only record first positive bands in the range $v' = 4-12$. The LRS plates could record the $\Delta v = 2$ sequence and this enabled bands with $v' = 2$ and 3 to be recorded. On the other hand, there are several dips in the response v. wavelength curve and this meant that several bands in

in the $\Delta v = 3$ and 4 sequences could only be weakly detected whereas others blackened the plate so strongly that variations of intensity with conditions could not be detected. None of the bands in the $\Delta v = 5$ sequence could be observed on the LRS plates which are also more susceptible to fogging than the Astra III plates.

While errors in intensity measurements from Astra III plates were expected to be somewhat less than those obtained from LRS plates, it was desirable to obtain information about as many of the vibrational levels of the upper state as possible. Judging from Tyte's results for the second positive system, the intensity variations in pure nitrogen were expected to be less than those in nitrogen helium mixtures. A few test plates were taken and showed that this was also true for the first positive system. For the experiments in pure nitrogen, LRS plates were used, while for the nitrogen + helium experiments both plates were used. In the latter case intensities of the $\Delta v = 2$ sequence were measured from the LRS plates and those for all the other bands were taken from Astra III plates and an attempt was made to correlate the values from the two plates. While this is obviously not as satisfactory as taking all the measurements from one plate for calculations in which all the bands are taken into account e.g. vibration temperature and transition moment variations, the calculations of variations with conditions should not be affected.

The experiments performed may be divided into the same two groups as those performed by Tyte on the second positive system.

a) Experiments in Pure Nitrogen:-

A series of experiments was performed with a discharge through pure

nitrogen. The following variations with conditions were investigated.

- i) Variation with current at a constant pressure of nitrogen. This was investigated at three nitrogen pressures, 0.2 mm., 1.0 mm., and 2.0 mm., of Hg the current varying between 10ma and 90 ma.
- ii) Variation with nitrogen pressure at a constant current of 50 ma.
- b) Experiments in Mixtures of Nitrogen and Helium:-

The remainder of the experiments were all performed in nitrogen diluted with helium. The variations investigated were:-

- i) Variations with helium pressure at a constant nitrogen pressure and current. The investigation was performed at 0.06 mm. N_2 with currents of 25 ma., 40 ma., 60 ma., 80 ma., and at 0.2 mm. and 0.4 mm. N_2 with a current of 40 ma.
- ii) Variations with the composition of a constant pressure mixture of nitrogen and helium at total pressures of 0.5 mm., 2.0 mm., and 5.0 mm., of Hg. The current in each case was 25 ma.
- iii) Variation with current in a constant mixture containing 0.25 mm. N_2 and 1.0 mm. He.

2. Results and Tables.

For each different set of conditions, the results were treated and analysed in the same way. The following quantities were investigated.

a) Intensities.

From each set of data, the integrated intensities were calculated using the method described in Chapter 2. They were then scaled with respect to the 7,4 band. This band was chosen because, though other bands had much greater intensities, the 7.4 band was in the most sensitive

TABLE 6

Intensities of Nitrogen First Positive Bands. 0.2mm Nitrogen, 35ma.

	Observed.	Predicted. (Cascade).
2, 0	6810	10524
3, 0	507	1371
3, 1	4795	8782
4, 1	1540	2018
4, 2	3000	4967
5, 1	300	220
5, 2	1812	1828
5, 3	1800	2158
6, 2	512	311
6, 3	2340	1483
6, 4	966	863
7, 3	359	330
7, 4	1000	1000
8, 4	256	264
8, 5	581	531
9, 5	269	155
9, 6	345	211
10, 6	313	74
10, 7	297	68
11, 7	381	31
11, 8	327	19
12, 8	261	11
12, 9	214	4

region of the photographic emulsion and, on the microphotometer traces, it had one of the largest areas and was therefore less susceptible to errors than other bands. Table 6 below shows a typical intensity distribution together with that calculated assuming that the main excitation process was process III (Chapter 3.4.) and using the populations obtained by Tyte for the $C^3\pi$ state under the same conditions. The agreement between the two sets of values is not very good, the calculated intensities being much higher than the experimental ones at low v' and much lower at high v' . This suggests that the cascade process was not the main one responsible for the formation of the first positive system.

b) Intensity Ratios.

For each set of conditions, the intensities of the bands in each v'' progression were normalised with respect to a suitable band in the same progression. This was one which gave a reasonably large area under the microphotometer trace and was not overlapped by any other emission lines or bands. The ratios obtained are listed in tables 7 to 15.

The main aims of these calculations were to examine the various Franck Condon factor arrays and to test the validity of the theory in Chapter 3 over a wide range of conditions. According to the theory the ratios should remain constant for all conditions. Any deviations from constancy would mean that the band strengths are not constants independent of the conditions.

As far as is known, this is the first time this effect has been investigated for the first positive system though similar investigations have been performed on the second positive. Smallwood (1961) and Pillow and Smallwood (1962) observed variations of several ratios with increasing

TABLE 7

Intensity Ratios of Nitrogen First Positive Bands.

Nitrogen Pressures of a) 0.2mm.Hg, b) 1.0mm.Hg, c) 2.0mm.Hg. Various Currents

Ratio	Current (ma.)									
	10	20	30	35	40	50	60	70	80	90
3,0/3,1	a)	.101	.102	.107	.118	.117	.126	.111	.114	.120
	b)		.147	.151	.142	.150	.146	.180	.164	.167
	c)		.091	.101	.116	.123	.171	.164	.182	.156
4,2/4,1	3.20	2.84	3.00	2.51	2.75	2.46	2.52	2.63	2.60	2.52
	2.93	2.84	2.81	2.27	2.10	2.34	2.36	2.64	2.29	2.54
		2.06	2.68	2.62	2.44	2.39	1.75	1.97	2.26	1.91
5,1/5,3			.088	.108	.095	.102	.113	.112	.113	.109
			.063	.115	.110	.111	.118	.119	.102	.096
			.063	.063	.082	.100	.113	.119	.111	.110
5,2/5,3	0.81	0.79	1.02	1.19	1.16	1.20	1.21	1.13	1.16	1.22
		1.09	1.01	1.17	1.20	1.01	1.23	1.12	0.93	0.81
		0.61	0.96	0.98	1.07	1.01	0.95	0.87	0.77	0.70
6,3/6,2	3.6	3.6	3.9	4.6	4.6	3.9	4.4	4.0	3.9	4.1
			4.7	5.1	4.8	5.6	6.7	6.8	5.5	4.8
			5.9	6.4	6.0	5.8	5.6	5.2	4.0	3.5
6,4/6,2		2.45	2.06	1.89	1.84	1.51	1.41	1.31	1.47	1.49
				2.56	3.28	3.40	3.39	3.21	2.71	2.87
			2.15	2.12	2.64	2.53	2.67	2.66	2.50	2.31
7,4/7,3		2.80	2.72	2.79	3.01	2.79	2.71	2.66	2.63	2.61
		2.29	2.81	2.81	3.11	3.47	3.19	2.66	2.27	2.01
			4.07	3.59	3.41	3.22	3.04	2.69	1.93	1.56
8,5/8,4			2.29	2.27	2.03	1.95	1.78	1.86	1.78	1.94
			2.01	1.77	1.73	1.97	2.15	1.70	1.47	1.28
			2.07	2.12	2.07	2.28	2.43	2.09	1.70	1.36
9,5/9,6		.66	.81	.78	.80	.69	.86	.93	.87	.68
			.75	.73	.73	.76	.64	.78	.82	.80
			.74	.69	.52	.62	.65	.72	1.03	1.34
10,6/10,7		.87	1.04	1.05	1.19	1.14	1.35	1.29	1.36	1.23
			1.49	1.23	1.10	1.02	1.15	1.31	1.27	1.58
			1.52	1.25	1.10	1.05	1.09	1.26	1.56	1.50
11,7/11,8			1.08	1.17	1.26	1.26	1.55	1.53	1.91	2.21
				2.03	1.92	1.84	1.91	2.59	2.65	2.51
				1.91	1.82	1.74	1.80	2.44	2.50	2.37
12,9/12,8			.92	.82	.89	.96	.89	.88	.90	.82
					.13	.28	.46	.72	.63	.56
					.30	.32	.43	.54	.57	.53

The expected errors in the ratios above and in the following tables are in the region 10-20%. For ratios involving weaker bands, the errors will be much larger

TABLE 8

Intensity Ratios of Nitrogen First Positive Bands.

Pure Nitrogen, 50ma, Various Nitrogen Pressures.

<u>Rq_{ratio}</u>	<u>Nitrogen Pressure (mm.)</u>									
	<u>0.05</u>	<u>0.1</u>	<u>0.2</u>	<u>0.3</u>	<u>0.5</u>	<u>1.0</u>	<u>2.0</u>	<u>3.0</u>	<u>5.0</u>	<u>7.5</u>
4,2/4,1	1.58	1.31	1.24	1.01	1.04	0.83	1.11	0.97	1.02	1.39
5,1/5,3	.271	.270	.280	.311	.304	.346	.253	.288	.263	.218
5,2/5,3	1.88	1.94	2.01	2.25	2.22	2.46	2.23	2.24	2.42	1.82
6,3/6,2	4.3	4.4	4.5	4.6	4.6	4.5	4.9	4.7	4.3	4.9
7,4/7,3	3.10	2.89	3.28	3.20	3.04	3.00	3.11	3.39	3.23	3.12
8,5/8,4	2.03	1.91	1.97	1.85	1.80	1.96	1.79	1.80	1.72	1.78
9,5/9,6	.71	.74	.78	.73	.77	.76	.75	.75	.80	.83
10,6/10,7	1.00	0.95	1.01	1.01	1.08	1.16	1.14	1.17	1.22	1.18
11,7/11,8	1.52	1.59	1.67	1.45	1.69	1.60	1.81	1.81	1.87	1.92
12,9/12,8	1.11	1.17		1.25	1.16	1.05	0.93	0.89	0.76	0.82

TABLE 9

Intensity Ratios of Nitrogen First Positive Bands.

0.06mm. Nitrogen: a)25ma., b)40ma., c)60ma., d)80ma.

Various Helium Pressures.

Ratio	Helium:Nitrogen Ratio					100
	0	3	8	27	50	
3,0/3,1	a).049	.065	.070	.059		
	b).073	.071	.098	.101		
	c).113	.118	.114	.130		
	d).115	.123	.108	.135		
4,2/4,1	1.32	1.26	1.19	1.21	1.36	
	1.08	1.52	1.18	1.26	1.19	
	1.28	1.55	1.15	1.21	1.05	
	1.47	1.36	1.28	1.11	1.27	
5,1/5,3	.202	.226	.225	.229		
	.222	.201	.217	.225	.280	
	.220	.207	.239	.244	.278	
	.194	.217	.232	.259	.280	
5,2/5,3	1.55	1.54	1.61	1.64	1.30	
	1.70	1.46	1.62	1.74	1.74	
	1.66	1.54	1.79	1.82	1.92	
	1.57	1.48	1.74	2.00	1.77	
6,3/6,2	5.1	4.3	4.2	4.6	4.9	
	3.8	4.2	4.6	4.3	5.1	
	4.7	4.4	4.6	4.5	6.3	
	4.9	4.8	4.5	4.5	6.4	
6,4/6,2	2.46	2.20	1.95	2.06	2.39	
	1.89	1.99	1.77	1.80	1.98	
	1.80	1.75	1.44	1.69	1.64	
	1.71	1.78	1.55	1.60	1.73	
7,4/7,3	3.02	2.93	2.92	2.86	2.71	
	3.27	2.85	3.00	2.86	2.95	2.47
	2.86	2.89	2.84	2.75	2.91	2.66
	2.91	2.77	2.79	2.77	2.98	2.61
8,5/8,4	2.84	2.39	1.96	1.99	1.87	
	2.31	2.18	2.05	2.02	1.90	1.41
	2.09	2.15	2.12	2.07	1.78	1.54
	2.09	2.17	2.09	2.11	1.80	1.49
9,4/9,6				.203		
		.186	.158	.172	0.210	
		.157	.160	.176		

TABLE 9(continued)

Ratio	Helium:Nitrogen Ratio					<u>100</u>
	<u>0</u>	<u>2</u>	<u>8</u>	<u>27</u>	<u>50</u>	
9,5/9,6	.90	.57	.78	.83	.82	.91
	.57	.74	.72	.82	.86	
	.75	.69	.62	.94	.98	
	.81	.69	.75	.41	1.05	
10,5/10,7				.236		
			.218	.264		
		.228	.259	.265	.313	
		.242	.239	.246	.335	
10,6/10,7	1.26	1.08	0.98	1.03	1.11	0.73
	1.11	0.95	1.02	1.14	1.31	
	0.99	0.97	1.11	1.20	1.44	
	0.99	1.12	1.09	1.04	1.43	
11,6/11,8			.37	.42		
		.37	.38	.47	.45	
		.44	.48	.52	.46	
	.35	.41	.45	.48	.44	
11,7/11,8		1.30	1.59	1.77	1.41	
	1.40	1.54	1.92	1.94	1.74	
	1.58	1.99	1.92	2.06	1.84	
	1.85	1.91	1.79	1.98	1.81	
12,7/12,8			.43	.40		
		.36	.35	.44	.52	
		.40	.42	.44	.59	
	.31	.41	.39	.46	.54	
12,9/12,8		1.02	0.87	0.73		
	1.14	0.88	0.74	0.66	.81	
	0.96	0.77	0.64	0.59	.84	
	0.84	0.70	0.62	0.60	.79	

TABLE 10

Intensity Ratios of Nitrogen First Positive Bands.

0.2mm. Nitrogen, 40ma., Various Helium Pressures.

Ratio	Helium:Nitrogen Ratio								
	<u>0</u>	<u>1.5</u>	<u>2.5</u>	<u>5</u>	<u>10</u>	<u>15</u>	<u>25</u>	<u>50</u>	<u>100</u>
3,0/3,1	.57	.62	.61	.62	.59	.45			
4,2/4,1	1.01	0.92	0.86	0.98	0.91	0.83	1.05	0.67	
5,1/5,3	.145	.131	.135	.145	.146	.164	.174		
5,2/5,3	1.01	0.97	1.16	1.27	1.17	1.37	1.24	1.49	
6,3/6,2	5.6	4.9	5.1	5.9	5.3	5.4	5.3	5.6	4.5
6,4/6,2	1.48	1.53	1.38	1.62	1.55	1.71	2.24	2.24	
7,4/7,3	3.42	3.10	2.97	3.10	3.14	3.07	3.27	3.08	3.01
8,5/8,4	2.20	2.07	2.04	1.97	1.98	1.97	2.04	2.15	2.04
9,4/9,6				.213	.200	.208	.320		
9,5/9,6	.75	.76	.73	.86	.87	.82	.80	.88	.95
10,5/10,7		.40	.32	.26	.24	.26	.35		
10,6/10,7	1.00	1.20	1.10	1.04	1.10	1.15	1.19	1.08	1.25
11,6/11,8		.57	.55	.47	.48	.46	.61		
11,7/11,8	1.24	1.76	1.87	1.88	2.14	1.82	2.00	1.10	
12,7/12,8		.54	.46	.41	.41	.42	.55		
12,9/12,8	.92	.75	.72	.64	.62	.57	.58		

TABLE 11

Intensity Ratios of Nitrogen First Positive Bands.

0.4mm. Nitrogen, 40ma., Various Helium Pressures

	Helium:Nitrogen Ratio								
	<u>0</u>	<u>1</u>	<u>2.5</u>	<u>5</u>	<u>7.5</u>	<u>12.5</u>	<u>25</u>	<u>50</u>	<u>75</u>
3,0/3,1	.124	.124	.111	.159	.147				
4,2/4,1	1.52	1.71	1.61	1.61	1.51	1.52	1.24		
5,1/5,3	.218	.178	.180	.184	.174	.201			
5,2/5,3	1.63	1.58	1.54	1.58	1.45	1.68	1.91		
6,3/6,2	5.6	5.5	4.9	5.2	4.8	5.7	5.8	4.2	3.8
6,4/6,2	1.52	1.82	1.74	1.75	1.64	1.66	1.13		
7,4/7,3	2.85	2.97	3.01	3.11	3.25	3.18	3.12	2.91	2.86
8,5/8,4	2.34	2.15	2.33	2.03	2.20	2.19	2.15	2.15	2.21
9,4/9,6				.159	.140	.195			
9,5/9,6	.75	.71	.72	.70	.67	.76	.69	.75	.87
10,5/10,7			.209	.219	.222	.228			
10,6/10,7	0.97	1.02	1.09	1.05	0.99	1.10	1.16	1.00	0.92
11,6/11,8			.38	.42	.39	.38			
11,7/11,8	1.42	1.71	1.78	1.88	1.77	1.75	1.68		
12,7/12,8			.36	.44	.41	.42			
12,9/12,8		1.14	0.80	0.76	0.76	0.76			

TABLE 12

Intensity Ratios of Nitrogen First Positive Bands.

Total Pressure (Nitrogen+Helium) = 0.5mm. Current = 25ma.

Ratio	% N ₂						
	4	10	20	30	40	50	100
3,0/3,1	.122	.165	.154	.156	.140	.162	.130
4,2/4,1	2.73	2.53	3.04	3.42	3.40	2.28	2.99
5,1/5,3	.062	.077	.095	.082	.088	.081	
5,2/5,3	.60	.78	.84	.77	.93	.79	.59
6,3/6,2	4.0	4.5	4.3	4.7	4.6	4.5	4.0
6,4/6,2		4.0	3.5	3.5	3.4	3.1	
7,4/7,3	2.36	2.53	2.54	2.53	2.75	2.50	2.72
8,5/8,4	1.17	1.61	1.83	1.96	1.81	1.81	1.50
9,5/9,6	1.34	0.92	0.74	0.80	0.84	0.86	1.04
10,6/10,7	1.64	1.33	1.30	1.20	1.22	1.21	1.58
11,7/11,8	2.71	2.10	1.86	2.00	2.00	1.78	2.45
12,9/12,8	.44	.53	.67	.69	.68	.63	.84

TABLE 13

Intensity Ratios of Nitrogen First Positive Bands.

Total Pressure (Nitrogen + Helium) = 2.0mm: 25ma.

	% N ₂							
<u>Ratio</u>	<u>2.5</u>	<u>5</u>	<u>10</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>50</u>	<u>100</u>
4,2/4,1	1.79	2.86	2.60	3.19	2.43	1.90	2.15	1.33
5,1/5,3	.197		.126	.115	.147	.172	.167	.248
5,2/5,3	1.27	0.45	0.85	0.85	0.93	1.17	1.10	1.49
6,3/6,2	4.8	3.9	4.8	4.1	3.9	4.0	4.4	4.4
6,4/6,2	1.80		2.80	2.93	2.33	2.14	2.16	
7,4/7,3	2.89	2.58	3.07	3.06	3.09	3.30	3.01	3.08
8,5/8,4	1.82	1.60	2.16	1.97	2.06	1.97	2.02	1.98
9,4/9,6			.154	.142	.138	.189		.205
9,5/9,6	.74	.88	.80	.69	.76	.89	.71	.72
10,5/10,7		.218	.250	.215	.207	.216	.226	.252
10,6/10,7	1.17	1.00	.106	0.99	0.93	0.97	1.07	1.08
11,6/11,8		.36	.49	.40	.41	.41	.41	.39
11,7/11,8	2.32	1.37	1.83	1.48	1.50	1.67	1.54	1.40
12,7/12,8		.43	.52	.46	.43	.41	.40	.46
12,9/12,8		.75	.69	.76	.79	.74	.75	.80

TABLE 14

Intensity Ratios of Nitrogen First Positive Bands.

Total Pressure (Nitrogen + Helium)=5.0mm. 25ma.

<u>Ratio</u>	% N ₂							
	<u>2</u>	<u>5</u>	<u>10</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>50</u>	<u>100</u>
3,0/3,1			.092	.105	.118	.072	.101	
4,2/4,1	1.69	1.61	1.73	1.88	1.81	1.91	2.23	2.09
5,1/5,3	.156	.185	.174	.147	.174	.158	.127	.148
5,2/5,3	1.03	1.21	1.10	0.93	1.06	1.12	0.97	1.08
6,3/6,2	4.4	5.1	4.1	4.4	3.9	4.8	5.0	4.7
6,4/6,2		2.52	2.21	2.37	2.29	2.61	3.15	2.77
7,4/7,3	3.03	2.84	2.85	2.85	2.80	2.93	2.92	3.16
8,3/8,4		.290	.261	.262	.278	.309		.152
8,5/8,4	1.78	2.13	2.08	1.90	2.01	1.97	2.21	1.80
9,4/9,6		.180	.176	.210	.180	.201	.201	.169
9,5/9,6	.80	.70	.71	.82	.72	.76	.72	.82
10,5/10,7	.256	.242	.240	.257	.243	.242	.248	.244
10,6/10,7	1.05	1.12	1.03	1.04	1.35	0.93	0.98	1.20
11,6/11,8	.59	.40	.39	.38	.40	.39	.46	.46
11,7/11,8	1.68	1.72	1.71	1.57	1.87	1.59	1.78	1.98
12,7/12,8	.55	.45	.40	.42	.34	.43	.50	.46
12,9/12,8	.81	.68	.64	.72	.60	.71	.78	.78

TABLE 15

Intensity Ratios of Nitrogen First Positive Bands.

0.25mm. Nitrogen, 1.0mm. Helium, Various Currents.

Ratio	Current(ma.)									
	<u>10</u>	<u>20</u>	<u>30</u>	<u>35</u>	<u>40</u>	<u>50</u>	<u>60</u>	<u>70</u>	<u>80</u>	<u>90</u>
3,0/3,1	.024	.081	.151	.148	.145	.130	.138	.149	.161	.160
4,2/4,1	1.70	2.39	2.75	3.09	2.88	2.77	2.62	2.93	3.77	4.35
5,1/5,3	.220	.181	.126	.116	.123	.111	.113	.102	.082	.076
5,2/5,3	1.51	1.26	0.84	0.80	0.89	0.84	0.86	0.76	0.65	0.59
6,3/6,2	5.7	6.0	6.0	5.8	5.3	4.3	4.3	4.5	4.9	4.7
6,4/6,2	1.95	1.89	2.97	2.87	3.28	2.47	2.30	2.77	3.65	4.04
7,4/7,3	2.97	2.90	2.72	2.51	2.17	2.29	2.38	2.39	2.51	2.49
8,3/8,4						.183	.177	.153	.182	.187
8,5/8,4	1.81	1.89	2.07	1.93	2.08	2.01	2.00	1.84	1.82	1.86
9,4/9,6			.131	.125	.147	.154	.145	.149	.147	.137
9,5/9,6	.67	.80	.88	.87	.80	.80	.82	.73	.65	.61
10,5/10,7	.167	.210	.209	.201	.222	.183	.194	.207	.210	.211
10,6/10,7	1.10	0.87	0.91	0.86	1.26	0.98	0.98	1.23	1.06	1.27
11,6/11,8	.37	.47	.42	.41	.46	.38	.37	.40	.41	.38
11,7/11,8	1.58	1.79	1.72	1.86	1.97	1.61	1.52	1.94	1.96	1.75
12,7/12,8	.37	.48	.44	.39	.40	.42	.37	.33	.34	.37
12,9/12,8	.75	.74	.72	.65	.69	.71	.64	.53	.55	.52

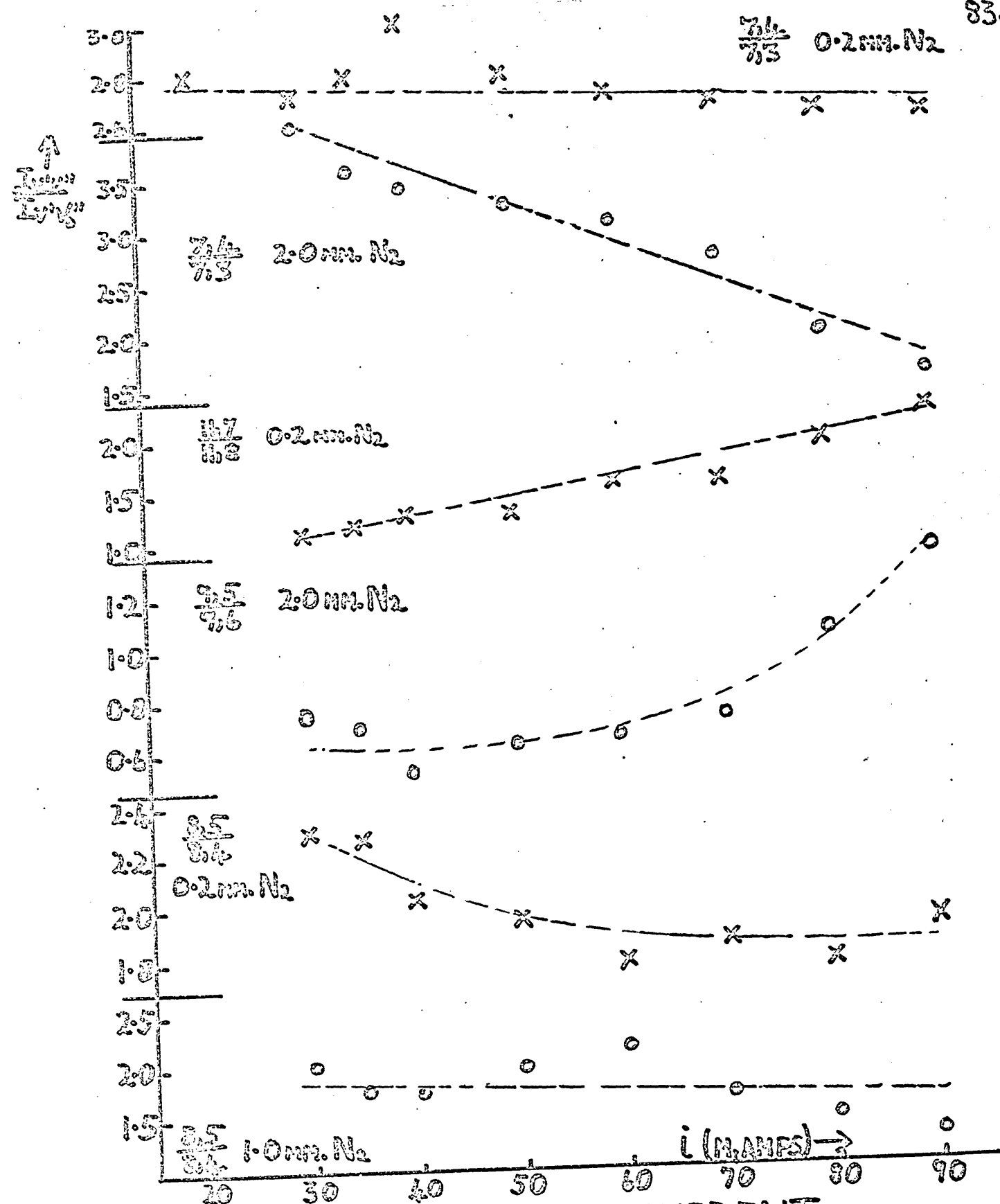


FIG. 9 INTENSITY RATIO v. CURRENT

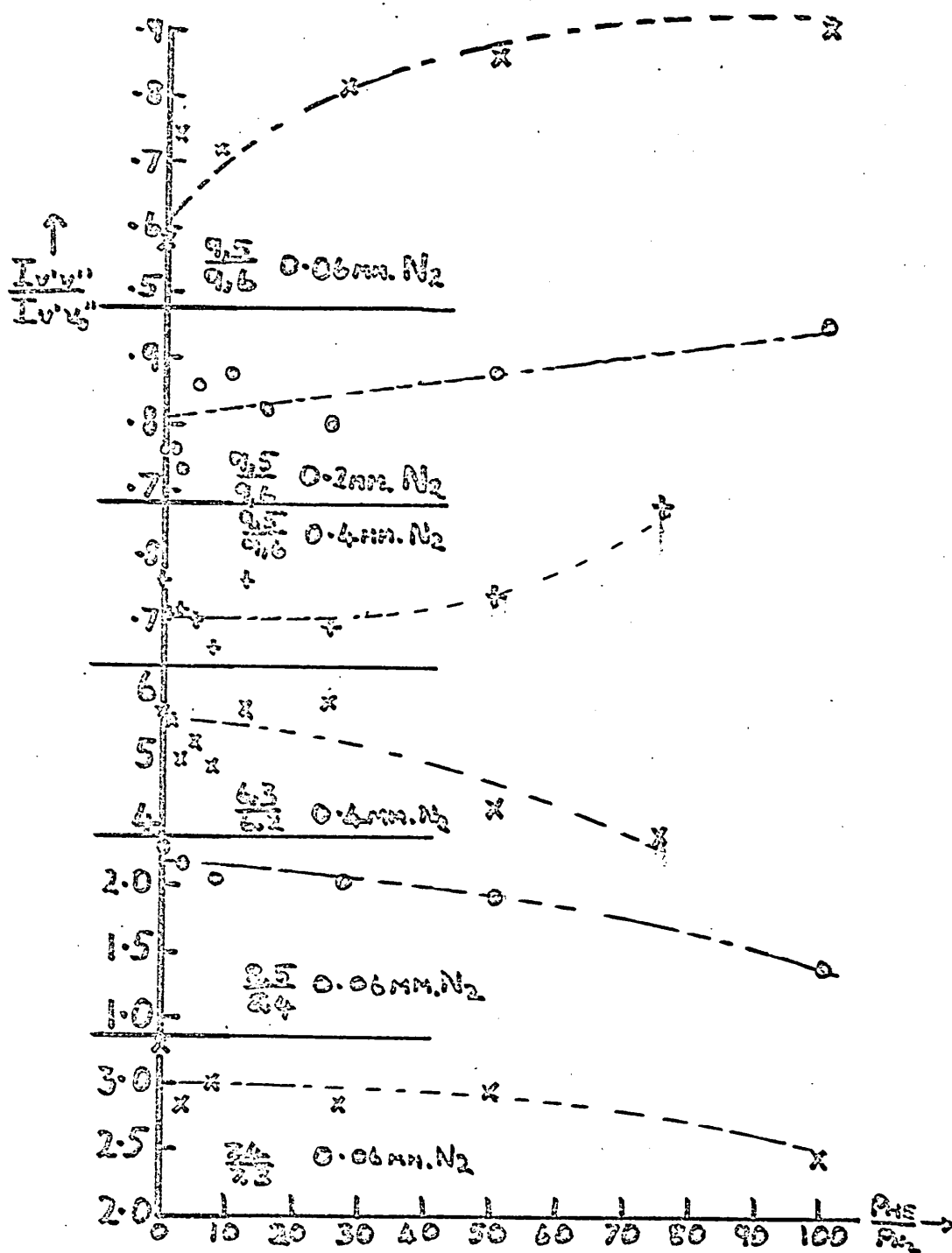


FIG. 10 INTENSITY RATIO v. $\frac{P_{H_2}}{P_{N_2}}$

current in a D.C discharge in pure nitrogen. Tyte (1965) used two discharge tubes and covered a very wide range of current densities. He also observed a systematic variation in the ratios. In the experiments using the present discharge tube, Tyte (1962 a,b,c,) observed no variations of relative intensity with current but did observe some large variations with pressure when helium was introduced into the tube.

It was observed on careful examination of the tables that there were variations in several of the ratios. In order to obtain a clearer visual picture of how the ratios were changing, they were plotted against the varying parameters for all conditions. Some of these plots are shown in figs. 9 and 10. The results are discussed more fully in Chapter 6.

c) Populations.

From the measured intensities and the values of $S_{v'v''} = R_e^2 q_{v'v''}$ calculated using equation 4.4. and the Franck Condon factors of Zare et.al. (1965), values of $(I\lambda^4/q)_{v'v''}$ and $(I\lambda^4/S)_{v'v''}$ were computed. Table 16 is a typical sample of the values obtained. The average values for each v' are also listed and these represent the populations of the vibrational levels of the upper state using $q_{v'v''}$ and $S_{v'v''}$ as the band strengths. It was observed that the values for $v' = 7 - 12$ were similar in both cases but for the other levels, the values using $S_{v'v''}$ were in general lower than those using $q_{v'v''}$. This was expected as, in the region measured, the variation of the transition moment is only noticeable for the $\Delta v = 2$ sequence (fig. 8.) and bands were only observed in this sequence up to $v' = 6$. An examination of the standard deviations in table 16 shows that, for $v' = 3-6$, the errors using $S_{v'v''}$ were less than those

TABLE 16

Comparison of Calculations of Populations of $B^3\Pi$ State.

0.1mm. Nitrogen, 0.4mm. Helium, 25ma.

		Zare q values					
Band		Average			Average		
		$\left(\frac{I_{\lambda}}{q}\right)^4_{v'v''}$	$\left(\frac{I_{\lambda}}{q}\right)^4_{v'}$	σ	$\left(\frac{I_{\lambda}}{S}\right)^4_{v'v''}$	$\left(\frac{I_{\lambda}}{S}\right)^4_{v'}$	σ^*
2	0	3925	3925	0%	2840	2840	0%
3	0	1316	1396	5.7%	1235	1174	5.1%
3	1	1477			1114		
4	1	1249	1476	15.4%	1191	1269	6.1%
4	2	1703			1346		
5	1	702	770	7.7%	711	712	2.7%
5	2	762			736		
5	3	846			690		
6	2	555	610	15.1%	578	576	10.9%
6	3	503			498		
6	4	773			653		
7	3	216	199	8.5%	219	200	9%
7	4	182			182		
8	4	96	91	5.5%	97	92	4.3%
8	5	86			88		
9	5	78	77	1.3%	80	78	6.8%
9	6	76			77		
10	6	96	87	9.2%	95	88	6.8%
10	7	79			82		
11	7	76	71	7.0%	72	71	1.4%
11	8	66			70		

* Similar values of the standard deviation were obtained for all conditions. The figures in the last column therefore are an estimate of the random errors in the populations for all conditions. Systematic errors may make the errors for $v'=2$ & 3 as large as 30%.

TABLE 17

Comparison of $B^3\Pi$ State Populations Using Different q Values.

0.1mm. Nitrogen, 0.4mm. Helium, 25ma.

<u>Benesch q values</u>					<u>Nicholls q values</u>		
			Average			Average	
		$\left(\frac{I\lambda}{S}\right)_{v'v''}^4$	$\left(\frac{I\lambda}{S}\right)_{v'}^4$	σ	$\left(\frac{I\lambda}{S}\right)_{v'v''}^4$	$\left(\frac{I\lambda}{S}\right)_{v'}^4$	σ
2	0	2488	2488	0%	1835	1835	0%
3	0	1070	1039	3.0%	698	769	9.2%
3	1	1008			841		
4	1	1073	1163	7.7%	746	997	25.1%
4	2	1252			1248		
5	1	683	681	1.0%	476	609	23.8%
5	2	689			539		
5	3	670			811		
6	2	566	574	14.1%	452	681	50.8%
6	3	479			422		
6	4	678			1169		
7	3	216	199	8.5%	189	185	1.6%
7	4	182			182		
8	4	99	96	3.1%	90	98	8.2%
8	5	93			107		
9	5	86	86	0%	91	105	13.3%
9	6	86			119		
10	6	105	101	3.0%	131	149	12.1%
10	7	98			166		
11	7	83	87	4.6%	111	183	39.3%
11	8	91			255		

using $q_{v',v''}$. For $v' = 7-12$, the deviations were about the same.

This was observed for all conditions which indicates that the calculated variation of the electron transition moment is real. Further evidence for this will be given later. All further populations quoted in this work have been calculated using $S_{v',v''}$ calculated from Zare's Franck Condon factors.

Table 17 lists values of $\lambda^4 / S_{v',v''}$ using the Franck Condon factor arrays of Nicholls (1961) and Benesch et.al.(1966b). The difference between the populations calculated using Zare's and Benesch's q values is small but there is a large difference between these and populations calculated using Nicholls' q values for which the standard deviations are much larger. This is further evidence for believing that Nicholls' q values are not as accurate as the others.

For each set of conditions, the populations were calculated using both Zare's and Nicholls' q values, and in every case, Zare's fitted the experimental data more satisfactorily. Benesch's tables did not appear till after these calculations were performed and they were not examined so thoroughly. Judging from the results in Chapter 4, and by Table 17, the results would not be greatly changed by using them instead of Zare's values. The populations obtained for the various conditions are all listed in tables 18 to 26. To obtain a clearer idea of the population distribution and also to facilitate comparison with calculated values assuming the cascade process III, tables 27 to 35 were compiled. In each of these, the populations have been scaled to $N_7 = 100$ and, where possible, compared with those obtained from the cascade calculations.

The general agreement between the observed and calculated values was poor, once again suggesting that the cascade process does not play a major role in populating the $B^3\Pi$ state.

It was observed in examining the intensity ratios that, for ratios involving bands in the $\Delta v=2$ sequence and the $v' = 3$ bands, there were extremely large variations. In these cases, all the bands mentioned had been measured from LRS plates while all the others were taken from Astra III plates. It was observed also that there were large differences between the values of $(I\lambda^4/S)_{v'v''}$ for these bands and other bands in the same v'' progression. It was also noted that the ratio $\frac{(I\lambda^4/S)_{\text{ave. } v'=5}}{(I\lambda^4/S)_{5,3}}$

was a constant for all the exposures on one pair of plates. This also applied to similar ratios for $v' = 4$ and 6 which suggested that there had been a systematic error in correlating the results from the two plates. The populations in the tables were derived as follows. The values for $v' = 4$ to 12 were calculated ignoring the bands in the $\Delta v=2$ sequence. For the bands in the $v'=2$ and 3 progressions, the values obtained from the plates were multiplied by the constant ratio above to bring them to the same scale. This did not affect the variation with conditions but did alter the population distribution. This means that the populations N_2 and N_3 are subject to larger errors than the other values but it is felt that this procedure was justified and gives a more realistic distribution.

d) Vibration Temperature.

For each set of conditions graphs were plotted of $\log_e N_v$ against $G'(v')$ and a least squares straight line was fitted to the points. From

TABLE 18

Populations, N_{v1} , of $B^3\Pi$ State

0.2mm. Nitrogen, Various Currents.

a) Observed b) Calculated - Process III

v_1	Current(ma.)										
	5	10	20	30	35	40	50	60	70	80	90
2 a)		1099	1654	2751	3601	3822	4651	6168	6474	7108	7270
b)	3534		4946		6930		7588				15311
3		435	484	766	1086	1170	1465	2153	2087	2426	2625
	1557		2146		3145		3360				7032
4		374	616	749	954	1000	1258	1462	1482	1745	1897
	732		1085		1536		1627				3279
5	252	283	395	602	735	787	997	1274	1409	1574	1784
	338		505		753		791				1514
6	204	265	339	493	576	695	845	1040	1135	1173	1220
	168		275		482		449				803
7		100	152*	175	202	228	297	394	420	472	559
	82		152*		231		250				426
8			55	91	97	107	132	166	193	248	300
	37		75		111		123				203
9			48	56	64	76	104	126	145	178	221
	14		30		44		49				80
10			45	52	57	66	95	120	123	162	192
	5		11		16		17				29
11			31	63	65	69	81	95	97	125	146
	2		3		5		6				9
12				24	25	25	29	33	37	44	55
	1		1		2		2				2

* Set equal for comparison

TABLE 19Observed Populations, $N_{v'}$, of $B^3\Pi$ State.

1.0mm. Nitrogen, Various Currents

v'	Current(ma.)									
	<u>10</u>	<u>20</u>	<u>30</u>	<u>35</u>	<u>40</u>	<u>50</u>	<u>60</u>	<u>70</u>	<u>80</u>	<u>90</u>
2	2102	2395	3125	3214	3813	4761	5040	5723	6268	6779
3	481	619	769	900	1012	1296	1521	1798	2027	2421
4	498	591	753	884	1025	1286	1542	1778	1975	2167
5	367	460	611	783	926	1116	1388	1559	1696	1852
6	285	403	546	646	744	899	1023	1122	1263	1322
7	100	156	202	258	292	385	433	503	566	633
8	39	53	100	136	161	220	266	334	389	439
9		35	72	92	108	159	218	258	336	369
10			65	81	94	144	175	225	263	331
11			58	64	72	106	131	158	204	253
12				25	35	39	48	59	73	88

TABLE 20Observed Populations, $N_{v'}$, of $B^3\Pi$ State

2.0mm. Nitrogen, Various Currents

	Currents(ma.)								
v'	<u>20</u>	<u>30</u>	<u>35</u>	<u>40</u>	<u>50</u>	<u>60</u>	<u>70</u>	<u>80</u>	<u>90</u>
2	1797	2809	3206	3267	4021	4347	5312	5450	6021
3	485	655	763	823	1063	1440	1728	2094	2315
4	426	690	815	866	1090	1567	1730	1838	2082
5	376	513	589	693	985	1111	1362	1540	1675
6	250	447	530	613	695	785	891	1075	1183
7	100	168	220	263	338	380	431	557	645
8	38	100	127	153	218	304	361	457	562
9	17	67	92	123	145	184	251	360	457
10	15	58	72	87	121	158	199	412	393
11		40	51	57	91	126	162	218	236
12		18	20	25	35	44	56	78	94

TABLE 21.

Observed Populations, $N_{v'}$, of $B^3\Pi$ State. Pure Nitrogen, 50ma.

Various Pressures.

Nitrogen Pressure (mm).

v'	0.05	0.1	0.2	0.3	0.5	1.0	2.0	3.0	5.0	7.5
2	1426	1490	1848	1856	1893	2184	2096	2074	2402	2209
3	623	541	653	703	504	553	523	602	756	735
4	402	478	505	537	483	497	480	529	621	559
5	366	394	408	428	402	427	451	505	594	547
6	266	295	297	299	279	284	304	321	383	343
7	100	114	112	117	113	122	139	156	211	193
8	41	49	50	53	55	67	91	106	158	139
9	32	37	39	40	42	49	62	75	104	102
10	30	35	36	40	40	45	52	60	81	72
11	26	29	29	31	31	36	40	44	56	51
12	10	11	11	11	11	12	13	15	20	18

TABLE 22.

Observed Populations, $N_{v'}$, of $B^3\Pi$ State. 0.2mm. Nitrogen, 40ma. Various Helium Pressures.

Helium: Nitrogen Ratio.

v'	0	1.5	2.5	5	10	15	25	50	100	150
2	1308	1532	1451	1361	1079	899	671	345		
3	486	540	540	555	545	513	396			
4	526	765	800	778	735	641	354	177	159	
5	383	489	565	617	588	556	391	195	107	62
6	303	436	493	535	520	469	296	173	128	68
7	100	167	189	226	230	221	147	91	70	49
8	43	72	89	109	112	102	68	44	38	26
9	36	63	81	123	132	126	96	39	28	
10	31	68	79	99	118	106	78	34	21	
11	27	50	59	78	90	79	52	29		
12	10	20	26	35	39	36	21	10		

TABLE 23.

Observed Populations, $N_{v'}$, of $B^3\pi$ State.
 Total Pressure (Nitrogen+Helium) = 0.5mm. 25 ma.

v'	% N_2							
	2	4	10	20	30	40	50	100
2		1200	1641	2664	2826	2597	2530	1641
3		516	755	1102	930	902	798	519
4	117	407	732	1190	1082	933	817	433
5	149	290	472	669	594	561	475	348
6	93	246	455	540	510	499	442	251
7	46	112	164	188	173	165	142	100
8		59	75	87	81	74	67	50
9		53	65	74	69	63	59	29
10	31	45	66	83	74	64	55	24
11	22	31	51	67	58	49	45	20
12		20	28	30	26	23	21	10

TABLE 24.

Observed Populations, $N_{v'}$, of $B^3\pi$ State.
 Total Pressure (Nitrogen+Helium) = 2.0mm., 25ma.

v'	% N_2							
	2.5	5	10	20	30	40	50	100
2	567	1220	1290	2020	1600	1500	1520	1400
3	246	607	547	688	542	474	481	331
4	424	411	625	856	692	628	590	570
5	410	449	549	636	544	531	493	438
6	275	295	412	489	412	382	364	358
7	100	123	187	209	178	176	140	138
8	60	57	85	100	90	84	78	73
9	39	73	102	99	88	76	64	68
10	36	68	101	105	87	79	65	60
11	26	49	77	79	70	65	57	52
12	10	22	37	37	30	28	23	22

TABLE 25

Observed Populations, $N_{v'}$, of $B^3\pi$ State.
 Total Pressure (Nitrogen+Helium) = 5.0mm, 25ma.

v'	% N_2							
	2	5	10	20	30	40	50	100
2		586	785	1014	1007	1113	1156	1661
3		246	264	337	315	255	300	439
4	226	361	479	557	542	447	386	489
5	238	370	466	488	469	424	382	476
6	198	316	364	388	366	341	302	339
7	100	166	195	215	187	154	126	184
8	47	105	133	138	140	119	72	144
9	46	83	99	93	91	76	67	85
10	48	80	97	85	94	65	55	63
11	32	60	77	75	76	57	44	47
12	16	26	34	30	31	22	19	19

TABLE 26

Observed Populations, $N_{v'}$, of $B^3\pi$ State. 0.25 mm. Nitrogen, 1.0 mm. Helium,
 Various Currents.

v'	Current (ma)									
	10	20	30	35	40	50	60	70	80	90
2	809	1060	1300	1430	1670	1800	1630	1880	2190	2400
3	235	369	505	550	619	725	705	842	1060	1190
4	432	452	507	553	636	661	666	729	821	852
5	253	328	391	427	517	600	631	657	715	736
6	228	302	346	378	405	485	540	557	577	617
7	100	122	131	147	193	213	235	254	250	261
8	50	62	69	75	101	118	134	149	142	147
9	46	59	65	67	98	116	126	132	136	147
10	40	56	65	70	89	110	112	126	117	128
11	38	50	57	64	73	88	92	106	102	105
12	16	23	24	27	33	37	40	46	46	46

TABLE 27

Relative Populations, $100N_{v'}/N_7$, of $B^3\Pi$ State.

0.2mm. Nitrogen, Various Currents

a) Observed:				b) Calculated- Process III						
v'	Current(ma.)									
	10	20	30	35	40	50	60	70	80	90
2 a)	1100	1090	1570	1780	1670	1560	1560	1540	1500	1290
b)		3250		3000		3030				3590
3	435	318 1460	437	538 1360	512	492 1340	545	497	512	470 1650
4	374	405 713	428	472 665	439	424 650	371	353	370	339 770
5	283	260 332	344	364 326	345	336 316	323	335	333	319 355
6	265	223 181	282	285 183	305	285 180	264	270	248	218 189
7	100	100 100	100	100 100	100	100 100	100	100	100	100 100
8		36 49	52	48 48	47	44 49	42	46	53	54 48
9		32 20	32	32 19	33	35 20	32	35	38	40 19
10		29 7	30	28 7	29	32 7	30	29	34	34 7
11		20 2	36	32 2	30	27 2	24	23	27	26 2
12			14	12 1	11	10 1	8	9	9	10 1

TABLE 28

Observed Relative Populations, $100 N_{v'}/N_7$, of the $B^3\Pi$ State.

Pure Nitrogen, 50 ma, Various Nitrogen Pressures.

Nitrogen Pressure (mm).

<u>v'</u>	<u>0.05</u>	<u>0.1</u>	<u>0.2</u>	<u>0.3</u>	<u>0.5</u>	<u>1.0</u>	<u>2.0</u>	<u>3.0</u>	<u>5.0</u>	<u>7.5</u>
2	1420	1300	1650	1590	1670	1790	1510	1330	1140	1150
3	623	474	582	605	446	453	376	386	358	382
4	402	419	451	468	427	407	345	339	294	290
5	366	346	364	366	356	350	324	325	282	283
6	266	258	264	256	248	234	218	205	182	178
7	100	100	100	100	100	100	100	100	100	100
8	41	43	44	46	49	55	66	68	75	72
9	32	33	35	35	37	40	45	48	49	53
10	30	31	32	34	36	37	37	39	39	37
11	26	26	26	27	28	30	29	28	27	26
12	10	10	10	9	10	10	9	10	9	9

TABLE 29

Relative Populations, $100N_{v'}/N_7$, of $B^3\Pi$ State.

0.06mm. Nitrogen, 40ma., Various Helium Pressures

a) Observed

b) Calculated-Process III

 P_{He}/P_{N_2}

v'	0	3	8*	27	50	100
2	a) 1657 b) 4928	1619 3525	1064 3202	900 2234	613 1936	2130
3	430 2187	462 1587	350 1419	270 971	285 842	974
4	517 1031	523 794	457 716	350 533	335 477	557
5	379 468	383 388	336 351	319 282	238 268	176 304
6	305 218	285 200	234 189	226 172	214 171	168 180
7	100 100	100 100	100 100	100 100	100 100	100 100
8	40 43	46 46	44 47	47 50	47 50	48
9	23 16	41 18	40 19	48 20	45 20	50 19
10	25 5	34 6	41 7	50 7	49 7	33 7
11	21 2	32 2	30 2	37 2	39 2	35 2
12	9 1	13 1	15 1	17 1	15 1	1

* For calculated values $P_{He}/P_{N_2}=9$

TABLE 30

Relative Populations, $100N_{v'}/N_7$, of $B^3\Pi$ State.

0.2mm. Nitrogen, 40ma., Various Helium Pressures

a) Observed

b) Calculated- Process III

		Helium:Nitrogen Ratio								
v'	0	1.5	2.5	5	10	15	25	50	100	150
2 a)	1300	915	765	602	470	407	458	378		
b)		2790	2690	2650	2230		1960	2050	2130	
3	486	323	286	246	237	232	269			
		1210	1170	1190	968		872	906	945	
4	526	457	422	344	319	289	241	194	227	
		615	610	606	518		489	498	506	
5	383	293	298	273	255	251	266	213	151	126
		310	310	308	278		260	256	257	
6	303	260	260	237	226	212	201	189	182	138
		179	180	179	172		165	163	163	
7	100	100	100	100	100	100	100	100	100	100
		100	100	100	100		100	100	100	
8	43	43	47	48	49	46	47	48	54	53
		49	49	49	50		51	52	52	
9	36	38	42	54	57	57	65	42	40	
		20	20	20	20		21	22	22	
10	31	41	42	44	51	48	53	37	30	
		7	7	7	7		8	8	8	
11	28	30	31	34	39	36	35	31		
		2	2	2	2		3	3	3	
12	10	12	14	15	17	16	14	11		
		1	1	1	1		1	1	1	

TABLE 31Relative Populations, $100N_{v'}/N_7$, of $B^3\Pi$ State

0.4mm. Nitrogen, 40ma., Various Helium Pressures

a) Observed b) Calculated-Process III

Helium:Nitrogen Ratio

<u>v'</u>	<u>0</u>	<u>1</u>	<u>2.5</u>	<u>5</u>	<u>7.5</u>	<u>12.5</u>	<u>25</u>	<u>50</u>	<u>75</u>
2	a) 1890 b) 3030	1500 2810	1090 2490	737 2180	605 2240	537	536 1900	2030	
3	510 1380	467 1290	352 1150	345 1010	270 1010	230	193 837	878	
4	429 704	470 658	408 623	351 546	302 535	241	213 472	194 478	191
5	341 345	363 326	319 320	289 288	265 279	249	228 265	167 247	153
6	270 187	291 183	245 182	231 174	222 171	207	207 170	180 160	169
7	100 100	100 100	100 100	100 100	100 100	100	100 100	100 100	100
8	54 48	53 48	48 49	50 50	52 51	46	50 50	57 52	60
9	34 19	43 19	48 19	54 20	54 21	55	42 20	35 22	30
10	31 7	43 7	47 7	50 7	48 7	47	43 7	30 8	26
11	24 2	34 2	38 2	40 2	39 2	35	29 2	18 3	13
12	9 1	13 1	16 1	17 1	17 1	16	12 1	6 1	

TABLE 32

Observed Relative Populations, $100N_{v'}/N_7$, of $B^3\pi$ State.
 Total Pressure (Nitrogen+ Helium) = 0.5mm, 25ma.

v'	% N_2							
	2	4	10	20	30	40	50	100
2		1080	1000	1410	1630	1580	1780	1640
3		462	460	585	537	547	561	519
4	254	365	446	632	624	566	575	433
5	323	260	288	355	343	340	334	348
6	203	221	278	287	294	303	312	252
7	100	100	100	100	100	100	100	100
8		53	45	46	47	45	47	50
9		48	40	39	40	38	41	29
10	67	41	40	44	43	39	39	24
11	48	28	31	35	34	30	32	20
12		18	17	16	15	14	15	10

TABLE 33

Observed Relative Populations, $100 N_{v'}/N_7$, of $B^3\pi$ State
 Total Pressure (Nitrogen + Helium) = 2.0mm., 25 ma.

v'	% N_2							
	2.5	5	10	20	30	40	50	100
2	567	1000	691	972	904	857	1090	1010
3	246	494	292	330	305	270	344	239
4	424	335	334	410	390	357	422	336
5	410	366	294	305	306	302	352	317
6	230	297	220	234	232	217	260	259
7	100	100	100	100	100	100	100	100
8	60	47	45	48	51	48	55	53
9	39	60	55	47	50	43	46	49
10	36	55	54	51	49	45	46	44
11	26	40	41	38	40	37	41	38
12	10	18	20	18	17	16	16	16

TABLE 34

Observed Relative Populations, $100 N_{v'}/N_7$, of $B^3\pi$ State.
 Total Pressure(Nitrogen+Helium) = 5.0mm, 25ma.

	% N ₂							
v'	2	5	10	20	30	40	50	100
2		353	403	471	538	722	917	903
3		148	136	157	168	166	238	239
4	226	217	246	259	290	290	306	266
5	238	223	239	227	251	275	303	259
6	198	190	187	180	196	221	240	184
7	100	100	100	100	100	100	100	100
8	47	63	68	64	75	77	57	78
9	46	50	51	43	49	49	53	46
10	48	48	50	40	50	42	43	34
11	32	36	39	35	40	37	35	26
12	16	16	17	14	17	14	15	10

TABLE 35

Observed Relative Populations, $100 N_{v'}/N_7$, of $B^3\pi$ State.
 0.25mm. Nitrogen, 1.0 mm. Helium, Various Currents

	<u>Current (ma)</u>									
v'	10	20	30	35	40	50	60	70	80	90
2	809	871	995	977	867	848	693	739	877	919
3	235	302	385	374	321	340	300	331	422	456
4	432	370	387	376	330	310	283	287	328	326
5	253	269	298	290	268	282	268	259	286	282
6	228	248	264	257	210	228	230	219	231	236
7	100	100	100	100	100	100	100	100	100	100
8	50	51	53	51	52	55	57	59	57	56
9	46	48	50	46	51	54	54	52	54	56
10	40	46	50	48	46	52	48	50	47	49
11	38	41	44	44	38	41	39	42	41	40
12	16	19	18	18	17	17	17	18	18	18

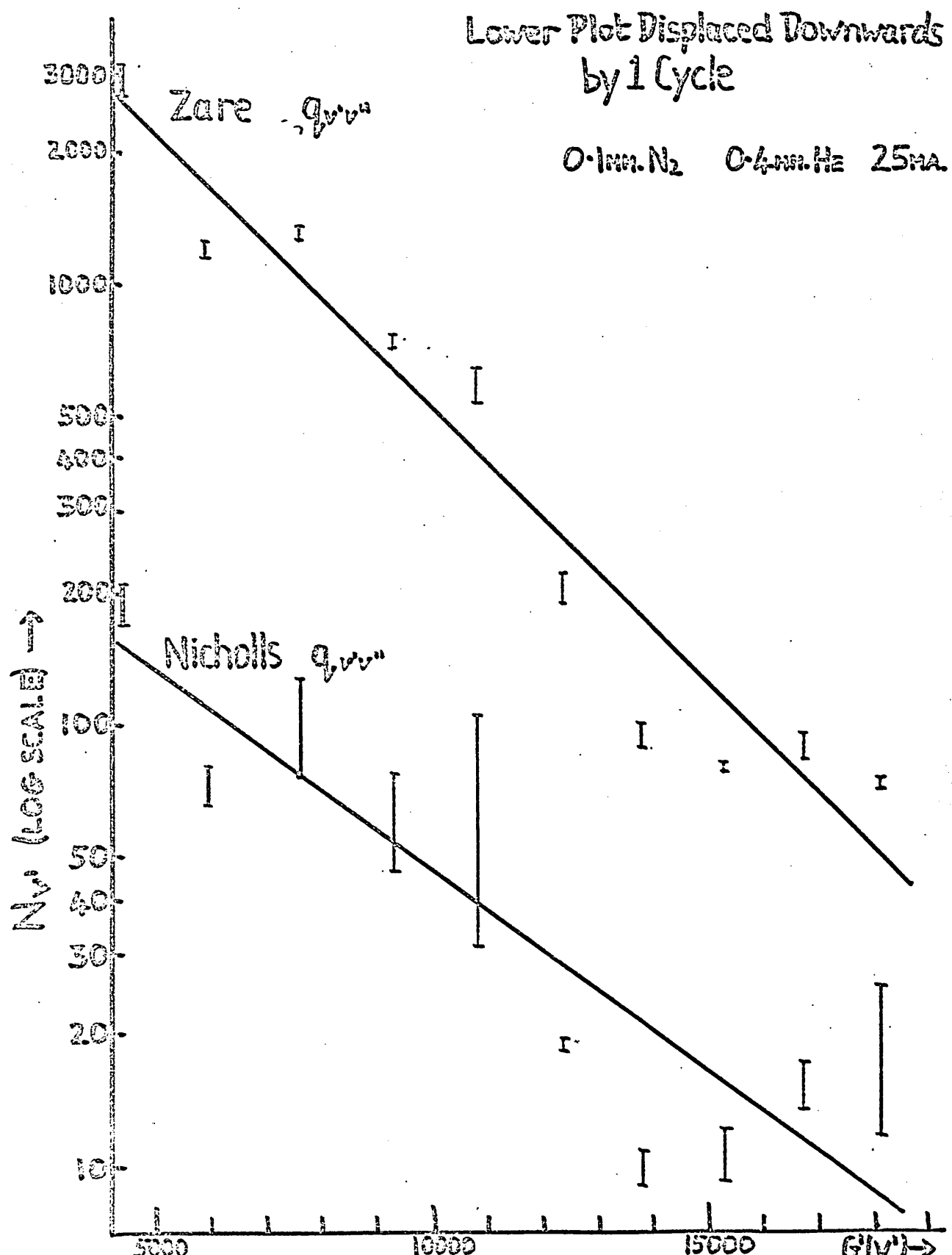


FIG.II POPULATION v. $G'(v')$

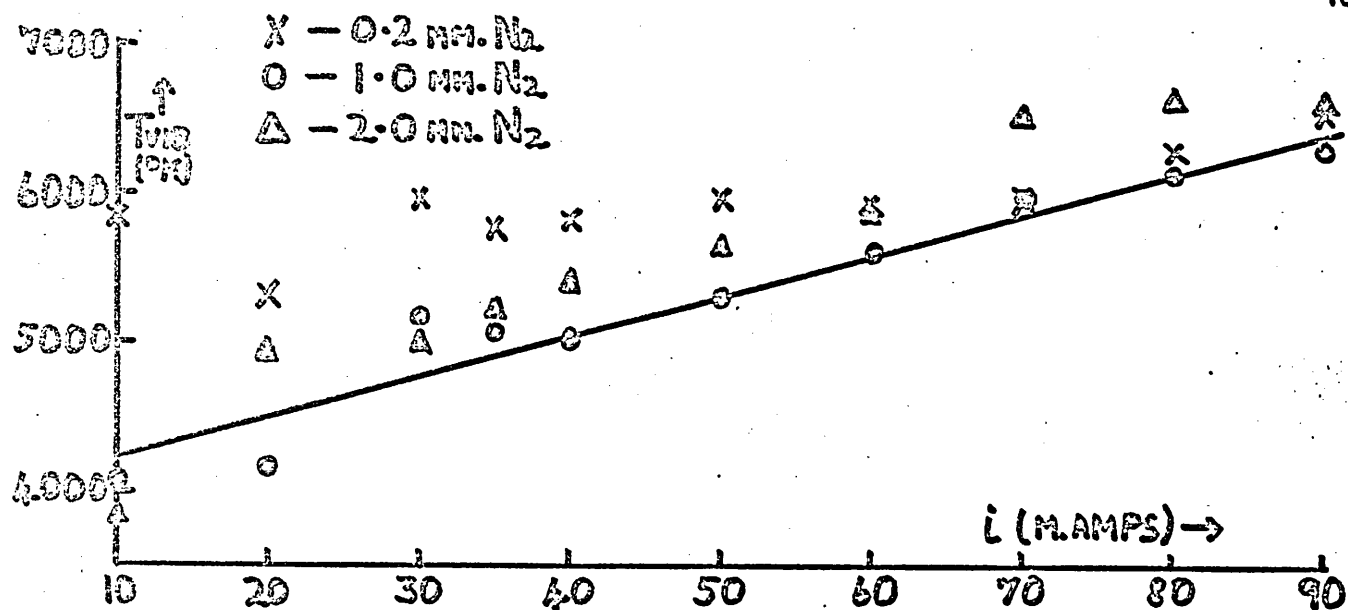
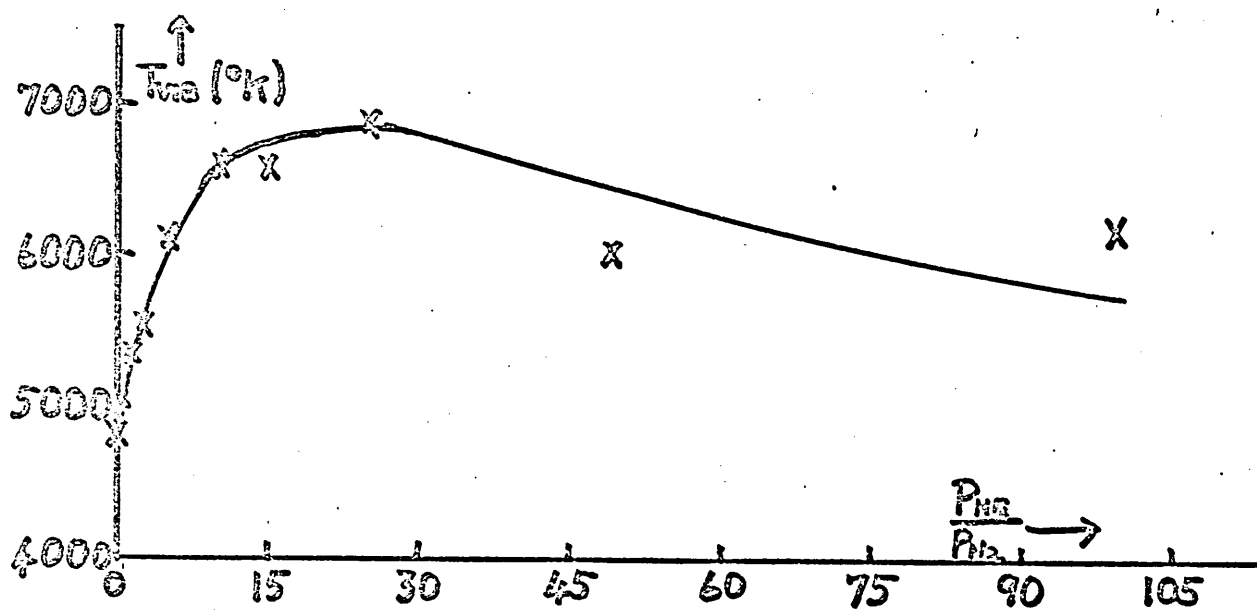


FIG. 12 EFFECTIVE VIBN. TEMP. v. CURRENT

FIG. 13 EFFECTIVE VIBN. TEMP. v. $\frac{P_{H_2}}{P_{N_2}}$ 0.2 mm. N_2

the slope of this line a value for the effective vibration temperature was obtained. Plots were made using values of N_v , that had been computed from both Zare's and Nicholls' Franck Condon factors. Fig.11 shows the two plots obtained for one set of conditions. $\log_{10} N_v$ has actually been plotted, so to obtain the temperature, a factor of $\log_{10} e$ must be introduced.

The points using Zare's q values lie closer to the line than those using Nicholls' values. The errors in the individual points are also much smaller. The difference between the two graphs was observed for all conditions demonstrating that Zare's values were more accurate and they were used in all further calculations.

As the straight line was only an approximate fit to a set of points not necessarily showing a linear variation, the actual values obtained for the vibration temperature have very little significance. The variations of the temperature with conditions are shown in figs.12 and 13 and serve as a guide in estimating at a glance how the distribution of the molecules in the excited states was affected by the conditions. Where applicable, temperatures were also calculated from the cascade calculations. These were much lower than the observed values indicating again that, if the cascade process were prominent, the lower levels would be more heavily populated and the higher ones hardly at all.

e) Electron Transition Moment.

For all the conditions, the values of $(I^{\lambda 4}/q)_{v',v''}/(I^{\lambda 4}/q)_{m,n}$ were calculated and brought to the same scale, as described in chapter 4. Table 36 gives a typical set of results. The results obtained do not show a large enough variation to justify fitting a quadratic curve (parabola) through them. This was to be expected from examination

of fig. 8. as the present experiments only covered the range $1.346 \text{ \AA} < \bar{r}_{v'v''} < 1.608 \text{ \AA}$ in which the variation was observed to be small. In spite of this it was felt that, if there were a real variation of R_e with $\bar{r}_{v'v''}$, then this might show in the similarity of the fitted curves for each set of conditions. If the scatter of the points were purely random, the parabolae fitted to each set of results obtained would not be expected to show similar trends.

Fig. 14 shows the values in table 36 plotted against the r-centroids. The continuous curve is the least squares parabola fitted to the experimental points and is represented by the equation.

$$R_e(\bar{r}) = \text{const} \times (1 - 1.32 \bar{r} + 0.45 \bar{r}^2) \quad 5.1.$$

which is exactly the same formula as that obtained using Turner and Nicholls' (1954b) results which covered a wider range of r-centroids. Repetition of this calculation for all conditions in which all the intensities were measured from one plate (see below) gave a similar result on nearly all occasions, certainly far more times than would be statistically expected if the variation were caused by random errors. Though this is by no means conclusive evidence, the consistency of the results and the agreement with Turner and Nicholls does indicate that there is a real variation of R_e with $\bar{r}_{v'v''}$ of the same order as that obtained from Turner and Nicholls' results. This could be confirmed only by extending the investigation further into the infra-red. Because of the small variation of R_e in the region investigated this method was not reliable enough to use in determining whether changing conditions affected the transition moment variation. The intensity ratios were used to study

this effect.

It was stated that the above calculation was performed only when the measurements were taken from one plate. It was mentioned previously that when results were taken from two plates, the intensities from the LRS plates i.e. for the $\Delta v = 2$ sequence appeared to be too low and this would give a false variation in the transition moment calculations. It was possible to draw a smooth curve through the points and, though this did not accurately represent the transition moment variation, it was still useful in detecting bands for which the points lay consistently off the curves for all conditions.

There were 3 bands that were observed to constantly fall off the curves. They were:-

- 12,9: This was above the curve for all conditions, the extent of the deviation varying with the conditions. This was probably due to overlap by the 4,0 band.
- 12,8: Nearly always fell below the curve. This was probably because of the deviation of the 12,9 band. Owing to the method of bringing the values for each v'' - progression to the same scale, a deviation in one of the bands in a v'' -progression could produce a deviation in the opposite direction in the others.
- 8,3: This band consistently fell above the curve, the deviation being independent of conditions. This indicated that the Franck-Condon factor was possibly too low.

All the calculations above were performed using Zare's (1965) Franck Condon factors. The same calculations were also performed using

Nicholls' (1961) values. This had the same effect as that noted in the earlier discussion (chapter 4). The variation in all cases was larger than that observed using Zare's Franck Condon factors and the standard deviation of the experimental points from the curves was greater, indicating that Zare's values were more accurate.

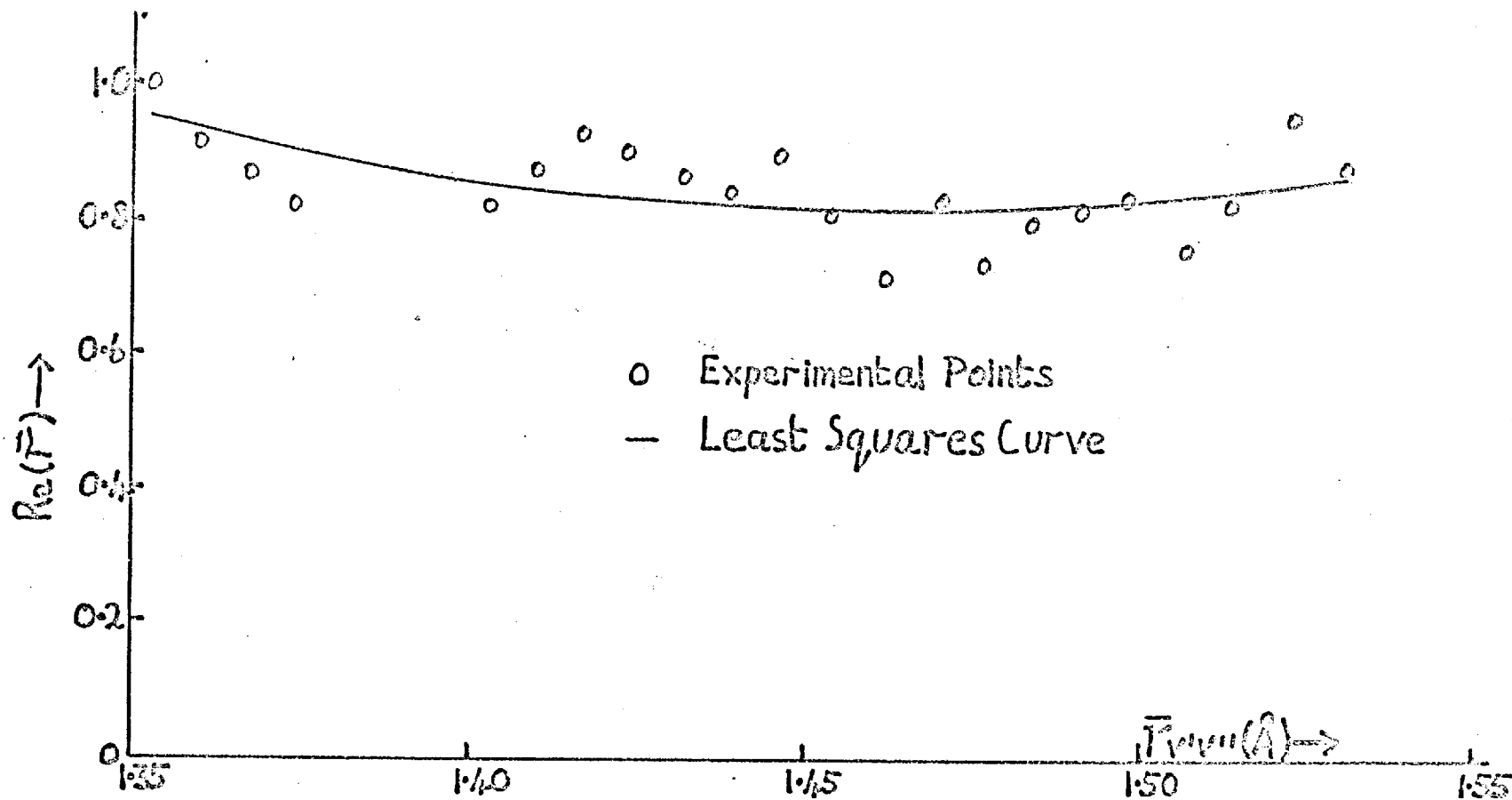


FIG. 14 $R_2(\bar{F})$ v. $\bar{F}$

0.1mm. N_2 0.4mm. H_2

CHAPTER 6.

DISCUSSION OF RESULTS.

1. Intensity Ratios and Examination of Franck Condon Factors.

The intensity ratios in tables 7 to 15 were used to estimate the reliability of the various Franck Condon factor arrays available. Except for conditions for which large variations were observed, all the values for each ratio were averaged and compared with the theoretical values calculated from equation 3.18 using the q values of Zare et.al. (1965), Benesch et.al. (1966b) and Nicholls (1961). These theoretical ratios are listed in table 37.

As well as the averaged ratios from the present experiments, values were calculated from the published intensities of earlier investigations. These are listed in table 38 and were taken from the following experiments.

Elliott and Cameron (1934) measured integrated intensities photographically using three different sources. Their results are shown in columns 1 to 3.

The sources were:-

1. Active nitrogen source in which only bands with $v' = 10, 11$ and 12 were emitted.
2. D.C. discharge
3. High frequency discharge.

Tawde and Patankar (1944, 1947) measured peak intensities photographically. Their results are listed in columns 4 and 5. The sources used were:-

4. D.C. discharge in pure nitrogen

5. Same discharge in air.

Turner and Nicholls (1954a), in the most extensive determination yet performed, measured integrated intensities photoelectrically. Their measurements extended up to $17000 \text{ \AA}$. The source used was a water cooled Pearse-Hunter discharge in pure nitrogen. Their results are listed in column 6.

Column 7 contains the integrated intensities of Petrie and Small (1953) from an Auroral spectrogram.

Further auroral measurements by Omholt (1957) are shown in column 8.

The averaged results from the present experiments are in column 9.

Examination of table 38 shows that there is, in general, good agreement between the ratios determined from laboratory measurements. The main discrepancies lie in the measurements of Tawde and Patankar, taken from peak intensities which are subject to larger errors than integrated measurements. For most bands the values all lie within the range of experimental errors which suggests that, if the intensity ratios do change with source conditions, the variations are small. The auroral measurements of Petrie and Small (1953) agree with the laboratory measurements except for $6,3/6,2$ and $5,1/5,2$. Omholt's values do not agree with any of the other determinations. Auroral measurements are not expected to be as accurate as laboratory measurements as the auroral spectrum contains many lines and bands and there is a great deal of overlapping.

Comparison of the ratios in table 38 with the theoretical values in table 37 shows that, for all the ratios, the q values of Zare et.al.(1965) and Benesch et.al. (1966b) give closer agreement with experiment than

TABLE 37

THEORETICAL INTENSITY RATIOS.

q values.

	Zare	Benesch	Nicholls.
3,0/3,1	.138	.130	.180
4,2/4,1	2.75	2.91	1.94
5,1/5,2	.115	.104	.133
5,3/5,2	1.31	1.37	0.81
5,1/5,3	.088	.076	.165
5,2/5,3	.77	.73	1.24
6,3/6,2	4.9	5.4	4.1
6,4/6,2	3.12	3.49	1.25
7,4/7,3	3.08	3.35	2.45
8,3/8,4	.134	.129	.139
8,5/8,4	2.02	2.15	1.51
9,4/9,6	.139	.132	.221
9,5/9,6	.75	.71	1.10
10,5/10,7	.284	.287	.548
10,6/10,7	1.13	1.13	1.94
11, ~~7~~ /11,8	1.76	1.85	3.85
12,7/12,8	.37	.40	.47
12,9/12,8	.302	.264	.086
11,6/11,8	.569	.678	1.59

TABLE 38

Comparison of Intensity Ratios From Various Experiments

Ratio	Elliott & Cameron			Tayde Patankar		Turner Nicholls	Petrie & Small	Omholt	Present Experiments
	1	2	3	4	5	6	7	8	9
3,0/3,1						.170		.209	.138
4,2/4,1						2.60	2.42	1.97	2.71
5,1/5,2		.096	.109	.152	.135	.145	.075		.108
5,3/5,2						1.17	1.25	0.79	1.18
6,3/6,2		5.9	5.3	5.6	5.7	4.9	8.2		4.8
6,4/6,2						3.26			3.04
7,4/7,3		3.35	3.27	3.25	3.31	3.29	4.62		2.98
8,3/8,4				.183	.148	.152			.176
8,5/8,4		2.03	2.20	2.20	2.33	2.11	2.31		1.96
9,4/9,6		.124	.128	.171	.129	.123			.150
9,5/9,6		.77	.77	.65	.59	.69	.61		.76
10,5/10,7		.200	.188	.495	.356	.195			.247
10,6/10,7	1.29	1.19	1.20	1.03	1.00	1.00			1.15
11,6/11,8	.38	.44	.43	1.21	.97	.35			.43
11,7/11,8	1.93	1.91	1.89	2.18	1.94	1.60			1.82
12,7/12,8	.31	.28	.31	.75	.61	.31			.43
12,9/12,8	.29	.64	.62	.46	.44				

those of Nicholls (1961). In general, the agreement is excellent, the largest discrepancies occurring for the ratios 8,3/8,4, 10,5/10,7; and 11,6/11,8 which all involve weak bands for which the errors in measurement are quite large. As in earlier calculations, both Zare's and Benesch's q -values fit the experimental data equally well, the differences between the theoretical ratios being less than the variations in the experimental values.

The largest variations in the experimental ratios occur for the ratio 12,9/12,8. Table 38 shows that this is due to the overlapping of the 12,9 band by the 4,0 band. In column 1, for an active nitrogen source in which the 4,0 band did not appear, the ratio agrees with the theoretical value whereas, for all the other sources, the ratio is much larger.

2. Variation of Intensity Ratios.

For all the sets of conditions employed, the intensity ratios for all the bands were plotted against the conditions (current and pressure). Several examples of these graphs have been shown (figs. 9 and 10). All the plots were carefully examined to see if there were any systematic variations that could not reasonably be accounted for by experimental errors. The following points were noted.

a) Variation with Current.

For the experiments in pure nitrogen, nearly all the ratios showed deviations larger than the expected errors, and most of these showed some systematic variation with the current, though this variation differed from band to band. For most, though not all bands, the largest variations occurred at lower currents. This agreed with the hypothesis, proposed by Tyte (1962a) on the basis of his and Smallwood's (1961) results for the

second positive system, that variations occur at low current densities, At a nitrogen pressure of 0.2 mm. Hg, the graphs did show systematic variations of the ratios, but in most cases the range covered by the ratios was within the expected experimental errors. It was therefore difficult to attach much significance to these results. The variations were, in most cases, larger at the two higher pressures (1.0 mm., 2.0 mm.), the plots showing similar trends at each of these pressures (fig.9.). The variations were usually in the same direction as the much smaller ones observed at 0.2 mm.

When there was helium in the tube, any systematic trend that could be picked out always appeared opposite to that observed in pure nitrogen.

The inference to be drawn from the above observations is that the assumptions made in the basic theory do not hold over a wide range of conditions. It was suggested by Tyte (1965) that changing source conditions may 'distort' the molecule and cause some change in the molecular potential function and hence the band strengths.

The hypothetical case is now taken in which it is assumed that the molecule is distorted and that the potential functions for the electronic states have been changed by an increase in current from those calculated by Zare et.al. (1965) to the Morse potentials used by Nicholls (1961). The intensity ratios expected for each of these potentials have been listed in table 37, and from these it can be seen that, in the case under consideration, the following ratios would increase with increasing current:-
 3,0/3,1; 5,1/5,3; 5,2/5,3; 8,3/8,4; 9,4/9,6; 9,5/9,6; 10,5/10,7; 10,6/10,7;
 11,6/11,8; 11,7/11,8; 12,7/12,8;

All the other ratios would decrease.

The above case obviously does not represent the physical situation, but both potential functions are reasonable representations, especially for the lower v 's. It is therefore not unreasonable to expect that, if the potential function is distorted, then the above group of ratios will all change in the same direction, the remainder changing in the opposite direction with the possible exception of transitions from higher v 's. This can be tested further by comparing the ratios expected from the potential functions calculated by Zare et.al.(1965) and Benesch et.al. (1966b). Both these are expected to be more realistic than the Morse potential and are in fact very similar to each other. It can be said that one potential is a slight distortion of the other. In this case, the following ratios would all change in one direction:-

3,0/3,1; 5,1/5,3; 5,2/5,3; 8,3/8,4; 9,4/9,6; 9,5/9,6; 10,6/10,7,
12,9/12,8;

With the exception of the $v' = 11$ and 12 bands this is the same group as before. The above ratios, up to $v'=10$, are therefore expected to vary in the same direction if the potential function is distorted.

An examination of the graphs representing the variation with current showed that the following ratios increased with increasing current

3,0/3,1; 5,1/5,3; 5,2/5,3; 9,5/9,6; 10,6/10,7; 11,7/11,8; 12,9/12,8.

The ratios below decreased with increasing current.

4,2/4,1; 6,3/6,2; 6,4/6,2; 7,4/7,3; 8,5/8,4;

The $\Delta v = 5$ sequence was not measured in these experiments and the behaviour of the ratio 12,9/12,8 is of little significance as the 12,9

band is overlapped by the 4,0 band.

The above groups are the same as those predicted in the above discussion and this suggests that the idea of distortion is not unreasonable. Nothing more definite than this can be stated as the above model is obviously an over simplification.

b) Variation with Pressure.

With pure nitrogen in the tube, all the variations in the ratios were within the expected errors and no definite trends were observed.

When there was a constant pressure of nitrogen and the pressure of helium was varied it was observed that several of the ratios were constant at low pressures but showed variations at high helium pressures. This effect was more marked at 0.06 mm. nitrogen than at the higher nitrogen pressures which suggests that it was the ratio of the helium and nitrogen pressures that was the influencing factor in determining this effect.

The following ratios were observed to increase with increasing helium pressure.

3,0/3,1; 5,1/5,3; 5,2/5,3; 9,4/9,6; 9,5/9,6; 10,5/10,7; 10,6/10,7;
11,6/11,8, 12,7/12,8:

The ratios which decreased with increasing helium pressure were:-

4,2/4,1; 6,3/6,2; 7,4/7,3; 8,5/8,4; 12,9/12,8:

It was difficult to pick out any systematic trend for the ratio 11,7/11,8 and, as before, no meaning can be attached to the variation of the ratio 12,9/12,8. Once again, the ratios appear to fall into the same two groups as in the previous discussions.

It must be pointed out here that in nearly all cases, especially at

the higher nitrogen pressures, the total variation was within the limits of experimental accuracy so that it would be dangerous to attach any significance to any of the plots taken on their own. However, the variations have been plotted for six different sets of conditions, i.e. 3 different nitrogen pressures and 4 different currents at 0.06 mm. N_2 . For each ratio the variation, though small, showed the same trend on each of the six plots indicating that they were ~~not~~ random variations. The consistency of the grouping of the ratios, mentioned above, also indicated that the variations were real and that the molecule could be distorted when there was a large excess of helium present. This agrees with the observations made by Tyte (1962c) on the second positive system.

The only ratios showing larger variations than expected were 6,3/6,2 at all pressures, 8,5/8,4 and 10,6/10,7 at 0.06mm. N_2 .

No large or systematic variations were observed with changing composition in the N_2 -He mixtures at total pressures of 2.0 and 5.0 mm. When the total pressure was 0.05 mm., some of the ratios showed large variations when the nitrogen concentration was very low ($<10\%$). This, together with the results obtained at constant nitrogen pressures, suggested that the distortion effect was most marked at very low nitrogen pressures with a large excess of helium. The ratios for which the effect was most marked were:-

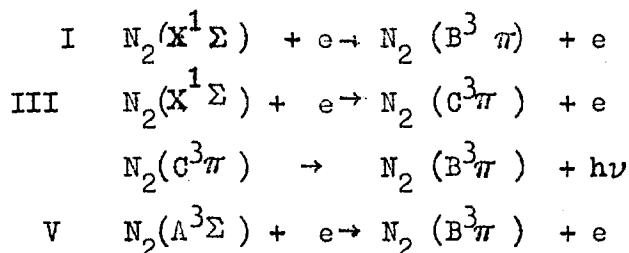
8,5/8,4;	Increased with increasing N_2 concentration
9,5/9,6; 11,6/11,8; 11,7/11,8;	Decreased " " " "

Though the variations observed could not be accounted for by random errors, they may have been due to systematic errors. The main systematic errors would be expected to arise from i) an incorrect temperature of

the standard lamp leading to poor calibration of the plates, and ii) errors caused by overlapping of bands. Incorrect calibration would lead to erroneous values of the ratios, but not to the observed variations with conditions. The generally good agreement between the values obtained from these and previous experiments (table 38) suggests that the calibration was accurate. If the variations were caused by overlapping, then the variation of the ratios with current would be expected to be similar in a nitrogen-helium mixture to that in pure nitrogen, as the intensities were observed to increase in the same way. As this was not the case, it would appear that overlapping could not account for the observed variations.

3. Theoretical Estimation of Relative Populations.

Table 39 shows the values of $N_B(v)$ calculated from the processes



The calculations were all performed assuming various temperatures to represent the population distribution in the initial states. Equations 3.35, 3.36, 3.38, 3.39 were used and the q-values of Benesch et.al. (1966) were taken as the band strengths, the variation of the transition moment being ignored. This was accurate enough for the present purpose of making a rough comparison between theoretical and experimental results.

Figure 15 shows the variation of the relative populations of the B state from process I as the temperature of the ground state increases.

TABLE 39

Predicted Relative Populations of $B^3\Pi$ State Assuming Various Excitation Processes

v'	Vibration Temperature Of Initial State ($^{\circ}\text{K}$)						∞
	0	1000	2000	3000	5000	10000	
0	a) 506	508	550	634	781	861	571
	b) 34303	33484	25586	18426	11715	6907	3100
	c)	421704	17930	5752	2212	1016	413
1	942	934	854	770	683	607	440
	13496	13229	10566	8049	5602	3798	2295
		292136	10953	3412	1344	667	318
2	1003	988	843	697	547	439	354
	6222	6093	4871	3788	2795	2101	1592
		116353	5523	1940	641	460	256
3	824	810	678	549	418	325	297
	2930	2866	2261	1730	1248	905	620
		35103	2629	1079	536	329	214
4	557	548	465	382	298	237	252
	1336	1310	1058	834	629	480	345
		9065	1189	596	347	241	182
5	340	335	294	253	209	176	209
	589	580	489	403	321	255	182
		2128	526	328	227	179	154
6	189	187	174	159	143	131	147
	247	245	223	201	180	161	138
		471	230	181	150	133	126
7	100	100	100	100	100	100	100
	100	100	100	100	100	100	100
		100	100	100	100	100	100
8	51	51	56	62	70	77	90
	39	40	43	46	50	53	58
		21	44	56	67	77	83
9	24	25	30	38	49	59	66
	14	14	16	18	20	23	26
		4	19	31	46	60	76
10	12	12	17	24	35	47	60
	5	5	6	7	8	9	10
		1	8	18	31	48	69

TABLE 39(continued)

Vibration Temperature of Initial State							
<u>v'</u>	<u>0</u>	<u>1000</u>	<u>2000</u>	<u>3000</u>	<u>5000</u>	<u>10000</u>	<u>∞</u>
11	5	6	9	15	25	37	47
	1	1	2	3	3	3	4
		0	4	10	22	38	59
12	3	3	5	10	18	30	42
	0	0	1	1	1	1	1
		0	2	6	15	30	55

a) $X^1\Sigma \rightarrow B^3\Pi$ b) $A^3\Sigma \rightarrow B^3\Pi$ c) $X^1\Sigma \rightarrow C^3\Pi \rightarrow B^3\Pi$

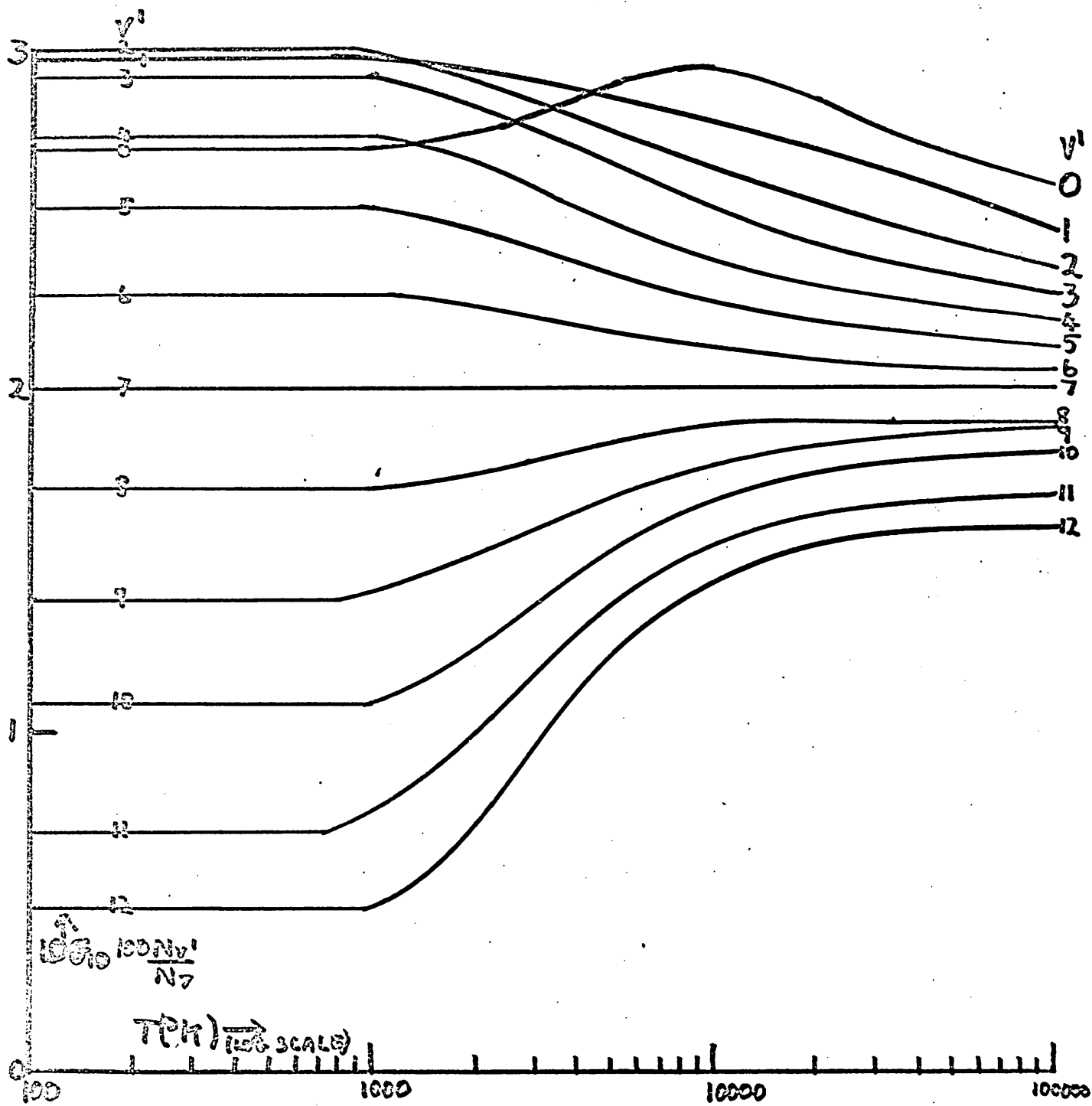


FIG.15 $\log_{10} \frac{100N_{v'}}{N_7} (B^3\pi) V. TEMP. (X'\Sigma)$

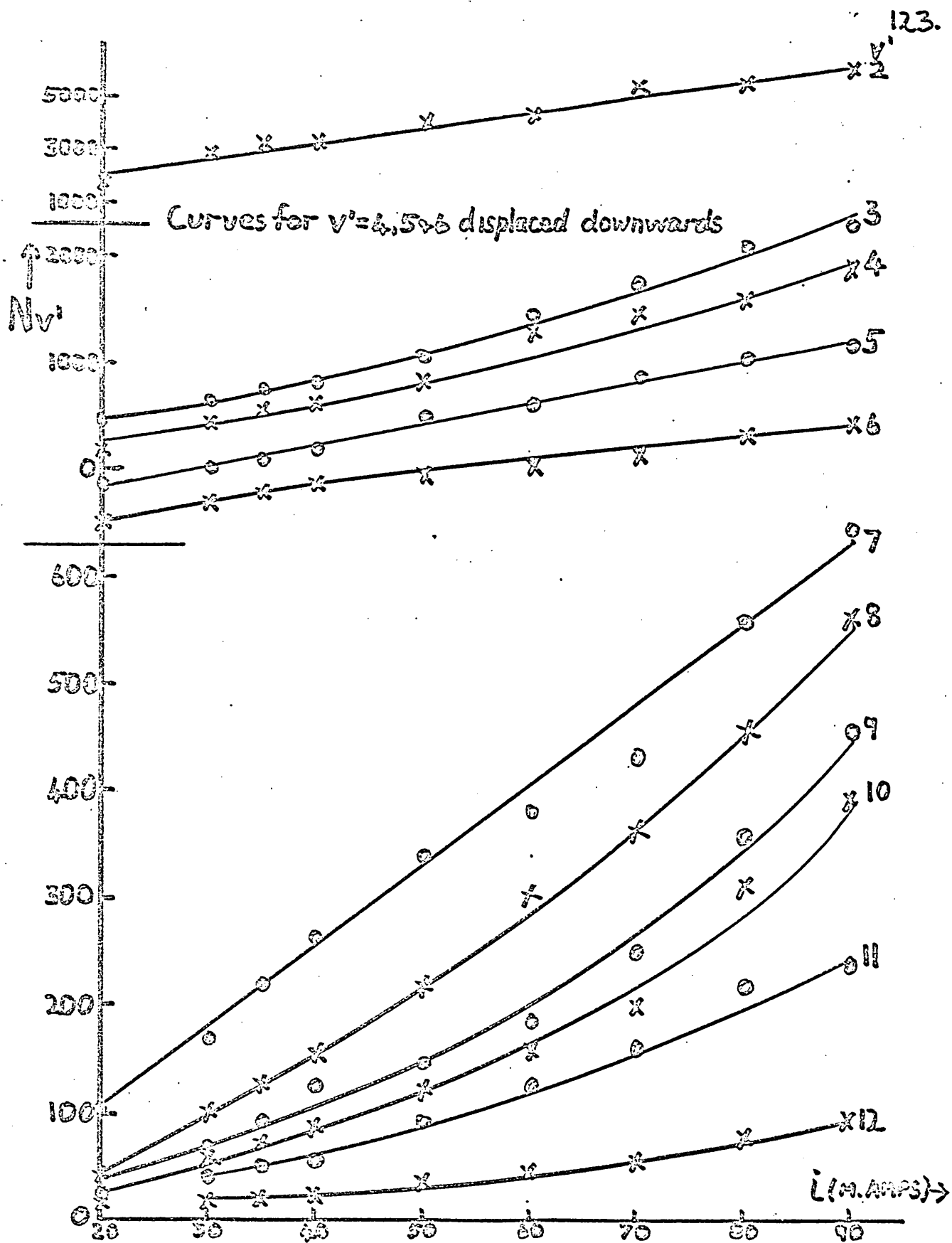


FIG. 16 POPULATION v. CURRENT 2.0 mm. N_2

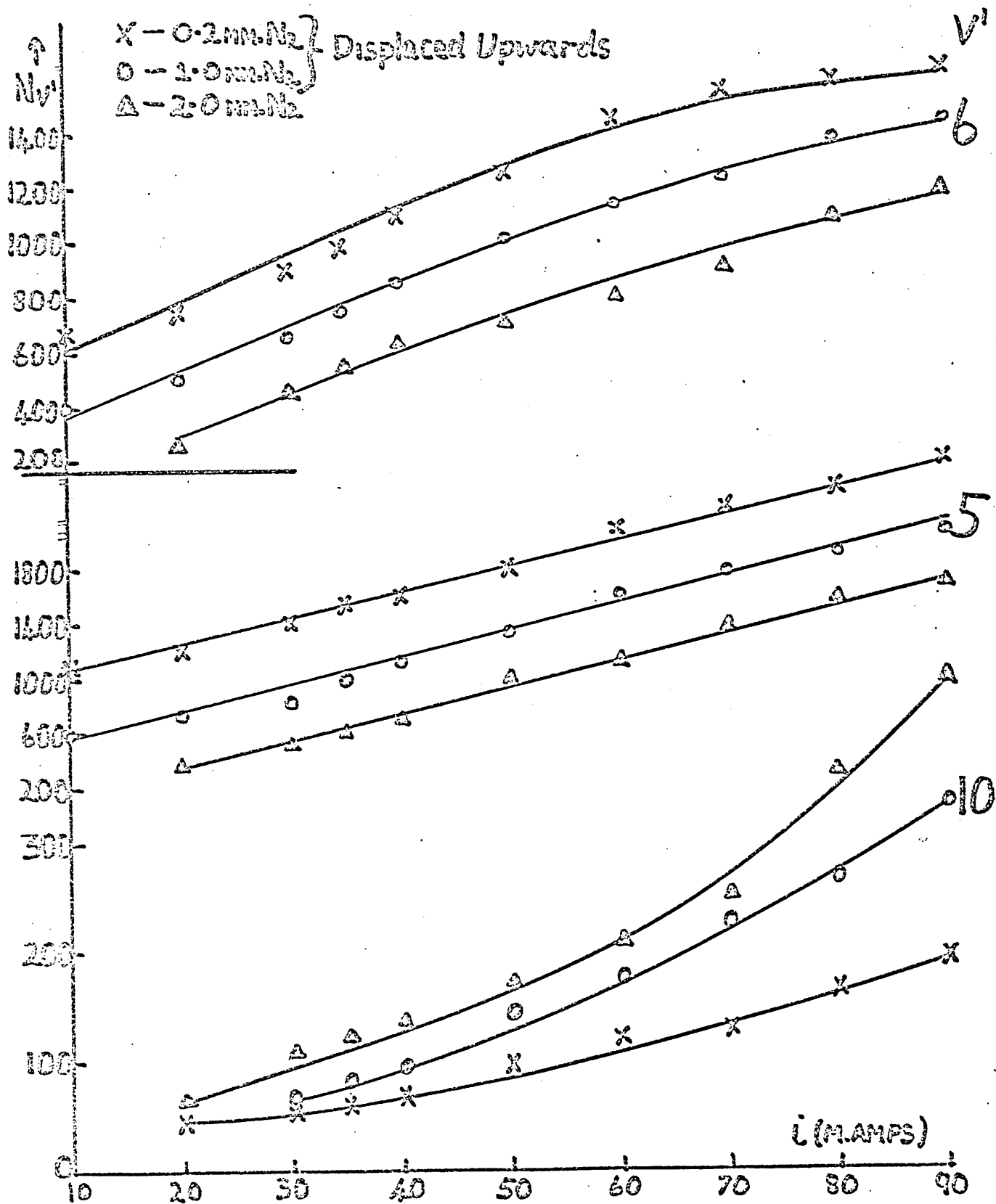


FIG. 17 POPULATION v. CURRENT

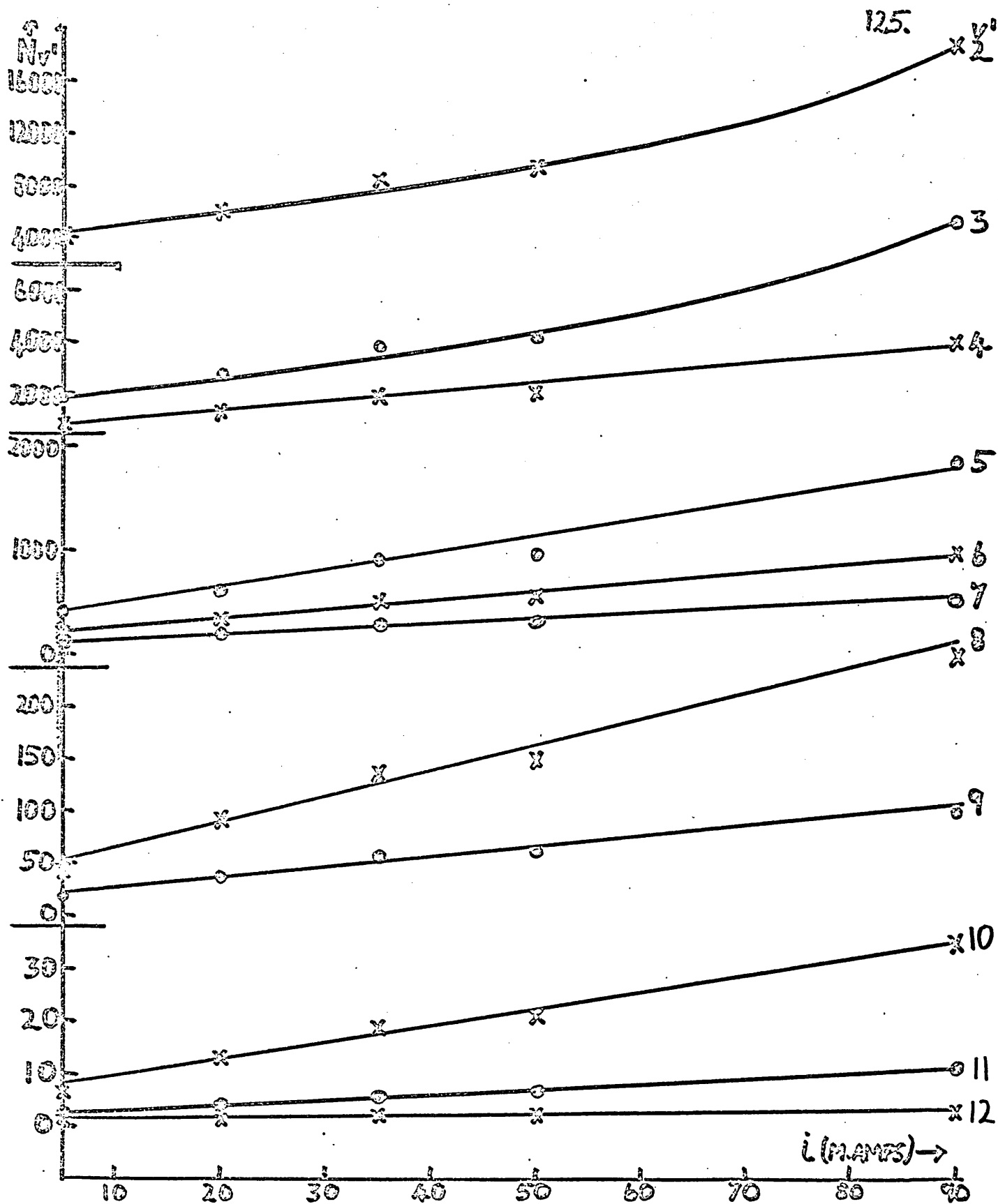


FIG. 18 CASCADe POPULATION v. CURRENT 0.2mm. N₂

The interesting feature is the behaviour of the lower levels. At low temperatures, $v = 2$ has the largest population but as the temperature increases, the distribution takes on a more normal appearance with $N_v > N_{v-1}$ for all v . In an earlier discussion (chapter 5) it was deduced that process III only played a very small part in populating the $B^3\pi$ state. Process V would appear from table 39 to populate mainly the lower levels except at very high temperatures. Process I was the only one for which calculations were performed that showed any agreement with the experimental distributions. (tables 27 to 35).

4. Populations.

a) Variation with Current.

The variation of the populations of the excited states as the current was varied at a constant nitrogen pressure is shown in fig.16. The variations for each level were similar at each of the nitrogen pressures used (fig.17). The curves do not behave in the orderly manner shown by those plotted for the 2nd positive system (Tyte 1962 a,b) which is a preliminary indication that the excitation processes involved were more complex.

The following features were observed:-

The variations for the levels $v' = 2, 5$ and 7 were linear.

The levels $v' = 3, 4, 8, 9, 10, 11, 12$ gave concave curves. The curvature was fairly small and was largest for $v' = 9, 10$, and 11 .

The level $v' = 6$ gave a convex curve.

Examination of the collision processes most likely to populate the $B^3\pi$ state (chapter 3) led to the following conclusions on the expected

variations with current.

Process I.

The population of the B state, N_B , should be proportional to the number of neutral ground state molecules (a constant as the pressure was constant), and the electron density i.e. proportional to the current.

Process II.

N_B is proportional to the number of ions and the number of electrons. The number of ions is proportional to the number of neutral molecules (constant) and the number of electrons.

$$\text{Hence } N_B \propto i^2$$

Process III.

N_B is proportional to the population of the C state. Tyte (1962) showed that this was mainly caused by electron excitation to the C state, and by ionisation followed by recombination, the latter process being one tenth as important as the former. This led to the following results.

$$N_C(v=0) \propto i + 0.1i^2$$

$$N_C(1) \propto i + 0.03i^2$$

$$N_C(2), N_C(3), N_C(4) \propto i$$

It is therefore expected that, from the cascade process, $N_B \propto i$ except for the levels which receive an appreciable part of their population by transitions from the $v = 0$ and 1 levels of the C state. For these levels, $N_B \propto i + ki^2$ where k is a constant depending on how much population they received from the $v_c = 0$ and 1 levels respectively. Benesch, Tilford and Vanderslice (1966) have recently published a list of transition probabilities ($S \nu^3$) $\frac{1}{v^4 v''}$ for the second positive system. The relevant

values are listed in table 40 below.

<u>Table 40</u>					
$v'(C^3\pi) \backslash v''(B^3\pi)$	0	1	2	3	4
0	1.00	0.67	0.27	0.085	
1	0.93	0.046	0.42	0.38	0.19

From these values it can be seen that only the plots for the $v = 0, 1, 2, 3$ and 4 (only very slightly) levels of the B state would be expected to show any curvature, the amount of curvature decreasing rapidly as v increases. This is illustrated in fig.18 where the populations calculated from the cascade process are plotted against the current. The populations of the C state were taken from Tyte's (1962a) tables.

Process IV

N_B is proportional to the population of the $a^1\pi$ state which is proportional to the current, and to the current.

$$\text{Hence } N_B \propto i^2$$

Process V

N_B is proportional to the population of the $\Lambda^3\Sigma$ state (N_A) and the current. If it is assumed that the $\Lambda^3\Sigma$ state is populated by electron collisions with the ground state, then $N_A \propto i$.

$$\text{Hence } N_B \propto i^2$$

By comparing the theoretical values with the experimental results, it was observed that processes III and V gave poor agreement with experiment. Process V would also be expected to give a noticeable curvature to the

plots of population against current for all v' . As no calculation was performed for process II it is difficult to assess the expected distribution. Using the potential data in Lofthus (1960) and applying the classical Franck Condon principle of vertical transitions between points on the potential curves, it would appear that the lower levels would be heavily populated and the higher levels hardly at all. The plots in fig.16 would also all be expected to be curves so it would appear that this process is not the major one. Process IV is even more difficult to assess as regards the expected distribution but curvature of all the plots in fig.16 would be expected if this process were the main one.

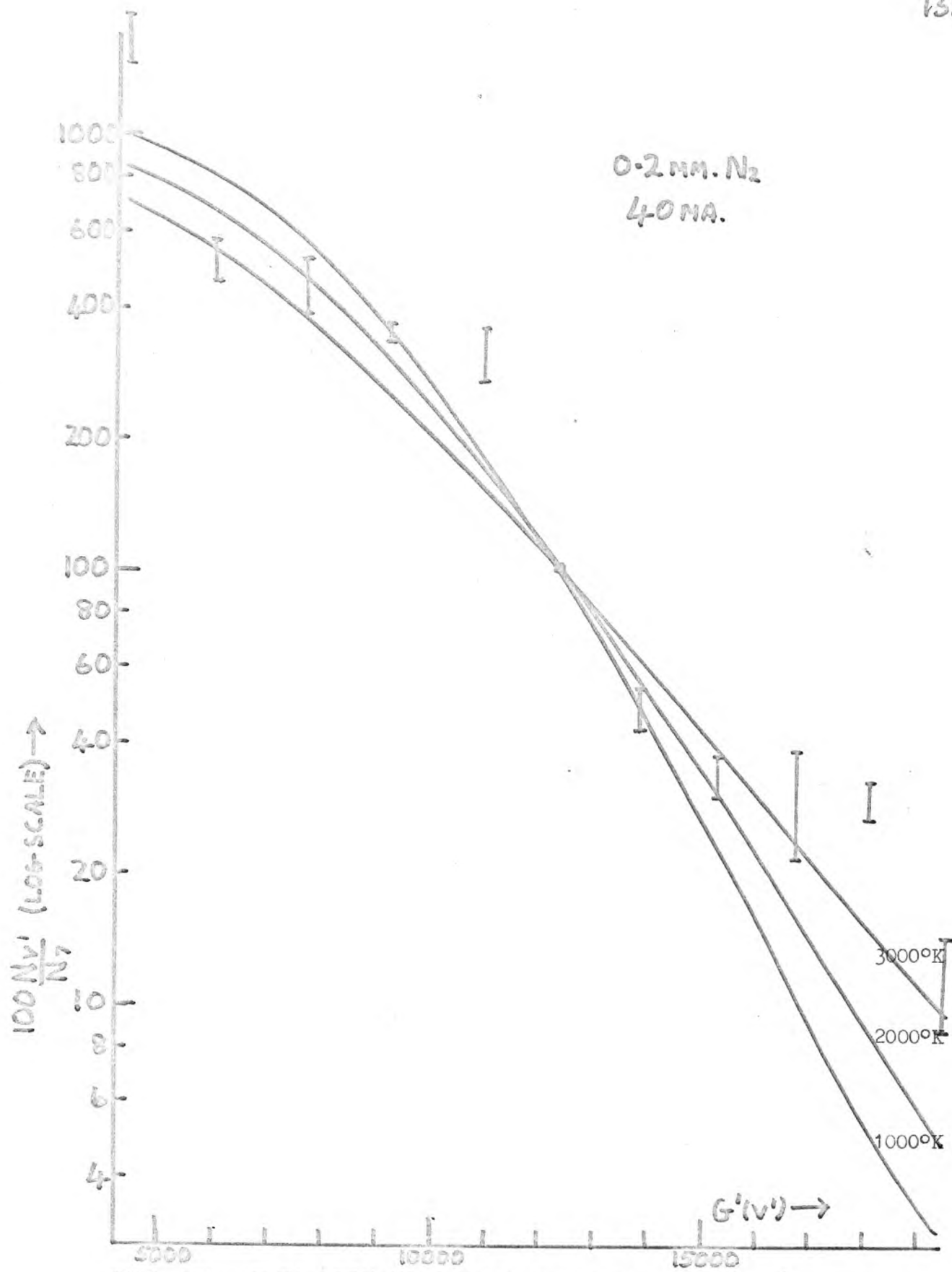
The curvature of the plots for $v' = 3$ and to a lesser extent $v' = 4$ and the linearity of those for $v' = 5$ and 7, are consistent with the population of the B state arising mainly from process I with a small contribution from process III. As processes II and V also affect mainly the lower levels, they would impose more curvature on the plots for these levels than on the higher levels, therefore a small contribution may arise from these processes. The importance of process IV cannot be estimated without more information. As the accuracy of the results for $v' = 2$ is poor, it is possible that the plot for $v' = 2$ is a curve, but the errors in measurement were too large to detect the curvature.

The above mechanism cannot explain the large curvature of the higher levels, especially $v' = 9, 10, 11$ nor the behaviour of the curve for $v' = 6$. Further information on the distribution was obtained by plotting $\log_{10} N_{v'}$ against $G'(v')$ (fig.19) for a typical set of experimental results. On the same graph, several theoretical distributions calculated for process I

were plotted, each corresponding to a different vibration temperature in the ground state. Examination of the curves then determined approximately which one best fitted the experimental points thus giving an indication of the ground state distribution. The best curve in fig.19 would be one for T between 2000 and 3000°K. It can be seen that the experimental points appear to oscillate about the theoretical curve indicating that direct electron excitation may be the main process, but that there are secondary processes occurring that cause a redistribution among the vibrational levels. The levels $v' = 6, 10$ and 11 appear strongly enhanced and $v' = 3$ and 8 reduced compared with the expected populations. Fig.16 indicates additional processes occurring for the higher levels which would cause them to be enhanced. The curve for $v' = 6$ shows that, as the current increases, the process responsible for the enhancement of $v' = 6$ becomes less important.

It is well known that, in the afterglow in active nitrogen, there is a very strong selective enhancement of $v' = 11$ and, to a lesser extent, $v' = 6, 10$ and 12 . As these levels also appeared enhanced in the present experiments it is possible that the afterglow mechanism was present to a very small extent in the discharge, and acted in addition to process I to produce the observed results.

From an examination of the potential curves (Benesch et.al. 1965) it seems possible that process IV may lead to a similar distribution as process I. This is very indefinite as it was impossible to perform a numerical calculation, but it means that, though process I gives good agreement with experiment, the possibility of process IV being important

FIG. 19 RELATIVE POPULATION v. $G'(v')$

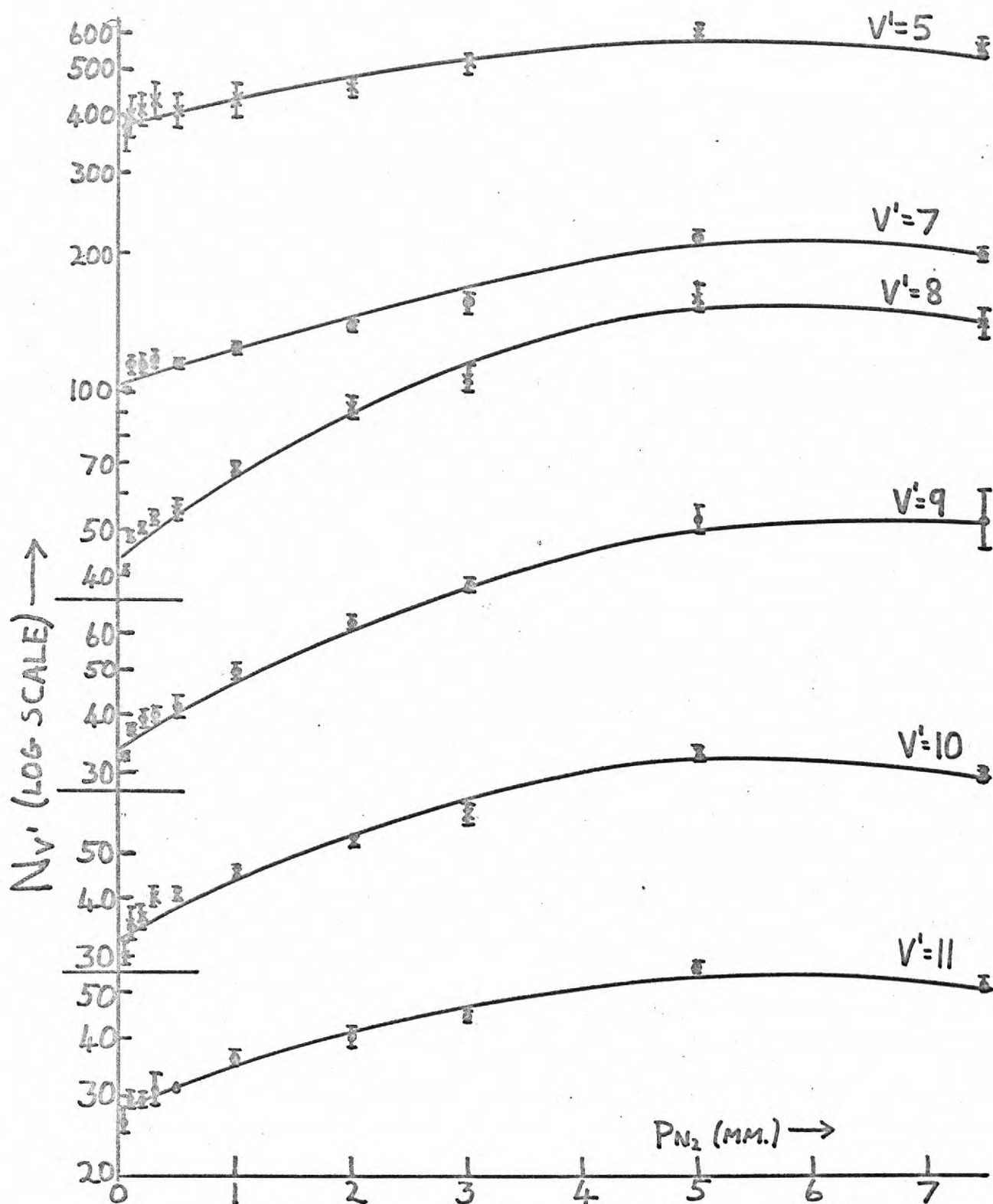
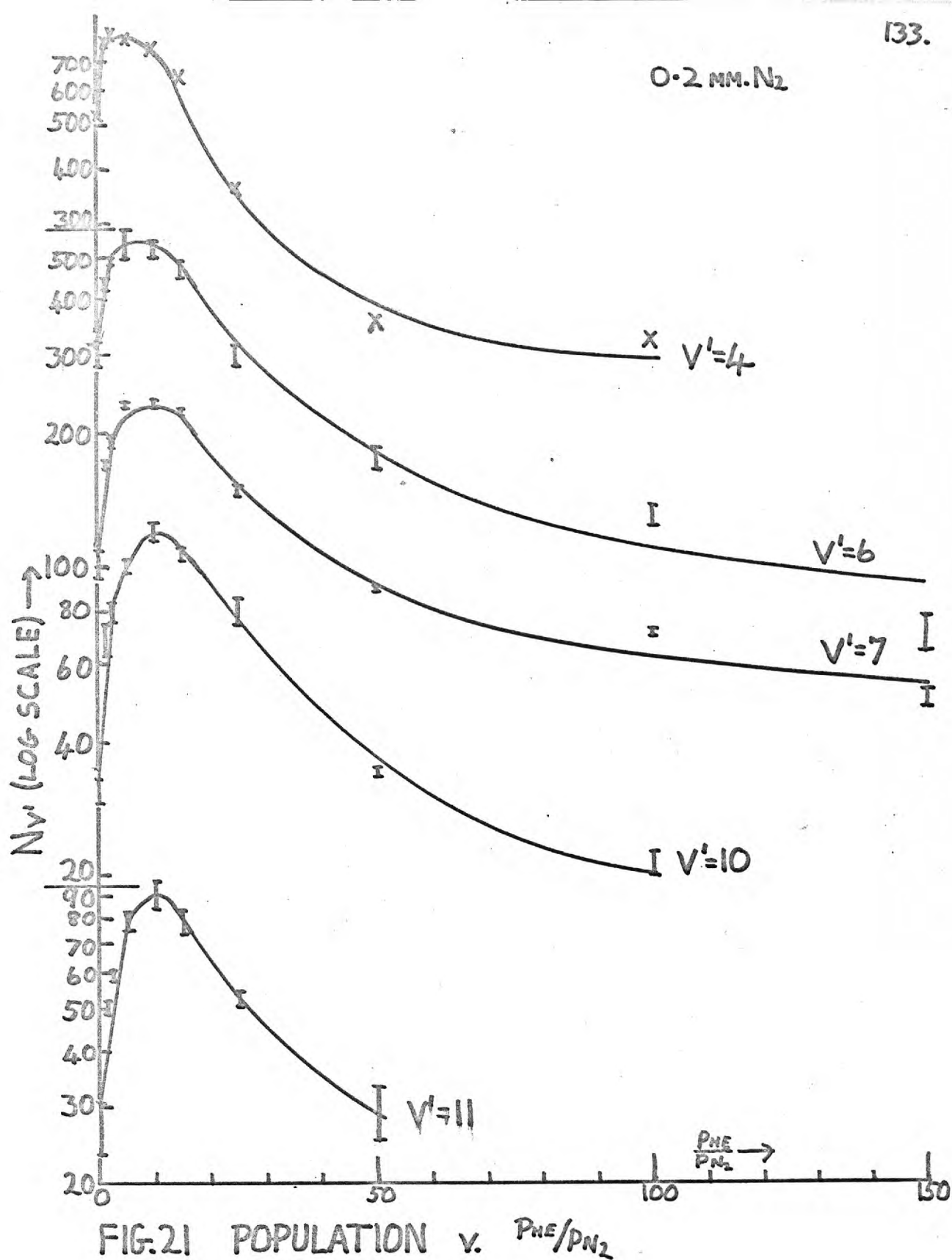


FIG. 20 POPULATION v. PRESSURE PURE N_2

0.2 mm. N₂FIG. 21 POPULATION v. P_{HE}/P_{N_2}

TOTAL PRESSURE = 2.0 mm.

134.

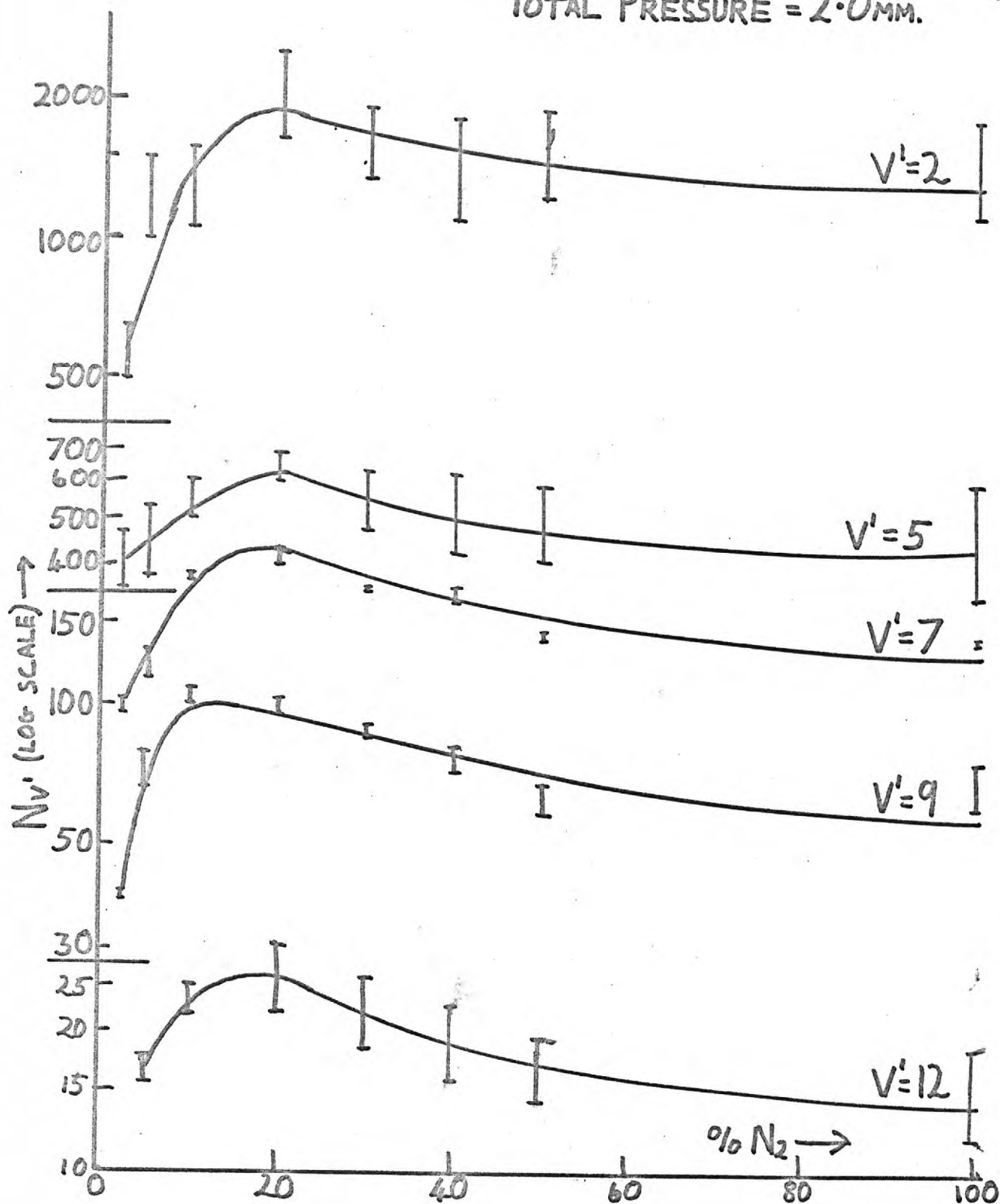


FIG. 22

POPULATION v. $\% N_2$

cannot be discounted.

b) Variation with Pressure.

i) Pure Nitrogen

Fig.20 shows the variation of the populations of the vibrational levels of the B state with the nitrogen pressure. For each level there was an initial rise in population to about 5 mm. pressure after which the population appeared to fall. As it was difficult to maintain the discharge in pure nitrogen at pressures higher than 7.5 mm., the behaviour around the maxima could not be determined with certainty.

An interesting point arising from these measurements was the relative behaviour of the 1st and 2nd positive systems. It was observed on the plate from which the intensities were measured that, corresponding to the increase in intensity (hence populations) of the 1st positive bands, there was a decrease in the intensity of the 2nd positive bands. No quantitative estimate of this effect was made, but Sharma (1959) measured the intensity of the 0,0 band of the 2nd positive system and this decreased sharply as the pressure was varied from 0.25 to 1.5 mm. Although this was the only band he measured, Sharma observed a decrease in the intensity of the system as a whole. He also observed a decrease in vibrational temperature and increase in rotational temperature until, at a pressure of about 1 atmosphere in an arc, the rotational structure of the 0,0 band extended over the whole $\Delta v = 0$ sequence while none of the other bands appeared. This was first observed by Feast (1950b) who also found a similar effect with the first positive bands. This indicates that the behaviour of the two systems is similar at high pressures.

The opposite behaviour of the two systems at low pressures confirms the earlier suggestion that the cascade process plays only a very minor role in populating the $B^3\pi$ state. The behaviour is consistent with the direct electron excitation mechanism. As the pressure increases, the electrons will make more frequent collisions with the nitrogen molecules. This will decrease the electron mean free path and there will be fewer electrons with sufficient energy to excite the $C^3\pi$ state. Some of these electrons will still have sufficient energy to excite the B state. Thus, electrons which excite the C state at low pressures, no longer have sufficient energy to do so at higher pressures and excite the B state instead. The first positive system is therefore enhanced at the expense of the second positive. As the pressure is increased further, the electron energy will decrease ~~further and~~ eventually the population of the B state will decrease.

The observed variations are also consistent with Nicholls' two step mechanism, process IV. For the second positive system, the metastable b states are produced by the initial excitation. In the above argument, the $C^3\pi$ and $B^3\pi$ states can be replaced by the b and $a'\pi$ states respectively and the same conclusions would be reached.

ii) Nitrogen Helium Mixture.

The variation of the populations of some of the excited levels with the ratio of helium to nitrogen pressure is shown in fig.21, for the case in which the nitrogen pressure was kept constant at 0.2 mm. The curves for all v' have the same shape as do the curves for the other nitrogen pressures used. There are probably several contributory factors to the

decrease of population with increasing pressure at higher helium pressures. There will be an increasing number of helium nitrogen collisions that could depopulate the B state levels before radiation occurred. The increase in helium pressure would reduce the probability of electron nitrogen collisions thus decreasing the rate of population of the excited levels. The mean electron energy would also decrease with increasing pressure and there would be fewer capable of exciting the B state. The initial increase at low pressures could be due to the increased number of electrons present as helium was added. This can be seen by the fact that the N_2^+ spectrum was enhanced when helium was added, thus the number of ions and hence the number of electrons available for collisions with the N_2 molecules must have increased. The same variations were observed by Tyte (1962a,c) for the second positive system.

In fig.22 the variation of the populations of the excited levels is shown as the percentage of nitrogen in the constant pressure mixture was increased. The curves have the same shape as those obtained for the second positive system by Tyte (1962 a,c) who proposed a mechanism to explain the variation. The same mechanism is thought to explain the present results.

5. Population Distributions.

Fig.23 shows the variation of $\log N_{v'}$ with $G'(v')$ for pure nitrogen at various pressures and in fig.24, the variation is plotted for a constant pressure of nitrogen and various helium pressures. For each set of points, the theoretical distribution from process I which best fitted the experimental data has been drawn through the points. The curves give an estimate of the distribution in the ground state if process I is assumed

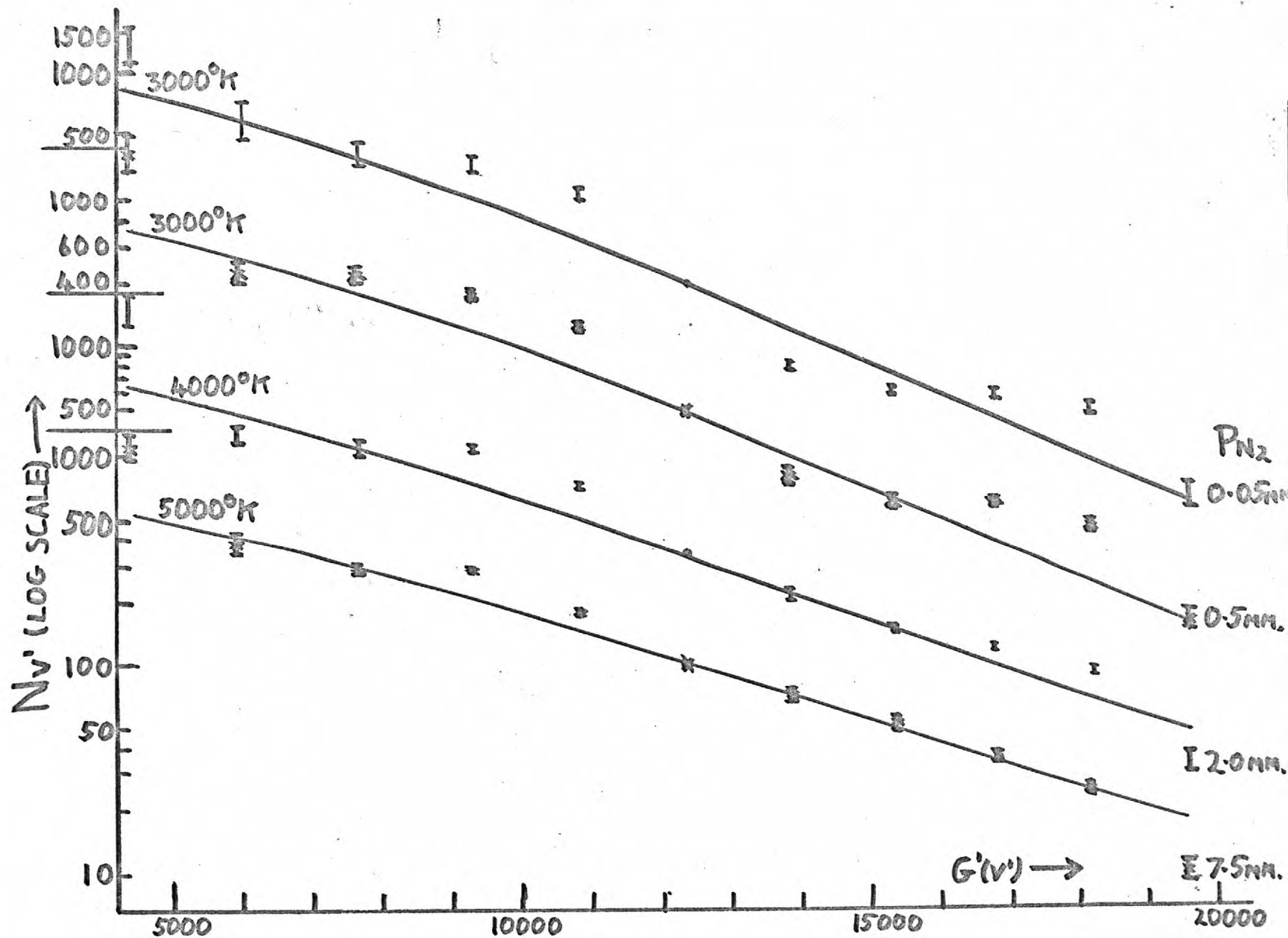
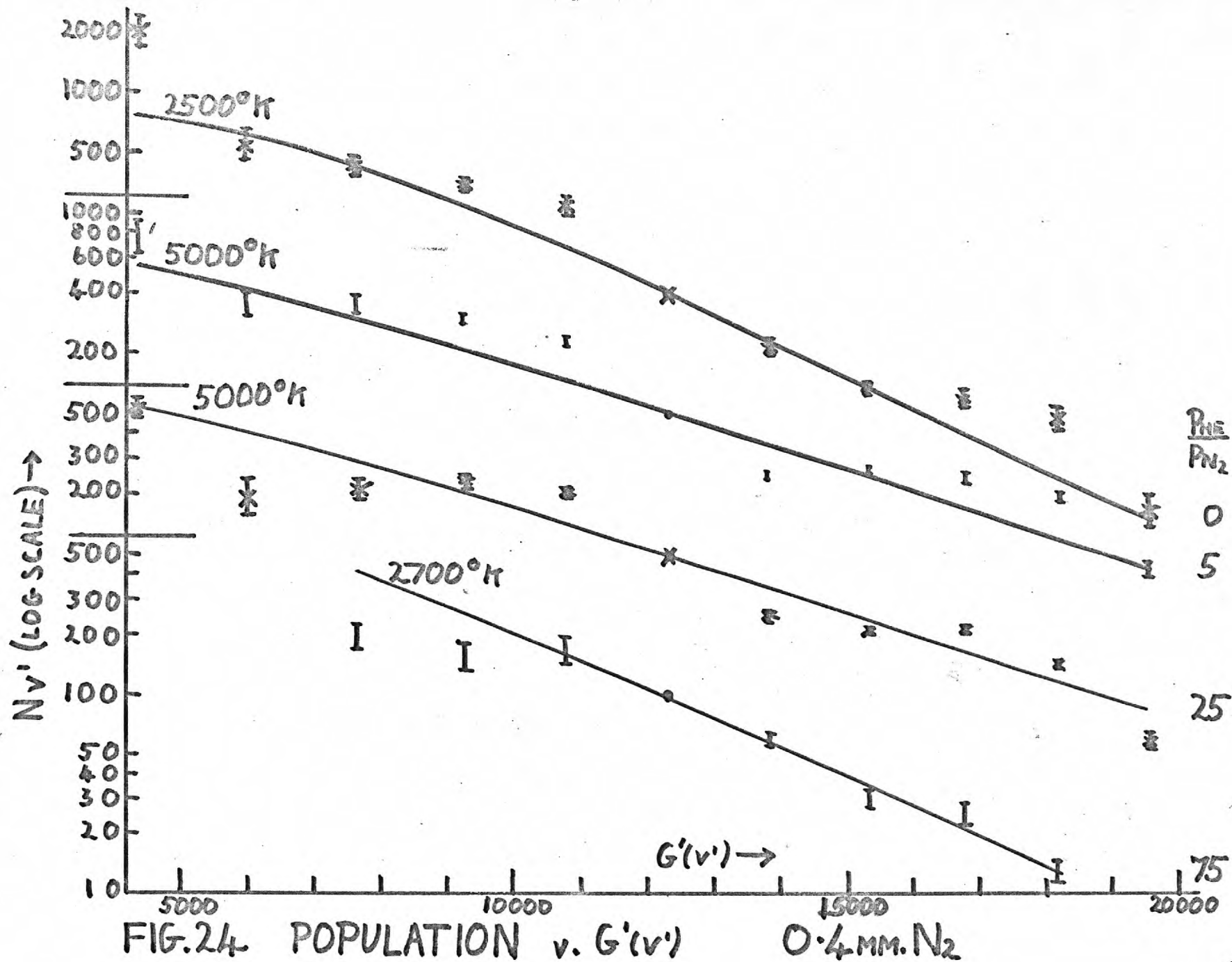


FIG.23

POPULATION v. $G'(v')$

PURE N_2 50mA.

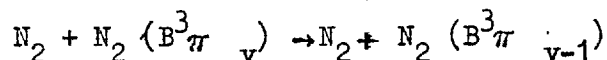


to be prominent. It was observed that the theoretical curves are very nearly linear which means that the distribution obtained by direct electron excitation from the ground state very nearly obeys the Boltzmann law.

a) Processes in Pure Nitrogen.

Fig.23 illustrates the way in which the various vibrational levels behaved as the pressure of nitrogen increased. At low pressures, the distribution was similar to that in fig.19. The populations of $v' = 2, 5, 6, 10, 11$ were enhanced and that of $v' = 8$ reduced. As the pressure was increased most of the abnormalities decreased and the observed distributions lay much closer to the theoretical curve. The curves became less steep indicating an increase in the temperature of the ground state as the pressure increased.

Stanley (1954, 1957), in his experiments on active nitrogen, has shown that the distribution becomes more normal as the pressure increases and he attributed this to a redistribution among the vibrational levels due to $N_2 - N_2$ collisions of the type



From his experiments he showed that there is a finite chance of this process occurring and that the probability increases with pressure. It is felt that this mechanism might explain most of the variations in fig.23.

It was also observed that the point for $v' = 2$ lay consistently above the curves at all nitrogen pressures. It has already been pointed out that the values for $v' = 2$ are not very reliable and this could partly explain the observed deviation. Also, if processes II, III and V were occurring in addition to the main excitation mechanism, they would

affect $v' = 2$ more than the other observed levels and this would cause the point to lie above the curve. If this were the case, then the points for $v' = 1$ and 0 would also lie above the curve but, as no observations were made on these levels, this could not be tested.

As the pressure increased, the point for $v' = 12$ fell below the curve. No mechanism has been found to explain this effect. The values for $v' = 12$ were subject to larger errors than most of the other levels.

b) Processes in a Mixture of Nitrogen and Helium.

For a constant nitrogen pressure and varying helium pressures, the general features of the distribution (vibration temperature) showed the same variation with pressure as in pure nitrogen. Fig.24 shows that above a certain pressure, the apparent vibration temperature of the ground state decreased, a feature not observed in pure nitrogen as the highest pressure attained (7.5 mm) was too low.

The detailed behaviour of the individual vibrational levels differed from that in pure nitrogen. The abnormalities in the higher levels disappeared at high helium pressures, an effect similar to that observed in the pure gas, though the helium pressure required for this to occur was much higher than the pressure required in pure nitrogen. This is consistent with the idea of vibrational redistribution through collisions as the effects of a collision depend on the nature of the colliding particles. A collision between a nitrogen molecule and a light helium atom would be expected to have less effect on the molecule than a collision with a heavier nitrogen molecule. It would therefore require a higher pressure (i.e. more helium, hence more helium nitrogen collisions) before the

distribution would correspond to the theoretical curve.

The behaviour of the lower levels ($v' = 2-5$) differed considerably from that observed in pure nitrogen. As the pressure increased, the enhancement of $v' = 2$ decreased. The populations of $v' = 3, 4$ and 5 also decreased relative to those of the higher levels until, at the highest pressure obtained (30 mm.He), the points for $v' = 4$ and 5 lay well below the curve. At this pressure, the $v' = 2$ and 3 bands were too weak to be observed, an indication that the populations were low and would also fall below the curve.

A close examination of the various graphs in fig.24 and of tables 29,30 and 31 shows that, as the helium pressure was increased, the population of $v' = 4$, N_4 , became greater than N_3 . After a further increase in pressure, N_5 became greater than N_4 , and at a higher pressure still, N_6 became greater than N_5 which then fell with respect to N_4 . These effects were observed to occur at the same total pressure for both 0.2 mm. and 0.4 mm. N_2 . They were not observed with 0.06mm. N_2 as the total pressure used was not high enough. The same systematic enhancement of successive levels was not observed in pure nitrogen but table 28 shows that N_5 increased relative to N_4 as the pressure increased.

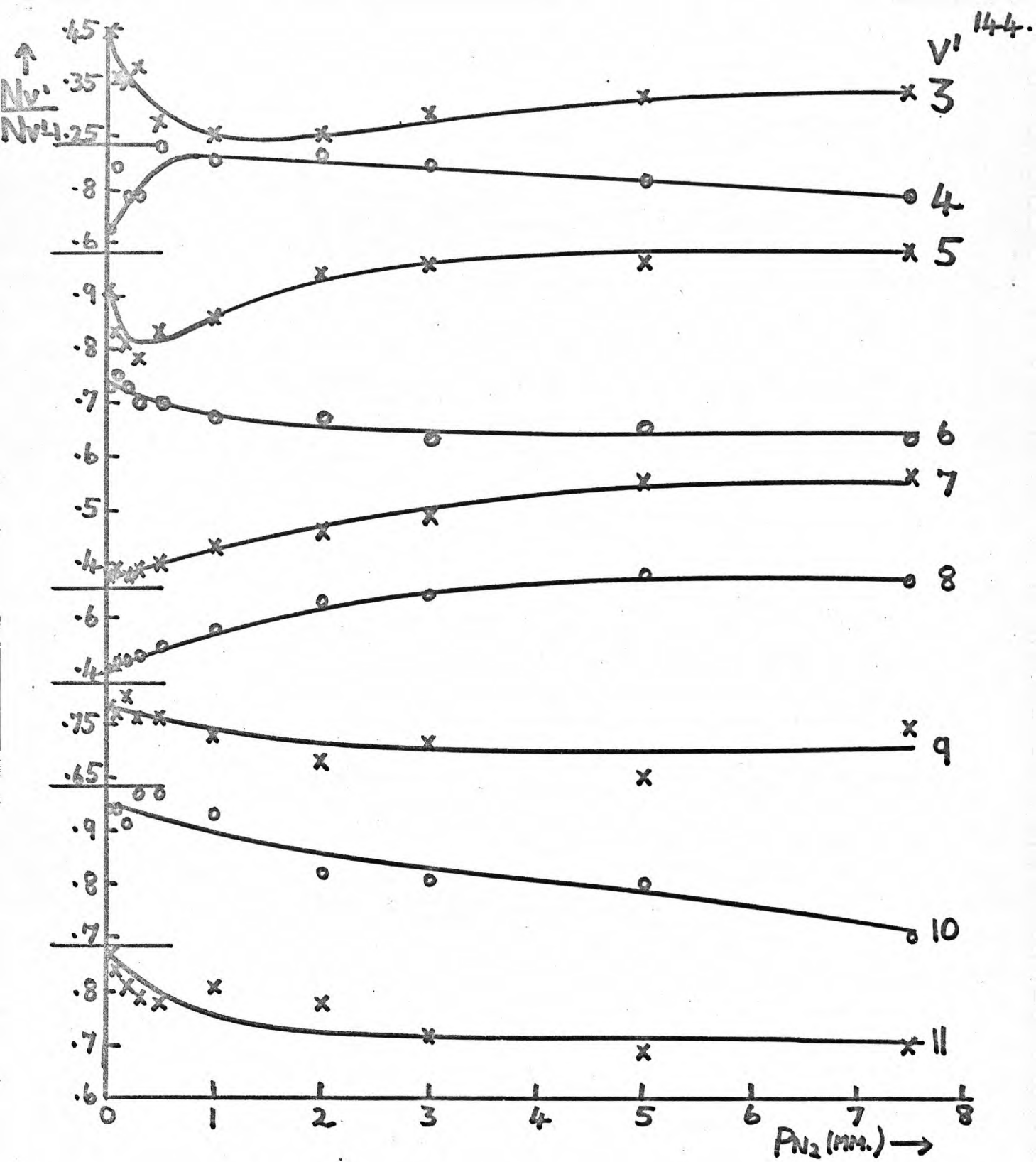
In order to examine this effect more closely, the ratios $N_{v'}/N_{v'-1}$ were calculated for both pure nitrogen and the nitrogen-helium mixture. The results are displayed in tables 41 and 42, and in figs. 25 and 26 the ratios are plotted against the pressure. For $v' = 3$ to 6 in the N_2 -He mixture, the ratios were steady at low pressures then rose sharply to a peak and fell off again. For each v' , the rise and the maximum occurred at a higher pressure than that for the preceding v' . The curves

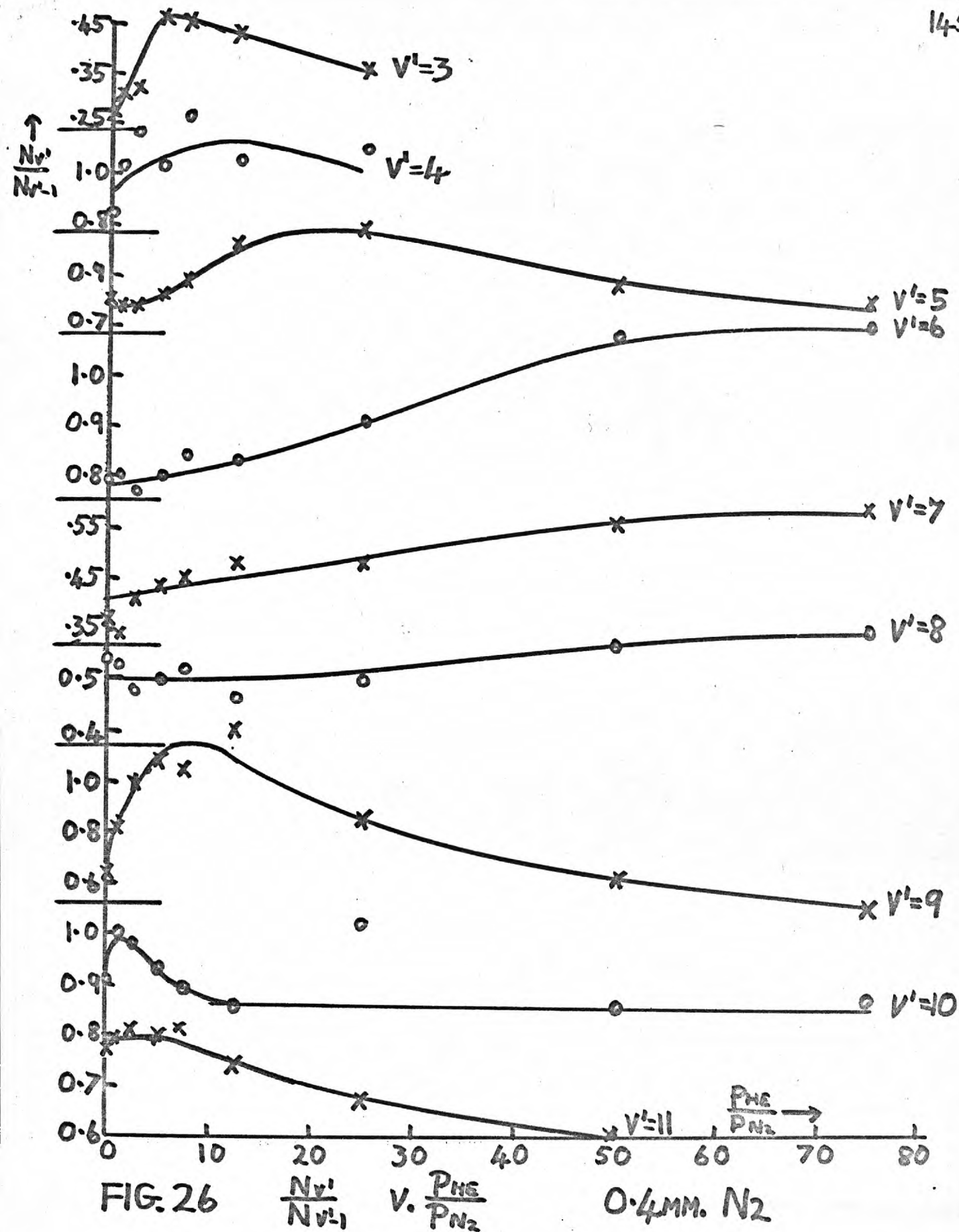
TABLE 41 $N_{v'}/N_{v'-1}$: Pure Nitrogen, 50ma., Various Nitrogen Pressures

	Nitrogen Pressure(mm)									
	0.05	0.1	0.2	0.3	0.5	1.0	2.0	3.0	5.0	7.5
N_3/N_2	.44	.36	.35	.38	.27	.25	.25	.29	.32	.33
N_4/N_3	.65	.88	.77	.77	.96	.90	.92	.88	.82	.76
N_5/N_4	.91	.83	.81	.78	.83	.86	.94	.96	.96	.98
N_6/N_5	.73	.75	.73	.70	.70	.67	.67	.63	.65	.63
N_7/N_6	.38	.39	.38	.39	.40	.43	.46	.49	.55	.56
N_8/N_7	.41	.43	.44	.46	.49	.55	.66	.68	.75	.72
N_9/N_8	.78	.77	.80	.76	.76	.73	.68	.71	.65	.74
N_{10}/N_9	.94	.94	.91	.97	.97	.93	.82	.81	.80	.70
N_{11}/N_{10}	.87	.84	.81	.79	.78	.81	.78	.72	.69	.70

TABLE 42 $N_{v'}/N_{v'-1}$: 0.2mm. Nitrogen, 40ma., Various Helium Pressures

	Helium:Nitrogen Ratio									
	0	1.5	2.5	5	10	15	25	50	100	150
N_3/N_2	.37	.35	.37	.41	.50	.57	.59			
N_4/N_3	1.08	1.41	1.48	1.40	1.35	1.24	0.90			
N_5/N_4	.73	.64	.71	.79	.80	.87	1.10	1.10	.67	
N_6/N_5	.79	.89	.87	.87	.89	.84	.76	.89	1.21	1.10
N_7/N_6	.33	.38	.38	.42	.44	.47	.50	.53	.55	.72
N_8/N_7	.43	.43	.77	.48	.49	.46	.47	.48	.54	.53
N_9/N_8	0.84	0.88	0.89	1.13	1.16	1.24	1.38	0.88	0.74	
N_{10}/N_9	0.86	1.08	1.00	0.81	0.89	0.84	0.82	0.88	0.75	
N_{11}/N_{10}	.90	.73	.74	.77	.76	.75	.66	.84		





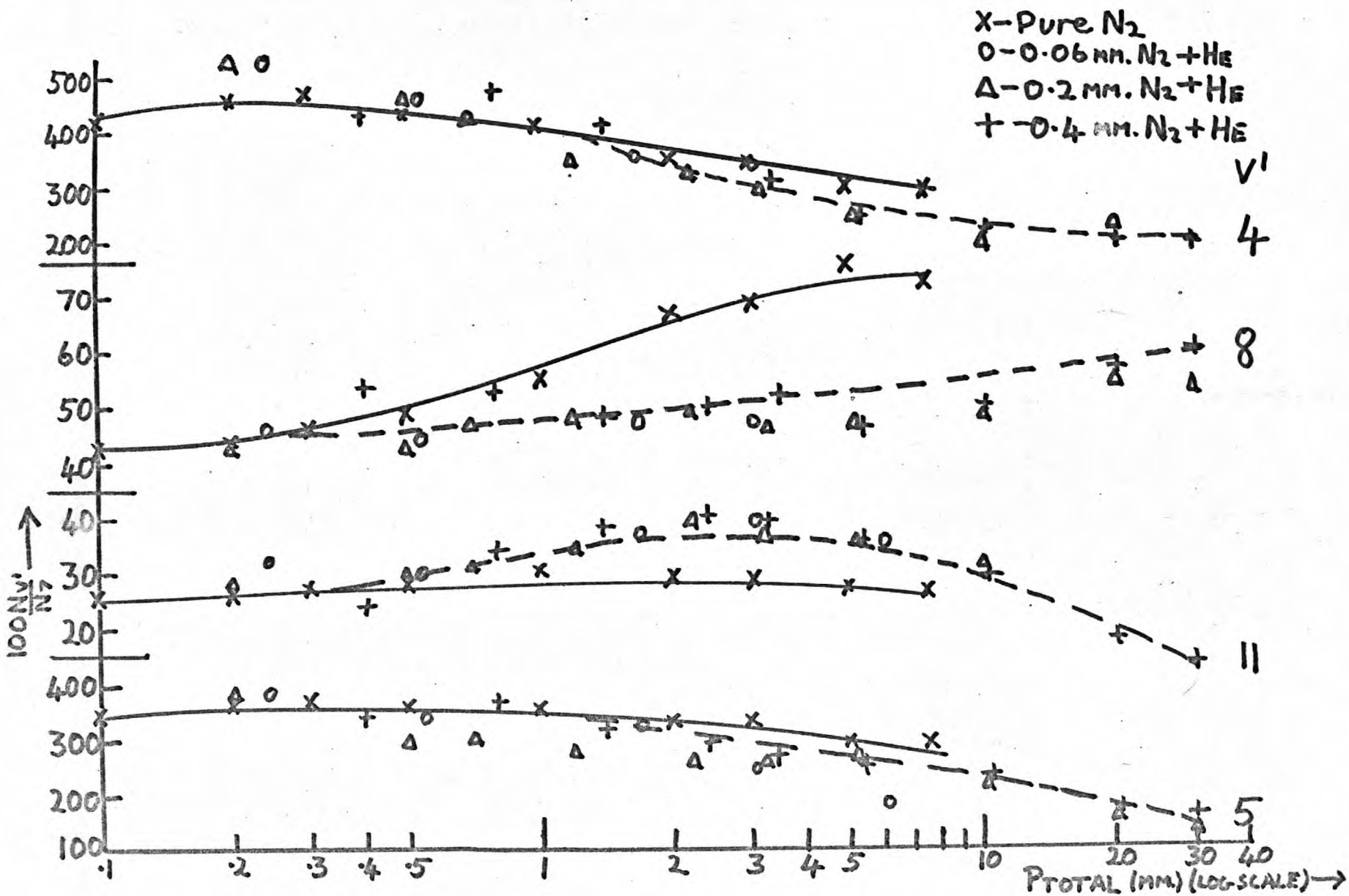


FIG. 27 RELATIVE POPULATION v. TOTAL PRESSURE

for $v' = 7$ and 8 showed no maximum, but both showed the sharp rise at high pressures conforming to the above pattern. The curves for $v' = 9$ and 10 both had maxima at low pressures, the one for $v' = 9$ occurring at a higher pressure than that for $v' = 10$, reversing the pattern shown by the lower levels. The curves for pure nitrogen did not show the same systematic features, the main point of interest being the rise in N_5/N_4 corresponding to a fall in N_6/N_5 and a rise in N_7/N_6 .

In order to explain the variations, a process is required that will, as the pressure increases, successively populate vibrational levels at the expense of the ones immediately below them. The initial rise in each of the curves indicates that the probability of the process occurring increases with increasing pressure, therefore it is likely to be a collision process. To explain the curves, $v' = 2$ will be taken as the starting point for discussion. As N_2 is higher than the other populations, the largest number of collisions will take place with molecules with $v' = 2$. As the pressure increases, the probability of the transition $v' = 2 \rightarrow 3$ by this process will increase and N_3/N_2 will increase. There will now be more molecules with $v' = 3$ and more transitions $v' = 3 \rightarrow 4$ will take place and, as the pressure increases further, N_4/N_3 will increase. As this happens N_3/N_2 will tend to decrease. With a further increase in pressure the transition $v' = 4 \rightarrow 5$ will become more probable, N_5/N_4 will increase thus decreasing N_4/N_3 .

It now remains to determine the nature of the collision process. As the variations only occurred with helium in the discharge the process must depend on the presence of helium. The obvious conclusion is that

N_2 - He collisions give the molecule a quantum of vibrational energy. Zener (1931) has shown theoretically that the chance of vibrational energy exchange in this type of collision is very small. Stanley (1954) has shown that vibrational energy transfer in N_2 - N_2 collisions is more probable than theoretically predicted so the same could apply to N_2 -He collisions. In this case it would appear (Stanley 1957) that downward transitions ($v' \rightarrow v' - 1$) would be far more likely than the upward ones needed to explain the curves in fig.26. It therefore seems that nitrogen-helium collisions will not provide the required process.

Oldenberg (1931) pointed out that an electron of about 5eV can give a molecule a quantum of vibrational energy in a collision without changing the molecular electronic state. Tyte (1962c) has proposed this mechanism as a possible explanation of the increasing populations of the $v' = 3$ and 4 levels of the $C^3\pi$ state as the helium pressure was increased. This mechanism would also explain the present observations. As the helium pressure increased, the intensities of the helium lines were observed to increase. This indicated that, as the pressure increased, the electrons made an increasing number of inelastic collisions with the helium atoms. This would reduce the mean electron energy and there would be more slow electrons available, increasing the probability of the above process occurring. It has been mentioned previously that the increase in intensity of the ion spectrum with increasing helium pressure indicated an increase in the number of electrons present. This would further increase the probability of the required electron-nitrogen collisions. The ion spectrum was not noticeably enhanced in pure nitrogen and this process

would therefore not be expected to occur so readily as in the N_2 -He mixture.

The difference in the pattern for $v' = 9, 10, 11$ is not unexpected. It is apparent from the enhancement of $v' = 10$ and 11 at low pressures that the processes populating these levels were more complex than for the lower levels. It is therefore not surprising that the ratios $N_{v'}/N_{v'-1}$ should behave differently for these levels. The curves for $v' = 10$ and 9 are consistent with a decrease of one in the vibrational quantum number, produced by a nitrogen - helium collision.

In pure nitrogen, $v' = 6$ was strongly enhanced at low pressures, the enhancement decreasing with increasing pressure. This was explained on the basis of nitrogen - nitrogen collisions causing a loss of one quantum of vibrational energy ($v' = 6 \rightarrow 5$). This mechanism would decrease the ratio N_6/N_5 and increase the ratios N_5/N_4 and N_7/N_6 . The fact that the curves in fig.25 behave in this way is added evidence in favour of this mechanism.

c) Dependence on Total Pressure.

Tyte concluded from his measurements on the second positive system that it was the total pressure rather than the constituents that determined the population distribution and hence the effective vibrational temperature of the excited state. It would appear from the above observations and discussion that this is not entirely true for the first positive system.

Examination of tables 32, 33 and 34 shows that in general, for a given total pressure, the relative populations of the vibrational levels were independent of the composition of the mixture. There were a few

exceptions to this for 100% nitrogen (no helium) and also when the percentage of nitrogen in the mixture was very small. Fig.27 shows the variation with the total pressure of the relative populations of several levels for all conditions used in the experiments. In all cases, the points for the helium nitrogen mixtures appear to lie on one curve while those representing pure nitrogen show a definite deviation from this curve, especially at high pressures. The deviation is more marked for some levels than for others.

The current used for the experiments in pure nitrogen was 50 ma, whereas that used for the nitrogen helium mixture was 40 ma. Examination of the tables shows that the relative populations hardly vary with the current, so a direct comparison of the two sets of results is valid.

6. Comparison of Populations with Previous Results.

Populations were calculated from the experimental results of all the workers mentioned in connection with the intensity ratios in table 38. The results are shown in table 43, the numbers of the columns referring to the same experiments as those listed in connection with table 38. Plots of some of these distributions are shown in fig.28.

Considering the differences in discharge conditions, the agreement between all the laboratory plots is very good. The enhancement of $v' = 11$ can be seen for both Elliott and Cameron's (1934) sources while $v' = 6$ appears enhanced in the D.C. discharges of Elliott and Cameron (1934) and Tawde and Patankar (1944,1947). Turner and Nicholls' (1954a) experiment was the only one for which bands with $v' = 0$ and 1 were observed and the plot for this experiment shows a maximum at $v' = 1$, consistent with a direct electron excitation mechanism. All the points for $v' = 0 - 6$ on this plot lie well below the theoretical curve, a feature not observed in the present

experiments in pure nitrogen. As the discharge conditions were different and the processes occurring in a discharge are known to be complex, some differences are to be expected.

Both the auroral distributions fit quite well the theoretical curve for direct electron excitation from the ground state at a temperature of 2000°K . Benesch, Vanderslice and Tilford (1966b) have recently performed calculations on excitation rates to the levels of the $\text{C}^3\pi$ state, the upper state of the second positive system. They have fitted their results to several auroral distributions and found that the intensity measurements of Broadfoot and Hunter (1964) on the 2nd positive system led to a temperature of 2000°K for the ground state. This particular set of intensity measurements was picked out as it was the only instance in which a band with $v' = 3$ was measured. Previously, only those with $v' = 0, 1$ and 2 had been measured and the addition of the extra level enabled a more definite determination of the distribution to be made. As the calculations for the first and second positive systems led to the same temperature and there was very little deviation of the measured points from the calculated curve, it would appear that the auroral spectrum of the N_2 1st and 2nd positive systems can be explained satisfactorily on the basis of direct electron excitation.

At lower v' , the results of Petrie and Small show some deviation from the curve and these deviations are similar to those observed in the present experiments at low nitrogen pressures.

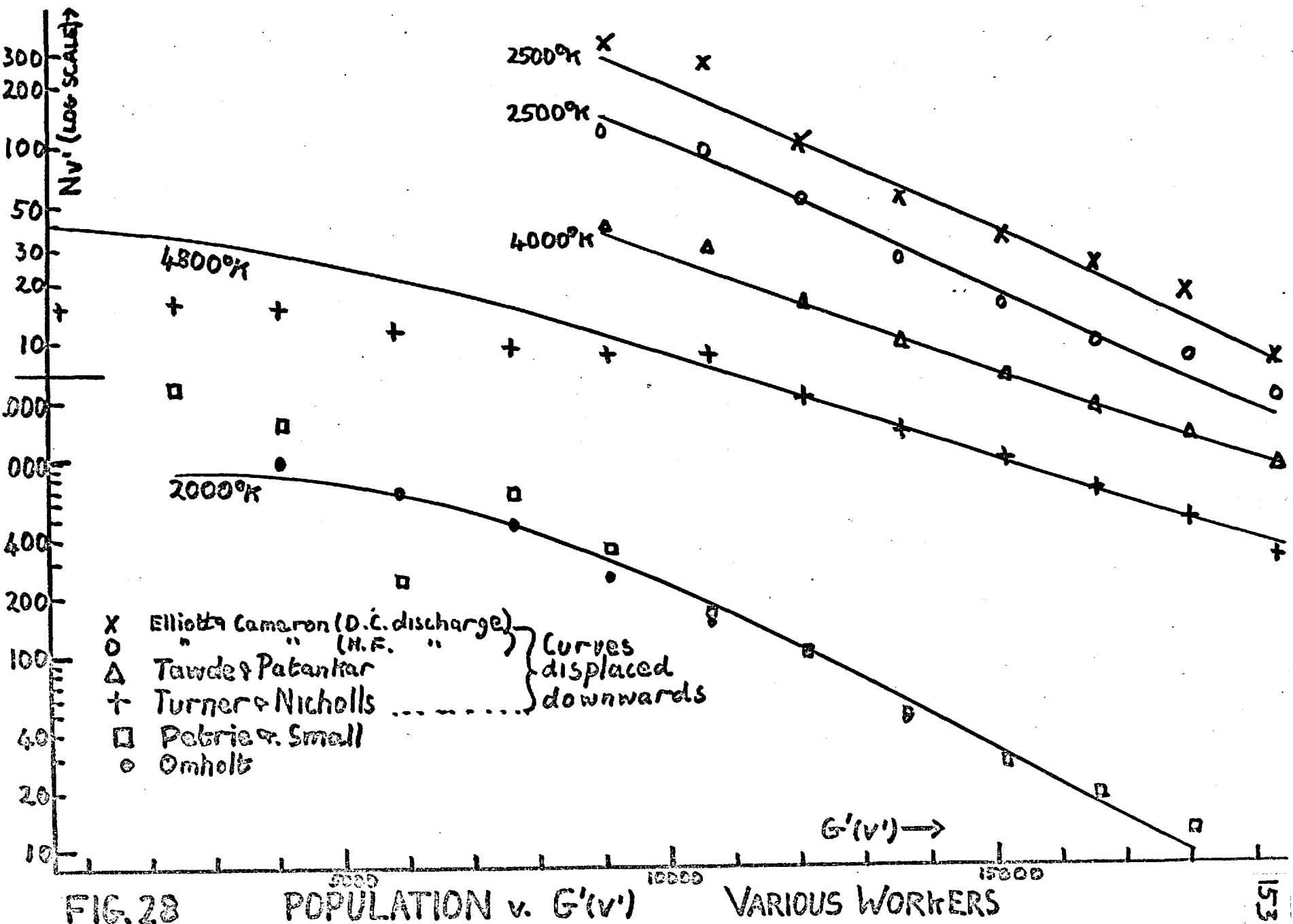
7. Energy Exchange in Collisions between Nitrogen Molecules.

There are several metastable nitrogen states, apart from the ground state that lie below some or all of the vibrational levels of the $\text{B}^3\pi$

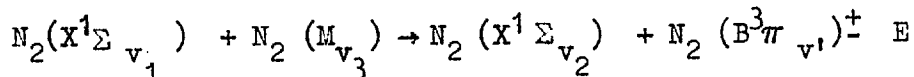
TABLE 43

Comparison of Relative Populations From Various Experiments

v'	Elliott & Cameron			Tawde & Patankar		Turner & Nicholls	Petrie & Small	Omholt
	1	2	3	4	5	6	7	8
0						294		
1						307	2275	
2						291	1545	965
3						220	243	670
4						181	665	441
5		319	224	247	232	167	333	241
6		251	177	195	198	162	160	143
7		100	100	100	100	100	100	100
8		54	50	64	59	68	47	46
9		33	30	42	41	49	27	
10		24	19	30	29	33	18	
11		17	16	21	21	24	12	
12		8	10	15	15	15		



state. Three such states together with approximate radiative lifetimes are $A^3\Sigma(0.1 \text{ sec})$, $a'^1\Sigma(10^{-3} \text{ secs.})$ and $a^1\pi(10^{-4} \text{ secs.})$. Collisions between molecules in one of these states and a ground state molecule therefore seem quite probable. It is therefore possible that one such collision might selectively populate one of the levels of the B state by the process



where M represents a metastable state and E is the energy difference between the two sides. The probability, P, of the process occurring will depend on

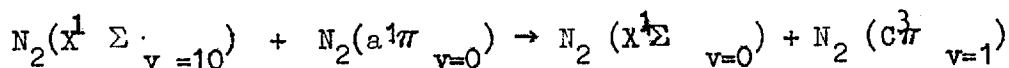
- 1) The populations of the states $X^1\Sigma_{v_1}$ and M_{v_3} . As the populations of the lower levels are usually greater than those of higher levels, P will be larger for low v_1 and v_3
- 2) The value of E.

Collisions are most likely for near resonance conditions i.e. when $E \sim 0$. P will be greatest when $E \sim 0$ and fall off as E increases.

- 3) The lifetime, τ , of the metastable state.

P will be greater for larger τ

Tyte (1962a) proposed the following mechanism to explain the observed enhancement of the $v' = 1$ level in the second positive system.

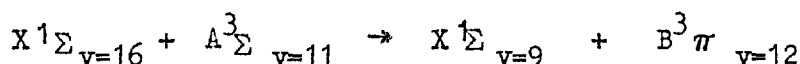


$E = 15 \text{ cm}^{-1}$ so, energetically, the process would seem probable.

There would also appear to be an appreciable population of the initial states.

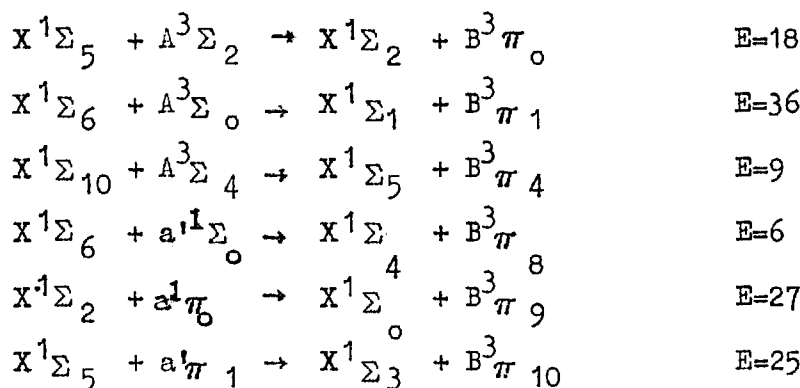
An examination of all possible collisions between ground and metastable state molecules was performed to see if any would populate the $B^3\pi$ state. All those for which $E < 100 \text{ cm}^{-1}$ were noted and it was found that

there were about 500 possible processes. Most of these could be discarded on the grounds of lack of population of the initial states. One such process was



In this case $E = 0$, but it was unlikely that there would be appreciable populations of either initial state and the probability of such a collision occurring must be negligible.

Some of the more probable collisions were



There were many other similar processes.

In order to determine the relative probabilities of these processes information is needed on the populations of all the states involved and also the relationship between P and E . Using the lifetime criterion, collisions between $X^1\Sigma$ and $A^3\Sigma$ would seem most likely and a collision could be found to populate each level of the B state. For the other collisions $X^1\Sigma + a'^1\Sigma$ and $a'^1\pi$, only the higher B levels are populated. The overall effect would be a slight enhancement of the higher levels but it is not thought that this would be significant. It does not appear that this mechanism can account for the large observed enhancements in the first positive system. The energy values used in

these calculations were taken from Benesch et.al. (1965).

B. Conclusions and Suggestions for Further Work.

The first point to emerge from this work was the extremely important part the arrays of Franck Condon factors play in this type of research. It has been demonstrated how two different arrays, calculated in different ways, can cause very large differences in the calculated transition moment variation and population distribution. As the latter is used in determining the processes occurring, it is vital that the Franck Condon factors should be accurate. Great care was taken that none of the observed effects was due to bad q values. The arrays of Zare et.al. (1965) and Benesch et.al. (1966b) both fitted the experimental data equally well and it was concluded that their accuracy was good.

The investigation into variation of intensity ratios was not very conclusive. The variations appeared consistent and it was shown that they could possibly be explained on the basis of distortion of the molecule, indicating that the 'isolated molecule' model used in the theory is not valid under all conditions. As the observed variations often lay within the experimental errors and the theoretical model used for comparison was very crude, the results only indicated possibilities. An investigation using a far wider range of currents and pressures is needed before any degree of certainty can be attached to the findings. The variations previously observed for the second positive system were much larger than those for the first positive. This is another point in favour of the distortion theory as when the molecule is in the $C^3\pi$ state, the outer electron orbit is further out than that for the $B^3\pi$ state, and would therefore be more susceptible to

distortions.

The examination of the relative populations of the excited levels demonstrated the complexity of discharge processes. From the variation of the distribution with conditions it has been possible to suggest mechanisms to explain some of the observed effects.

Extensive calculations were performed in order to produce theoretical population distributions for comparison with experiment. All the results indicated that the main process populating the $B^3\pi$ state was excitation by direct electron impact with ground state molecules. Other processes were suggested which probably played a minor role and some evidence was presented for this. The two step process of Nicholls (1948) may also be appreciable but there was no way of investigating this quantitatively.

There are many possibilities for future work. The continued estimation of Franck Condon factor arrays for other band systems would be of value. It would also be worthwhile extending the experiments on the first positive system to cover the infra red region. This would enable bands with $v' = 0$ and 1 to be measured. An investigation at higher pressures than those used in the present experiments would indicate whether the trends observed, both as regards intensity ratios and collision processes, continued as expected or whether some other processes were taking place. In order to gain a greater insight into the processes occurring, it would be of interest to examine several band systems simultaneously, as only by having an overall picture of the transitions occurring can one hope to obtain a more complete picture of the excitation and de-activation processes.

All the theoretical calculations performed were dependent on assumptions about the distribution of molecules in the ground state. If this distribution could be determined experimentally then the observations could be interpreted with greater certainty. Unfortunately this would prove extremely difficult. Intensity measurements on systems involving the ground state (Vegard-Kaplan, Lyman-Birge-Hopfield etc.) would yield little as these transitions are all forbidden and form only a small fraction of the processes populating the ground state. Radiative transitions between the vibrational levels of the ground state would yield the populations, but these are forbidden transitions and it is doubtful whether they could be observed with sufficient intensity. The only other possibility is to set up a very intense continuum source behind the discharge and try and obtain absorption bands of ground state transitions. This would be a difficult experiment to perform accurately.

Another interesting experiment would be a systematic investigation into the effects of all the rare gases on the nitrogen band systems. In chapter 1 the possibility was mentioned of energy exchange between unexcited nitrogen molecules and metastable rare gas atoms producing selective enhancement of some nitrogen bands. A systematic quantitative investigation would give more insight into this type of process. This could also help in determining whether the enhancement of the ion spectrum in helium is a result of the energetics of nitrogen-helium collisions, or whether the helium just reduces the diffusion of the ions to the walls of the tube. During this investigation, the examination of collision processes and variations with conditions could be extended to the other rare gases and

this may lead to determining the dependence of the observed processes on the mass of the colliding particles.

Finally, further development of computer programmes for use in this kind of work would be very useful. Without the use of a computer, it would have been impossible to perform many of the calculations, and the production of a library of computer programmes for use in analysis of intensity measurements would be extremely valuable.

CHAPTER 7.OXYGEN SECOND NEGATIVE SYSTEM.1. Classification of Bands.

The O_2^+ second negative system results from a ${}^2\Pi - {}^2\Pi$ transition, the upper state being Hund's case b and the lower state case a. It is a system of red-degraded double-headed bands, the separation of the heads of a $v' \rightarrow v''$ transition being 200 cm^{-1} . The system extends from 1900 to 6500 Angstroms.

The bands were first observed by Johnson (1924b) who identified them and measured them in the region 2318 to 4403 Angstroms. The system was further extended by Ellsworth and Hopfield (1927), Mulliken and Stevens (1933), Lal (1948), Feast (1950a) and Byrne (1961). Rotational analyses on several of the bands have been performed by Stevens (1931) and Bozoky (1937). A fairly comprehensive list of band - head wavelengths has been published by Wallace (1962).

Johnson analysed the system and found that it could be represented by the Deslandres formula

$$\nu = \frac{1620}{1420} + 16.945 p^2 - 13.37 m^2 \quad 7.1.$$

Birge (1925) assigned a $v' - v''$ scheme to the system and computed the constants producing the following formula used by Ellsworth and Hopfield.

$$\nu = \frac{38308}{38108} + (887 v' - 13.4 v'^2) - (1859.9 v'' - 16.53 v''^2). \quad 7.2$$

Johnson's assignments fall into the general vibrational scheme if we put

$$v' = 33 - m \quad \text{and} \quad v'' = 55 - p$$

The above formula (7.2.) gave quite large deviations between the observed and calculated values of ν , and Feast in his calculations, used constants given by Jevons (1932), producing the formula

$$\nu = \frac{38596}{38796} + [898.9(v' + \frac{1}{2}) - 13.7 (v' + \frac{1}{2})^2] - [1876.4(v'' + \frac{1}{2}) - 16.53(v'' + \frac{1}{2})^2] \quad 7.3$$

This gives far better agreement between observed and calculated values than the previous formula.

It was noted during the course of the investigation that there were several discrepancies in the assignments and wavelengths of some of the bands as measured by different workers. It was therefore thought worthwhile to compute the expected wavenumbers for all the bands in the system using the formula 7.3. These were then compared with the experimental values from the above references and table 44 was compiled giving the best values obtained so far for each band.

During the course of the present experiment, several bands were observed which had not been previously identified. The wavelengths were measured using the helium lines on the spectrogram as standards, and quantum numbers were assigned. The accuracy was not too good because of the wide slit used.

Comments on Table 44.

Wallace's table contains the most complete and up to date list of the band head wavelengths, being compiled from all the above references with the exception of Byrne. Byrne's results have been added, and several additions and alterations have been made to the table. These are outlined

below.

- a. 2318.7 ^{λ} This band was assigned the values $p = 55$, $m=27$ by Johnson i.e. $v' = 6$ $v'' = 0$. Ellsworth and Hopfield later measured the 6,0 band at 2317.9 Å and the 2318.7 Å band has been assigned the values $v' = 9$, $v'' = 1$ which fits the calculated value more accurately.
- b. 2526.8 This band was in Lal's table. It was ~~not~~ marked as new but it had not been previously recorded.
- c. 2602.6, 2602.9 These have been interchanged as they fit the calculated values more accurately.
- d. 2688.5 This was measured and identified by Johnson. The wavelength given in Wallace must be a misprint.
- e. 2703.2 This was measured in the present experiment. Previously the 3,2(ii) and the 5,3 (i) bands had been given the same wavelength. The plate shows clearly that the two bands are separated and the present value gives good agreement with that calculated for the 3,2 band.
- f. 2806.1 This was measured by Johnson but not assigned any quantum numbers. The assignment given here is backed up by the fact that the second head for this band was observed at 2821.0 Å
- g. 2877.3 This band was measured by Feast. It corresponds more closely to the calculated value than Johnson's measurement which was used by Wallace.

	λ	
h.	2962.0	Previously measured at 2963.4 by Lal. The present value is closer to the calculated one.
i.	2980.0	New band, see plate 1a.
j.	3143.0	Previously measured at 3141.0. The 3143.0 band corresponds more closely in wavelength and intensity to the 1,4 band. The 3141.0 band also appears and fits the assignment 5,6 (i)
k.	3127.9, 3148.1	Previously measured by Lal as 3130.0 and 3149.0 on a smaller spectrograph. Present measurements give better agreement with calculated values.
l.	3277.2	New band, see plate 1a.
m.	3700.5	Wallace gives Johnson's value 3701.2. Feast's is closer to calculated value.
n.	4219.1	Measured by Johnson but left unassigned. Band measured and identified by Byrne at 4218.0 was probably same band. Johnson's wavelength agrees better with calculation.
o.	4820	Given by Wallace as 4826. Probably a misprint.
p.	5154.8	Measured by Byrne. Given by Wallace as 5143 Å.

None of Byrne's results appear in Wallace's table and several of them have been reassigned different quantum numbers from those originally given by Byrne.

q.	2548.1	Given as 11-5 band. Present assignment gives better agreement with theory.
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- r. λ 5736.1 Given as 1-13 band, but discrepancy with theoretical value is too large. No reasonable assignment was found.
- s. λ 6433.0 Given as 3-16 band, but 0-14 fits the values more
6531.8 closely.

In addition to the above, there are large differences between observed and calculated wavenumbers in most of Lal's measurements. This is probably because he used a small spectrograph and his assignments are probably correct.

There are still several bands which Johnson measured but for which no quantum numbers have been found. A thorough check on the expected wavenumbers of bands of the system has so far failed to reveal a way in which these bands may be fitted into the system.

TABLE 44

Band Heads of the O_2^+ Second Negative System						
λ (Observed)	Intensity	ν (Observed)	ν (Calculated)	ν'	ν''	Ref
1942*		51493	51420	23	0 1	6
1956*		51125	51152	22	0 1	
1966*		50865	50885	21	0 1	
1977*		50582	50532	20	0	
1985*		50378	50332	19	0 1	
1991.5		50213	50181	18	0	
2005.9		49837	49803	17	0	
2013.7		49644	49603	16	0	
2022.0		49440	49397	15	0	
2029.9		49248	49197	14	0	
2039.8		49009	48964	13	0	3
2048.1		48810	48764	12	0	
2059.7		48536	48503	11	0	
2068.3		48334	48303	10	0	
2080.0		48042	48016	9	0	
2090.3		47824	47816	8	0	
2103.7		47520	47500	7	0	
2112.2		47329	47300	6	0	
2128.4		46969	46958	5	0	
2138.6		46745	46758	4	0	
2155.3		46383	46387	3	0	2
2164.0		46197	46187	2	0	
2183.9*		45789	45790	1	0 1	
2213.8*		45172	45165	0	0	
2224.4*		44957	44965	11	1	
2243.5		44559	44544	10	0 1	
2252.8		44375	44344	9	0	
2246.9*		44505	44513	8	0	
2275.3*		43949	43947	7	0	
2285.8*		43749	43747	6	0	
2281.3*		43835	43833	5	0	1a
2291.8*		43633	43633	4	1	
2307.2		43329	43322	3	0	
2318.7		43114	43122	2	0	
2317.9	1	43129	43126	1	0	
2328.7		42929	42926	0	0	
2343.3	1	42662	42669	10	1	
2354.3	1	42462	42469	9	1	
2371.8		42149	42136	8	2 1	
2381.0	3	41986	41990	7	1	
2392.6	3	41783	41790	6	1	1
2421.8	2	41279	41283	5	1	
2433.5	3	41081	41083	4	2	
2446.9	1	40856	40859	3	2	
2458.6	1	40661	40659	2		

TABLE 44(Continued)

λ (Observed)	Intensity	ν (observed)	ν (Calculated)	ν'	ν''	Ref.
2465.8	2	40543	40548	5	1	1
2478.0	4	40343	40348			
2488.3	6	40176	40179	7	2	
2500.6	6	39978	39979	4	1 i	
2512.9	3	39783	39786	4	1 ii	4b
2526.8		39564	39586	6	2	1
2532.8	6	39470	39472			
2545.5	7	39273	39272	11	4	6q
2548.1		39233	39212			5
2562.5	2	39013	39012	3	1	4
2564.0		38990	38997			
2577.6		38784	38797	5	2	1
2581.0	8	38733	38738	10	4 i	
2594.3	8	38535	38538	10	4 ii	4&6c
2588.9	4	38615	38615	7	3 i	5c
2602.6	4	38412	38415	7	3 ii	4
2602.9		38407	38402	2	1	
2617.3		38196	38202	4	2	1
2617.3		38196	38180	6	3	
2630.7		38001	37980	8	4	5
2632.7	6	37973	37976	3	2 i	
2646.7	6	37772	37776	3	2 ii	7e
2652.3	4	37692	37695	5	3	1
2666.5	4	37491	37495	2	2	
2677.8	1	37333	37338	4	3	1
2691.5	1	37143	37138	8	5 i	
2688.5		37184	37187	8	5 ii	7f
2703.2		36982	36987	3	3	1
2705.3	7	36954	36961	7	5 i	
2720.0	7	36754	36761	7	5 ii	5g
2749.1		36365	36370	2	3	1
2763.0		36182	36170	4	4	
2761.9	7	36196	36199	8	5 i	f
2776.7	7	36003	35999	8	5 ii	
2806.1		35626	35627	3	3	1
2821.0		35438	35427	7	5 i	
2823.7	9	35404	35409	7	5 ii	5g
2839.7	9	35205	35209	2	3	1
2861.0	3	34943	34947	4	4	
2877.3	5	34745	34747	6	5 ii	5
2890.3	7	34588	34593	1	3 i	7h
2907.1	5	34388	34393	1	3 ii	
2901.9	7	34450	34455	3	4 i	1
2919.8	8	34239	34255			
2937.1	2	34037	34040			1
2962.0		33751	33749			
2980.0		33547	33549			1
2970.0	7	33660	33665			
2987.5	8	33463	33465			

TABLE 44 (Continued)

λ (Observed)	Intensity	ν (Observed)	ν (Calculated)	ν'	ν''	Ref.
3005.0	2	33268	33269	7	6	5
3022.8	2	33072	33069	2	4	1
3043.6	8	32846	32849	4	5	4
3062.8	8	32640	32649	6	6	5
3052.5		32750	32743	8	7	
3071.3		32550	32543	1	4 i	1
3070.0	5	32563	32562	1	4 ii	7j
3088.7	5	32367	32362	5	6 i	1
3096	2	32290	32304	3	5	7k
3113.6	2	32108	32104	7	7 i	5
3123.1	5	32010	32004	2	5	1
3143.0	5	31808	31804	0	4	
3141.0		31828	31827	11	9 i	5
3127.9		31961	31954	8	8 i	
3148.1		31756	31754	8	8 ii	7l
3160.7		31629	31624	1	5	1
3210.8	8	31136	31137(3)	3	6 i	4
3231.2	8	30939	30933(7)	5	7	5
3225.8		30991	30988	7	8 ii	
3257.6		30689	30692	2	6	1
3277.2		30505	30492	0	5	
3300.3	6	30292	30293	10	10 i	5
3322.6	6	30088	30093	1	6	1
3303.9		30259	30276	9	10	5
3312.7		30178	30182	2	7	1
3334.2		29984	29982	0	6	
3353.5	3	29811	29812	2	7	1
3393.1	4	29463	29459	8	10 i	5
3416.2	2	29264	29259	3	8 i	5 m
3397.8	8	29422	29422	3	8 ii	
3421.2	8	29221	29222	1	7	1
3465.9	1	28844	28844	0	6	
3494.2	7	28611	28615	9	10	5
3517.7	8	28420	28415	2	7	1
3542.0	4	28225	28219	0	6	
3567.7	4	28021	28019	8	10 i	5
3594.5	2	27812	27814	3	8 i	
3620.1	2	27616	27614	3	8 ii	
3603.7	7	27741	27744	1	7	1
3629.8	8	27542	27544	0	7	
3653.0	2	27367	27367	8	10 i	5
3700.5		27016	27019	3	8 i	
3727.5		26820	26819	3	8 ii	
3706.6	8	26971	26970	1	7	1
3733.9	8	26774	26770	0	7	
3830.5	8	26099	26099	5	10	5
3859.5	8	25903	25899	3	9	
3929.0	7	25445	25446(0)	1	8	6
3959.4	6	25249	25240(6)			
3943.6		25350	25358			
3972.0		25169	25158			

TABLE 44 (Continued)

λ (Observed)	Intensity	ν (Observed)	ν (Calculated)	ν'	ν''	Ref.
4050.1		24604	24604	4	10i	6
4059.9		24624	24624	2	9	
4092.0		24431	24424			
4082.4	8	24488	24487	0	8	1
4115.8	8	24290	24287			
4182.2		23904	23895	3	10 i	6
4219.1		23695	23695	3	10ii	1n
4237.0		23595	23589			
4271.8		23403	23389	11	14	6
4313.4		23177	23171	4	11	
4351.0		22977	22971			
4331.5		23080	23078	2	10i	2
4363.1		22913	22908	0	9	
4399.4		22724	22708			
4466.5		22383	22382	3	11i	6
4495.9		22236	22234	1	10	
4536.3		22038	22034			
4636.5		21562	21565	2	11i	3
4679		21368	21362	0	10	
4721		21177	21162			
4760	3	21003	21007	5	13	5
4803	3	20815	20807			
4783.8		20898	20902	3	12i	6
4820		20714	20721	1	11	o
4878		20496	20521			3
5035		19855	19850	0	11	5
5086		19655	19650			
5102		19595	19593	5	14i	
5154.8		19394	19393	5	14ii	p
5308.6		18832	18831			6
5364.2		18637	18631	4	14	
5443		18367	18370			
5498		18182	18170	0	12	3
5678		17606	17595	1	13i	6r
5729.1		17450	17451	4	15i	
5736.1		17429				
6103		16381	16381	1	14i	3
6433		15541	15510			6s
6531.8		15305	15310	0	14	

References:

1. Johnson
2. Ellsworth & Hopfield
3. Mulliken & Stevens
4. Lal
5. Feast
6. Byrne
7. Measurements obtained in present experiment

The letters in the reference column refer to the comments on the previous pages.

* denotes vacuum wavelengths.

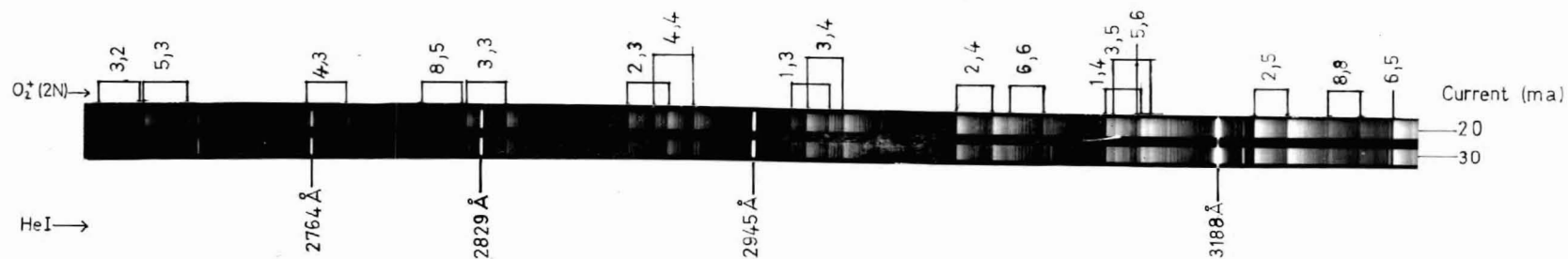


PLATE Ia

0.005 mm. Oxygen

1.0 mm. Helium

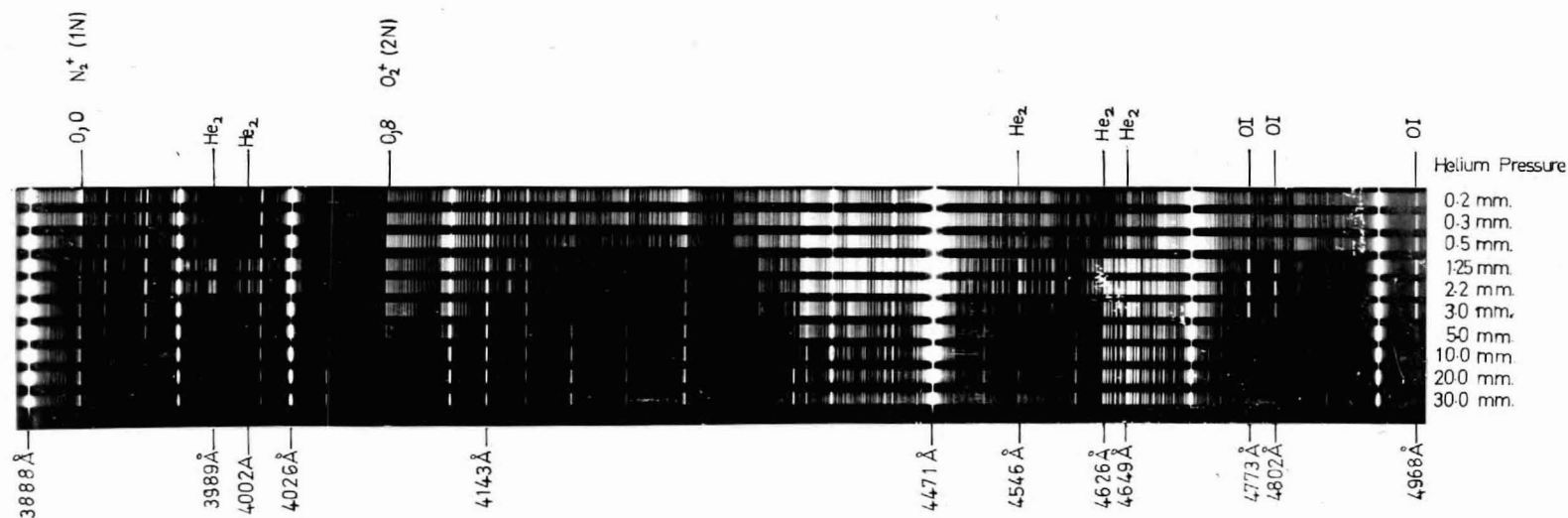


PLATE Ib

0.01 mm. Oxygen

50 mamps

2. Variation of Intensities with Conditions.

a. Introduction.

In chapter 1 it was mentioned that the second negative system is not very suitable for accurate intensity measurements. The two main difficulties are caused by overlapping of the bands and calibration.

Every band in the system is overlapped to some extent by a neighbouring band. It was hoped that cooling the tube would cut this down sufficiently to enable accurate intensity measurements to be made. On examining the plates and microphotometer traces obtained it was found that the decrease in the rotational structure brought to light several more bands that in 'hotter' sources had been masked by the rotational structure of the stronger bands. There was still enough overlapping to make intensity measurements unreliable. The system was only excited with any intensity when there was helium present and further difficulty was caused by the strong emission of the helium spectrum in the same region. It would be possible to make a reasonably accurate analysis by using a high dispersion instrument, measuring individual rotational lines and applying the method of Robinson and Nicholls (1961) for overlapped bands. Unfortunately, there was not sufficient time to perform this investigation and it was decided to obtain a qualitative idea of the variations with conditions as a preliminary to future quantitative investigations.

The second difficulty arose because the emission from the tungsten lamp was very weak below about $3000 \text{ \AA}$ making calibration difficult below this wavelength.

b. Experimental

The apparatus was the same as that used in the investigation on the

nitrogen first positive system. The oxygen was taken from a commercial cylinder.

Two sets of experiments were performed, one using the quartz optics of the spectrograph and slit width of 0.08 mm. This helped to blend together the rotational lines so that the microphotometer traces obtained from the plates gave an indication of the integrated intensities of the bands. The plates (Zenith Astronomical) were exposed for 3 minutes in the region $2700 \text{ \AA} - 4100 \text{ \AA}$. In the second set of experiments the glass optics were used in the range $3800 \text{ \AA} - 5000 \text{ \AA}$ with a slit width of 0.03 mm. This enabled more detailed features, such as rotational structure, to be observed. Zenith Astronomical plates were again used and exposed for 15 minutes.

c. Variations with Current

Four plates were taken corresponding to experiments in which the pressures of oxygen and helium were kept constant and the current varied. The pressures were 0.005 mm., 0.01 mm., 0.05 mm., and 0.1 mm. of oxygen with, in each case, 1 mm. of helium. For the two lowest oxygen pressures, the intensities of the bands appeared to decrease with increasing current after a slight increase at the lowest currents used (10 to 20 m.a.) whereas, at the two highest pressures, the intensities increased with current. At all oxygen pressures the helium line spectrum appeared strongly and at 0.005 mm. oxygen, the He_2 bands also appeared very bright. There were slight traces of nitrogen impurity (2nd positive and 1st negative) and, in all cases, these bands behaved in exactly the opposite way to the oxygen bands.

d. Variations with Helium Pressure.

The variation in intensities of the oxygen bands with increasing helium pressure was similar to the corresponding variation observed in the nitrogen first positive bands (chapter 6). The intensities increased initially then decreased as the helium pressure was increased further. The nitrogen impurity bands behaved in exactly the opposite fashion indicating the influence the presence of oxygen has on the nitrogen spectrum. Plate 1b was taken with the glass optics and shows the variation with helium pressure at 0.01 mm. oxygen and a current of 50 m a. The main feature of interest is the difference in appearance of the spectrum at 1.25 mm. and 2.2 mm. helium caused by the sudden appearance of the He_2 molecular bands and the oxygen lines at $4773 \text{ \AA}$, $4801 \text{ \AA}$ and $4968 \text{ \AA}$. The helium bands at $3989 \text{ \AA}$, $4002 \text{ \AA}$ and $4546 \text{ \AA}$ almost disappeared at the other pressures whereas those at $4625 \text{ \AA}$ and $4648 \text{ \AA}$ still remained strong. The oxygen lines mentioned above were also extremely weak at other pressures. The opposite behaviour of the nitrogen and oxygen bands is best illustrated by the $(0,0) \text{ N}_2^+$ 1st negative band at $3914 \text{ \AA}$ and the $(0,8) \text{ O}_2^+$ 2nd negative band at $4082 \text{ \AA}$. On a plate taken using the quartz optics and extending further into the ultraviolet region, several more He_2 bands appeared under the same conditions as above, only those at $3665 \text{ \AA}$ and $3676 \text{ \AA}$ remaining at higher helium pressures. Table 45 lists the OI lines and He_2 bands which appear strongly at the above pressures together with the details of the transitions. It was observed that the helium bands remaining at higher pressures belong to the same series whereas all the others belong to other series.

TABLE 45

Strong OI lines and He₂ Bands Appearing at 0.01mm. Oxygen + 1.25mm.
and 2.2mm. Helium.

$\lambda(\text{\AA})$ (approx.)	Transition	Comments
<u>OI Lines</u>		
3947	$3^5S^o-4^5P$	Fairly strong at low He pressures. Vanish at high He.
4368	$3^3S^o-4^3P$	Strong-low He. Weak-high He.
4772 4773	$3^5P-7^5D^o$	} Very weak - low He. Strong - 1.25mm., 2.2mm. He. Vanish - high He.
4801 4802	$3^5P-8^5S^o$	
4968 4969	$3^5P-6^5D^o$	
<u>He₂ Bands</u>		
3665 3676	$i^3\Pi_g-a^3\Sigma^+_u$	} Very strong - 1.25mm., 2.2mm. He. Weaker - higher He.
4625 4648	$e^3\Pi_g-a^3\Sigma^+_u$	
3356 3777 3989 4001 4158 4546	$1^3\Pi_g-a^3\Sigma^+_u$ $q^3\Sigma^+_u-b^3\Pi_g$ $m^3\Sigma^+_u-b^3\Pi_g$ $k^3\Sigma^+_u-b^3\Pi_g$ $l^3\Sigma^+_u-b^3\Pi_g$ $h^3\Sigma^+_u-b^3\Pi_g$	} Only appear at 1.25mm., 2.2mm. He.

Several other weak He₂ bands appeared at 1.25mm. and 2.2mm. He.

Some plates were taken in which the O_2^+ 1st negative bands appeared. As far as could be observed, the variations with conditions appeared similar to those observed for the 2nd negative system.

3. Theoretical Intensity Distribution.

Table 46 shows the expected intensity distribution for the 2nd negative system. A temperature of the upper state of $1000^{\circ}K$ has been assumed, equation 3.14 was used and the q values of Nicholls (1965a) were taken as the band strengths.

Using $q_{v', v''}$ instead of $S_{v', v''}$ would appear reasonable in the present case. Robinson and Nicholls (1958) measured integrated intensities of the bands in the system and, adopting the usual procedure, derived the following variation of the transition moment.

$$R_e(\bar{r}) = \text{const.} \times (-1 + 1.5386 \bar{r} - 0.5872 \bar{r}^2) \quad 7.4.$$

A glance at the diagram in their paper shows that the experimental points all appear to fall within a range of about 20%. Considering the nature of the band system, the expected errors would be of that order and the use of $q_{v', v''}$ instead of $S_{v', v''}$ would appear to be a reasonable approximation. The only Franck Condon factors available have been calculated by Nicholls (1965a) using a Morse potential and it is possible, as with the N_2 first positive, that some of them ~~may~~ be in error. This would affect the calculated values of $R_e(\bar{r}_{v', v''})$.

The intensity ratios, calculated from equation 3.18, are listed in table 47 together with those calculated from Robinson and Nicholls' (1958) results. For several of the ratios, the agreement between experiment and theory is very good. Where large deviations occur, they could be due to either experimental errors or inaccurate Franck Condon factors.

TABLE 46

Predicted Intensity Distribution in the Oxygen Second Negative System											
$v' \backslash v''$	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
0	0	0	1	8	25	57	100	138	155	141	105
1	0	1	8	28	67	113	134	109	55	10	0
2	0	3	17	50	92	108	75	22	0	14	28
3	0	6	27	63	85	62	16	0	17	23	8
4	1	10	34	62	57	20	0	12	19	5	0
5	1	13	36	49	28	2	6	16	6	0	6
6	2	15	34	33	9	0	11	8	0	4	4
7	3	15	28	19	1	4	9	1	1	4	0
8	3	14	21	9	0	6	5	0	3	2	0
9	3	13	15	3	1	6	1	0	3	0	1
10	3	11	10	0	2	4	0	1	1	0	1

TABLE 47

Intensity Ratios of Oxygen Second Negative Bands.

<u>Ratio</u>	<u>Predicted</u>	<u>Experimental</u> (Robinson & Nicholls)
0,5/0,6	0.57	0.88
0,7/0,6	1.4	1.1
1,4/1,5	0.60	0.45
1,6/1,5	1.2	0.9
1,7/1,5	0.98	0.75
2,3/2,5	0.47	0.46
2,4/2,5	0.86	0.90
2,7/2,5	0.21	0.20
3,4/3,3	1.34	0.99

4. Conclusions.

The work on the intensity variations in oxygen was purely observational and serves mainly as a guide for future research. The main feature of interest was the sudden appearance of He_2 bands and OI lines on plate 1b. A systematic investigation of this effect together with intensity measurements of the O_2^+ 2nd negative bands, preferably at higher dispersion, should give some insight into the processes taking place. It would also be of use to compute Franck Condon factors for the system using an RKR potential and numerical methods and compare with the values obtained by Nicholls (1965a). The two sets of values could then be assessed in a similar way to that used for the N_2 1st positive system.

CHAPTER 8.

COMPUTATIONAL PROCEDURE.

1. Introduction

The calculations involved in analysing the experimental results are very simple in nature but had to be performed many times for various experimental conditions. In order that the amount of data obtained should not be limited by the time necessary to perform the calculations, it was decided to make use of the computer facilities available. Several programmes have been written in Fortran IV for processing on an IBM 7090 computer. These covered all the calculations necessary for a complete analysis of the experimental results. This has made it possible to make far more experimental observations than would otherwise have been feasible. In addition to speeding up the analysis of experimental data, several theoretical calculations have been performed which it would otherwise have been impossible to carry out in the time. It was necessary to check each programme carefully before use but, once this had been done, all the computations could be guaranteed accurate. An account of all the programmes written is given below.

2. General Programmes.

There were several programmes involving standard mathematical procedures which were used regularly.

Programme 1-Curve Fitting:

This programme used the method of least squares to fit a polynomial of any degree to a set of points. Part of the routine involved matrix

inversion and a standard inversion subroutine was obtained from the programme library.

Programme 2-Graph Plot.

This was a standard library subroutine which scaled and plotted any set of data.

3. Transition Moment Calculations

Programme 3 recalculated Turner and Nicholls' (1954b) results using different arrays of Franck Condon factors and printed out the results obtained in table 3.

Programme 4 took the output from programme 3 and performed the scaling procedure outlined in Turner and Nicholls' paper. The programme was checked by using the results from Turner and Nicholls' table I as input and comparing the output with their table III. It was in checking this programme that the error mentioned in chapter 4 was observed.

Programme 5 used the output from programme 4, the r-centroids, and programme 1 to fit a polynomial of specified degree to give $R_e(\bar{r}_{v',v''})$ in terms of $\bar{r}_{v',v''}$. Once again, this was checked first using all Turner and Nicholls' data.

4. Reduction of Experimental Results.

Programme 6- Calibration.

The process making photographic photometry far more laborious than the photoelectric method is the calibration of the plates and the production of intensities from the calibration curves. In order to cut down this labour an attempt was made to fit a polynomial to the graph of intensity against area. The polynomial was of the form.

$$I_0 = a_0 + a_1 \Lambda + a_2 \Lambda^2 \dots$$

where I_0 represents the intensity on a scale of 64 (see Chapter 2), and A is the area. Second and third degree polynomials were fitted for each band and the standard deviation of the experimental points from the fitted curve was calculated. Programme 2 was used to plot the fitted curves and the experimental points so that it could be seen at a glance which polynomial was the better fit and whether it was a reasonably accurate representation of the calibration curve. It was found in most cases that the cubic fit was adequate. In the few cases where this was not so, the calibration curve had to be plotted by hand and the intensities taken from it.

Programme 7

This programme converted all the values of I_0 calculated in programme 6 into I_{band} using equation 2.5. The programme then used these values to calculate the intensity ratios, $(I\lambda^4/q)_{v'v''}$ for each band, the average $(I\lambda^4/q)_{v'}$ for each v'' progression and the vibration temperature. The latter was calculated by fitting a least squares straight line to the values of $\log_e (I\lambda^4/q)_{v'}$ and $G'(v')$ which were also plotted using programme 2.

Programme 8

This performed the same calculations as programme 7, using the band strengths, $S_{v'v''}$, in place of $q_{v'v''}$.

Programme 9

The output from programme 8 was taken together with the source conditions and fed into programme 2 which plotted all the required variations with conditions.

Programme 10

The input to this programme consisted of the values of $(I\lambda^4/q)v'v''$ from programme 7 and the r-centroids. The variation of the transition moment was then calculated using the same procedure as in programmes 4 and 5. Programme 2 was then used to plot both the experimental values of $(I\lambda^4/q)v'v''/(I\lambda^4/q)_{mn}$ and the fitted curve for each set of conditions. This facilitated the task of searching for systematic deviations of individual bands from the curve.

All the above programmes (7-10) were arranged so that the calculations could be performed using different Franck Condon factor arrays in order that comparisons could be made.

Programme 11 - Wavelength Determinations

For the O_2^+ second negative system some wavelength measurements were necessary and a programme was written to perform the calculations. The main input consisted of the comparator readings, d, and wavelengths, λ , for the standards, and the comparator readings of the unknown lines or bands together with any identifications. Polynomials for λ of successive degrees in d were fitted to the standards until one was found for which the standard deviation was less than the required accuracy which had been fed in with the input. This polynomial was then used to calculate the wavelengths of the unknown lines or bands. In order that any errors in identification of standards should not spoil the calculations, it was arranged for the programme to discard any standard for which the difference between the actual and the calculated wavelengths was greater than a certain factor (fed in with the input) multiplied by the standard

deviation. The calculation was then repeated without this line.

5. Theoretical Calculations

Programme 12 - Cascade Calculations

Tyte's values of populations of the $C^3\pi$ state of nitrogen were fed in as input and the calculations outlined in chapter 3 were performed to find the populations of the $B^3\pi$ levels expected from a cascade process. The expected intensities of the first positive bands were also calculated.

Programme 13 - Electron Excitation Calculations

This programme used the theory of chapter 3 to compute the expected populations of the $B^3\pi$ state by various electron excitation mechanisms at various temperatures of the initial state.

Programme 14 - Examination of Collisions.

The energetics of all possible collisions between metastable and ground state nitrogen molecules were examined. Collisions for which the initial and final energies balanced to within a specified amount were printed out. This programme is perfectly general in that collisions between any states of any molecule can be examined.

Programme 15

This was a short programme to calculate the expected intensity ratios using equation 3.18 and several arrays of Franck Condon Factors.

Programme 16

This was a simple short programme to calculate the wavenumbers of all bands (observed and unobserved) of the O_2^+ second negative system using equation 7.3.

Programme 17

The intensity distribution expected in the O_2^+ second negative system was computed for a specified vibration temperature of the upper state.

Nearly all the programmes used are generally applicable to any intensity calculations of this type. In their present form, they have been written to conform to the specific requirements of the work performed. They can easily be adapted to fit other band systems and it is hoped in the near future to make them more general so that they may be available for use, without amendment, with any band system.

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