

EFFECT OF AN INERT GAS ON THE INTENSITY
DISTRIBUTION ON THE ROTATIONAL COMPONENTS
OF THE NEGATIVE NITROGEN BAND 3914A

and

CORONA SPECTRUM OF AIR, NITROGEN AND OXYGEN.

by

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- I. Introduction and General Theory of Band Spectra.
 - 1. Frequency Relation.
 - 2. Intensity Relations.
 - a. Thermal Equilibrium.
 - b. Resonance Fluorescence.
 - II. Anomolous Results.
 - 1. Herzberg.
 - 2. Byck.
 - III. Experimental.
 - IV. Results.
 - V. Conclusion.
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OF THE NEGATIVE NITROGEN BAND 3914A.

Introduction.

There are three principal types of band spectra, first the pure rotation bands in the far infra red, secondly the vibration rotation bands in the infra red, and the electronic bands in the ultra violet, visible and infra red. As their names imply the rotation bands are emitted by changes in the rotational energy of the molecule only, vibration rotation bands by simultaneous changes in the vibrational and rotational states, and electronic bands by changes in the electronic, vibrational, and rotational configurations.

The frequency of the emitted radiation is then determined by three groups of quantum numbers, firstly a group of quantum numbers which to a first approximation define the energy the molecule would have were the nuclei stationary, secondly, a quantum number which defines the interatomic vibrations of the molecule, lastly, a group connected with the rotation of the nuclei and the finer structure of the electronic components. In a particular

case ($l \geq 1$) the last group reduces to a single quantum number K belonging to the rotation of the nuclei but in general there are interactions between electronic motions and nuclear rotations. In many cases to a first approximation, however, the energy levels can be calculated using only K . In the N_2 band 3914A which is emitted by electronic change $2 \rightarrow 2$ the resulting frequencies determined by K will not give the finer structure of the rotational components which are of the order of a few hundredths of an angström and hence will not affect the result since the sum intensity of the doublets should just equal the intensity calculated on the simple theory for the single line.

Therefore if the above case consider a rigid rotation and neglect all electronic and vibrational effects.

Let $r_1 \theta_1 \phi_1$, $r_2 \theta_2 \phi_2$ be the coordinates of the two nuclei with respect to their centre of gravity let

$$u_1 = \frac{m_1 m_2}{m_1 + m_2} = \frac{m}{2} \text{ in case of a symmetrical molecule}$$

$$r = r_1 + r_2$$

$$\begin{aligned} \therefore \text{Kinetic energy} &= \left(\frac{m_1 r_1^2 + m_2 r_2^2}{2} \right) (\sin^2 \theta \dot{\phi}^2 + \dot{\theta}^2) \\ &= I (\sin^2 \theta \dot{\phi}^2 + \dot{\theta}^2) \end{aligned}$$

from wave equation

$$\sum_{m_1} \frac{\nabla^2 \psi}{m_1} + \frac{8\pi^2}{h^2} (E - V) \psi = 0$$

E = total energy, V = potential energy = 0.

$$\therefore \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2}{h^2} \mu r^2 E \psi$$

Let $\psi = \theta \phi$ θ is function of value θ alone
 ϕ " " " ϕ "

and let $K'(K'+1) = 8\pi^2 E I / h^2$

$$\therefore \frac{\sin \theta}{\theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \theta}{\partial \theta} \right) + K'(K'+1) \sin^2 \theta = \frac{1}{\phi} \frac{\partial^2 \phi}{\partial \phi^2}$$

Since first two terms are functions of θ alone and the last a function of ϕ alone therefore each must equal a constant = $\pm m^2$ say

$$\therefore \frac{\partial^2 \phi}{\partial \phi^2} + m^2 \phi = 0$$

$$\phi = e^{im(\phi - \alpha_m)}$$

in order that this shall be single valued m must be an integer.

$$\therefore \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \theta}{\partial \theta} \right) + (K'(K'+1) \mp \frac{m^2 \theta}{\sin^2 \theta}) = 0$$

Single valued solutions $P_{K'm}(\theta)$ are allowable only if K' is an integer such that $m \leq K'$

$$\therefore \psi = \theta \phi = P_{K'm} e^{im(\phi - \alpha_m)}$$

$$\therefore E_{K'} = K'(K'+1) h^2 / 8 \pi^2 I'$$

$$E_{K''} = K''(K''+1) h^2 / 8 \pi^2 I''$$

We assume here that vibrational effects are zero hence - $\underline{I' = I''}$

$$V_{K', K''} = \frac{(K'^2 + K' - (K''^2 + K'')) h^2}{8 \pi^2 I h}$$

for the R branch $K'' = K' - 1$

$$P \quad K'' = K' + 1$$

$$\therefore \text{for R Branch } V_{K', K'-1}^R = 2K'h / 8 \pi^2 I$$

$$P \quad V_{K', K'+1}^R = -2(K'+1) / 8 \pi^2 I$$

\therefore the frequency of the emitted light is given by

$$V = V^e + V^v + K'h / 8 \pi^2 I \quad - \quad R \text{ branch.}$$

$$V = V^e + V^v + (K'+1) / 8 \pi^2 I \quad P \text{ branch.}$$

The general appearance of a band depends on the arrangement and relative intensities of the lines. In absorption spectra and in thermally excited spectra the initial distribution is that corresponding to some initial temperature. In practice the observed intensity is of this type even when there is no apparent reason to expect such equilibrium. The actual distribution in such a case is determined as follows:

By Boltzman's law the number of molecules with rotational energy between E and $E+dE$ is $dN \propto e^{\frac{-E}{kT}}$.

Therefore the number of molecules with energy

$$= K(K'+1) / 8 \pi^2 I$$

will be proportional to $e^{\frac{-K'(K'+1)h^2}{8\pi^2 I}}$ but the emitted light has frequency $\propto K'$ in the R branch and proportional to $(K'+1)$ in the P branch, and since the energy in the quantum is proportional to the frequency therefore the intensity of the lines will be given by

$$\text{R branch } I_{K'} = C K' e^{\frac{-K'(K'+1)/8 \pi^2}{h I T}}$$

$$\text{P branch } I_{K'} = C (K'+1) e^{\frac{-K'(K'+1)/8 \pi^2}{h I T}}$$

where K' is the quantum number in the initial state.

In the R branch the line of maximum intensity will be given by

$$\frac{\partial I_{K'}}{\partial K'} = 0 = C e^{\frac{-K'(K'+1)/8 \pi^2}{h I T}} \left(1 - K' \frac{(2K'+1)/8 \pi^2}{h I T} \right)$$

$$\therefore T = K'_m (2K'_m + 1) / \frac{8 \pi^2}{h I}$$

$$(\approx 2.96 K'_m (2K'_m + 1) \text{ for } N_2)$$

It has been shown by Hand, Kronig, and others that in the case of symmetrical molecules there are two complete sets of energy levels termed symmetric and anti-symmetric and such that transitions from symmetric to symmetric states or anti-symmetric to anti-symmetric are the only ones allowed. The probability of a molecule being in a symmetric state is however less than the probability of its being in an anti-symmetric state, hence the lines emitted by changes in symmetric states are relatively weak. In the N_2^+ molecule these are even termed components of the band.

A marked change from these types of distribution is present in the resonance fluorescence spectra of a molecule. If the exciting radiation is sufficiently monochromatic to cover only one absorption line then all molecules receiving energy will be in the same initial state. The possible changes in the rotational quantum numbers are given by $\Delta K = \pm 1$ or 0 or in the case where the molecule does not emit a Q branch $\Delta K = \pm 1$. If \bar{K} is the quantum number of the molecule in the initial, K' the value in the excited state, and K'' the final value then $K'' = K' \pm 1 = \bar{K} \pm 1$

$$\therefore K'' = \bar{K} \text{ or } \bar{K} \pm 2$$

the frequency shift due to the rotational quantum number change will be $= B((K+2)(K+3) - (K+1)K)$

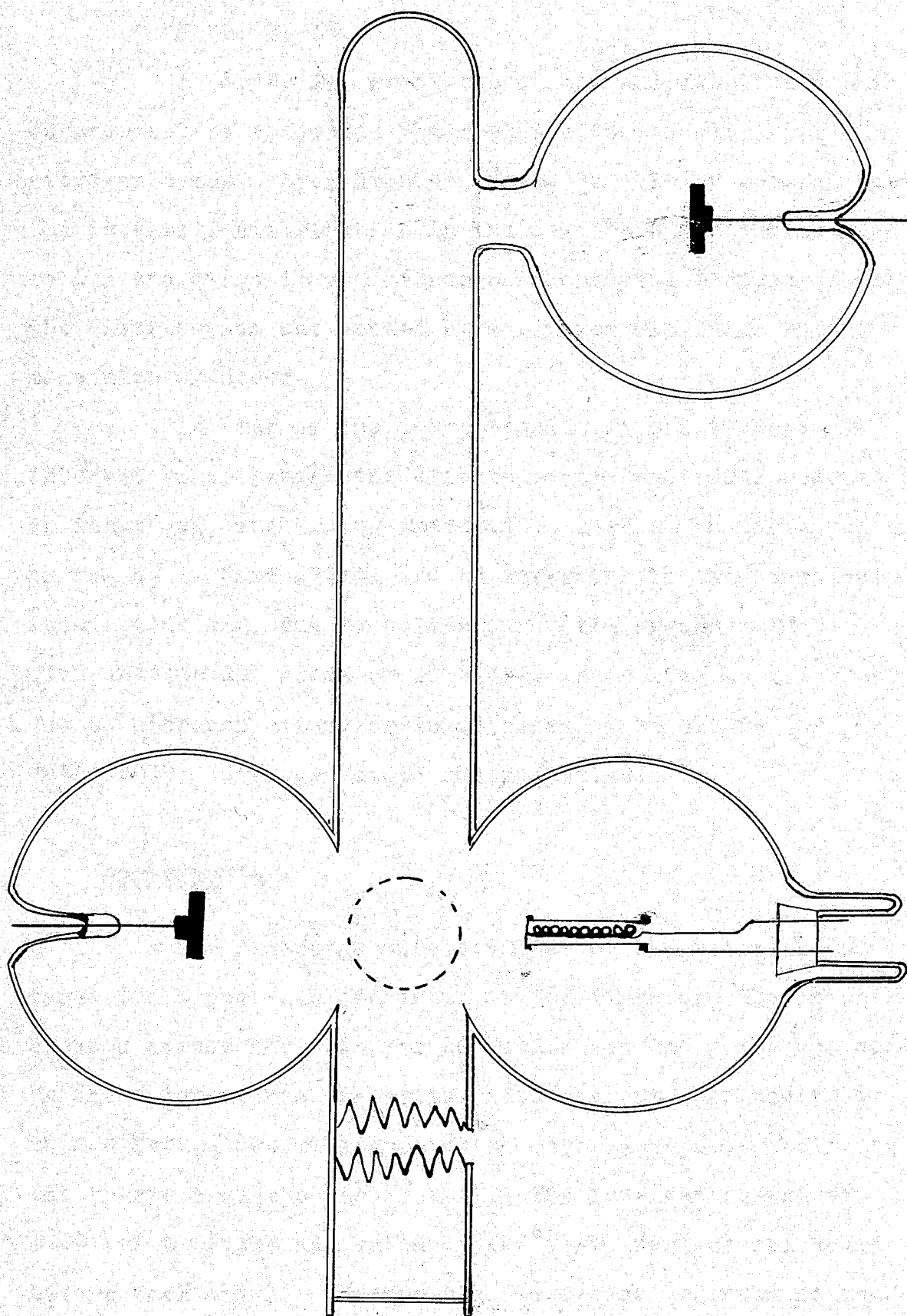
$$= B(4K+6)$$

$$\text{or} \quad = B((K-2)(K-1) - K(K+1))$$

$$= -B(4K-2)$$

we thus have a series of doublets of approximately constant frequency difference, determined by the change in the vibrational quantum number which is unrestricted. That is we have two lines of each band showing.

In investigating the spectrum excited by the nitrogen afterglow in organic molecules Herzberg found intensity relationships which did not agree with the normal C.N. spectrum but in which a few lines were greatly enhanced. In the bands 4216A 3883A he found the lines



P 5, 8, 16

R 3, 6, 14 greatly enhanced and attributed this enhancement to resonance fluorescence due to ultra violet nitrogen bands. Byck however disproved this by showing that the intensity distribution in the C.N. band was not influenced by the radiation from a nitrogen discharge and suggested that the distribution was caused by collision with high energy molecules or atoms.

In view of the above results it was thought of interest to determine the effects of pressure and presence of an inert gas, with known metastable levels, on the spectrum of the N_2^+ band 3914A; and to determine if the anomalous intensities were due to collision of the second kind with metastable atoms or molecules in as much as the spectrum due to nitrogen afterglow is believed to be excited by metastable nitrogen atoms and molecules.

Experimental.

The discharge tube used was of the hot cathode type; the types used are shown in the figures. The potential applied across the tube was 200 volts and the power consumed by the filament was 465 watts. The current thru the tube ranged from a few milliamperes to several amps depending on the pressure of the gas present. The tube was pumped to $1/50$ of a micron and baked at 350° Cent. for several hours before each trial. However the electrodes absorbed so much

gas that it was difficult to state very accurately any low pressures, measured by a McLeod gauge a considerable distance from the discharge tube.

A Hilger Quartz spectrograph was used to obtain spectrograms of the discharge. The plates used were Eastman seed 33 which were very satisfactory for use with the Moll recording microphotometer.

The intensity of the lines was measured qualitatively by the height of the line on the microphotometer tracing. In most of the tracings it was impossible to measure the intensity accurately due to unknown background and insufficient dispersion.

Results.

		type of distribution.	Temperature.
N ₂	A		
3u	0	Thermal	500°A.
3u	30	R3,6,12,16 enhanced	-
80	0	Thermal except near null line	700°A
80	1	" "	700°A
80	80	Irregular very roughly thermal R3, 6 enhanced even terms, very weak.	700°A
80	5000	Approximately thermal R6, enhanced.	800°A

As there was insufficient dispersion to separate the lines of the P branch it was impossible to check that certain initial levels were relatively more probable in mixtures of argon and nitrogen. But it is clear since metastable argon has insufficient energy, 12.5 and 12.96 volts, to directly excite the negative bands that the process cannot be one of direct excitation by impact, but is probably caused by ultra-violet radiation either from the argon or from nitrogen molecules excited by the metastable argon. Byek's explanation of the enhancement by collision could also be ruled out as excitation by collision does not appear to be the same highly selective excitation that is present in the case of resonance fluorescence phenomena.

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CORONA SPECTRUM OF AIR, NITROGEN AND OXYGEN.

I. Historical.

II. Experimental.

1. High Potential Source.
2. Corona tube.
3. Analyzing Instruments.

III. Results.

1. Air.
2. Nitrogen.
3. Oxygen.

IV. Conclusion.

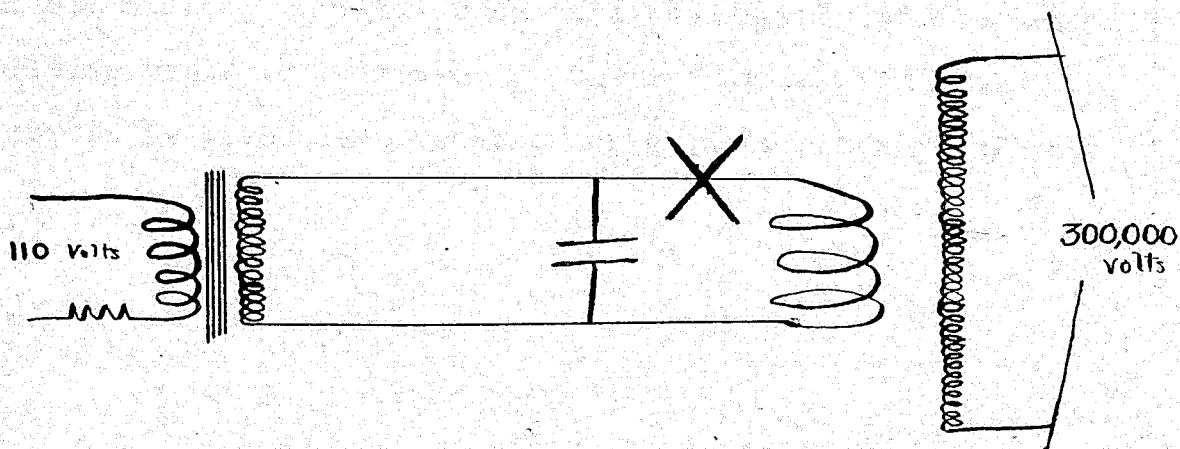
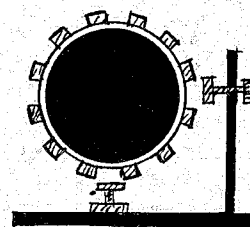
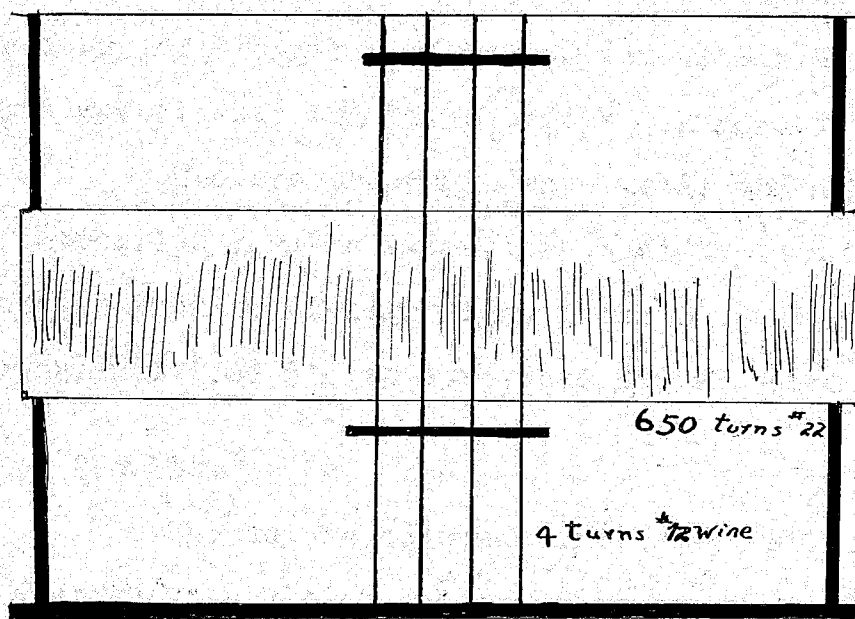
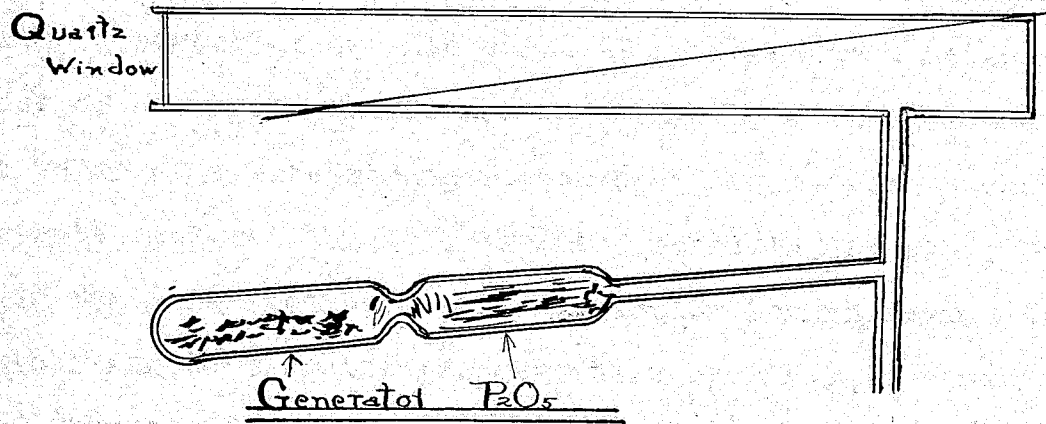
CORONA SPECTRUM OF AIR, NITROGEN AND OXYGEN

Historical.

Peek and Whitehead in their work on Corona state that the voltage gradient in the corona is the same as in a spark, that is, the spark is limiting effect of the corona when the breakdown gradient extends between two electrodes. In support of this Zebrowski found that the corona spectrum of air consisted entirely of spark lines of nitrogen and oxygen but with a peculiar intensity distribution.

Experimental.

The apparatus consists of three main groups, the high potential source, the corona tube, and the spectrographs. The high potential source was of two stages, first the raising of the potential to about 20,000 volts with an oil immersed stepup transformer taking 1 KVA. This was then connected thru a condenser and rotary spark gap to the primary of a testa coil as shown in figure (1). An oudin coil was used initially, but discarded due to insulation difficulties under sustained load. The testa coil gave potentials up to 300,000 volts but as the corona tube could not sustain these voltages it was necessary to reduce the voltage to approximately 100,000 volts.



A sectional view of the corona tube is given in figure 2. When taking spectrograms of air it was necessary to keep a stream of dry air circulating thru the tube as oxides of nitrogen were formed very rapidly. Pictures were also taken of a wire strung in the open air between glass electrodes and was found to be the same as in dry air. The oxygen was generated by heating potassium permanganate crystals and passing the gas generated over P_2O_5 to remove water vapour. The nitrogen was generated by heating a mixture of sodium azide and alumina, and again drying the gas. The pressure of the gas used was approximately atmosphere and the tube was flushed and baked before taking spectrograms.

Two spectrographs were used; one a Hilger quartz spectrograph for the ultraviolet and the other a specially made instrument of high light power for the visible region. Hypersensitized plates were used for all these spectrograms.

Results.

The corona spectrum in air and nitrogen has a characteristic violet colour in oxygen a yellow colour. The radiation in air and nitrogen consisted mainly of the second positive bands of nitrogen. A table of all wavelengths observed is given here together with their classification.

4917.5	2nd positive group or N ₂
4814.7	" "
4722.7	" "
4665.8	" "
4648.6	" "
4573.5	" "
4489.4	" "
4415.9	" "
4356.9	" "
4343.8	" "
4269.1	" "
4201	" "
4141.1	" "
4094.2	" "
4058.7	" "
3997.8	" "
3942.	" "
3914	1st negative of N ₂
3894	2nd positive
3884	1st negative
3857	1st negative or 2nd positive or combine.
3805	2nd positive
3755	"
3710	"
3671	"
3642	"
3577	"
3536	"
3500	"
3469	"
3446	"
3371	"
3339	"
3309	"
3285	"
3267	"
3159	"
3136	"
3116	"
3104	"
2977	"
2962	"
2953	"
2820	"
2814	"
2445	may be 2nd negative or 4th positive.

Several bands due probably to compounds
in air not present in N₂.

In N_2 the first negative bands were relatively stronger than in air. The exposure required for these pictures was four hours. For oxygen, however, the light was so weak that exposure for twenty-four hours produced no effect on the plate. However on widening the slit and again taking a twenty-four hour exposure a slight darkening of the plate was observed in the region 6,000A. This was probably caused by the negative bands of oxygen.

Conclusion.

From the absence of spark lines we may infer that the corona discharge is one of comparatively weak excitation as well as weak intensity. Unfortunately the intensity is not sufficient to use high dispersion and so obtain the temperature of the gas. It is definitely shown that Zebrowski was mistaken in assigning the spectra to the spark spectra of air. Lee and Kuirelmyer state that the corona spectra of oxygen is of the same colour as that of air or nitrogen. This discrepancy is caused by the fact that they used impure oxygen, as it requires only a very small amount of nitrogen in oxygen to change the colour of the discharge from yellow to the violet characteristic of nitrogen. From the intensities in the spectrograms it appears that not more than a few percent of the molecules of the gas are ionized and practically none are dissociated in the case of nitrogen. In the case of oxygen there is not sufficient data to draw conclusions. It would appear therefore

that the corona in nitrogen exists till sufficient energy is available to cause dissociation of the molecules when a spark discharge passes.

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Head of the Department