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Effects of Pressure on the Visible Band Spectra of Nitrogen

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(1) The visible band spectrum of nitrogen produced by an electrodeless discharge has been studied at pressures ranging from 0.002 to 4 mm. (2) At the lowest pressures the spectrum was almost entirely composed of the first negative bands due to N_2^+ . The first positive bands appeared very faintly. As the pressure of the discharge was increased, the first and second positive band systems greatly increased in

intensity up to a pressure of 0.2 mm. At still higher pressures the second positive bands were found to fade until at pressures of 4 mm they were just noticeable. (3) In the case of the first negative bands, it is found that increase of pressure increases the number of N_2^+ ions in the higher rotational states.

EXPERIMENTAL

THE spectra were excited by means of an electrodeless discharge. A high-frequency oscillation was maintained in a copper helix in the center of which was the discharge tube. The oscillator circuit was similar to that recently described by Hunt and Schumb.¹ The exciting coil was made of 1/8" copper tubing wound in a helix 4" in diameter, the turns being 1/2" apart. A 50-watt oscillator (De Forest Type 503A) was used. When adjustments were made, the plate current was 60 m.a. when there was no discharge in the tube. This was convenient because when the glow in the discharge tube was highest the plate current rose to 100 m.a.

The wave-length of the oscillator was 16 meters (19×10^6 cycles). There is every reason to believe that the excitation was electrostatic rather than electromagnetic.² The oscillator produced a continuous wave, so that the rate of change of magnetic flux was small. Uniform glow was obtained throughout the tube, and no indication of ring discharge was noticeable. The pressure range over which the discharge could be obtained was very considerable. From 20 mm

down to the lowest pressures obtainable with diffusion pumps and a liquid air trap, certainly less than 10^{-6} mm, light glows were obtained. At the lowest pressures, the gray glow formed when the discharge was turned on, disappeared in a few seconds and gave way to brilliant variegated colors on the inner surface of the tube.

The discharge tube was of quartz and was 12" long and 3/4" in diameter. A quartz optical window was fused on an end. A quartz tube is very desirable even when working with visible spectra since it can be heated in vacuo to high temperatures to remove adsorbed impurities. It was connected to the rest of the apparatus by a quartz to Pyrex seal. A liquid-air trap was inserted between the tube and the rest of the apparatus which served to keep mercury from the diffusion pumps and other impurities from the tube. The gas was admitted to the tube through this trap.

A large Universal Schmidt and Haensch Spectrograph was employed. For visible regions the optical system contained two Rutherford prisms, dispersion (C-F $6^\circ 52'$). The slit mechanism of the spectroscope was placed close to the quartz window of the tube without an intervening lens.

Tank nitrogen was used in most of the observations. This was found justifiable since the spectrum obtained was identical with that obtained by nitrogen prepared by heating potassium nitrite. Spectra were obtained at pressures of 0.002, 0.007, 0.013, 0.025, 0.05, 0.13, 0.2, 0.4,

* The material contained in this contribution constituted part of a dissertation presented by Eugene R. Brownscumbe to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1932.

¹ Hunt and Schumb, *J. Am. Chem. Soc.* **52**, 3152 (1930).

² MacKinnon, *Phil. Mag.* **8**, 605 (1909); Brasfield, *Phys. Rev.* **35**, 1073 (1930); Lynch and Hilberry, *ibid.* **37**, 1091 (1931); Knipp and Knipp, *ibid.* **38**, 948 (1931).

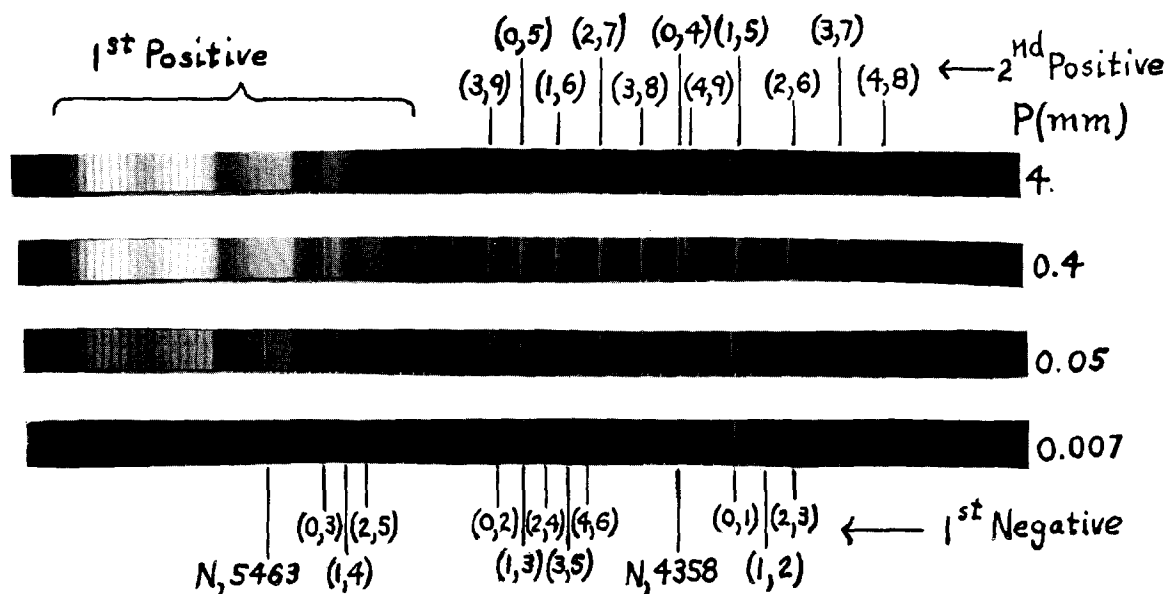


FIG. 1. Effect of pressure on the band spectrum of nitrogen.

0.8, 2.2 and 4 mm. Five-minute exposures were used.

RESULTS AND DISCUSSION

The effects of pressure on the entire visible band spectrum are illustrated by Fig. 1, in which photographs obtained at the pressures indicated at the right are shown.³ At the lowest pressure, every line observable at wave-lengths less than 5500Å is due to the spectrum of the first negative group due to N_2^+ with the exception of the two lines of atomic nitrogen indicated at 5463Å and 4358Å. The vibration-band heads of this system of bands are indicated and designated by the vibrational quantum numbers given at the bottom of the illustration. At the red end, the first positive group of bands due to neutral nitrogen appear faintly. As the pressure is increased, the first positive group increases greatly in intensity, and there also appears at pressures above 0.01 mm another band system due to neutral nitrogen and designated the second positive group. The vibration-band heads of the second positive group are marked and designated by their vibrational quantum numbers at the top of the illustration. Upon closer observation

it is interesting to note that the intensity of the second positive group increases up to a pressure of 0.2 mm and then decreases with further increase in pressure until at a pressure of 4 mm it is just noticeable. This particular point is more clearly indicated in Fig. 2 in which an enlargement of that part of the spectrum in Fig. 1 which includes the (0, 1) and (1, 2) bands of the first

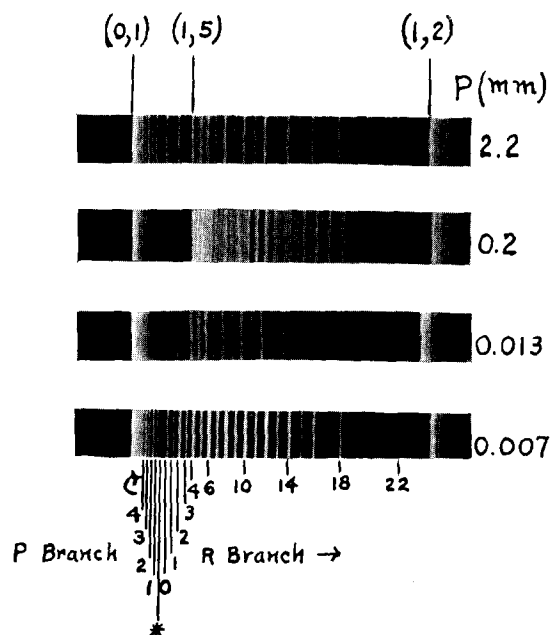


FIG. 2. The (0, 1) and (1, 2) first negative bands and the (1, 5) band of the second positive.

³For a general discussion of these band systems, see Weizel, *Bandenspektren*, pp. 346-361, *Handbuch der experimentellen Physik, Ergänzungswerk*, Band 1, Akad. Verlagsgesellschaft, Leipzig, 1931.

negative group and the (1, 5) band of the second positive group is shown.

In discharges of this kind, it is to be expected that the negative bands or atomic lines persist at all pressures, since the presence of both positive ions and electrons are necessary in order for the discharge to persist. In similar experiments with oxygen, the second negative bands due to O_2^+ were found to be intense over a large pressure range. In the case of hydrogen, it is well known that no spectrum due to H_2^+ appears, but in this case the atomic lines are very intense at all pressures as are those due to the band spectrum of H_2 . Thus, the presence of bands due to N_2^+ is to be expected. Further, an activated neutral molecule can result from a three-body collision between a positive ion, a molecule and an electron, so that at the higher pressures we may expect the appearance of the positive groups of bands. The fact that the second positive group decreases in intensity at the higher pressures shows that the energy exchanges bear a complicated relation to the number of collisions. Under the conditions of these experiments, the energy contributed to the gas in producing the discharge was nearly the same at all pressures. Similar results were obtained in the region of the (0, 0) band of N_2^+ at 3195 Å.

The structure of the first negative bands has been studied by Fassbender⁴ and Herzberg⁴ and is of the $^2\Sigma-^2\Sigma$ type. The rotation structure possesses a *P* and an *R* branch but no *Q* branch. The well-known phenomenon of alternating intensities in these lines appears very clearly. Measurements of the lines of the N_2^+ bands from the plates obtained at 0.007 mm and 4 mm were made and were found to agree within ± 0.1 of a wave number. These measurements with vacuum correction also agreed within the same limits with the values given by Fassbender. The equations for the two branches,

$$P(K) = 23391.01 - 3.99K + 0.19K^2$$

and

$$P(R) = 23391.01 + 3.99(K+1) + 0.19(K+1)^2,$$

were found to represent the measurements to within ± 0.05 of a wave number. From this, the

⁴ Fassbender, *Zeits. f. Physik* 30, 73 (1924); Herzberg, *Ann. d. Physik* 86, 189 (1928).

moments of inertia of the lower and higher vibrational states were found to be

$$I' = (13.23 \pm 0.05) \times 10^{-40} \text{ g} \cdot \text{cm}^2$$

and

$$I'' = (14.56 \pm 0.05) \times 10^{-40} \text{ g} \cdot \text{cm}^2.$$

13.35 and 14.41 have been given for I' and I'' of the (0, 0) band.⁵ The origin of the band and some of the rotational quantum numbers of the *P* and *R* branches are indicated at the bottom of Fig. 2. The structure of the second positive band is a $^3\Pi-^3\Pi$ type.⁶ No attempt was made to measure the lines of this band. One further fact was observed from microphotometer traces obtained at the higher and lower pressures. At higher pressures, the intensity of the lines at higher quantum numbers was relatively greater than their intensities at lower pressure. This is illustrated clearly in Fig. 3 where the intensities, roughly determined from the microphotometer traces, are plotted against the rotational quantum numbers, in this case the even numbers, at pressures of 0.007 and 2.2 mm. The odd-numbered lines show an exactly similar behavior. Since between the quantum numbers 4 and 10 the N_2^+ lines are augmented in intensity by the lines of the second positive band, it is roughly estimated that the distribution of intensities is more truly represented by the solid line than by the dotted one given by the measurement. There seems to be little doubt that pressure increases the number of N_2^+ ions in the higher rotational quantum states.

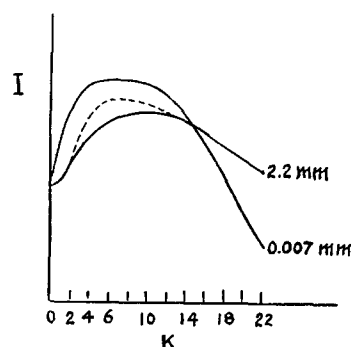


FIG. 3. Intensities of the lines of (0, 1) first negative band of nitrogen.

⁵ International Critical Tables 5, 415 (1929). McGraw-Hill Book Company.

⁶ Lindau, *Zeits. f. Physik* 25, 247 (1924); 26, 343 (1924); 30, 187 (1924).