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THE DISSOCIATION OF NITROGEN BY ELECTRON IMPACT

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Abstract

The $2p^23s\ ^4P-2p^23p\ ^4P^\circ$ N I lines near 8200 A.U. are produced by bombarding N_2 molecules with electrons having energies of 23 ± 1 volts or more. Experiments with different currents and pressures indicate that the rate of production of excited atoms depends on a single impact and not upon successive double impacts. A discussion is given of the possibility that the lines are emitted following the recombination with electrons of N^+ ions, shown by positive ray experiments to be produced at this voltage.

IN THE course of an investigation of active nitrogen produced by the electrodeless discharge Herzberg[1] found that certain lines of the N I spectrum were emitted with great intensity. These lines belonged to the various multiplets in the region near 8000 A.U. emitted by transitions from the $2p^23p$ configuration to the $2p^23s$ configuration. They were emitted with undiminished intensity even when the condition of the walls of the tube was such that the afterglow of the active nitrogen was quenched. On the assumption that this quenching was an indication of a great reduction in the concentration of atomic nitrogen Herzberg came to the conclusion that, because of the undiminished intensity of the red lines, their production must be independent of the concentration of the nitrogen atoms, i.e., the $2p^23p$ excited atoms must be produced by some primary process of excitation of nitrogen molecules and not by excitation of nitrogen atoms already present. The purpose of the experiments here described was to test this conclusion by a more direct experiment and to endeavor to determine the minimum energy of bombarding electrons which would cause the appearance of these lines. The experiment is essentially the same as that of Kondratjew[2] who investigated the appearance of certain of the violet N I lines. Because of the relative lack of sensitivity of the photographic plate for the infra-red lines, however, we did not find it feasible to work with such low pressures as did Kondratjew.

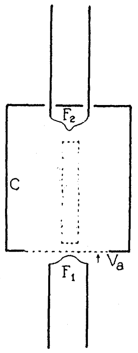

Fig 1. Diagram of electrodes.

The electrodes of the experimental tube were arranged as indicated in Fig. 1. The source of the bombarding electrons was the filament F_1, an oxide-coated, notched strip of either platinum or nickel. C was a closed cylinder with platinum gauze on the bottom towards F_1, and a slit in the side for spectroscopic observation. The electrons from F_1 were accelerated into C by a variable applied accelerating voltage, V_a. The correction to this applied

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[1] G. Herzberg, Zeits. f. Physik **49**, 512 (1928).

[2] V. Kondratjew, Zeits. f. Physik **38**, 346 (1926).

voltage, necessary on account of the potential drop in F_1, contact difference of potential, etc., was found by determination of the apparent ionizing potential of mercury vapor always present in the tube. The Hertz[3] method was used. F_2 was a fine tungsten filament from which the space-charge limited current was drawn for this purpose. Nitrogen generated by the reaction between bromine and ammonia was stored over P_2O_5 and then flowed through a liquid air trap and the experimental apparatus, the pressure and rate of flow being regulated by adjustable capillary leaks. Mercury vapor was always present in the tube. The Hg^+ ions formed served to prevent the setting up by space-charge effects of strong fields in C. The spectrum was photographed with a Steinheil glass spectrograph of large light power(1:3). Eastman infra-red plates, ammonia bathed, were used.

It was found that of all the lines emitted in the $2p^23s-2p^23p$ transition only those of the $^4P-^4P^\circ$ multiplet, all of wave-lengths close to 8200 A.U., were sufficiently separate from strong first positive bands to be detected readily when weak. Fortunately, this is the region of maximum sensitivity of the Eastman infra-red plates. In all that follows "the infra-red lines" will refer solely to those of the $^4P-^4P^\circ$ multiplet.

The question as to whether these lines were emitted as the result of a primary dissociation was investigated by varying the bombarding current and the pressure. Two exposures were made on the same plate, the pressure being 0.04 mm and the voltage 40, one with a current of 7 milliamperes for 18 hours, the other with an average current of 40 milliamperes for 3 hours. These two exposures gave almost identical results, the intensity of the infra-red lines and of every band being practically the same in both. Another such pair of exposures was made with the higher pressure of 0.24 mm and at 40 volts, one with a current of 4.5 milliamperes for 4 hours, the other with a current of 35 milliamperes for 1/2 hour. Again the two exposures gave practically the same results. The plate was not quite so heavily exposed as was the first one made at the lower pressure, but the intensity of the infra-red lines relative to the bands was apparently the same in all four spectra. If successive electron impacts with molecules or molecular ions or excitation of already formed atomic nitrogen had been of importance in the production of these lines the exposures with higher currents and at the higher pressure would presumably have shown the lines stronger with respect to the bands. The concentration of atoms present in the tube must have been fairly small, and dependent upon the current, since there was a great clean-up effect of the gas by such a discharge. It appears then that either the excited atoms which emit the infra-red lines are produced by a dissociation of the nitrogen molecules immediately upon collision with electrons having sufficient velocity, or that metastable excited molecules are produced which break up to give the excited atoms upon collision with other molecules, or that atomic ions are somehow produced and give rise to the excited atoms upon recombination with electrons.

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[3] G. Hertz, Zeits. f. Physik **18**, 311 (1923).

The only other N I line which can be distinguished on these plates (region from 4700 to 9000 A.U.) is a line at 4935.0 A.U., one of those identified by Kiess.[4] It is the $2p^23s\ ^2P_{1\frac{1}{2}}-2p^24p\ ^2S$ line. The companion $2p^23s\ ^2P_{\frac{1}{2}}-2p^24p\ ^2S$ line at 4915 A.U. is presumably obscured by the very heavy broad Hg line at 4916. On these plates the 4935 line appears weaker than the infra-red lines but its intensity also seems to behave the same way and to bear the same relation to the intensities of the bands in the four exposures described above.

A series of exposures at different voltages was made in the attempt to determine the critical energy necessary to cause the appearance of the infra-red lines. For these the pressure was kept at about 0.04 mm, the time of the exposure being about 15 to 20 hours. It is, of course, difficult under the most favorable circumstances to determine the exact voltage for disappearance of a spectrum line, but it was even more difficult in this work because of the extremely low intensity of the infra-red lines and especially because of changes of several tenths of a volt in the contact difference of potential in the course of an exposure. These changes are presumably connected with the formation of layers on the electrodes by atomic nitrogen. They could be followed by frequent observation of the apparent ionizing potential of the mercury vapor. The changes were greater the higher the pressure of nitrogen. The final conclusion is that the infra-red lines appear at 23 ± 1 volts. This is 0.7 volt higher than the value reported at the Washington meeting of the American Physical Society[5] because it was found later in the course of the work on the negative bands, described in the following paper, that the method of correcting the voltage scale was giving too large a correction and, therefore, low corrected voltages.

Unfortunately, the presence of the 4935 line was not detected until after this work was completed so that the exposures do not give any very exact idea of the minimum voltage for the appearance of that line. It does not appear on the plates in which the infra-red lines are just barely visible, but being much weaker would not be expected to appear even if the light were present with the same relative intensity as at higher voltages. One plate, taken at 25.3 volts shows the 4935 line with much the same intensity relative to that of the infra-red lines as at higher voltages.

This critical value of 23 ± 1 volts is just 7 volts higher than the new value of the ionizing potential of nitrogen discussed in the following paper and agrees, therefore, with the critical voltage for the appearance of N^+ ions in the positive ray experiments of Smyth[6] and of Hogness and Lunn.[7] They give a value of 24.1 ± 1 volts, but that is based on the assumption of a value of 16.9 volts for the ordinary ionizing potential of nitrogen. The agreement of these critical voltages suggests that the appearance of the N^+ ions in those experiments and of the infra-red lines in these may be different mani-

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[4] C. C. Kiess, Jour. Op. Soc. Am. **11,** 1 (1925).

[5] Louis A. Turner and E. W. Samson, Phys. Rev. **33,** 1085 (1929) (Abstract).

[6] H. D. Smyth, Proc. Roy. Soc. **104A,** 121 (1923).

[7] T. R. Hogness and E. G. Lunn, Phys. Rev. **26,** 786 (1925).

festations of the same original process. The positive ray experiments indicate that the primary process is the formation of excited molecular ions which dissociate into atoms and atomic ions upon collision. The infra-red lines would appear, then, following the recombination of the N^+ ions with electrons. The available energy is not great enough for the production of molecular ions which could dissociate into atomic ions and excited atoms in the $2p^23p$ configuration. The behavior of the infra-red lines with changes of current and pressure discussed above shows that if they are emitted as the result of recombination, the probability that an atomic ion once produced will recombine in the cylinder must be independent of the electron density and of the pressure. This is quite plausible since the region within the cylinder is presumably nearly field-free, the positive ions are not drawn out rapidly, and a high concentration of slow electrons can be built up. The atomic ions which are all neutralized eventually must nearly all be neutralized in the cylinder in the gas or at the walls. The recent experiments of Oliphant[8] show that helium ions, at least, are neutralized to give excited helium atoms upon contact with a metal tube through which they are passing.

This agreement of the critical voltage with that for the production of the N^+ ions may, however, be merely a coincidence. The infra-red lines may be produced by an immediate dissociation of molecules into normal and excited atoms or by the dissociation of metastable highly excited molecules. The behavior of the 4935 lines suggests that the immediate dissociation can give rise to various types of excited atoms or that various metastable highly excited molecules can be formed. It is also consistent with the hypothesis of recombination. Further experiments will have to be performed before the question can be settled. Both direct production of excited atoms and recombination may take place.

In many experiments with this tube with various pressures of nitrogen the currents showed a tendency to become unsteady near 23 volts. Often there was an increase in the current from F_1 accompanied by a decrease in the thermionic current from F_2. This is apparently the same effect as the decrease of the thermionic current caused by ordinary active nitrogen in an arc found by Kenty and Turner.[8] In the present experiment, however, the phenomenon seems to occur at the voltage at which atomic lines appear and is thus most definitely and directly connected with the appearance of atomic nitrogen. It is of interest in this connection to recall that Storch and Olsen[9] found a great increase in the rate of formation of ammonia in mixtures of hydrogen and nitrogen at this voltage.

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[8] M. L. E. Oliphant, Proc. Roy. Soc. **A124**, 228 (1929).

[8] Carl Kenty and Louis A. Turner, Phys. Rev. **32**, 799 (1928).

[9] H. H. Storch and A. R. Olsen, J. Am. Chem. Soc. **45**, 1605 (1923).