A NOTE ON THE EXCITATION OF THE ARC SPECTRUM OF NITROGEN

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ABSTRACT

The arc spectrum of nitrogen has been excited with low voltage arcs in mixtures of argon and nitrogen. A comparison of the intensities of the lines showed that the strong N I lines were as intense as the moderately strong argon lines. The excitation takes place probably in two steps, the first being the dissociation of the nitrogen molecules into normal and metastable nitrogen atoms by collisions with metastable argon atoms, and the second being the excitation of the metastable nitrogen atoms by collisions with metastable argon atoms.

Introduction

It is known from the work of Johnson,[1] Cameron,[2] McLennan and Shrum[3] and others that the presence of a rare gas often modifies the character of the spectra emitted by diatomic gases. By this means Merton and Pilley[4] excited the arc spectrum of nitrogen by passing a discharge through a Geissler tube containing helium and a trace of nitrogen. They also tried mixtures of argon and nitrogen but with moderate currents obtained no evidence of the N I lines. They accounted for the emission by assuming that the helium atoms acted as safety valves limiting the electron velocities to 20.5 volts, which is greater than that required to excite the arc lines but less than the excitation potential of the spark lines. At about the same time Compton[5] suggested that metastable helium atoms were the effective agents. He showed that in mixtures of helium and nitrogen a high current density should be favorable to the dissociation of the nitrogen molecules into neutral atoms by collisions with metastable helium atoms.

Many new N I lines were found by Duffendack and Wolfe[6] who used a high current density in mixtures of helium and nitrogen. They found that the lines were more intense in low voltage arcs than in Geissler discharges. This is in agreement with Compton, since the higher current density of the low voltage arc tends to produce a higher concentration of metastable helium atoms. Compton predicted that the N I spectrum would not be excited in mixtures of argon and nitrogen, since at the time the heat of dissociation of the nitrogen molecule was believed to be about 19 volts, which was much

[1] Johnson, Roy. Soc. Proc. **A108**, 343 (1924); Phil. Mag. **48**, 1069 (1924); Roy. Soc. Proc. **A106**, 195 (1924).
[2] Cameron, Phil. Mag. **1**, 405 (1926).
[3] McLennan and Shrum, Roy. Soc. Proc. **A108**, 501 (1925).
[4] Merton and Pilley, Roy. Soc. Proc. **A107**, 411, (1925).
[5] Compton, Phil. Mag. **50**, 512, (1925).
[6] Duffendack and Wolfe, Phys. Rev. **34**, 409 (1929).

higher than any of the resonance potentials of argon. According to the work of Kaplan,[7] however, the heat of dissociation of molecular nitrogen must be taken as 9.1 volts rather than 19 volts and since there are strong metastable levels of argon at 11.5 and 11.67 volts, which are sufficient to dissociate the nitrogen, it seemed reasonable to expect that under favorable conditions the N I spectrum could be excited in mixtures of argon and nitrogen.

Experimental

In accordance with the above considerations a low voltage arc discharge tube was used in this investigation. It was made of Pyrex glass 25 mm in diameter and 50 cm in length, with the electrodes in bulbs sealed to the side of the tube. This design made it possible to use the tube "end-on" so as to increase the intensity. The hot cathode consisted of an internally heated nickel cylinder coated with a thin layer of barium and calcium oxides. Liquid air traps were used wherever necessary to keep the tube free of mercury vapor.

Before each set of experiments the discharge tube was thoroughly exhausted and baked at a temperature of 350°C. For purposes of degassing the electrodes were brought to a red heat by passing a high current discharge through the tube.

It was found convenient to use commercial argon purified by means of a magnesium arc, while the nitrogen was generated by heating a mixture of sodium azide and alumina.

The argon pressure most suitable to the passage of high currents was found to be 1 to 3 mm while a nitrogen partial pressure of 0.01 to 0.3 mm was found satisfactory for the excitation of the N I lines. The best results were obtained with discharge currents of the order of 2 amperes at 70 volts.

A Hilger E-I quartz spectrograph for the region 3200 to 6000A and a Hilger constant deviation spectrograph with a flint glass prism for the region 6000 to 9000A were used. With the quartz spectrograph one hour exposures were sufficient to record all the N I lines observed. The strong lines could easily be photographed in ten minutes. With the flint glass spectrograph one hour exposures were taken.

The wave-lengths of the lines were measured by using international iron lines for comparison, and the relative intensities determined with a Moll selfregistering microphotometer.

Results

In the region from 3400 to 5000A the plates showed most of the intense lines and many of the weak lines of the N I spectrum found by Merton and Pilley and by Duffendack and Wolfe. Many of the weaker lines were obscured by the positive bands of nitrogen which were usually present when the arc lines were strong. The negative bands of nitrogen were not present on any of the plates. It was found that higher nitrogen pressures were required to bring out the arc lines in the longer wave-length regions than in the violet and ultraviolet. The higher pressures also brought out the first positive

[7] Kaplan, Phys. Rev. **33**, 638, (1929).

bands prominently and this together with the small dispersion prevented the identification of any lines in the region 5000 to 8000A. Some of the more intense lines above 8000A were photographed by using the flint glass spectrograph and infrared sensitive plates.

A comparison of photographic densities made from the microphotometer curves showed that the relative intensities of the lines were, in most cases, the same as those found by Duffendack and Wolfe in mixtures of helium and nitrogen. It was found that the stronger arc lines were as intense as the moderately strong argon lines. The lines observed are given in Table I.

TABLE I. *Observed lines of N I. The first two columns contain the wave-lengths and the intensities of the lines in helium mixtures as given by Duffendack and Wolfe. In the third column are listed the estimated intensities in argon-nitrogen mixtures.*

Wave-lengths (I.A.)	Intensity in He mixture	Intensity in A mixture	Wave-lengths (I.A.)	Intensity in He mixture	Intensity in A mixture
8711.9	2	2	4554.21	1	1
8703.4	2	unresolved	4553.38	1	1
			4503.53	1	0
8686.4	3	5	4502.27	2	2
8683.6	4	unresolved			
8680.3	5	unresolved	4499.08	0	1
			4492.40	7	4
8629.5	4	2			
			4358.27	10	8
8594.3	3	1	4313.11	4	2
			4305.46	6	4
8242.5	4	3			
			4230.35	4	2
8223.3	5	10	4224.74	4	2
8216.45	7	unresolved	4223.04	5	3
8210.9	3	unresolved	4215.92	2	1
			4214.73	5	3
8188.2	5	7			
8185.0	5	unresolved	4187.06	1*d*	1*d*
			4151.46	12	9
4935.03	10	10	4143.42	obscured by He	1
4914.90	5	4	4137.63	7	2
			4114.00	6	4
4881.79	1	1	4109.98	12	12
4753.13	2	2	4099.94	9	10
4669.77	3	6	3834.84	2	1
4660.05	2	3	3834.24	4	3
4657.72	1	0	3830.39	9	4
4656.65	1	0	3822.07	6	2
4651.08	1	3			
			3650.19	5	1
			3532.65	4	0

DISCUSSION

The two important agencies for the dissociation of the nitrogen molecules and for the excitation of the atomic spectrum are collisions with electrons and with metastable argon atoms. Many experimenters have shown that electron impacts seldom produce simple dissociation of nitrogen molecules. In fact, Duncan[8] has shown that the only atomic spectrum excited by electron bombardment is the spark spectrum, and this results only when the electrons have energy of 70 volts or more. He found that electrons with energy of the same order as the heat of dissociation of the nitrogen molecule or as the resonance potentials of argon did not excite any line spectrum of nitrogen, but were evidently totally consumed in exciting the molecular spectra. It seems reasonable to assume that since the nitrogen molecules are not dissociated by electron impacts, they must be dissociated by collisions with metastable argon atoms. Moreover a metastable argon atom has sufficient energy (11.5 or 11.67 volts) to dissociate a nitrogen molecule into a normal atom and a metastable atom, since this requires the sum of the energy required to dissociate the molecule into two normal atoms (about 9 volts[7,9]), and the energy necessary to raise one of the atoms from the normal state $^4S_{1\frac{1}{2}}(2p^3)$ to the metastable $^2D_{2\frac{1}{2},1\frac{1}{2}}(2p^3)$ states (2.37 volts), a total of about 14 volts. As this is in close resonance with the energy of the metastable argon atoms it is probable that a nitrogen molecule would be dissociated into a normal atom and a metastable atom by a collision with a metastable argon atom.

It is also probable that the metastable argon atoms are the active agents for the excitation of the nitrogen atoms. According to the classification of Ingram[10] and of Compton and Boyce[11] the nitrogen atom has energy levels varying from 10.3 to 14.2 volts, as well as metastable levels at 2.37 and 3.56 volts. Thus a metastable argon atom could excite a normal nitrogen atom to levels as high as 11.67 volts energy, or a metastable nitrogen atom (2.37 volts) to levels as high as 14 volts energy. Also it is known that there is a high concentration of metastable argon atoms in high current low voltage arcs. Thus the nitrogen arc spectrum could be excited with considerable intensity by metastable argon atoms. Electrons with energy of the same order are present in the discharge and could also excite the nitrogen atoms. However the number of collisions between electrons and nitrogen atoms is small compared with the number of collisions between electrons and argon atoms because the nitrogen pressure is much lower than the argon pressure. Thus, since the stronger N I lines are of the same order of intensity as the argon lines, it is probable that metastable argon atoms are the most important agents in the excitation of the nitrogen atoms.

According to the classification of the N I lines, the initial levels of the lines reported arise from the configurations $3p^2 3p$ and $3p^2 4p$. The excitation potentials of all these levels lie between 11.7 volts for the $^4D_{\frac{1}{2}}$ state (built upon ^3P, $2p^2$ of the ion) and 13.85 volts for the $2P_{1\frac{1}{2}}$ state (built upon $^1D_2$, $2p^2$ of the ion). Thus a metastable argon atom has sufficient energy to raise a metastable nitrogen atom to any of these levels, but has not sufficient energy to raise a normal nitrogen atom to them. Hence the N I lines observed are probably excited by collisions of metastable argon atoms with metastable

[8] Duncan, Astrophys. J. **62,** 145 (1925).

[9] Birge, Phys. Rev. **34,** 1062 (1929).

[10] Ingram, Phys. Rev. **34,** 421 (1929).

[11] Compton and Boyce, Phys. Rev. **33,** 145 (1929).

nitrogen atoms. Nevertheless the metastable argon atoms have sufficient energy to excite the normal nitrogen atoms to the levels $3p^2 3s\, ^2P_{1\frac{1}{2},\frac{1}{2}}$ and $3p^2 3s\, ^4P_{2\frac{1}{2},1\frac{1}{2},\frac{1}{2}}$ (energies 10.6 and 10.3 volts respectively). Also it has been found by Compton and Boyce[11] and by Ekefors[12] that these are initial levels for transitions giving rise to ultraviolet lines. Moreover the transitions from the $3p^2 3s\, ^2P_{1\frac{1}{2},\frac{1}{2}}$ states are to the metastable states of 2.37 and 3.56 volts energy and not to the normal state of zero energy. In addition the $3p^2 3s\, ^2P_{1\frac{1}{2},\frac{1}{2}}$ states are the final levels of many of the transitions giving rise to the more intense lines reported. Hence many of the metastable atoms that are further excited return to the metastable state in two steps, radiating visible and ultraviolet light. Thus since metastable atoms result from the dissociation of the nitrogen molecules and from the radiation of light by excited atoms, it is probable that there is a high concentration of metastable nitrogen atoms in the discharge. These are probably excited to the initial levels of the lines reported by collisions with metastable argon atoms.

The experiments with argon indicate therefore that the excitation of the N I lines takes place probably in two steps, the first being the dissociation of the nitrogen molecules into neutral and metastable nitrogen atoms by collisions with metastable argon atoms, and the second being the excitation of the metastable nitrogen atoms by collisions with metastable argon atoms.

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[12] Ekefors, Zeits. f. Physik **63**, 437 (1930).