Band Spectra in Nitrogen at Atmospheric Pressure. A Source of Band Spectra Excitation

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An apparatus, essentially an ozonizer, consisting of a cylindrical condenser, a portion of the dielectric of which is a gas, has been used as a source of band spectra excitation. Such a source can be operated with the gas at atmospheric pressure and at a temperature which is practically that of the walls. Nitrogen bands $A \rightarrow X$ have been photographed in emission at atmospheric pressure under resolution sufficient to permit measurement of part of their rotational structure. The rotational structure of four of the present bands has been computed by using the rotational constants which have been determined from other band systems in nitrogen. The agreement with the measured values is satisfactory, and makes more certain the identi-fication of this band system. The alternation of intensity in the rotational lines is clearly visible, measurements indicating that the ratio of the intensities is 2 : 1. In this source of excitation the first positive group of nitrogen is considerably weaker relative to the second positive group than in an ordinary glow discharge. The rather striking difference between this type of source and a high voltage, low current arc at atmospheric pressure is illustrated by band spectra in oxygen containing a small amount of nitrogen. In the latter source the principal emission is the Runge bands of oxygen while in the former the only prominent material is the second positive group of nitrogen.

A N ORDINARY all-glass ozonizer in operation is luminescent, and affords a source of band spectra excitation which may be of use because of the unique conditions under which it operates. In particular two conditions, which are at times desirable, can be met by using such a source; first, the gas may be excited at atmospheric pressure and second, it may, at the same time, be held at room temperature. Either one of these conditions can be met in other sources but ordinarily not both at the same time. In arc and flame excitation, while at atmospheric pressure, the gas is usually at high temperature while in the glow discharge the gas is at low pressure. In the present work emission spectra of nitrogen from the above-mentioned source have been studied, and, in particular, it has been found that certain bands otherwise difficult to excite may be obtained in this way.

APPARATUS

While there are many forms of ozonizers, the type used in the present work, shown in Fig. 1, consisted of two coaxial glass tubes separated by a gas space of a few millimeters. The outside of the outer cylinder and the inside of the inner cylinder were covered with metal coatings, thus forming essentially a Leyden jar with a portion of the dielectric a gas. The inlet and outlet tubes at either end were connected by a closed circuit of glass tubing consisting of a trap for immersion in liquid air or a portion of tubing containing
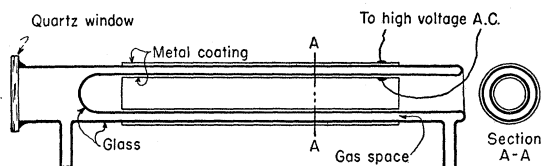

FIG. 1. Source of excitation.

material such as metallic sodium to be used as a purifying agent. A quartz window was cemented on the end of the ozonizer, through which the emission could be viewed. The spectrograph was so oriented that the extended plane of the slit and the collimater axis was tangent to the cylindrical annular, luminous gas space.

Tank nitrogen dried in liquid air was used in the work. The gamma-bands of NO, arising from the small amount of oxygen in the nitrogen, showed strongly in the emission, and since these bands interfered with the observation of the bands of interest, several methods were tried in an effort to remove the oxygen. First, a tungsten filament was heated in the gas. This formed large amounts of tungsten oxide without appreciably reducing the intensity of the NO bands. Second, hydrogen was added with a liquid-air trap in the system to freeze out the water formed. In order to reduce greatly the intensity of the NO bands, an excess of hydrogen was required. This brought out a continuous background of emission. Third, metallic sodium was introduced in the system and distilled along it, reducing greatly the intensity of the NO bands but not removing them completely. Fourth, aluminum foil was placed in the discharge space. This reduced the intensity of the NO bands to about the same extent as did the sodium. It appears that the excitation of the NO bands is a very sensitive test for small amounts of oxygen in nitrogen. All plates in the present work used for measurement were taken with an apparatus in which the oxygen had been reduced by means of metallic sodium. A large Hilger quartz spectrograph, with a 170-cm focus, was employed.

Mechanism of Excitation

The discharge in the ozonizer consists of a myriad of tiny sparks which may under certain conditions become so finely and uniformly distributed as to cause the appearance of a uniform glow. The character of the discharge is similar to that of the Tesla luminescence,[1] though the discharge between double dielectrics with small gas

space separation is probably more completely distributed in the form of many fine discharges than is the Tesla luminescence as commonly used, and it can be produced without special apparatus.

The mechanism of the ozonizer action has been the subject of a large amount of work[2] which we shall not attempt to discuss here. The character of the discharge, however, seems to be in accord with the following description. Since an ozonizer does not operate under steady direct-current voltages, some important difference must be found in the conditions when alternating or pulsating direct voltages are applied. On the rise of voltage in the first quarter cycle there is a sweeping of the residual ions in the gas to the walls of the dielectric. Were the voltage change to stop here, that is, as in the application of a steady direct-current voltage, no further change would occur in the gas. In striking the walls of the dielectric, the ions, which are swept out of the gas by the rise of voltage in the first quarter cycle, eject electrons from the dielectric material. Thereafter these are also included in the process of sweeping, and they produce ionization in the gas as they move under the potential gradient. If the frequency is sufficiently high, as is the case at 60 cycles, this ionization produced in the gas does not disappear entirely in the time between voltage peaks. The ionization rises from the moment of applying the alternating potential until it comes to a steady-state condition, at which the average rate of the removal of ions by sweeping and by recombination is equal to the average rate at which ions are being produced.

Thus a short time after the application of the alternating potential the gas has become a conducting medium, still perhaps of rather high resistance, but nevertheless able to give appreciable currents at the voltages applied. Discharge phenomena occur in the gas space, therefore, but these are manifestations not so much of breakdown as of the carrying of current by the partially ionized gas. Now it is known that in a low pressure gas discharge, the cross section of the discharge decreases with increasing pressure. At

[1] N. Tesla, *Experiments in Alternate Currents of High Potential and High Frequency* (McGraw-Hill, 1904), p. 29 *et seq.*; H. Kauffman, Zeits. f. physik. Chemie **26**, 719 (1898); **28**, 673 (1899); McVicker, Marsh and Stewart, J. Chem. Soc. **123**, 642 (1923); **129**, 17 (1926).

[2] See for example G. Glockler and S. C. Lind, *The Electrochemistry of Gases and Other Dielectrics* (John Wiley and Sons, New York); M. Moeller, *Das Ozon*, (Vieweg, Braunschweig, 1921).
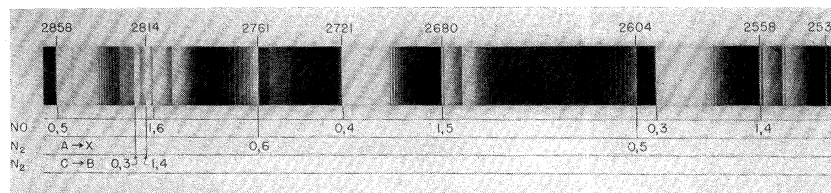
FIG. 2. Portion of ultraviolet emission from ozonizer filled with nitrogen at atmospheric pressure.

a given pressure, moreover, the cross section of the current stream in the gas decreases with decreasing current. Thus with increase of gas pressure and decrease of the current carried, the cross section of the current stream decreases. In the source of excitation used in the present work, one has these two conditions in the extreme; the pressure is atmospheric, and, because no single onset of current can discharge more than a small area of the ion layer on the dielectric surface, the current is very low. This results in a localized discharge which is probably of very small cross section. Such discharges occur at many places along the surface of the dielectric since, because no single discharge can clear more than a very small area, another such discharge can occur in the immediate neighborhood. Each of the tiny sparks consists of an extremely weak electric discharge. The total effect represents, nevertheless, appreciable light, especially when the annular space of the ozonizer is observed end-on. When the apparatus shown in Fig. 1 is operated at 15,000–25,000 volts and 60 cycles, the current indicated by an ordinary a.c. milliameter is of the order of a milliampere.

RESULTS AND DISCUSSION

With dry nitrogen at atmospheric pressure in the ozonizer, the emission observed consisted principally of the second positive group of nitrogen and the gamma-bands of NO, which appear to be of roughly the same intensity. The first positive group of nitrogen in this source is very much weaker relative to the second positive group than in an ordinary glow discharge. Other spectra can be seen on the plates and in particular the bands which have been observed by Vegard[3] and by Kaplan[4] and which are be-

lieved to be due to the intersystem transition $A\ ^3\Sigma_u{}^+ \rightarrow X\ ^1\Sigma_g{}^+$. Their intensity is relatively weak and the emission of the NO bands interferes greatly in observing them. However, by reducing the oxygen content a few of these intersystem transition bands were observed free of overlapping emission.

Figure 2 is an enlargement of a portion of a spectrogram showing some of the intersystem nitrogen bands in which part of the rotational structure is clearly visible. The rotational structure, although distinct, cannot, however, be accurately measured because of low resolution; this is due partly to the wide slit employed (0.05 mm), but chiefly to variation in room temperature during the exposure times of seven to eight hours. In the vicinity of the heads the lines are not resolved. In one weaker exposure with a slit width of 0.02 mm and less than the ordinary temperature variation, the lines were sharper and the diffuse lines near the head were weakened relative to those further removed. This indicated that they were composed of multiple overlapping lines. The rotational structure has been partially measured for the bands $0-5$, $0-6$, $1-4$ and $1-5$ and is given in Table I, the most satisfactory measurements are those for the bands $0-5$ and $0-6$.

The rotational constants for both the upper and lower levels of the $A \rightarrow X$ transition have been determined from other band systems in nitrogen better than could be done from the

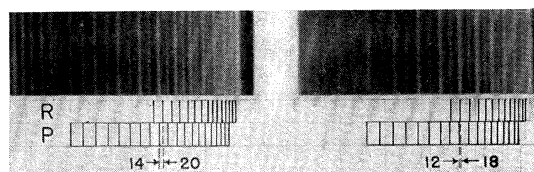[3] L. Vegard, Zeits. f. Physik 75, 30 (1932).
[4] J. Kaplan, Phys. Rev. 44, 947 (1933); 45, 675 (1934); and 45, 898 (1934). Nature 141, 645 (1938) and 141, 1139 (1938).

FIG. 3. The bands $0-6$ and $0-5$ of the $A \rightarrow X$ transition in N_2.

FIG. 4. Comparison of ozonizer and arc excitation in oxygen.

present spectrograms. In Table I the observed values for the lines are compared with those computed from the rotational constants given by Sponer[5] and from an estimated position of the origin of each band. Each band is considered to consist of a single P and R branch, and further fine structure is neglected. The agreements seem to be as good as can be expected and make more certain the identification of the emitter of the bands. As shown in Table I higher members of the R branch lie in nearly the same positions as lower members of the P branch. In Table II a comparison is made of three sets of combination differences. It seems probable that, because of the relative intensities, the measured values almost correspond to the P branch lines. Fig. 3 shows the bands $0-5$ and $0-6$ with a portion of the rotational structure of each sketched below. The alternation of intensity in the band lines can be clearly seen.

It happens that it is the stronger lines of each branch which nearly overlap so that the intensity alternation is visible, and is not partially masked as would be the case if the stronger lines of the one branch overlapped the weaker lines of the other branch. An approximate determination of the intensity ratio, based on ten lines from one plate in each of the two bands $0-5$ and $0-6$, gave 1.94 as the average of sixteen values. These lay in the range 1.82 to 2.08 and were individually the average of the two ratios for three consecutive lines. This latter averaging was made to correct for the general change in intensity of the lines with change of quantum number. Correction was not made for background. The result indicates that the ratio is 2 : 1, in accord with the two units of spin ($i = 1$) possessed by the N^{14} nucleus.

TABLE I. *Rotational structure of* $(0-6)$, $(0-5)$, $(1-5)$ *and* $(1-4)$ *bands.*

K''	P CALC. (CM⁻¹) VAC.	OBS. (CM⁻¹) VAC.	R CALC. (CM⁻¹) VAC.	K''	K''	P CALC. (CM⁻¹) VAC.	OBS. (CM⁻¹) VAC.	R CALC. (CM⁻¹) VAC.	K''
	2761A band (0−6) estimated origin at 36201.0 cm⁻¹					2604A band (0−5) estimated origin at 38389.0 cm⁻¹			
		*	36203.9	0			*	38391.9	0
		*	205.8	1			*	393.8	1
		*	206.9	2			*	394.8	2
		36207.5	207.1	3			*	394.9	3
		*	206.4	4			38394.7	394.0	4
		*	204.8	5			*	392.3	5
		*	202.3	6			*	389.5	6
1	36197.2	*	198.9	7	1	38385.2	*	385.9	7
2	192.6	193.6	194.6	8	2	380.5	380.4	381.3	8
3	187.0	*	189.5	9	3	374.8	*	375.8	9
4	180.6	182.3	183.4	10	4	368.2	368.3	369.4	10
5	173.2	*	176.4	11	5	360.7	359.4	362.0	11
6	165.0	166.0	168.5	12	6	352.3	352.2	353.7	12
7	155.9	156.0	159.8	13	7	342.9	345.3	344.4	13
8	145.9	147.1	150.1	14	8	332.6	334.1	334.4	14
9	135.0	134.0	139.6	15	9	321.3	321.8	323.3	15
10	123.1	123.7	128.2	16	10	309.2	310.3	311.3	16
11	110.4	110.2	115.8	17	11	296.1	297.5	298.3	17
12	96.9	99.1	102.6	18	12	282.0	283.0	284.5	18
13	82.4	83.2	88.5	19	13	267.1	267.8	269.7	19
14	67.0	69.2	73.5	20	14	251.2	251.8	253.9	20
15	50.7	52.2	57.6	21	15	234.4	235.4		
16	33.5	36.3	40.8	22	16	216.6	218.1		
17	15.5	16.5			17	198.0	199.6		
18	35996.5	35998.6			18	178.3	180.0		
19	976.6	979.3			19	157.8	156.8		
20	955.9	958.3			20	136.3	139.5		
21	934.3	938.5							
22	911.7	916.7							
	2510A band (1−5) estimated origin at 39820.0 cm⁻¹					2378A band (1−4) estimated origin at 42036.0 cm⁻¹			
		*	39822.8	0			*	42038.8	0
		*	824.7	1			*	40.7	1
		*	825.7	2			42041.5	41.5	2
		*	825.6	3			*	41.4	3
		39823.6	824.6	4			*	40.3	4
		*	822.7	5			*	38.2	5
		*	819.8	6			*	35.0	6
1	39816.2	*	815.9	7	1	42032.2	*	30.9	7
2	811.4	811.8	811.1	8	2	27.3	25.3	25.8	8
3	805.7	*	805.3	9	3	21.5	*	19.7	9
4	799.1	800.0	798.6	10	4	14.7	13.2	12.6	10
5	791.4	*	790.9	11	5	6.9	*	4.6	11
6	782.9	782.9	782.3	12	6	41998.1	41997.4	41995.5	12
7	773.3	774.2	772.7	13	7	988.3	987.0	985.4	13
8	762.8	763.0	762.1	14	8	977.5	976.2	974.4	14
9	751.4	752.2	750.6	15	9	965.7	964.6	962.3	15
10	738.9	738.9	738.1	16	10	953.0	952.5		
11	725.6	726.1	724.7	17	11	939.2	938.8		
12	711.3	710.5	710.3	18	12	925.5	924.8		
13	696.0	699.3			13	907.7	907.8		
14	679.7	680.8			14	892.0	893.2		
15	662.5	665.5			15	874.2			
16	644.4	645.5			16	855.5	853.6		
17	625.3	626.4							
18	605.2	606.5							

* The first measured lines are broad and diffuse and cover the starred assignments.

5 H. Sponer, *Molekülspektren* (Springer, Berlin, 1935).

TABLE II. *Combination differences of the bands.*

K''	$R(K)-P(K)$ (0−6)	(0−5)	CALC.	$R(K-1)-P(K+1)$ (0−5)	(1−5)	CALC.	$R(K)-P(K)$ (1−5)	(1−4)	CALC.
12	66.9	69.2	71.7	91.6		94.9	72.4	72.6	71.0
13	72.8	77.5	77.3	100.4	102.1	102.5	74.9	79.2	76.7
14	77.9	82.3	83.2	109.9	108.7	110.0	82.2	83.0	82.4
15	81.8	86.4	88.9	116.0	117.5	117.8	86.7		88.1
16	87.4	92.2	94.7	122.2	125.8	125.3	93.4	98.9	93.7
17	93.7	97.9	100.3	130.3	132.4	133.0	99.7		99.4
18	100.5	103.0	106.2	140.7		140.5	104.0		105.1
19	103.9	111.0	111.9	143.5		148.2			
20	110.9	112.3	116.9						

The source of excitation used in the present work possesses some usefulness in band spectra research because of the two conditions of high gas pressure and low temperature that can be simultaneously met. The difference between two sources of excitation which do not have these two factors in common is illustrated in Fig. 4 in which some emission of oxygen containing a small amount of nitrogen is shown. The emission in the upper picture is from the ozonizer while in the lower picture it is from a high voltage, low current arc operated by the same type of transformer. In both cases the gas was at atmospheric pressure. In the lower picture the principal emission is the Runge bands of oxygen,[6] while from the ozonizer it is the second positive group of nitrogen. A further study is being made of the mechanism of excitation in the ozonizer.

The authors gratefully acknowledge the assistance given them by Mrs. L. S. Deming and Mr. R. T. O'Connor in the course of this work.

[6] C. Runge, Physica 1, 254 (1921).

The Analysis of Nuclear Binding Energies

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The fine structure of the mass defect curve has been studied, especially with reference to the nuclear symmetry character. From the analysis it has been found possible to obtain satisfactory empirical curves for the functions L and E_0 appearing in Wigner's theory. The behavior of these curves allows deductions to be made regarding nuclear shells, and binding energies of both known and as yet unknown, unstable, nuclei. About 150 masses have been computed in this way.

INTRODUCTION

THE light nuclei are well known to exhibit a marked periodicity of four, which may be interpreted as a consequence of the operation of the Pauli principle in systems containing two kinds of heavy particles. One may obtain an instructive representation of this behavior by plotting, as a function of the mass number A, the change in binding energy observed on the addition of successive particles. Such a plot (corresponding to the familiar graphs of ionization potentials for atomic electrons) is shown in Fig. 1. The effect is exhibited for two methods of building up atoms:

$$\nu+H+\nu+H+\nu+H+\cdots,$$

and $$\nu+\nu+H+H+\nu+\nu+\cdots,$$

where ν and H represent, respectively, a neutron and a hydrogen atom. The following facts are made evident without a detailed study by this method of displaying the empirical information on atomic masses.

(1) Successive particles entering the same period or level are bound with energies increasing in a roughly linear way for small mass numbers, but later a depression of the proton points takes place.

(2) The heights of the peaks decrease as the mass number increases.

(3) The binding energy of the last proton in Ne^{20} is abnormally high compared to that in O^{16}. This is probably to be correlated with the unusually low total binding energy of Ne^{20} noticed by Hafstad and Teller.[1] (We shall later adduce evidence that Ne^{20} is at the end of the $2s$ sub-shell.)

E. Wigner[2] has studied the consequences of a detailed application of the Pauli principle to a many-body nuclear model in which the specifically nuclear forces are equal between all pairs of particles and do not depend on the spin ("1th approximation"). Although it is now well known, particularly from the neutron-proton scattering

[1] L. R. Hafstad and E. Teller, Phys. Rev. 54, 684 (1938).
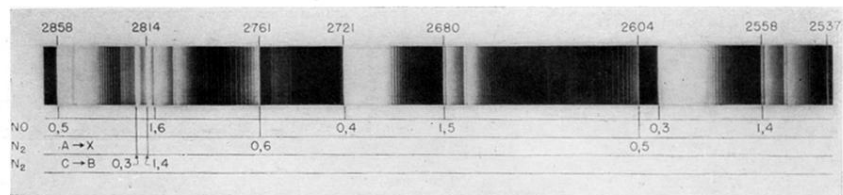[2] E. Wigner, Phys. Rev. 51, 947 (1937).

FIG. 2. Portion of ultraviolet emission from ozonizer filled with nitrogen at atmospheric pressure.

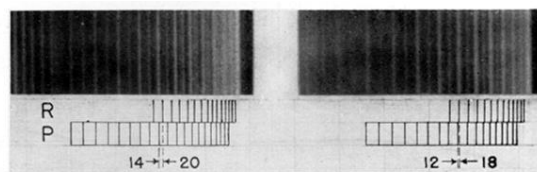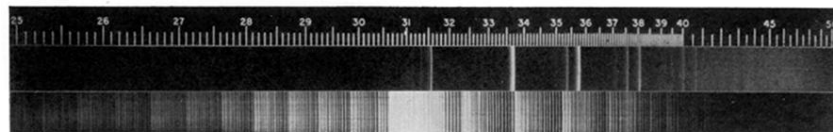FIG. 3. The bands $0-6$ and $0-5$ of the $A \rightarrow X$ transition in N_2.

Fig. 4. Comparison of ozonizer and arc excitation in oxygen.