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Spectra Emitted from Solid Nitrogen Condensed at 4.2°K from a Gas Discharge*

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Products of an electrical discharge in flowing nitrogen are frozen at liquid helium temperatures. The solid material emits a glow. Emission spectra have been obtained in the region 2200 A to 7000 A. The most intense features of these spectra, five sharp lines near 5230 A and three diffuse lines between 5530 A and 5670 A, are attributed to radiation from nitrogen atoms as affected by the solid lattice. There is a less intense series of bands, degraded to the red, extending from 3500 A to 6400 A. This system most probably arises from a transition of the N_2 molecule, probably to the $A^3\Sigma_u^+$ state. In the same region there is a group of very weak diffuse bands which may be emission from NO_2. In addition several weak bands are attributed to the beta and gamma systems of NO and to NH.

When the flow of nitrogen and the electrical discharge are removed, an afterglow from the solid is observed. The spectrum of the afterglow shows only the group near 5230 A and a weak line at 5944 A. The half-life of this afterglow radiation is about 15 seconds. Intensities of all other features decay to zero in less than one second.

I. INTRODUCTION

IN recent years several laboratories have attempted to form solids containing large concentrations of free radicals. These efforts have led to some very interesting phenomena[1–3] and to the tentative conclusion that free radicals can be stored in solids at low temperature.

While investigating a solid condensed at liquid helium temperature from the products of an electrical discharge through nitrogen gas, a glow was observed from the solid.[4] Spectra have been obtained and wavelengths of the radiation have been measured between 2200 A and 7000 A. Many of the observed lines and bands reported here have been explained in terms of the interaction between nitrogen atoms and nitrogen molecules and the solid.[5] In many respects these spectra are similar to those first observed by Vegard[6] and by McLennan and Shrum[7] in 1924, who bombarded solid nitrogen with electrons and "canal rays." Since the early work of Vegard[8,9] and of McLennan and co-workers,[10] no further work has been reported on experiments of this sort.

The strongest features of the radiation observed in the present experiments are five relatively sharp lines near 5230 A and three diffuse lines between 5530 A and 5670 A. This radiation is thought to be caused by transitions of nitrogen atoms in the solid.[5] There is a striking, though less intense, series of bands degraded to the red which extend from 6390 A to 3572 A. These bands are probably due to a $^5\Sigma_g^+ - A^3\Sigma_u^+$ transition of the nitrogen molecule. Some bands of the first positive system of N_2 also are observed in long exposures. Over much of this same region, there are also some very weak diffuse bands which appear to be related to the emission system of the NO_2 molecule. In the ultraviolet and blue regions, there are two series of bands which increase in intensity with oxygen impurity and which most probably are the beta and gamma systems of NO. The $A^3\Pi_i - X^3\Sigma^-$ and $c^1\Pi - a^1\Delta$ bands of NH also are present.

When the flow of nitrogen and the discharge are stopped, the solid continues to glow. The radiation consists of the emission near 5230 A, with a much smaller contribution at 5944 A. The half-life of this radiation varies between 12 and 22 seconds; all other radiation decays rapidly with a half-life considerably less than one second.

II. DESCRIPTION OF APPARATUS

Two types of apparatus were used in these experiments. The original apparatus, constructed of Pyrex glass, is illustrated in Fig. 1. Nitrogen gas is admitted through a control stopcock from a cylinder of nitrogen and passes through an electrodeless discharge. The discharge is maintained in the wave-guide resonator by a 2450-Mc/sec power supply (125 watts input power). The surface, S, immersed in liquid helium acts as a trap by freezing out all gases except helium, and thus is an effective high-speed pump for maintaining the flow of nitrogen. In order to prevent the solidification of discharge products at temperatures above 4.2°K, the gas is carried to the cold walls within a passageway near room temperature. This relatively high tempera-

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[1] F. O. Rice and M. Freamo, J. Am. Chem. Soc. **73**, 5529 (1951); **75**, 548 (1953).

[2] Giguere, Secco, and Eaton, Discussions Faraday Soc. **14**, 104 (1953); J. Chem. Phys. **22**, 2085 (1954).

[3] H. P. Broida and J. R. Pellam, J. Chem. Phys. **23**, 409 (1955).

[4] H. P. Broida and J. R. Pellam, Phys. Rev. **95**, 845 (1954).

[5] C. M. Herzfeld and H. P. Broida, Phys. Rev. **101**, 606 (1956).

[6] L. Vegard, Nature **113**, 716 (1924).

[7] J. C. McLennan and G. M. Shrum, Proc. Roy. Soc. (London) **A106**, 138 (1924).

[8] L. Vegard, Compt. rend. **180**, 1084 (1925); Ann Physik **79**, 377 (1926); Leiden Comm. **16**, No. 175 (1924–1926); Leiden Comm. **19**, No. 205 (1929–1931).

[9] Vegard published a large number of articles on his studies but it is difficult to summarize his results. Some of his more complete publications are given in reference 8.

[10] McLennan, Ireton, and Thompson, Nature **118**, 408 (1926).

ture is maintained by forcing warm helium gas between the compound walls, *D*, surrounding the channel, *E*.

This apparatus had the disadvantage of requiring observations of spectra through five layers of glass, two liquids, and the solid deposit. Furthermore it was impossible to observe wavelengths shorter than that of the cutoff of Pyrex glass near 3100 A. The second apparatus was designed[11] to overcome these difficulties. It is a metal Dewar system of the type described by Duerig and Mador.[12] The modified system is illustrated in Fig. 2. The discharge tube and the tube for carrying discharge products to the cold surface are the same as in Fig. 1. Products from the discharge are collected upon a copper wedge kept cold by thermal contact through copper bars to the liquid helium reservoir. Early tests showed that the glowing material could be deposited on clean copper, and also on quartz and on sodium chloride suspended between the copper bars. Since thicker layers of material were deposited on sections of metal facing the direction of gas flow, a wedge-shaped collecting surface was used. Our later experience showed that the use of this wedge did not greatly increase the brightness of the glow.

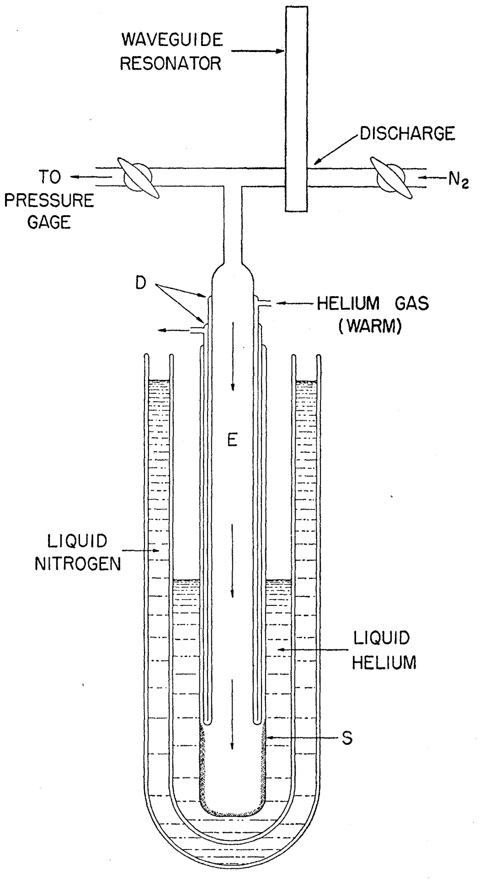

FIG. 1. Pyrex Dewar and collection system.

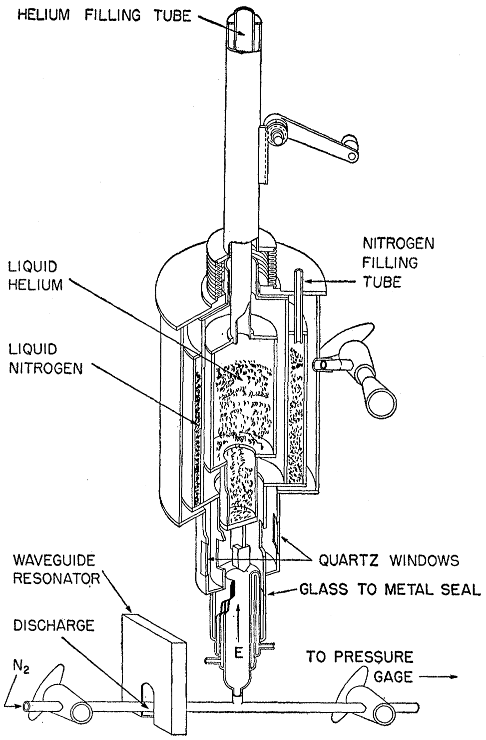

FIG. 2. Metal Dewar and collection system.

Under our best operating conditions, the glow in the metal system was maintained for 1 hour while depositing about 1.5 g of nitrogen and using approximately 2.5 liters of liquid helium. In the glass system the glow has been maintained for 45 min while depositing 5.5 g of nitrogen and using 7 liters of liquid helium. Part of the helium was used to cool the apparatus from 77°K to 4.2°K.

Radiation was observed through quartz windows on both sides of the wedge and was focused by quartz lenses onto the slits of the spectrographs. Two prism spectrographs and a direct reading grating monochromator were used simultaneously. Each prism instrument has interchangeable quartz and glass optics; both sets of optics were used in each instrument. One has an $F/10$ optical train giving, with the slit widths used, a resolution of about 1.5 A at 5200 A (glass) and 0.5 A at 2600 A (quartz). The other spectrograph has a $F/4$ camera giving an increase in photographic speed speed of 6.5 times; with the slits used it gave a resolution of about 4 A at 5200 A (glass) and 0.8 A at 2600 A (quartz). The direct reading monochromator[13] uses photomultiplier detection and the signal is amplified and transferred to a pen recorder.[14] Because of the low

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[11] A Dewar constructed at the Johns Hopkins University Applied Physics Laboratory, was loaned to us by Dr. R. C. Herman.

[12] W. H. Duerig and I. L. Mador, Rev. Sci. Instr. **23**, 421 (1952).

[13] W. G. Fastie, J. Opt. Soc. Am. **42**, 641 (1952).

[14] This instrument was constructed by the Research Department of the Leeds and Northrup Company and loaned to the National Bureau of Standards on a field trial.

TABLE I. Observed lines and bands emitted by a solid of condensed products of a discharge through nitrogen gas.

Wavelength A (air)	Wave number cm^{-1} (vacuum)	Intensity	System					
2368.7	42 204.3	20					E	
2448.5	40 829.0	5					E	
77.3	40 354.3	40					E	
2509.0	39 844.5	1		X				
23.6	39 614.0	3					E	
59.1	39 064.5	20					E	
95.1	38 522.6	30					E	
2613.8	38 247.1	1				D		
29.7	38 015.8	5				D		
38.0	37 896.2	5			C		E	
79.4	37 310.7	10					E	
2721.8	36 729.5	20					E	
53.5	36 306.7	3					E	
56.0	36 273.8	3				D		
61.8	36 197.6	3			C		E	
2810.4	35 571.7	10					E	H?
35.4	35 258.0	1		X				
58.9	34 968.2	7					E	
94.8	34 534.6	7				D		
97.2	34 506.0	3					E	
2902.7	34 440.6	10			C			
51.4	33 872.4	10					E	H?
61.8	33 753.4	1				D		H?
76.5	33 586.7	1						H?
83.6	33 506.8	3					E	
3007.6	33 239.4	7					E	
45.6	32 824.7	15				D	E	
54.5	32 729.1	30			C			
80.2	32 456.0	15	J					
89.0	32 363.6	20	J				E	
3157.8	31 658.5	20						H?
68.5	31 551.6	10					E	
3200.6	31 235.1	3					E	
09.2	31 151 4	10				D		
19.4	31 052.8	30			C			
58.5	30 680.2	10		X				
67.2	30 598.4	5						H?
72.1	30 552.6	10					E	
3359.2	29 760.5	40	F					
70.6	29 659.8	30	F					H?
87.3	29 513.6	5				D		
98.0	29 420.7	20			C			
3442.6	29 039.5	5					E	H?
57.3	28 916.0	5				D	E	
69.6	28 813.5	1						H?
3531	28 312	7 max		B				
72.4	27 984.4	20	A					
76.2	27 954.7	5	A					H?
87.0	27 870.5	5				D		
98.0	27 785.3	40			C			
3740	26 730	7 max		B				
69.5	26 521.2	40	A					
76.7	26 470.6	10	A					
3803.5	26 284.1	10				D		H?
3818.9	26 178.1	30			C			
85.9	25 726.8	40				D		
3985.8	25 082.0	60	A					
91.3	25 047.4	10	A					
97	25 012	5	A					H?
4100	24 383	8 max		B				
4224.0	23 667.6	90	A					
31.0	23 628.4	10	A					
4316	23 163	10 max		B				
4487.6	22 277.4	100	A					
96.0	22 235.8	10	A					
4621	21 634	7 max		B				
4782.0	20 905.9	80	A					
87.4	20 882.3	1	A					
92.0	20 862.3	5	A					
4938	20 245	5		B				
5026	19 891	2		B				
5111.7	19 557.5	60	A					
19.6	19 527.4	5	A					
22	19 518	5	A					
5214.2	19 173.1	40					α	
20.1	19 151.4	100					α	
28.5	19 120.6	200					α	
35.0	19 096.9	150					α	
40.4	19 077.2	80					α	
5483.3	18 232.1	50	A					
93	18 200	1	A					
5549	18 016	200					β	
5616	17 801	150					β	
5657	17 672	130					β	
5906.1	16 927	20	A					
43.8	16 820	30					α'	
6319	15 821	5					G	
90	15 645	40	A				G	
6456	15 485	10					G	
6528	15 314	20					G	
6612	15 120	20					G	
6692	14 939	5					G	

Tentative assignments

α, β—atomic nitrogen transitions
α'—unidentified, probably atomic
A—$^5\Sigma-{}^3\Sigma$, N_2
B—NO_2, diffuse bands. Position of maximum intensity tabulated.
C—NO β, diffuse bands. Band head position tabulated.
D—NO β, shorter λ of doublet, degraded to red.
E—NO γ, longest λ of 4 observable heads, degraded to violet.
F—NH, heads
G—N_2, first positive
H—N_2, second positive
J—OH, (0,0) Q_1, Q_2
X—Unidentified

light intensity a wide slit (about 50 microns) was used, permitting a resolution of the order of 0.5 A.

III. VISUAL OBSERVATIONS

While the discharge is maintained, the collecting surfaces (Figs. 1 and 2) emit visible radiation strong enough to be seen in daylight. The color of this glow changes from a blue-green to a yellow-green with increasing nitrogen flow rate. At too high a flow the glow disappears, and in the metal system the deposited solid evaporates. The glow does not always begin as soon as discharge products are collected on the cold walls. Even though the correct flow and discharge conditions are established the glow may not appear for the first minute or two. We do not know if the condition of the surface is critical for the appearance of the glow. However, the glow has been observed with products of discharges through nitrogen deposited on clean glass, copper, silver, fused silica, sodium chloride, and solid oxygen. A primary requirement is that the surface be below 35°K. It appears that the brightest glow occurs at a few degrees above 4.2°K.

Another characteristic of the surface glow is the random occurrence of local bright spots while material is depositing. Brilliant blue flashes can be observed on (or in) the surface. In the glass apparatus the region of the blue flash is a few millimeters wide. It appears to be an explosive reaction spreading in a fraction of a second for several centimeters within the deposited material. In the metal apparatus, similar flashing occurs and, in addition, a more usual occurrence is for the green to disappear leaving a blue surface. This latter effect occurs with different relative brightness every few seconds. Photoelectric measurements of this phenomenon were made and are discussed below.

If the flow of nitrogen is stopped, the discharge goes out and an afterglow from the cold collected material persists for as long as 5 minutes. During this time the intensity diminishes steadily with no spontaneous flashing. The addition of more nitrogen through the discharge causes the material again to glow brightly. In one case the afterglow lasted more than 4 minutes even though the added deposition was for less than 10 seconds.

When the green afterglow has disappeared, warming the surface (by the addition of warm nitrogen or helium or by removal of liquid helium) causes a blue-green afterglow. Under conditions in which the temperature does not change rapidly this afterglow has been observed for an hour. Indications are that the blue-green afterglow occurs only within a few degrees below 35°K. In two experiments using the glass apparatus, after the disappearance of both the green and blue afterglows, reimmersion of the vessel into liquid helium resulted in the reappearance of a somewhat weakened green afterglow.

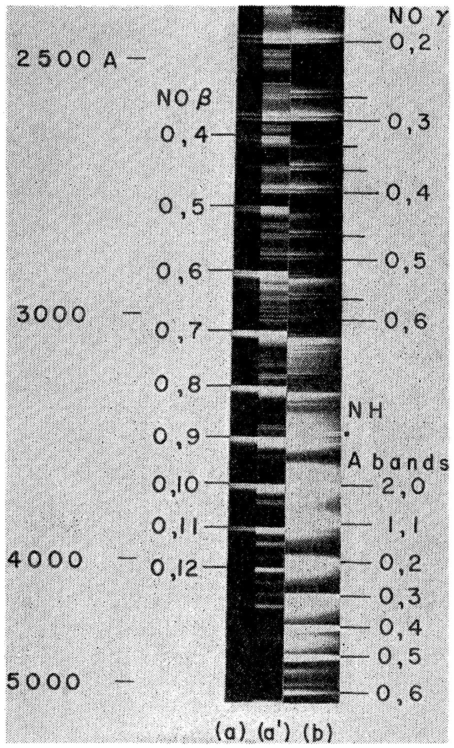

FIG. 3. (a) Spectrum of afterglow in flowing nitrogen gas at pressure of 4 mm Hg. The glow was observed 20 cm from the discharge in a path length of 5 cm, $F/4$ quartz prism instrument; slit width 0.03 mm; *I-F* (3) plate; exposure time 15 min. (a′) Same as (a), but exposure time 50 min. (b) Spectrum from solid at 4.2°K while products from a discharge through nitrogen are being collected. Slit width 0.014 mm; 103a-0 plate; exposure time 10 min.

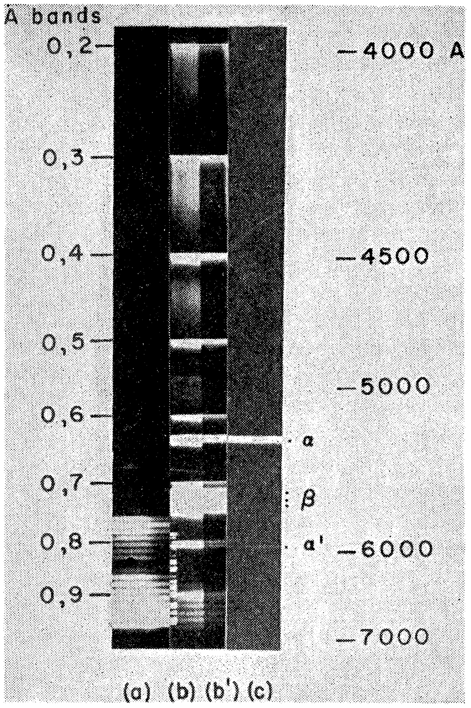

FIG. 4. (a) Spectrum of afterglow in flowing nitrogen gas at pressure of 4 mm Hg. The glow was observed 20 cm from the discharge in a path length of 5 cm, $F/4$ glass prism instrument slit width 0.020 mm; 103*a-F* plate; exposure time 15 min. (b) Spectrum from solid at 4.2°K while products from a discharge through nitrogen are being collected. Slit width 0.041 mm; exposure time 25 min. (b′) Same as (b), but exposure time 5 min. (c) Spectrum of green afterglow from solid nitrogen near 4.2°K; discharge off. Total accumulated exposure time 30 min.

The glows originate from the solid or from the surface where deposition occurs. This is apparent to the observer and has been verified in two ways. In the metal system with the same nitrogen flow and the same discharge conditions, but without a cold surface for condensing the material, no spectrum is obtained in more than 10 times the exposure time needed to obtain the stronger features when a deposit is formed. Furthermore in one experiment a green afterglow was obtained and then a small tip on the bottom of S (Fig. 1) purposely was broken to allow helium at 4.2°K into the vessel. Although one atmosphere of cold helium gas was admitted, the glow was not observably affected.

IV. SPECTROSCOPIC OBSERVATIONS

The spectra were photographed under various conditions. Figures 3 and 4 show representative spectra.

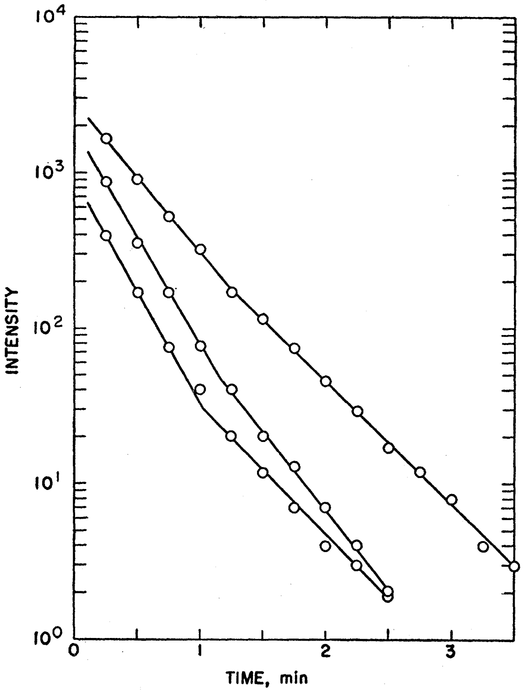

FIG. 5. Logarithm of measured intensity at 5228 A (α) as function of time after the discharge is turned off. Three separate runs are shown. The difference in slopes is unexplained.

Table I lists the wavelengths of most of the prominent features together with eye estimates of the relative intensities on an arbitrary scale of 1 to 200. Intensity of 1 indicates the faintest feature visible in an exposure time of 25 minutes for the *F*/4 glass instrument with 103*a*-*F* plates. The same intensity estimate represents an exposure time of 10 minutes for the *F*/4 quartz instrument with 103*a*-0 plates. The intensity estimate of 200 is assigned to the most intense lines which can be photographed with the *F*/10 instrument in less than 1 minute on a 103*a*-*F* plate. The symbols in the fourth column of Table I indicate the lines or bands that are associated with each other, i.e., appear under the same conditions, have a similar structure, or can be identified from gas spectra. Tentative assignments of the various bands also are given.

Commercial cylinder nitrogen was used. Nitrogen flow rates about 20 cm^3/min (NTP) were found to give the brightest green glow in the metal apparatus; in the glass apparatus the optimum flow rate was 105 cm^3/min. Two types of nitrogen gas were used—Matheson Chemical Company prepurified nitrogen containing less than 10 parts per million of both hydrogen and oxygen; and Southern Oxygen Company superdry nitrogen containing less than 1 part per million of hydrogen and a few tenths of one percent of oxygen. The same phenomena were observed with both types of nitrogen. In one experiment a leak developed at the quartz windows. This addition of air enhanced the band systems of molecules containing oxygen. Figure 3 (b), shows the spectrum obtained under these conditions.

TABLE II. Intensity changes of features of the solid glow, coincident with the blue flash.

Wavelength, A	System	% Change	Half-life, sec
5565	β	<±10	<0.10
5230	α	−250	12–22
4782	*A*	+ 20	<0.25
4379	*B*	+100	<0.25

Figures 3 and 4 also show for comparison some gas afterglow spectra obtained under the brightest conditions in the same flowing nitrogen gas at a pressure of 4 to 5 mm Hg, more than 5 times the pressure used while obtaining the solid glow.

Photoelectric measurements were used to supplement visual observations of changing conditions. Table II contains a summary of some observed intensity changes which accompany the blue flashes. Column 1 gives the wavelengths at which the intensity was observed. Column 2 gives the designation of the other lines or bands having the same behavior. Column 3 shows the maximum percentage change of signal occurring simultaneously with an observed blue flash. A minus (−) sign means that the intensity decreased and a plus (+) sign means that the intensity increased. The right-hand column gives the time after the discharge is off for the intensity to decay to one-half its value. With the exception of the α radiation, all intensities dropped to zero more rapidly than the pen recorder could indicate. Three representative plots of the decay of the α radiation are shown in Fig. 5.

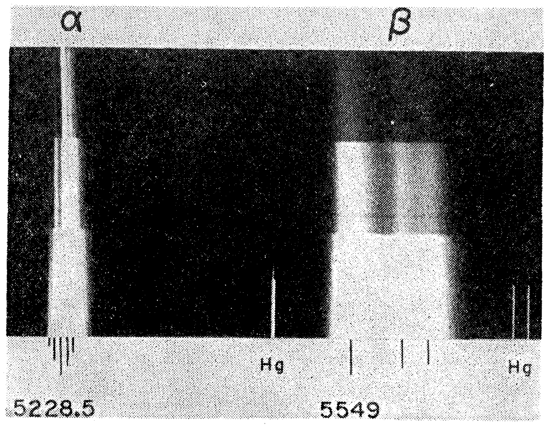

FIG. 6. Spectra of the α and β lines emitted by the solid near 4.2°K while the discharge is on. *F*/10 glass prism instrument; 103-*F*(3) plate; exposure time—3, 9, and 27 minutes.

V. DISCUSSION

The spectra observed from the solid nitrogen are quite different from those obtained from either the nitrogen discharge or the nitrogen afterglow. Tentative assignments have been made for the observed systems in the spectra obtained from the solid material.

The α and β lines, (see Fig. 6) are thought to be emission from nitrogen atoms as affected by the solid. The relative intensity of these lines varies with flow rate, the β lines coming out more strongly at higher flow. As Fig. 6 shows, the α lines are quite narrow, with a sharp edge on the short wavelength side. The β lines are quite diffuse, having an average width of about 30 A. Herzfeld and Broida[5] postulate that the α lines near 5230 A result from the $^2D-^4S$ transition of atomic nitrogen. The ^2D state in the gas has a lifetime of several hours.[15] while the lifetime in the solid is of the order of 15 seconds. No explanation has yet been made of the line at 5944 A, but the line is thought to originate in a manner similar to the α lines because it occurs under the same conditions.

Herzfeld and Broida[5] also tentatively assign the A bands to the $^5\Sigma_g{}^+-A^3\Sigma_u{}^+$ transition of molecular nitrogen. These 10 bands fit the following equation to within the experimental error of measurement, $\pm 0.5\ \text{cm}^{-1}$:

$$\nu=27961.1+12.1v'-(1462.2v''-10.20v''^2+1.6\times10^{-2}v''^3+1.0\times10^{-5}v''^6).$$

The E bands are the γ system of NO ($A^2\Sigma^+-X^2\Pi$). There may be a small shift (about 0.6 A) to shorter wavelengths of the bands in the solid as compared to those in the gas afterglow. Table III lists the measured wavelengths of the four heads ($^\circ P_{12}$, P_2, P_1, Q_1) in the solid and in the gas afterglow, as well as the vibrational quantum numbers.[16,17] The intensity estimates, for the spectra from the gas and the solid, were made from our photographs on our arbitrary scale of 0 to 10. This is a different scale from that described for Table I, but represents a self-consistent scale for this table. Curiously enough (Fig. 3) the vibrational and rotational intensity distributions indicate a higher "temperature" in the solid than in the gas afterglow.

The D lines appear to be the bands of the β system of NO ($B^2\Pi-X^2\Pi$) shifted about 9.4 A (approximately 100 cm⁻¹) to longer wavelengths. Associated with each pair of D lines and on the long-wavelength side is a diffuse band C. The C-bands are quite broad, having a width of about 10 A. Table IV lists the measured wavelengths of the double heads in the solid and in the gas afterglow. Vibrational assignments are from Pearse and Gaydon.[17] The intensity estimates were made in the same manner as for Table III. If there is no rotation in the solid, the measured shift may in part be caused by the difference between the position of the origin and that of the band head and in part caused by solid state effects. Also it is possible that the diffuse bands C may be caused by hindered rotation as suggested for

TABLE III. Gamma system of NO ($A^2\Sigma^+-X^2\Pi$), E-bands, in the solid and in the gas afterglow. Band heads of the four branches, $^\circ P_{12}$, P_2, P_1, and Q_1 are listed.

Intensity			Wavelength, A	
Solid	Gas	v', v''	Solid	Gas[a]
5	6	0, 1	2361.8	2363.6
			2369.0	2370.2
3	2	1, 3	2440.0	2439.5
			2448.5	2447.3
10	10	0, 2	2470.0	2469.8
			2471.3	2470.9
				2477.0
			2477.3	2478.4
1	0	2, 5	2513.4	
			2515.1	2515.6
			2523.6	2523.2
5	2	1, 4	2550.3	2549.8
			2551.0	2550.6
			2557.6	2557.3
			2559.1	2558.6
8	8	0, 3	2586.0	2586.1
			2587.3	2587.0
			2594.1	2593.9
			2595.1	2595.3
2	0	2, 6	2629.7	2631.1
			2638.0	2638.9
3	2	1, 5	2669.9	2669.8
			2670.9	2671.4
			2678.4	2678.6
			2679.4	2679.6
5	5	0, 4	2711.5	2711.7
			2712.7	2713.4
			2720.7	2720.5
			2721.8	2721.9
1	0	2, 7	2753.5	2754.7
3	1	1, 6	2799.4	2799.9
			2800.9	2801.2
			2809.0	2809.2
			2810.4	2810.5
2	3	0, 5	2847.8	
			2849.5	2849.6
			2857.9	2857.9
			2858.9	2859.3
1	0	2, 8	2886.6	2888.9
			2897.2	2898.3
3	0	1, 7	2942.1	2941.6
			2951.4	2952.0
2	1	0, 6	2996.3	2997.4
			3007.6	3008.7
4		2, 9	3031.4	3032.5
			3045.6	3043.7
3		0, 7	3157.8	
			3168.5	
1		2, 10	3186.5	
			3200.6	3202.1
3		1, 9	3267.2	
			3272.1	3274.3
2		1, 10	3442.6	
			3457.3	

[a] Wavelength of the gas spectrum are taken from Rosen.[16]

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[15] G. Cario and L. H. Reinecke, Abhandl. Braunschweig Wiss. Ges. **1**, 11 (1949).

[16] B. Rosen, *Atlas des Longueurs d'Onde Caracteristiques des Bandes d'Émission et d'Absorption des Molécules Diatomiques* (Hermann and Cie, Paris, 1952).

[17] R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (Chapman and Hall, Ltd., London, 1950).

TABLE IV. Beta system of NO ($B^2\Pi - X^2\Pi$), *D* bands, in the solid and in the gas afterglow. Band heads of the two *R*-branches are listed.

Intensity Solid	Intensity Gas	v', v''	Wavelength A Solid	Wavelength A Gas[a]	Wave number difference cm^{-1}
0	1	2, 5	2613.8 2616.6	(2602.5) (2608.0)	166.0 126.0
1	2	0, 4	2629.7 2633.5	2620.5 2626.4	133.5 102.6
3	4	0, 5	2756.0 2761.8	2747.5 2754.2	112.2 99.9
5	8	0, 6	2894.8 2900.6	2885.3 2892.6	113.7 95.3
1	2	1, 7	2961.8	2943.2 2951.5	117.8
10	9	0, 7	3045.6 3051.8	3034.5 3043.0	120.1 94.8
8	10	0, 8	3209.2 3215.7	3197.7 3206.7	112.1 87.2
5	9	0, 9	3387.3 3395.2	3376.2 3386.2	97.0 78.3
1	1	1, 10	3457.3 3469.6	(3446.0) (3456.9)	94.9 105.9
3	7	0, 10	3587.0 3593.8	(3572.4) (3583.5)	113.9 79.9
2	5	0, 11	3803.5	3787.4	111.8

[a] Wavelengths tabulated in parentheses are taken from Pearse and Gaydon.[17]

the weak companion lines of the *A*-bands.[5] The measured frequencies of the shorter wavelength line fits the following equation within the experimental error:

$$\nu = 45\,742.1 + 1003.5v' - 4.0v'^2 - (1903.4v'' - 14.0v''^2 - 0.0195v''^3).$$

This indicates a change in the vibrational frequency of the upper state ($B^2\Pi$) of NO from 1037.0 cm^{-1} in the gas to 1003.5 cm^{-1} in the solid. There is not sufficient data to know if the change in the anharmonicity (from 7.6 to 4.0 cm^{-1}) is real. The change in the intensity distribution is very marked.

The rather prominent lines at 3359 A and 3370 A are the *Q* maxima of the 0,0 and 1,1 bands of NH ($A^3\Pi_i - X^3\Sigma^-$). Fine structure observed in this region is associated with this system and also with the system $c^1\Pi - a^1\Delta$ of NH for which the 0,0 band heads are observed near 3253 A and 3237 A.

The *B*-bands have very diffuse appearance, and are extremely broad, extending is some cases 50 to 100 A. In some regions a few sharper features may be distinguished within the diffuse bands. The positions of the maxima of intensity (listed in Table I) and of the sharper features show a fairly close correlation with the wavelengths of the emission and absorption spectra of NO_2.[17,18]

The group of bands labeled *G*, which is observed in the spectrum of the solid in the region between 6000 and 7000 A, is probably part of the first positive system ($B^3\Pi - A^3\Sigma$) of N_2. Table V compares the wavelengths of these bands with those of the first positive system as measured in a gas afterglow at a pressure of about 4 mm Hg and indicates a shift of 15 cm^{-1}. Our measured values for the spectrum of the gas differ from those listed in Pearse and Gaydon[17] because our small dispersion made it more convenient to measure at the positions of the centers of the bands rather than at the band heads. The intensity estimates were made in the same manner as for Table III. In addition to the bands listed in Table V, bands of the $\Delta v = 2$ progression have been observed on another plate. The vibrational intensity distribution from the solid differs from those in the discharge and in the gas afterglow. In particular the lack of appreciable intensity in the bands originating from $v' = 12$ is of interest in the interpretation of mechanisms of active nitrogen.

A number of very weak lines between 2800 A and 4000 A have been grouped together and marked *H*? in Table I. The positions of these lines are such as to indicate that these lines are part of the second positive system of N_2. However, a number of the more intense bands of the system which should be observable would fall in regions where they may be masked by other more intense features. The observations are suggestive of the occurrence of the second positive system, but the identification is quite tentative. It is possible that a small amount of light is reflected from the discharge, but there is no direct evidence of this.

VI. SUMMARY

On collecting, at liquid helium temperatures, the products of an electric discharge in nitrogen gas, several

TABLE V. First positive system of N_2 ($B^3\Pi - A^3\Sigma$), *G*-bands, in the solid and in the gas afterglow.

Intensity Solid	Intensity Gas	v', v''	Wavelength,[a] A Solid	Wavelength,[a] A Gas
	6	12, 8		5743
0	8	11, 7	[b]	5792
	6	10, 6		5842
	5	9, 5		5893
	4	8, 4		5948
	2	7, 3		5999
	2	6, 2		6055
	0	5, 1		6109
	1	12, 9 4. 0		6168
	5	11, 8		6233
1	6	10, 7	6319	6305
Masked	5	9, 6	6390	6381
5	7	8, 5	6456	6450
8	8	7, 4	6528	6524
10	10	6, 3	6612	6606
6	9	5, 2	6692	6688
3	7	4, 1	[b]	6769

[a] The position of the center of each group was measured.
[b] Band observed but position not measured.

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[18] F. H. Newman, Phil. Mag. **20**, 777 (1935); V. Kondratjew, Physik Z. Sowjetunion **11**, 320 (1937); Y. Tanaka and M. Shimazu, Tokyo Sci. Research Inst. **43**, 241 (1949).

types of glow are observed. Evidence that the observed glows are a solid phenomenon has been given above. The most intense features of the spectra, the α and β lines and the A-bands (Table I and Fig. 3), are quite different in appearance from the usual spectra obtained from gases. However, the NO γ bands (E) and the NH bands (F) show considerable rotational structure and, in addition, indicate a comparatively high rotational "temperature." It seems possible that local heating or "explosions" may form the excited molecules leading to these bands in the gas phase just above the surface. Band heads of the system attributed to NO β (B and C) from the solid are displaced on the average of 9.4 A from the gas NO β system and the system has a very much different structure and intensity distribution in the solid than in the gas. The intensity distribution of the N_2 first positive bands (G) differs in the solid from that in a gas discharge or in a gas afterglow, and the bands also may be shifted to longer wavelengths.

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Molecular Excitation in Beta Decay*

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The theory of molecular excitation in beta decay is developed for the general case of a polyatomic molecule. Calculations of the daughter molecule vibrational excitation are carried through for diatomic molecules, and the results are presented graphically. Finally, the formation of the $(He^3H^3)^+$ molecule ion in the decay of one nucleus of a tritium molecule is studied in detail. It is concluded that the $(He^3H^3)^+$ ground electronic state vibrational spectrum should be observable in the light spontaneously emitted by tritium. For example, neglecting nonradiative transitions, one expects approximately 10^{14} photons per second to be radiated at wave number $\cong 2.35\times 10^3$ cm^{-1} by every gram of tritium in the $1\rightarrow 0$ vibrational transition.

I. INTRODUCTION

When the nucleus of an atom undergoes beta decay, it is possible that the resulting daughter atom will be formed in an electronically excited or ionized state. A number of papers[1–9] have investigated the theory of this process both for electron (±) emission and for electron capture. In addition, the holes produced in the electronic shells and, in the case of K-capture, the ejected orbital electrons have been detected experimentally, with a probability in general agreement with the theoretical predictions.[10–15]

If the nucleus which decays is one of several in a molecule, the physical situation is more complicated. Not only can electronic excitation and ionization occur, but the daughter molecule can be left in an excited vibrational or rotational state. The former effect is due primarily to the sudden change in nuclear charge, while the latter essentially results from the recoil momentum given the decaying nucleus. Dissociation of the daughter molecule can also take place if this molecule is formed either in an unbound electronic state, or in a bound electronic state but in vibrational and rotational states with a combined energy exceeding the depth of the corresponding internuclear potential well.

The purpose of this paper is to present a theoretical treatment of the problem of molecular excitation in beta decay. It is divided into three parts. First, a general discussion is given for polyatomic molecules; time-dependent perturbation theory is used, and the direct interaction between the emitted electron and the molecular electrons is neglected. Second, the special case of diatomic molecules is treated. Here the Born-Oppenheimer[16] approximation gives simple vibrational and rotational wave functions for the nuclear motion so that the problem can be investigated in some detail. Also, a classical distribution of the daughter molecules over their final rotational states is given, and the possibility of experimental detection of the dependence of the final state population on the beta-decay coupling

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[1] A. Migdal, J. Phys. (U.S.S.R.) 4, 449 (1941).

[2] E. L. Feinberg, J. Phys. (U.S.S.R.) 4, 423 (1941).

[3] A. Winther, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **27**, No. 2 (1952).

[4] P. Benoist-Gueutal, Physica **18**, 1192 (1952).

[5] H. M. Schwartz, J. Chem. Phys. **21**, 45 (1953).

[6] H. Primakoff and F. T. Porter, Phys. Rev. **89**, 930 (1953).

[7] J. S. Levinger, Phys. Rev. **90**, 11 (1953).

[8] P. Benoist-Gueutal, Ann. phys. **8**, 593 (1953).

[9] M. Wolfsberg, Phys. Rev. **96**, 1712 (1954).

[10] G. Charpak, Compt. rend. **237**, 243 (1953).

[11] G. A. Renard, Compt. rend. **238**, 1991 (1954).

[12] T. B. Novey, Phys. Rev. **86**, 619 (1952).

[13] J. A. Miskel and M. L. Perlman, Phys. Rev. **94**, 1683 (1954).

[14] W. Rubinson and J. J. Howland, Phys. Rev. **96**, 1610 (1954).

[15] F. T. Porter and H. Hotz, Phys. Rev. **89**, 938 (1953).

[16] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

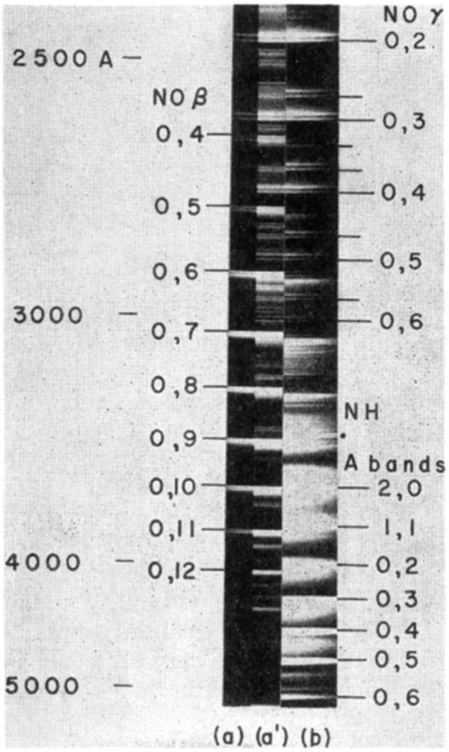

FIG. 3. (a) Spectrum of afterglow in flowing nitrogen gas at pressure of 4 mm Hg. The glow was observed 20 cm from the discharge in a path length of 5 cm, $F/4$ quartz prism instrument; slit width 0.03 mm; *I-F* (3) plate; exposure time 15 min. (a′) Same as (a), but exposure time 50 min. (b) Spectrum from solid at 4.2°K while products from a discharge through nitrogen are being collected. Slit width 0.014 mm; 103a-0 plate; exposure time 10 min.

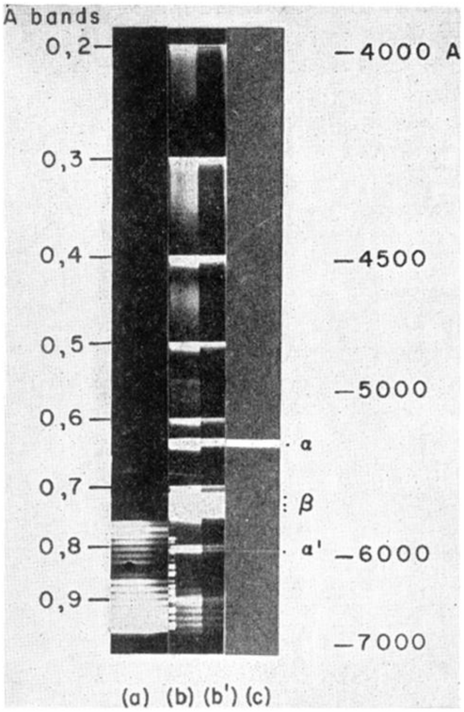

FIG. 4. (a) Spectrum of afterglow in flowing nitrogen gas at pressure of 4 mm Hg. The glow was observed 20 cm from the discharge in a path length of 5 cm, *F*/4 glass prism instrument slit width 0.020 mm; 103*a*-*F* plate; exposure time 15 min. (b) Spectrum from solid at 4.2°K while products from a discharge through nitrogen are being collected. Slit width 0.041 mm; exposure time 25 min. (b′) Same as (b), but exposure time 5 min. (c) Spectrum of green afterglow from solid nitrogen near 4.2°K; discharge off. Total accumulated exposure time 30 min.

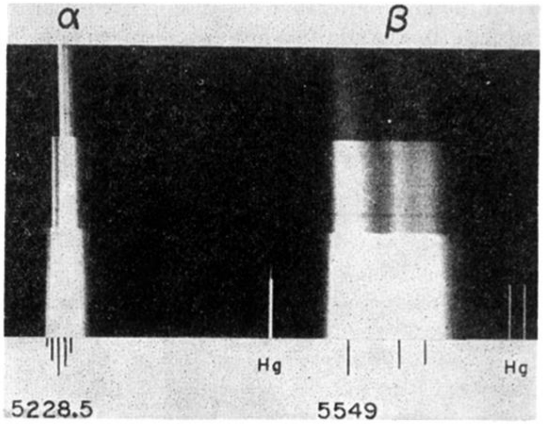

FIG. 6. Spectra of the α and β lines emitted by the solid near 4.2°K while the discharge is on. $F/10$ glass prism instrument; 103-F(3) plate; exposure time—3, 9, and 27 minutes.