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BAND SPECTRA IN THE EXTREME ULTRA-VIOLET EXCITED BY ACTIVE NITROGEN

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Abstract

To determine the amount of energy available in active nitrogen for the excitation of spectra, a vacuum grating spectrograph was used to observe spectra between 2500 and 1000A excited in certain gases in the afterglow. The gases were mixed with glowing nitrogen obtained by flowing nitrogen through a discharge tube containing an oscillatory discharge. H_2, O_2, N_2, CO and NO were studied, of which only CO and NO showed bands in the region mentioned.

NO bands excited by active nitrogen.—In addition to the β and γ bands of NO characteristic of the afterglow, a progression was found belonging to another system with the same final levels, i.e., levels associated with the normal electronic state of the molecule. The initial level, identified from published absorption data as an electronic state with zero vibration, is designated as level *C*, and the new system, as the δ band system of NO. The 0–0 δ-band is at 1915.7A, corresponding to 6.44 volts.

CO bands excited by active nitrogen.—A few bands of the fourth positive group of CO were obtained in the afterglow, corresponding to the excitation of vibration states $n'=1$ to 6 of electronic level A. The total energy of these levels is from 8.2 to 9.0 volts.

Mechanism of excitation by active nitrogen.—The results are discussed in the light of a possible mechanism of excitation proposed by Birge. It is assumed that atoms of nitrogen can combine to form an excited diatomic molecule if the encounter is such that the energy of formation and the relative kinetic energy of the atoms go over into electronic, vibrational, and rotational energy of the molecule. Such encounters will be rare, because both energy and momentum must be conserved in the recombination; therefore the active modification will have a relatively long life. On formation, the molecules have 11.4 ± 0.3 volts of energy; part of this is lost immediately by radiation of the α group bands, leaving from 9 to 10 volts in a configuration which is strongly metastable with respect to the normal electronic state. This metastable molecule is considered responsible for the excitation of spectra in the afterglow.

Introduction

E. P. LEWIS in 1900[1] called attention to the fact that discharge tubes containing nitrogen exhibit a glow which may under suitable conditions persist for a considerable time after the discharge is cut off; later[2] he showed that the afterglow excites spectra in gases or vapors mixed with it. The chemical activity of the afterglow was emphasized by Strutt,[3] who suggested that atoms of nitrogen recombining to form molecules might be responsible for the phenomenon. Recent attempts[4,5] to check this hypothesis spectrally have sought a connection between the heat of dissociation of nitrogen, known

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[1] E. P. Lewis, Astrophys. J. **12,** 8 (1900).
[2] E. P. Lewis, Astrophys. J. **20,** 49 (1904).
[3] R. J. Strutt, Proc. Roy. Soc. **85A,** 219 (1911).
[4] Ruark, Foote, Rudwick, and Chenault, J. Optical Soc. Am. **14,** 17 (1927).
[5] Okubo and Hamada, Phil. Mag. **5,** 372 (1928).

to be 11.4 ± 0.3 volts,[6] and the energy content of the levels found excited in the afterglow. The quartz prism spectrographs used are subject to the limitation that wave-lengths corresponding to energy changes of more than seven volts (1800A) are not transmitted by the prisms, and only the observation of transitions between excited states can establish the occurrence of excitation to higher levels. To observe transitions between levels above seven volts and the normal unexcited level, a vacuum grating spectrograph or a fluorite prism instrument is required.

The present investigation was undertaken to study spectra excited in the afterglow, beyond the limits of quartz, and to determine whether the entire association energy of nitrogen, 11.4 volts, is available for the excitation. The apparatus used and the results obtained with various gases are described in the following sections. No evidence was obtained of excitation higher than nine volts in the materials selected, and in the discussion which concludes the paper, a mechanism of excitation is suggested to account for the results obtained.

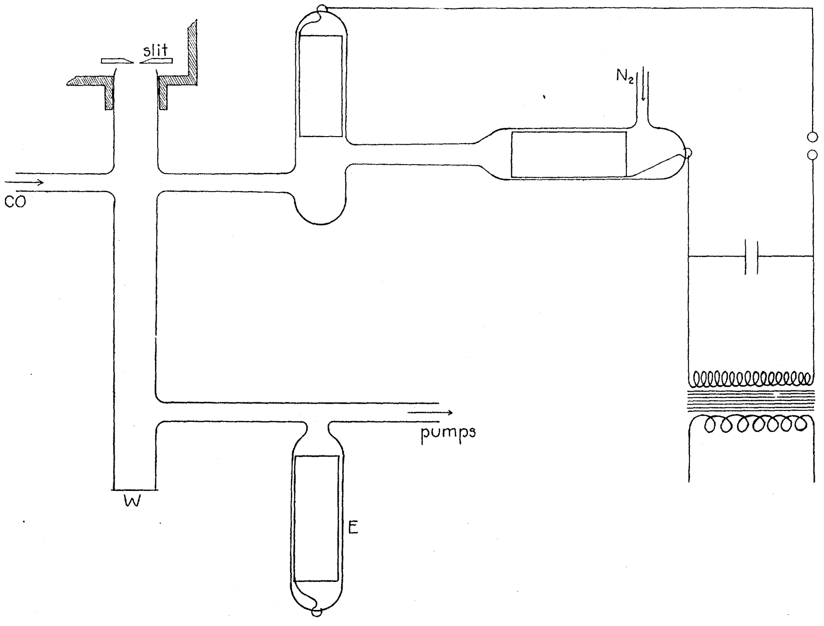

Fig. 1. Apparatus for observing spectra of gases excited in active nitrogen.

APPARATUS

The spectrograph used was designed by Hopfield and built in the department shop. A brass receiver contains a grating of one meter radius, ruled at the National Physical Laboratory, in England, and giving a dispersion of about 17.6 A/mm. Sealed to the receiver, and communicating with the interior through the slit, was the tube in which the gas to be excited was

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[6] H. Sponer, Zeits. f. Physik, **34,** 622 (1925).

mixed with active nitrogen. The arrangement is indicated in Fig. 1, which shows the slit of the spectrograph at one end of the viewing tube, a Pyrex window *W* at the opposite end, and the side tubes admitting the gas under test (marked CO in the figure) and active nitrogen respectively. The electrical connections indicated produce an oscillatory discharge through the L shaped discharge tube, which is placed so that light from the discharge is not reflected or scattered to the slit. The auxiliary electrode *E* is used in connection with one of the others to obtain an ordinary 60 cycle discharge through the viewing tube, yielding emission spectra for comparison purposes.

Commercial nitrogen from a steel cylinder was passed over hot copper to reduce the oxygen content, and over P_2O_5 to remove moisture, and admitted to the discharge tube at the point shown through a torsion capillary valve due to Hopfield.[7] The flow was maintained by pumps exhausting at the point indicated. Another pair of pumps in parallel was connected to the receiver of the spectrograph, thereby maintaining about the same pressure (about 2 mm) on both sides of the slit, and limiting the entry of active gas into the receiver to that which diffused through the slit.

The films used were either Schumann films prepared according to the method developed by Hopfield,[8] or commercial films treated with paraffine oil to obtain sensitivity in the extreme ultra-violet by fluorescence. There was little to choose between the two types, because the quicker response of the oiled films was counteracted by their readiness to fog. Exposures with the oiled films ran up to 22 hours, and with the Schumann films, to 48 hours.

The slit was made 0.25 mm wide to decrease the time of exposure required for the appearance of bands. The NO bands appeared distinctly with exposures of two hours on oiled film, or five hours on Schumann films.

NITROGEN

The known energy levels[9] of nitrogen are shown in Fig. 2. The constants of the normal unexcited state are known from the a_1-X transitions, measured by Birge and Hopfield.[10] The exact position of level *A* in the diagram is uncertain, since no connection has been found between *X* and any of the levels *A*, *B*, *C*, or *D*, which are inter-related in the first, second, and fourth positive groups of nitrogen. Accordingly, their position is assigned as a result of measurements on the energy of excitation by electron impact, combined with spectroscopic observation, made by Sponer.[6] During her stay in Berkeley, she also photographed the afterglow[11] with the grating used in the present work, running exposures up to 60 hours, in the hope of

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[7] J. J. Hopfield, J. Optical Soc. Am. **12,** 391 (1926).

[8] J. J. Hopfield, Phys. Rev. **20,** 573 (1922).

[9] See "Molecular Spectra in Gases," Bulletin 57 of the National Research Council. Fig. 2, above, embodies results that have been obtained since the preparation of Fig. 26, p. 244 of the Bulletin.

[10] Birge and Hopfield, Nature **116,** 15 (1925).

[11] H. Sponer, Proc. Nat. Acad. Sci. **13,** 100 (1927).

finding the predicted $A-X$ bands. No such bands appeared. Since then the grating has been inverted and refocused, and the diaphragms in the receiver have been readjusted, to obtain a speed possibly three or four times greater than before. Under the new conditions, a 48 hour exposure still failed to show either the known a_1-X or the expected $A-X$ bands. Her work on absorption in N_2, which yielded the Birge-Hopfield bands (a_1-X), has since been carried further by Hopfield[12] with the result that new levels have been found, but nothing involving the levels A, B, C, or D.

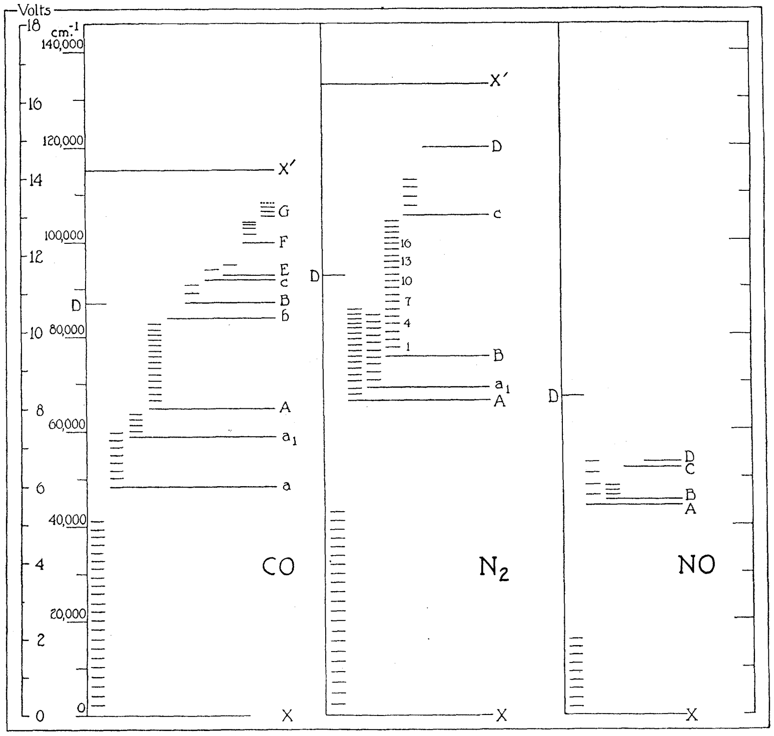

Fig. 2. Electronic and vibrational levels of CO, N_2, and NO.

The absence of the $A-X$ combinations indicates a high degree of metastability for the A level, and therefore has a direct bearing on the problem of the afterglow. The afterglow is characterized by the presence of certain bands, the α group, belonging to the first positive system, which arise from transitions to vibration states of electronic level A. Because the latter is metastable, the molecules cannot lose the electronic energy by radiation, but must return to the unexcited state by giving up the energy in second type collisions, or at the walls of the vessel.

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[12] J. J. Hopfield, Abstract No. 89, Washington Meeting, American Physical Soc. Apr. 1928.

Certain bands of the second positive group ($C-B$) are associated with the afterglow according to Ruark, Foote, Rudwick, and Chenault,[4] who worked with an electrodeless discharge at low pressures. These may have appeared because of a defect in the operation of the sectored disk which was used to hide the discharge, as suggested by Okubo and Hamada,[5] or if the effect was real, the occurrence of excitation to the C level at 13 volts could be explained as a four volt excitation of a metastable molecule carrying nine volts of energy. The non-appearance of the bands in the work of Okubo and Hamada might be due to the fact that they used a continuous flow method with pressures 100 times as great as those used in the electrodeless discharge method. In the present work, certain transitions of this system appeared on the afterglow films with intensities varying from film to film, but no critical study was made to decide whether these bands were due to stray discharge, to light reflected or scattered from the discharge tube, or to the afterglow proper.

HYDROGEN

The first excited electronic level of the hydrogen molecule has been shown by Dieke and Hopfield[13] to have an energy of 11.1 volts. Excitation to this level should be possible in the afterglow if 11.4 volts are available. Repeated attempts were made to obtain the molecular spectrum of hydrogen in the afterglow, but it failed to appear on any of the films. A comparison spectrum picture made at the pressure maintained for the afterglow experiments showed that the mixture of nitrogen and hydrogen in the receiver was transparent in the region under investigation. Both electrolytic hydrogen and the commercial product were employed, and the rate of admission was varied from the slowest, which left the appearance of the glow unchanged, to the most rapid, which almost quenched the visible glow.

OXYGEN

While the electrolytic generator was in service, it was easy to reverse the current and obtain oxygen. The comparison spectrum showed no bands in the region investigated under the conditions available, and a short trial exposure in the afterglow also gave no bands below 2000A. Since oxygen absorbs light very strongly in this region, no further attempt was made to use it.

NITRIC OXIDE

If any oxygen is present with the nitrogen in a discharge, NO is formed, and the characteristic β and γ bands of NO are observed in the afterglow. They correspond to transitions from electronic levels B and A respectively to X. (See Fig. 2.) A progression of bands belonging to another system with the same final states was observed, the data for which are given in Table I.

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[13] Dieke and Hopfield, Zeits. f. Physik **40**, 299 (1926) and Phys. Rev. **30**, 400 (1927).

TABLE I. *Delta bands of NO observed in active nitrogen.*

I*	$n'-n''$	λ (Head)	ν, cm^{-1}	$\Delta\nu$, obs	$\Delta\nu$, calc**	obs−calc
1	0–0	1913	52,274			
				1947	1874.4	+73
2	0–1	1987	50,327			
				1831	1846.6	−11
3	0–2	2062	48,496			
				1811	1818.9	− 8
4	0–3	2142	46,685			
				1822	1791.1	+31
3	0–4	2229	44,863			
				1760	1763.4	− 3
2	0–5	2320	43,103			

* The 0–0 γ-band has an intensity of 6 on this scale.
** From formula for vibrational levels of the normal state.

The bands degrade toward the violet, and the measurements given are for the heads. Since the $0-0$ band appears only faintly, because of self-reversal, and is difficult to measure accurately, the most probable value for its frequency is obtained indirectly by adding the known $\Delta\nu$ to the frequency of the $0-1$ band, yielding 52,201 cm^{-1} or 1915.7A, and placing the energy at 6.44 volts. This new system of afterglow bands is designated here as the δ band system of NO, and the initial level, the C level.

The level here found in emission is responsible for the absorption band found by Leifson[14] at 1910.6A. The discrepancy of 5A is due in part to the fact that Leifson's measurements were of the middle of the band, and those given here are of the heads. The width of the slit (0.25 mm) used in the present work tends to exaggerate the difference. Although Leifson grouped some of his absorption bands into series, the band at 1910.6A is not among them. Further work on the analysis of NO bands is under way in this laboratory.

CARBON MONOXIDE

Since carbon monoxide has a number of electronic levels between 6 and 12 volts (see Fig. 2), it was selected as the next gas to try. The gas was generated by the action of sulphuric acid on ammonium oxalate and was stored over water. It was passed through concentrated KOH solution to remove CO_2, dried with P_2O_5, and run through a liquid air trap and a torsion capillary valve into the afterglow.

Great difficulty was experienced in obtaining CO bands in the far ultraviolet in the afterglow. Two exposures, made with oiled films, contained very faint impressions of bands in the region in question, but attempts to obtain the bands more strongly with longer exposures resulted simply in fogging the films. The faintness of the results leaves open the possibility that the bands observed are not actually an afterglow phenomenon. However, comparison with a CO emission spectrum on the same film shows that the distribution of intensities is different, and that the bands of the third positive

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[14] S. W. Leifson, Astrophys. J. **63**, 73 (1926).

group, which are very strong in the emission spectrum, are definitely absent in the afterglow. Furthermore, analysis shows that the bands which appear are related in a manner consistent with the argument of a special type of excitation.

These facts are exhibited in Table II. Only the bands observed in the afterglow are listed, some thirty additional bands which appeared in the comparison spectrum being omitted. The wave-length measurements, made on the comparison spectrum, are uncertain by ±2A because the impressions obtained on oiled film are not sharply defined, particularly with a slit as wide as the one used here. In column 2 intensities on an arbitrary scale from 1 to 5 are given for the bands of the comparison spectrum. In column 3 intensities in the afterglow are indicated on a quite different scale: the strongest band is arbitrarily called 10, the others being numbered serially in the order of decreasing intensity. Several bands about which there might be some doubt are listed as of 0 intensity.

TABLE II. *Fourth positive group of CO excited in afterglow.*

1 λ	2 *I*, comp.	3 *I* in N_2	4 λ*	5 $n'-n''$*	6 *I**
1410	1	6	1409.0	6–1	2
1464	2	0	1463.7	4–1	3
1493 1496	1	2	1493.8 1497.8	3–1 6–3	3 3
1528	4	0	1527.6	5–3	3
1542	5	0	1542.2	3–2	5
1558	5	10	1559.3	1–1 4–3	5
1574	5	8	1576.5	2–2 5–4	4
1597	1	9	1597.4	0–1	3
			1596.1	6–5 3–3?	1
1648	0	7	1648.2	3–4 6–6?	5
1653	1		1653.3	0–2	4
1669	1	5	1669.9	1–3	6
1792	2	4	1792.6	1–5	10d
1810	1	3	1811.0	2–6	10d
2171	1	1	2173.3	5–13 1–10?	8
2194	1	1	2195.0	2–11	6
			2196.9	6–14	8

* See reference 15
d = double

The quantum designation of each of the observed bands is known from the analysis by Birge.[15] In column 4 are shown the wave-lengths as listed by Birge, alternative interpretations being suggested for a few of the bands because of the uncertainty of the present measurements. The quantum assignments made by Birge, and the intensities as listed by him, are given in columns 5 and 6 respectively.

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[15] R. T. Birge, Phys. Rev. **28,** 1157 (1926).

It will be seen that the initial vibration states which are present run from 1 to 6, carrying total energies from 8.2 volts to 9.0 volts. The absence of the bands of the third positive group $(b-a)$ indicates that the b level, carrying 10.35 volts of energy, is not excited.

DISCUSSION

Reference has already been made to the suggestion of Strutt[3] that recombining atoms might be responsible for the characteristics of the afterglow. Attention was diverted from this hypothesis by a paper of Saha and Sur[16] which applied the theory of collisions of the second kind[17] and ascribed the activity to an excited nitrogen molecule, with an energy which they estimated at 8.5 volts. Birge[18] pointed out that the α group of the afterglow was known to belong to the first positive system of nitrogen, with an initial level estimated to be at about 11.5 volts. The energy was checked within ±0.3 volts by Sponer's excitation potential measurements.[6] The electronic levels, both initial and final, of the first positive group of nitrogen, are "floating," i.e., no spectral connection between these levels and the normal level has been observed, therefore no spectral determination of the energy has been possible. Birge at that time suggested that the long life of the afterglow required the hypothesis that the initial level is for some reason metastable.

Meanwhile measurements on the rate of decay of the afterglow by Angerer[19] indicated that two activated entities are involved in each elementary process of light emission. Sponer[6] revived the atomic hypothesis, and sought to account for the long life of the afterglow by assuming that a triple collision is necessary to make recombination possible. In so doing, she referred to the case of hydrogen as studied by Bonhoeffer[20] where it was shown that atoms can recombine only at the walls, or in a triple collision including some third body that is capable of taking up the energy given out in recombination. In terms of this mechanism, then, a pair of nitrogen atoms colliding simultaneously with a third body, say a nitrogen molecule, can unite and give up the energy of association, 11.4 volts. Accordingly, the entire 11.4 volts might be available for excitation, and the process should be very efficient if the third body has energy levels at just under 11.4 volts.

Subsequent work of Bonhoeffer and Kaminsky[21] showed results in definite contradiction to the triple collision hypothesis. On keeping the partial pressure of active nitrogen constant, but increasing the partial pressure of N_2, the luminosity decreased, instead of increasing as required by the triple impact theory.

The analogy with hydrogen breaks down at a vital point. In hydrogen, the first excited electronic level[13] at 11.1 volts is far above the energy of

[16] Saha and Sur, Phil. Mag. **48**, 421 (1921).

[17] Klein and Rosseland, Zeits. f. Physik. **4**, 46 (1921).

[18] R. T. Birge, Nature **114**, 642 (1924).

[19] E. Angerer, Physik. Zeits. **22**, 97 (1921).

[20] K. F. Bonhoeffer, Zeits. f. Phys. Chem. **113**, 199 (1924).

[21] Bonhoeffer and Kaminsky, Zeits. f. Elektrochemie **32**, 536 (1926).

association, at 4.42 volts.[22] In nitrogen, on the other hand, the electronic levels A, a_1, and B are lower than the energy of association at 11.4 volts, and vibration-rotation levels are present which have total energies nearly equal to that value, so that spontaneous recombination with the formation of an excited molecule is possible. Since both energy and momentum must be conserved in such a process, the recombination can occur only in the rare cases where the relative kinetic energy of the atoms plus the potential energy is equal to the total energy of some particular quantum state in which the angular momentum of the molecule is equal to the angular momentum of the pair of atoms before collision. Some small tolerance must be assumed in such a process, otherwise the probability would be vanishingly small, and the life of the active state would be almost indefinite.

The assumption that recombination occurs in this manner offers an explanation of the long life of the afterglow. Birge[23] has shown that other afterglow phenomena, such as the variation of luminosity with temperature, can be described readily in terms of this mechanism. Bonhoeffer and Kaminsky's results have been considered by Bernard Lewis,[24] who shows that a two-body collision between atoms of nitrogen leads to results in agreement with their observations.

It is well known that the α bands characteristic of the afterglow are simply a set of bands selected from the first positive band system of nitrogen. The initial states represented are vibration levels 10, 11, and 12 of electronic level B, and the final states are vibration levels 5 to 8 of electronic level A, the observed bands lying in the green, the yellow, and the red. The emission of these bands, according to Birge, occurs immediately after recombination. Since the final levels are associated with electronic state A, which is strongly metastable, the molecules are thus left with considerable energy which cannot be lost directly by radiation, but which is available for the excitation of other atoms or molecules. It is possible to estimate the energy of these metastable molecules, by combining Sponer's data on excitation potentials[6] with spectral data[9] on the α bands. Assuming 11.4 volts to be the energy of the initial level 11, the energies of the final states run from about 9.0 to 9.5 volts. If the α bands extend into the infra-red, as might be inferred from the ordinary band spectrum of nitrogen, higher final levels would occur as well, up to say 10 volts. All of these values are uncertain within ± 0.3 volts, the experimental error of the excitation potential determinations. The most probable energy, corresponding to the most intense member of the α group, is 9.33 volts.

It should be noted that not all of this energy must necessarily be given up in a second type collision. Some of it may be lost by radiation in the infra-red with the loss of a quantum of vibrational energy. On the other hand, the molecule may be able to retain vibrational energy while returning to its normal electronic state in a second type collision. Thus the possibilities

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[22] R. T. Birge, Proc. Nat. Acad. Sci. **14,** 12 (1928).

[23] R. T. Birge, unpublished work.

[24] B. Lewis, Phys. Rev. **31,** 314 (A) (1928) and J. Amer. Chem. Soc. **50,** 27 (1928).

for excitation of other spectra are much greater than in the case of metastable atoms, and the richness of spectra excited in the afterglow is explained.

However, there is reason to believe that excitation of particular levels does not always occur, even though it is possible from considerations of energy alone. Thus Okubo and Hamada[5] find a level of mercury at 9.51 volts excited in the afterglow, but the next at 9.65 unexcited. This may mean that the energy available is less than 9.65 volts (which would be consistent with the mechanism discussed here) or that the 9.65 volt level has characteristics which prevent it from taking over the energy of a metastable nitrogen molecule.

The bands found in CO with 8.2 to 9.0 volts of energy receive somewhat less than the predicted maximum energy from the afterglow. The probable explanation for this has been given above. In the case of NO, it is possible that the β, γ and δ bands are a recombination phenomenon, since it is apparent from the energy diagrams (Fig. 2) that the metastable nitrogen molecule carries energy sufficient to dissociate NO.

Conclusion

Since the experimental evidence of this and other researches is that atoms and molecules in the afterglow are excited readily with energies up to nine volts, and probably not above 9.5 to 10 volts, the conclusion may be drawn that the excitation is caused by a nitrogen molecule in one of a series of metastable states carrying the corresponding energy. The view that atoms of nitrogen combine to form an excited molecule responsible first for the emission of α bands and later for the excitation of other spectra is thus supported by the results obtained in these experiments.

It is a pleasure to acknowledge the guidance received from Professor J. J. Hopfield and Professor R. T. Birge in carrying out this investigation.

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University of California,
April, 1928.