using Eqs. (11) and (12), we obtain

$$\phi_R(b)=\phi_R(a)e^{i\theta(b,a)}+\int_a^b dx\phi_{L0}(x)\rho(x)^{i\theta(b,x)}, \tag{28}$$

$$\phi_L(b)=\phi_L(a)e^{-i\theta(b,a)}+\int_a^b dx\phi_{R0}(x)\rho(x)e^{-i\theta(b,x)}. \tag{29}$$

The equations can be simplified by the introduction of two new parameters:

$$A=\int_a^b dx\rho(x)e^{-2i\theta(x,a)}, \quad \theta=\theta(b,a). \tag{30}$$

In terms of these, Eqs. (28) and (29) become

$$\phi_R(b)=\phi_R(a)e^{i\theta}+\phi_L(a)Ae^{i\theta}, \tag{31}$$

$$\phi_L(b)=\phi_L(a)e^{-i\theta}+\phi_R(a)A^*e^{-i\theta}. \tag{32}$$

θ is the phase shift per cell given by the ordinary WBK method. $|A|^2$ is the probability that the particle changes its direction of motion in going through one cell.

Floquet's theorem tell us that the solutions to the wave equation for a periodic potential can always be written in the form $u(x)\exp[i\mu x]$, where $u(x)$ has the periodicity of the lattice and μ is either purely real or purely imaginary. It is real for the energy levels corresponding to allowed levels, and imaginary for the stop bands between them. Equations (31) and (32) represent a linear transformation whose characteristic values are $\lambda=\exp[\pm i\mu x]$. The secular equation obtained from Eqs. (31) and (32) is

$$\lambda^2-2\lambda\cos\theta+(1-|A|^2)=0. \tag{33}$$

The roots of this equation are

$$\lambda=\cos\theta\pm(|A|^2-\sin^2\theta)^{\frac{1}{2}}. \tag{34}$$

Whenever the quantity in parentheses is negative, the equation has two imaginary roots, complex conjugates of each other. In this case

$$\lambda=\cos\theta\pm i(\sin^2\theta-|A|^2)^{\frac{1}{2}} \tag{35}$$

which to first order in $|A|$ satisfies $|\lambda|=1$. Whenever the quantity in parentheses is negative, we will be in an allowed energy range. As the energy is varied, for a given potential, $\sin\theta$ will repeatedly go through zero. When $\sin\theta$ comes close enough to zero, the term in parentheses in Eq. (34) becomes positive and both roots will be real. The roots, when real, will have their extreme values (i.e., farthest removed from unity) when $\sin\theta=0$. For that value of energy, we have

$$|\lambda|=1\pm|A|\simeq e^{\pm|A|} \tag{36}$$

to first order in $|A|$. The zone boundaries occur when the quantity in parentheses is negative, we will be in an $\sin\theta=\pm|A|$.

The fact that we have taken into account only the first-order correction makes our solution an approximate one, which is valid only if the coefficient $|A|$ is small compared with unity. The method is therefore valid only when the region between bands is narrow. This condition is not as restrictive as the one applicable to the usual perturbation theory approach.

It is possible that $|A|$ can be zero. In this case a particle can travel through the lattice without being reflected. The reflections caused by different parts of the cell must cancel in such a case. If $|A|$ vanishes at an energy for which $\sin\theta=0$, the spacing between adjacent bands vanishes and they touch each other.

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The Infrared Spectrum of Active Nitrogen

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Thirty-one bands, including the (0, 0) band at 10,440A, of the N_2 first positive system have been photographed in the Lewis-Rayleigh afterglow of active nitrogen. There is no indication that the $v=0$ level of the $B^3\Pi$ state is preferentially populated as required by the "resonance" theory of atomic re-association using $D(N_2)=7.383$ volts. The analogy between the Lewis-Rayleigh glow and the spectrum of the airglow is discussed briefly.

I. INTRODUCTION

MOST investigators of active nitrogen accept the hypothesis that the primary reaction leading to the Lewis-Rayleigh afterglow of active nitrogen is the recombination of two nitrogen atoms in the presence of a third body, the walls being conditioned in such a way as to inhibit recombination at the walls and allow the reaction to proceed slowly in the volume.[1] This reaction may be expected to give rise to a nitrogen

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[1] S. K. Mitra, *Active Nitrogen—A New Theory* (Indian Assoc. for the Cultivation of Science, Calcutta, 1945), p. 68. Mitra's theory of active N_2 involving nitrogen positive ions was based to a substantial degree of an analogy with processes in the night sky and the ionosphere. New experimental data on the upper atmosphere show that this analogy is quite remote, as is pointed out in the present paper. For this and other reasons Mitra's theory is no longer in general favor.

molecule in either the metastable $A^3\Sigma$-level or in the $v=0$ level of $B^3\Pi$, providing the dissociation energy of nitrogen is 7.383 ev. Admittedly, the magnitude of the dissociation energy of N_2 is a controversial point, since Gaydon's proposal[2] that it is 9.765 ev. In the spectrum of active nitrogen, Kaplan[3] has reported a marked enhancement of the (0, 0) band of the first positive system ($B^3\Pi-A^3\Sigma$) at 10,440A. This observation indicates that the $v=0$ level of $B^3\Pi$ is preferentially populated by the afterglow reactions. This may be interpreted as evidence, for both the nitrogen reassociation theory of active nitrogen and for the 7.383-ev dissociation energy, by the following argument.

Since the $v=0$ level of the $B^3\Pi$-state of N_2 has an excitation energy of 7.35 ev, and the $v=1$ level of this state lies above 7.383 ev, the only nonmetastable state of N_2 which can be excited by a re-association which has 7.383-ev energy available is the $v=0$ level of $B^3\Pi$. Hence, the only allowed radiation which this process could produce is the 10,440A (0, 0) band of the N_2 first positive system. Thus, if X represents the third body in the collision,

$$N(^4S)+N(^4S)+X\rightarrow N_2(v=0\ B^3\Pi)+X \tag{1}$$

followed by

$$N_2(v=0\ B^3\Pi)\rightarrow N_2(v\geq 0\ A^3\Sigma)+h\nu(\lambda\geq 10{,}440\text{A}). \tag{2}$$

Of course, the dissociation energy may be divided between the third body and the newly formed molecule.

This alternative reaction does not lead to molecular radiation[4]

$$N(^4S)+N(^4S)+X\rightarrow N_2(v\geq 0\ A^3\Sigma)+X^{\text{exc}}. \tag{3}$$

After reactions (1) and (2) or (3), the molecule is in the metastable $A^3\Sigma$-state. Subsequent collisions of the second kind, with atomic and molecular nitrogen in ground or metastable states, can be invoked to explain the excitation of the remainder of the afterglow spectrum (at least as far as the energetic requirements are concerned).[5] We conclude then, that *if* in the three-body collision the *entire* dissociation energy (of 7.383 ev) is given to the resulting nitrogen molecule in the form of electronic energy and none to the third body, then one would expect the strongest feature of the afterglow spectrum to be the 10,440A (0, 0) band of the first positive system.

Of course, the appearance of a very intense (0, 0) band of the first positive system of nitrogen in the afterglow would not in itself prove the correctness of the theory described above, nor would it prove that the dissociation energy of N_2 is 7.383 ev. However, the presence of this radiation with great intensity would make possible an experiment which would strongly support the 7.383-ev value for $D(N_2)$ if this is the correct value. The experiment is to study the infrared spectrum of the "dark modification" of active nitrogen. When active nitrogen is heated, or is subjected to a small electric current, the visible glow disappears or is greatly weakened, but the gas retains its activity.[1] This is demonstrated, in the first case, by the observation that when nitrogen flows through a tube, the central portion of which is heated, the glow is extinguished in the heated portion but recommences when the gas reaches the cooler part of the system. One assumes then that the primary reaction (three-body recombination in the volume) continues throughout the dark phase, and that the intermediate reactions leading to the excitation of visible light are interrupted by the heating (or the current.) The mechanism for this interruption might be the destruction of the metastable molecules which the recombination process produces. If the dissociation energy is 7.383 ev, then the primary reaction leads to radiation in the infrared only, so that the phase in which only the primary reaction proceeds would indeed appear "dark." An investigation of the infrared spectrum of the "dark modification" of active nitrogen should reveal the reportedly strong (0, 0) band of N_2 (first positive) at 10,440A with more or less undi-

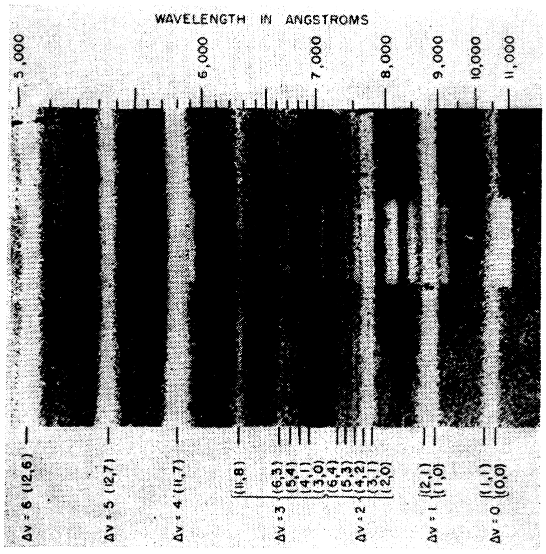

FIG. 1. Bands of first positive system of N_2 in active nitrogen. Type I–Z plate. Maximum infrared speed, 10,900A.

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[2] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 448. A. G. Gaydon, *Dissociation Energies* (John Wiley and Sons, Inc., New York, 1947), p. 152. Other values of $D(N_2)$ have been proposed, the most recent being 11.80 ev, by G. Glockler, J. Chem. Phys. **18**, 1518 (1950).

[3] J. Kaplan, "*The Laboratory Production of Auroral Afterglows*," in *The Emission Spectra of the Night Sky and Aurorae* (The Physical Society, London, 1948), p. 118.

[4] It has often been stated that because the available dissociation energy is almost exactly equal to the excitation energy of a certain level of the product molecule, the reaction exciting this level by "resonance" is very probable. However, owing to the interchange between the kinetic energy of vibration and translation with the electronic energy, it is by no means obvious that all of the energy involved in the recombination process will be transformed into electronic energy. The most probable products of the reaction may be left in a state of strong vibration, as is indicated in Eq. (3).

[5] A complete discussion of the reaction scheme for active nitrogen (which will not be undertaken here) must include also an analysis of the role played by the metastable $a^1\Pi$-state of the molecule.

minished intensity, if the mechanism described is operative. Such an observation would suggest strongly the value 7.383 ev for $D(N_2)$.

The early work on the infrared spectrum of active nitrogen was carried by Kichlu, Acharya,[6] and Cario.[7] The infrared limit of their photographic plates was about 8900A, so they were only able to observe the (3, 1), (2, 0), and probably the (3, 2), (2, 1), and perhaps (1, 0) bands of the first positive system in addition to the well-known visible bands originating on $v'=6$, 11, and 12. They could not have detected the (0, 0) band even if it had been much more intense than the bands originating on $v'>0$. More recently, Kaplan[3] has investigated the infrared spectra of nitrogen afterglows and has compared them with airglow and auroral spectra. He mentions a strong enhancement of the (0, 0) band of the first positive system in the Lewis-Rayleigh afterglow, though no details are given. Before undertaking the spectroscopy of the "dark modification," we had to confirm the abnormal intensity of the 10,440A band in the normal afterglow. These spectra of the Lewis-Rayleigh glow in active nitrogen, photographed with I–Z plates, are described in this paper.

II. EXPERIMENTAL APPARATUS

Commercial tank nitrogen was flowed over hot platinized asbestos and then phosphorous pentoxide to remove all of the hydrogen in the gas. A remaining trace of oxygen in the gas was allowed to remain as a helpful impurity and appeared in the spectra as bands of NO. The gas was passed through a dry ice-acetone trap, then a controlled leak, and finally through an uncoated cylindrical Vycor vessel 3″ in diameter and 12″ long. A self-excited 7-Mc oscillator with a maximum power output of 750 watts excited a discharge in the cylindrical vessel. Microswitches, operated by a rotating cam, turned on the oscillator for ½ second. The oscillator was then turned off, and about 0.05 sec later a shutter between the discharge vessel and the spectrograph slit opened. The shutter remained open, with the oscillator off, for 2½ sec, after which the shutter closed and the cycle began again. In this way the apparatus operated continuously, the spectrograph photographing the integrated spectrum from 0.05 to 2.50 sec in the afterglow. A neon Geissler tube was next to one end of the discharge vessel so that neon lines would appear on the plate if the shutter opened while the neon tube was excited. The neon tube was periodically excited by the same oscillator which produced the nitrogen discharge, and the fact that no neon lines appeared on the afterglow spectrograms proves that the shutter did not leak light from the very intense direct discharge. When the cycling apparatus was turned off, the afterglow was easily visible in a darkened room for one minute.

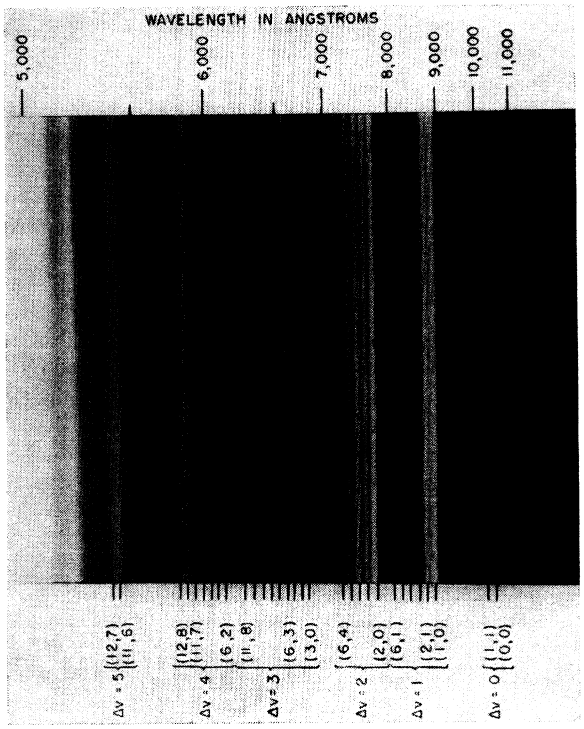

FIG. 2. Bands of first positive system of N_2 in active nitrogen. Type I–Z plate. Maximum infrared speed, 10,900A.

The spectrograph was a glass prism Zeiss instrument with a speed of f:2.7, an aperture of about 6 cm, and a slit width of 0.08 mm. A 30-sec exposure showed the visible spectrum quite satisfactorily, but preliminary exposures of 48 hr on I–Z plates hypersensitized in an ammonia-ethyl alcohol solution were not sufficient to show the band at 10,440A. The hypersensitized plates were then pre-fogged by a controlled exposure to a tungsten lamp through two Wratten 87 infrared filters.[8] After this pre-exposure, a 48-hr exposure brought out the (1, 0) band as well as the (0, 0) band. Since only a qualitative measure of the relative intensity of the (0, 0) band and the bands from higher initial vibrational levels was sought, a heterochromatic photometry was not employed. The manufacturer's data on the spectral sensitivity of the hypersensitized emulsion, as well as comparison of afterglow plates with spectrograms of the direct discharge, afford a sufficient indication of the order of magnitude of the relative intensities involved. The speed of the I–Z plate (hypersensitized) is roughly uniform from 7000 to 11,000A with a slight maximum around 10,900A.

III. RESULTS

Figure 1 shows an enlargement of a spectrogram of the infrared afterglow. The short lines in the center of the spectrogram are comparison spectra of He, A, and

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[6] Kichlu and Acharya, Nature **121**, 982 (1928); Proc. Roy. Soc. (London) **A103**, 168 (1929).

[7] G. Cario, Z. Physik **89**, 523 (1934).

[8] The details of the criteria used to determine the optimum pre-exposure will be published soon elsewhere.

Ne. The most prominent features of the spectrum are the well-known bands originating on $v'=12$ and 11. The characteristically anomalous intensity distribution in the progressions involving $v'=6$ are also apparent. In the infrared, the bands originating on $v'=1$, 2, and 3 are quite intense. Also, their intensity is quite comparable to that of the (0, 0) band. There is certainly no suggestion in this spectrum that the $v'=0$ level of $B^3\Pi$ is selectively populated, which the theory outlined above would require. Of the several two-day exposures which were made, the spectrum in Fig. 1 had the strongest (0, 0) band. The intensity distribution in the bands originating on levels with $v'<6$ appears very similar to the intensity distribution in the spectrum of the direct discharge.

Figure 2 shows an enlargement of another spectrogram in which (0, 0) appeared much weaker, although in this case it was at least in part due to an accidental fault in the hypersensitization procedure. This enlargement was made by mounting the printing paper on a rotating drum whose axis was perpendicular to the image of the spectral lines from the enlarger. In this way the effect of grain spoiling the resolution of the spectral lines was intentionally reduced, and many more bands are visible on careful inspection of the enlargement. In this spectrum the (1, 0) and (2, 1) bands were particularly intense, even more intense than the usually dominant (12, 7) and (11, 7) bands. The preferential population of $v'=6$ is particularly apparent, however. The $\Delta v=1$ and 2 progressions drop off abruptly in intensity at $v'=6$. The $\Delta v=3$ progression shows an abrupt decrease in intensity at $v'=6$ and then again at $v'=11$. The $\Delta v=4$ progression begins with (6, 2) and then gets much stronger at (11, 7) and (12, 8). A total of 31 bands of the N_2 first positive system are observed. In the green and blue regions of the spectrum, traces of the β-spectrum of NO and the violet system of CN appear. No atomic spectral lines were observed in the afterglow. Overlapping of NO and CN impurity bands and the very low dispersion make it impossible to exclude the possibility that N_2 second positive bands, or Vegard-Kaplan bands appear very faintly in the afterglow. These systems are not found by other authors in the Lewis-Rayleigh glow (though they may be found in the very short time afterglows). A weak feature at 4850A is unidentified and might be associated with the (2, 15) Vegard-Kaplan band which is degraded to the red and has its band head at 4837.1A. This band is listed by Pearse and Gaydon[9] as the most intense Vegard-Kaplan band observed by Bernard.

IV. ACTIVE NITROGEN AND THE AIRGLOW

The excitation process for the 10,440A band described at the beginning of the paper was first proposed with reference to a very strong radiation of about this wavelength in the airglow of the earth's atmosphere. When this radiation was first discovered[10–13] it was interpreted as the (0, 0) band of the N_2 first positive system, assuming the above reaction scheme. The altitude of emission of the airglow was, at that time, very uncertain. The possibility that this altitude might be as high as 200 km or more gave encouragement to efforts to explain the existence of the required density of atomic nitrogen in the atmosphere at night. Also, there appeared to be a marked similarity between the spectra of the airglow and the Lewis-Rayleigh nitrogen afterglow in the laboratory, especially when a little oxygen is introduced into the active nitrogen. This similarity also appeared to support the atomic nitrogen theory of excitation of the airglow, since this theory appeared to apply well to active nitrogen. Our failure to find a marked enhancement of the (0, 0) band at 10,440A is not surprising in view of the recent discovery by Meinel[14,15] that the infrared spectrum of the airglow must be identified as due to OH and not to N_2. Also, recent work indicates that the altitude of emission of the airglow is in the neighborhood[16] of 100 km, and it is very unlikely that an appreciable density of atomic nitrogen exists at this height. Hence, it appears that the analogy between the airglow and active nitrogen is rather remote.

The failure of both the nitrogen afterglow and the airglow to demonstrate the resonance theory of excitation of the first positive (0, 0) band of N_2 by recombination of atoms does not contradict the 7.383-ev value of the dissociation energy of N_2. Nor does the lack of preferential excitation of the (0, 0) band in active nitrogen disprove the hypothesis that the primary reaction is the recombination of atoms in three-body collisions. For even if $D(N_2)=7.383$ ev, the recombination product may be in the metastable $A^3\Sigma$-state (see Sec. I). Construction of the correct reaction scheme for active nitrogen must await an independent and final determination of the dissociation energy of nitrogen.

The author is grateful to Professor O. Oldenberg for many helpful discussions in connection with the spectrum of active nitrogen and this paper.

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[10] Stebbens, Whitford, and Swings, Astrophys. J. **101**, 39 (1945).

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[14] A. B. Meinel, Pub. Astron. Soc. Pacific **60**, 357 (1948); Astrophys. J. **111**, **207**, 433, **555**, and **112**, 131 (1950).

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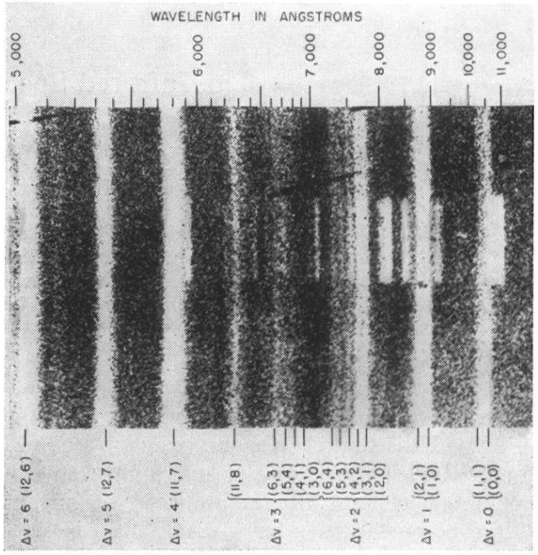

FIG. 1. Bands of first positive system of N_2 in active nitrogen. Type I–Z plate. Maximum infrared speed, 10,900A.

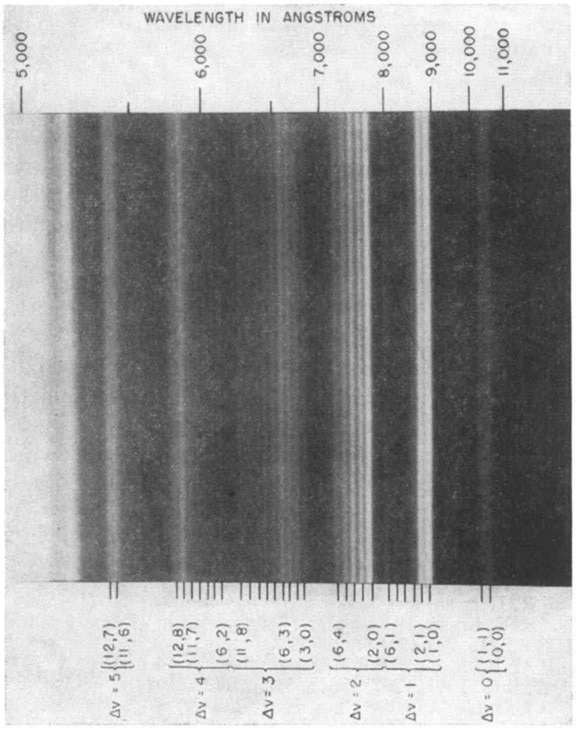

FIG. 2. Bands of first positive system of N_2 in active nitrogen. Type I–Z plate. Maximum infrared speed, 10,900A.