A STRONG INFRARED RADIATION FROM MOLECULAR NITROGEN IN THE NIGHT SKY*

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ABSTRACT

A new infrared radiation has been detected in the night sky, which is far more intense than the ordinary persistent aurora giving the green line at 5577 A. Measured with a photocell and filters, the wave length of the new radiation is 10,440 $\pm$ 25 A.

This night-sky radiation is identified with the (0, 0) band of the first positive group $B^3\Pi \rightarrow A^3\Sigma$ of N_2. The absence of other N_2 bands suggests that emission of the (0, 0) band involves conversion of the energy of dissociation $D(N_2)$ into excitation in a three-body collision:

$$N + N + N_2 \rightarrow N_2 + N_2^{exc}.$$
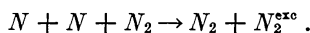
Since $D(N_2)$ is a little larger than the excitation energy of $B^3\Pi$, $v' = 0$, but smaller than $B^3\Pi$, $v' = 1$, only the bands arising from $B^3\Pi$, $v' = 0$, would be excited; and of the latter, only (0, 0) is observable. This mechanism implies the presence of a large number of nitrogen atoms in the high atmosphere. It can be effective only with the value 7.38v. of $D(N_2)$ advocated by Herzberg and Sponer.

In the year 1940 a program of measures of stars and nebulae in different spectral regions was begun by Stebbins and Whitford. With a photoelectric cell and suitable filters it was possible to isolate six regions ranging from 3530 A to 10,300 A. The observations were made with the 60-inch and 100-inch reflectors; and for measures of large objects, like the nebulae, the photometer was equipped with focal diaphragms up to 19 mm in diameter, giving an angular field of 8ʹ.6 on the 60-inch and 5ʹ.1 on the 100-inch reflector.

TABLE 1

COMPARISON OF STAR AND SKY

Filter	Ultraviolet λ3530	Violet λ4220	Blue λ4880	Green λ5700	Red λ7190	Infrared λ10,300 A
Deflection, star.......	8	8	10	8	8	8 mm
Deflection, sky.......	8	5	5	8	13	112 mm

On the very first exposure to a nebula, M 31, through an infrared filter giving an effective wave length of 10,300 A, the galvanometer deflection was unexpectedly large. A check exposure to neighboring blank sky, to determine the background effect, promptly showed that there was a strong infrared radiation in the night sky which would have to be eliminated from any measures of objects of low surface brightness, like the nebulae. This elimination of the sky background is readily accomplished by sliding the photometer on the telescope from object to blank sky and then back to object, this being the regular observing procedure for nebulae and clusters and for faint stars where with even the smallest practical diaphragm the relative sky effect is appreciable.

As a sample of the relative effects between a star and the sky, we have the data in Table 1. A star of type dF7 was selected as giving roughly the same deflection for each

spectral region with the cell and filters used. The infrared radiation is obviously much brighter than any other part of the spectrum, including the persistent auroral line at 5577 A, for which we have never found any effect. With allowance for the continuous sky spectrum, the infrared radiation is probably scores of times—perhaps even a hundred times—as strong as the line in the green. At first we thought that the infrared effect was caused by the line at 8600 A discovered by V. M. Slipher,[3] but it soon became evident that this assumption could not be true. An inspection of the curves for these filters[4] shows that the response at 8600 A should be greater for the red than for the infrared filter and that, while the increased sky deflection for the red may be caused by the line at 8600 A, the main source must be farther out, probably near 10,000 A, where it would be between the strong water-vapor absorption bands ρ and Φ, roughly at 9500 A and 11,300 A, respectively. The decreasing sensitivity of the photocell makes improbable anything beyond 11,500 A.

That the new radiation must be atmospheric was shown by its variation with the zenith distance, by its usual decrease through the night, and by its irregular variability from night to night and from season to season. Most of the measures were made with the 60-inch reflector incidentally to observations of stars and nebulae, for it never seemed worth while to devote the time of a large reflector to work which could be done with any f:5 condensing lens or even by pointing the photometer directly at the sky. But, despite the fragmentary character of our data (only three or four measures per night), a rough impression of the changes in this radiation could be formed. The brightness is greatest immediately after twilight, when, under standard conditions, an exposure to the sky near the pole with a 12-mm focal diaphragm on the 60-inch gives a galvanometer deflection of 100–150 mm. In general, this intensity decreases through the night until the deflection is, say, 70–100 mm before dawn.

During the night the telescope is being pointed to all parts of the sky; and the measurements show that the infrared intensity varies with the zenith distance. The intensity probably varies in proportion to sec z; but because of erratic changes in intensity this law could be more easily tested with a smaller telescope. Measures should be made at widely different zenith distances at intervals of time not greater than a minute and should be carried to near the horizon in order to estimate the height of the emitting layer above the earth's surface. All this sounds simple enough; but with the 60-inch the program on stars and nebulae includes measures in six colors, and the sky background must be eliminated in all six. There are also further complications when the moon is above the horizon. At that time the sky is bluer, as shown by the increased intensity in the ultraviolet, with progressively less change toward the infrared.

One night we had occasion to test the infrared sky during the approach of dawn. With the telescope pointed at the zenith, the galvanometer deflections increased in 20 minutes from 70 mm to a sharp maximum of 94 mm and then decreased to 66 mm by 20 minutes later. The maximum occurred within one minute of the computed time for the sun 18° below the horizon. This dependence of the infrared upon the incidence of solar radiation in the upper atmosphere should, of course, be investigated near both sunrise and sunset.

Renewed interest was awakened on July 20, 1944, when the infrared sky was found unexpectedly to be of nearly twice its ordinary brightness and to be fluctuating by 10 or 15 per cent within 10 minutes. Near midnight the deflections were up to about 200 mm, then dropped back to 100 mm before dawn. We seemed to be witnessing an infrared auroral display, but there was no disturbance of the magnetometer at Mount Wilson that night. By two nights later the deflections were back to normal or below; on a night in

[3] $M.N.$, **93**, 666, 1933. In a private communication Dr. Slipher states that he has detected other radiations near 10,000 A, but he has not determined the wave lengths. Whether or not his spectrograms extend out to 10,450 A is not clear; possibly they do.

[4] Stebbins and Whitford, $Mt.$ $W.$ $Contr.$, No. 680, p. 4; $Ap.$ $J.$, **98**, 23, 1943.

September, however, the deflections got up to 250 mm without minute-to-minute fluctuations.

In the course of a discussion of these outbursts in the night sky P. Swings suggested that the radiation was undoubtedly molecular in origin and very likely could be traced to the (0, 0) band of nitrogen at about 10,450 A. With this suggestion as a guide, it was proposed to determine the wave length in some way with the photocell and a suitable filter, since a photograph of the sky spectrum at 10,450 A would require an extremely long exposure. For the Schott filter UG6, 2 mm thick, the following transmissions are given by the maker (reflections neglected):

$$8500 \text{ A} \ldots \ldots 0.01 \quad 11,500 \text{ A} \ldots \ldots 0.79$$
$$9500 \ldots \ldots .25 \quad 13,000 \ldots \ldots 0.92$$
$$10,500 \ldots \ldots 0.59$$

One piece of this filter should absorb all wave lengths shorter than 8500 A; then, if the sky radiation is confined to a band near 10,000 A, each additional piece would transmit the same fraction of the light incident upon that piece.

Measures of the sky were obtained on several nights, giving the respective transmission ratios, two filters to one and three filters to one:

$$(2)/(1) = 0.565 \pm 0.007 \text{ (p.e.)}, \qquad (a)$$

$$(3)/(1) = 0.348 \pm 0.005, \qquad (b)$$

and, dividing (b) by (a),

$$(3)/(2) = 0.616 \pm 0.012. \qquad (c)$$

With only four filters available it was not convenient to measure (c) directly, but from the difference between (a) and (c) we conclude that there must be some radiation in addition to a narrow band. If the extra light is of longer wave length than the assumed

TABLE 2

CALIBRATION OF FILTERS

	10,336 A	10,407 A	10,478 A
Observed (2)/(1)...............	0.508±0.024	0.564±0.010	0.589±0.020
Observed (3)/(1)...............	0.264±0.000	0.318±0.011	0.361±0.012
Computed (3)/(2)...............	0.520±0.025	0.564±0.022	0.614±0.029

band, the correct ratio is less than (a); but if the extra light is of shorter wave length, the correct ratio is greater than (c). Anything but a monochromatic source in the region considered will give a higher ratio for each added filter. Still more pieces of the same filter, or, better yet, another filter with a transmission gradient of opposite sign, would settle the matter; but these were not available.

The average transmission-curves given by the maker cannot be relied upon for different melts of the same glass; hence we undertook the calibration of the UG6 filters. Our pieces were all cut from the same 2-inch square. A most convenient monochromator was found to be the 150-foot tower telescope, with the normal solar spectrum from a 75-foot grating. A visual setting at 5168 A in the second order gave 10,336 A in the first order; with a dispersion of 0.71 A/mm, other settings were made by moving the photometer along the spectrum. The mean results for each combination of filters for three regions at intervals of 10 cm are in Table 2. The differences between (2)/(1) and (3)/(2) are now within the accidental errors, showing that there was no scattered light and that the measured spectral regions were effectively pure.

To utilize all the data, including some additional measures at wave lengths other than those of Table 2, two linear equations were derived expressing the ratios as functions of the wave length. The ratios from the sky, $(2)/(1) = 0.565$ and $(3)/(1) = 0.348$, were then substituted in these equations to get the respective wave lengths. The details are not important because of the systematic difference between the two results. We find:

From $(2)/(1)$ . . . .   10,427 A
From $(3)/(1)$ 10,452

Mean. . . . . $10,440 \pm 25$ A

We see no better procedure than to take the mean of the two values and to estimate the probable error to be of the same order of magnitude as the difference between them. Although the resulting wave length could be improved by further measures with other filters, it should, even under present conditions, compare favorably with anything that could possibly be obtained so far out in the infrared with a spectrograph and the present photographic plates.

SPECTROSCOPIC COMMENTS

IDENTIFICATION

The only possibilities that suggest themselves for identification of a night-sky emission near λ 10440 are: (a) the forbidden $^2D - ^2P$ multiplet of N I; (b) the (0, 0) band of the $B^3\Pi \rightarrow A^3\Sigma$ (first positive) group of N_2.

FORBIDDEN LINES OF N I

Most observers agree that the doublet near λ 5200 is absent from the night sky, as should be expected from the transition probabilities in Table 3. They also agree that

TABLE 3

LINES OF [N I]

$^4S - ^2D$	λ 5197.8, EP 2.4 volts, trans. prob. 0.000021 λ 5200.1, EP 2.4 volts, trans. prob. 0.000014
$^4S - ^2P$	λ 3466.4, EP 3.6 volts, trans. prob. 0.0094
$^2D - ^2P$	λ 10407.3, EP 3.6 volts, trans. prob. 0.21 λ 10397.8, EP 3.6 volts, trans. prob. 0.25

λ 3466 is likewise absent from, or hardly visible in, the night sky, although it appears in the spectrum of diffuse aurorae. The strongest [N I] lines should be $\lambda\lambda$ 10407.3–10397.8, with mean wave length λ 10402.7. The emission at λ 10403 has the same upper level as λ 3466; hence the intensity ratio of λ 10403 to λ 3466 should be that of the transition probabilities $(0.21 + 0.25):0.0094$ or 49:1. Although λ 10403 should thus be the strongest [N I] emission, it would not be able to give rise to the intense night-sky emission observed, since λ 3466 is either absent or hardly visible. It should be noted that a line fifty times the intensity of λ 3466 would still be weak, compared to the green or red [O I] lines; and the green line is not detected by the photoelectric measurements. Hence it is safe to conclude that a [N I] emission cannot be a major contributor to the night-sky emission near λ 10440. Moreover, the wave length observed for the maximum intensity of the night-sky emission is found to be definitely longer than the [N I] line, and the difference in wave length appears greater than would be due to the experimental error.

On the other hand, since λ 3466 is observed in certain types of aurora, a reinforcement of infrared night-sky emission in an aurora may possibly be due, at least partly, to the contribution of λ 10403 [N I]. In such a case a shift of the intensity maximum toward the shorter wave lengths should be observed.

(0, 0) BAND OF THE FIRST POSITIVE GROUP OF NITROGEN

a) Wave length.—The (0, 0) band has been examined by A. H. Poetker[5] and by A. A. Frost and O. Oldenberg.[6] A thermopile with a prism spectrometer gave a maximum at 1.042 μ; with a grating, four peaks were recorded between 1.035 μ and 1.046 μ, the two strongest being at 1.041 μ and 1.043 μ. Individual lines were observed photographically but could not be measured accurately.

Frost and Oldenberg include a reproduction of part of the (0, 0) band taken with a 21-foot grating in the first order, on which many individual lines are resolved; but they give no analysis of the band.

From the well-measured N_2 bands of the visual region,[7] we may attempt to compute the intensity maximum of the (0, 0) band. But this is difficult and uncertain, especially since we ignore the temperature in the atmospheric regions where the infrared night-sky emission occurs. An estimated value of the wave length of the maximum is λ 10450. At any rate, the N_2 emission should be of wave length longer than the [N I] line. The agreement in wave length between the observed night-sky emission and the (0, 0) band of N_2 is quite satisfactory.

b) Intensity.—The (0, 0) band is by far the strongest transition in the $\Delta v = 0$ sequence and certainly one of the strongest bands of the whole first positive group.[8]

Yet, if we attribute the intense night-sky emission to the (0, 0) band, other transitions should be observable with fair intensity if the relative intensities were at all similar to those found in such laboratory sources as a discharge in gas. Several emissions observed in the night-sky spectrum in the region from λ 5000 to λ 6000 have been tentatively attributed to bands of the first positive group. But all these emissions are extremely weak, and many of the identifications are even very doubtful.

No appreciable emission is observed, photoelectrically, in the night sky at λ 8910, which is the maximum of the (1, 0) transition; this fact shows that very few N_2 molecules are actually brought to the level $v' = 1$ of $B^3\Pi$.

Hence the identification of the night-sky emission with the N_2 band requires a mechanism enhancing the (0, 0) band relative to the other vibrational transitions.

c) Suggested excitation mechanism.—The value generally accepted for the heat of dissociation of N_2, $D(N_2) = 7.383$v.,[9] is based on a discussion of predissociation phenomena. Recently A. G. Gaydon[10] has advocated a higher value $D(N_2) = 9.764$v. In this discussion we shall adopt the value $D(N_2) = 7.383$v. given by Herzberg. Actually, the excitation mechanism suggested for the (0, 0) band depends entirely on the correctness of this value.

The value 7.38v. agrees almost exactly with that of the $v' = 0$ level of the $B^3\Pi_g$ electronic state (which is the upper state of the first positive group, $B^3\Pi_g \rightarrow A^3\Sigma_u^+$). In fact, the heat of dissociation of N_2 is just a little higher than $B^3\Pi$, $v' = 0$, but lower than $B^3\Pi$, $v' = 1$ (Fig. 1).

[5] *Phys. Rev.*, **30**, 812, 1928.

[6] *Phys. Rev.*, **48**, 66, 1935.

[7] For a list of these bands see, for example, Pearse and Gaydon, *The Identification of Molecular Spectra* (London, 1941), p. 137.

[8] The absence of the N_2 band in absorption in the solar spectrum is due to the high energy of 6.1v. of the lower level $A^3\Sigma$.

[9] G. Herzberg and H. Sponer, *Zs. f. Phys. Chem.*, B, **26**, 1, 1934.

[10] *Nature*, **153**, 407, 1944.

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by S. Chapman[11] for the [O I] lines. Chapman suggests that the [O I] emission in the night sky is due, at least partly, to the recombination of O atoms formed by dissociation of O_2 during the day. Solar energy would be stored up during the day in the form of free atoms and released in the course of the night. Numerous other suggestions have been made to explain the [O I] and other night-sky emissions. Among the latest is the mutual neutralization of O^+ and O^- ions on impact,[12]

$$O^+ + O^- \rightarrow O^{\text{exc}} + O^{\text{exc}},$$
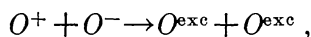
an electron leaking across from the negative ion and occupying a vacant level in the positive ion.

As far as the "nonpolar" part of the night-sky emission is concerned, the observations are well explained by Chapman's mechanism.[13] The mechanism suggested here is some analogue for nitrogen of Chapman's hypothesis concerning oxygen. Evidently, a general decrease in the intensity of the infrared emission in the course of the night is readily understood in the recombination hypothesis.

It is at present impossible to predict the range in wave length covered by a N_2 band emitted in the upper atmosphere according to the mechanism suggested here, but evidently the emitted radiation is not monochromatic. It is therefore not surprising that the observed ratios (a) and (c) mentioned on page 41 are slightly different.

d) Objections to the mechanism of nitrogen recombination.—The photodissociation[14] of N_2 differs from that of O_2. In fact, the difficulty of photodissociating N_2 molecules is the main reason why it has usually been assumed that atomic nitrogen, if present at all in the upper atmosphere, must be there only in very small amounts. On the contrary, at great heights in the atmosphere (above 100 km) most of the oxygen is supposed to be in the atomic form.

The question of the photodissociation of N_2 has recently been discussed by Ta-You Wu,[12] who concludes that photodissociation of N_2 should be appreciable in the region $\lambda < 500$ A, not yet explored in the laboratory. Modern evidence[15] points to the fact that the sun radiates much more energy in the far ultraviolet than would a black body at 6000° K, so that radiation would still be plentiful beyond λ 500 A. But, according to Dr. G. Herzberg,[16] there is actually no need for radiation of wave length shorter than λ 500 to produce a dissociation of nitrogen. It is very likely that N_2 molecules can be predissociated by radiation of wave length shorter than approximately 1400 A. Dr. Herzberg states that the higher vibrational levels of the $A^3\Sigma_u^+$ state can almost certainly predissociate into two normal N atoms. Although the transition probability from the ground state to the $A^3\Sigma_u^+$ state is small, it would suffice to produce a considerable dissociation of N_2 molecules in the upper atmosphere.

Another objection to the presence of atomic nitrogen in the atmosphere is the absence of strong [N I] emission in the night sky. Of course, to obtain a [N I] emission,

[11] *Phil. Mag.*, **23**, 657, 1937.

[12] H. S. W. Massey and D. R. Bates, *Reports on Progress in Physics*, **9**, 72, 1943. Incidentally, the mechanism suggested for [O I] by Massey and Bates would not be applicable to a [N I] emission, on account of the small electron affinity of the N atoms. For other suggestions see Ta-You Wu, *Phys. Rev.*, **66**, 65, 1944.

[13] C. T. Elvey, *Rev. Mod. Phys.*, **14**, 141, 1942.

[14] Evidently, N atoms may be formed by photodissociation of molecules other than N_2, such as NO. But such a process is not likely to give rise to a high abundance of N atoms.

[15] A. Hunter, *Reports on Progress in Physics*, **9**, 5, 1943.

[16] Private communication. The authors wish to thank Dr. Herzberg for his helpful comments.

appropriate excitation mechanism of sufficient efficiency must exist for the N atoms. If our suggested mechanism

$$N + N + N_2 \rightarrow N_2 + N_2^{exc}$$
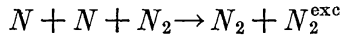
is correct, it would deplete considerably the less efficient recombination process

$$N + N + N \rightarrow N_2 + N^{exc}$$
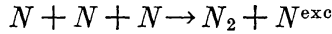
and would be much more frequent than any other excitation mechanism for N I.

Wu's discussion shows that, by supposing an appreciable abundance of free N atoms in the upper atmosphere, several important observations can be explained. It is possible, in this way, to reconcile the theoretical and observed densities in the E and F layers; to understand the observed recombination coefficients of electrons in these same E and F layers; and to explain the presence of N_2^+ and N_2 bands in high aurorae. We should add that numerous reactions between N atoms and oxygen or oxides of nitrogen may be of interest for the physics of the upper atmosphere.

e) Remarks.—

1. After emission of the first positive group, the N_2 molecules are left on the metastable level $A^3\Sigma^+$, from which part of them will fall down toward the ground electronic level $x^1\Sigma^+$ with emission of the forbidden Vegard-Kaplan bands.

2. The N_2 molecules on the metastable level $A^3\Sigma^+$ have been invoked on numerous occasions to explain the excitation of the $[O$ I$]$ lines, the peculiar behavior of the red lines of $[O$ I$]$ at twilight and in certain types of aurora, etc. Many of these attempts have lost their significance following investigation and discussion by Chapman, Götz, Nicolet, and others. But some of them may still be reconsidered in the light of the present result, since the population on the $A^3\Sigma$, $v = 0$ level must be appreciable.

3. Since the mechanism of emission suggested here seems to be the only one sufficiently plausible to explain the intense night-sky emission near λ 10440, it may be considered as an argument in favor of the value $D(N_2) = 7.38$ volts.