In conclusion, we wish to express our thanks to Dr. G. R. Toshniwal for many useful discussions and to Mr. K. B. Mathur and Dr. Rakshit for much help in the calculations.

SUMMARY

In this paper, the ray treatment of passage of e.m. waves through the ionosphere has been critically reviewed, and a wave treatment has been given for the *o*-wave for propagation in the magnetic equator. It has been shown that contrary to the implicit assumption in the ray treatment which requires complete reflection at the point in the ion-barrier where μ falls to zero, there may be considerable penetration by the wave of the barrier, even when the thickness of the barrier amounts to several kilometres.

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68. ON THE ACTION OF ULTRA-VIOLET SUNLIGHT UPON THE UPPER ATMOSPHERE

(*Proc. Roy. Soc. Lond.*, **A160**, 155, 1937)

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1—INTRODUCTION

The ordinary solar spectrum extends, as is well known, to about $\lambda 2913$, the more ultra-violet parts being cut off by ozone absorption in the upper atmosphere. We have thus no direct knowledge of the distribution of intensity in the solar spectrum beyond $\lambda 2913$, as it will appear to an observer situated outside the atmosphere of the earth. But it is now recognized that a number of physical phenomena is directly caused by the photochemical action of this part of sunlight on the constituents of the upper atmosphere. Such phenomena are (1) the luminous spectrum of the night sky and of the sunlit aurora,[1] (2) the ionization in the E, F and other layers which is now being intensely studied by radio-researchers all over the world[2], (3) the formation and equilibrium of ozone (see Ladenburg 1935), (4) magnetic storms and generally the electrical state of the atmosphere.

Formerly it was a debatable point whether some of these phenomena were not to be ascribed to the action of streams of charged particles emanating from the sun. There seems to be no doubt that the polar aurora and certain classes of magnetic storms are to be ascribed to the bombardment of molecules of N_2 and O_2 by such charged particles, for these phenomena show a period which is identical with the eleven year period of the sun, and are found in greater abundance, the nearer we approach the magnetic poles.[3] But there now exists no doubt that the ionization observed by means of radio-methods in the E and F_1 regions, their variation throughout day and night, and at different seasons is due to the action of ultra-violet sunlight. This was decisively proved by observations during several total solar eclipses since 1932 (Appleton and Chapman 1935). The luminous night-sky spectrum, though it has certain points of similarity to the polar aurora, is on the whole widely different, and is found on nights free from electrical disturbances. The prevailing opinion is that it is mainly due to the ultra-violet solar rays, i.e. in the course of the day sunlight is stored up by absorption by the molecules in the upper atmosphere, and again given up during the night, in one or several steps, as a fluorescence spectrum. According to S. Chapman (1930) the formation of the ozone layer and its equilibrium under different seasonal conditions is

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[1] For a general account of the spectrum of the luminous night sky, see Dejardin (1936).

[2] For general information regarding investigation on the ionosphere, see Mitra and others (1936) and Appleton (1936).

[3] See for general information article by Störmer (1931). The frequency of aurorae appears to reach a maximum 20° from the magnetic pole.

also to be mainly ascribed to the action of ultra-violet sunlight. In the following paper an attempt will be made to discuss some of these questions in as rigorous a way as is possible with our present knowledge. It is evident that an adequate discussion is possible only if we have a good knowledge of (1) the distribution of intensity in the solar spectrum beyond λ2900, (2) the photochemical action of light of shorter wave-length than λ2900 on the constituent molecules of the upper atmosphere, which are mainly oxygen and nitrogen. We shall first consider (1).

2—THE ULTRA-VIOLET SPECTRUM OF THE SUN

The disappearance of sunlight below λ2900 has long been known, through the researches of Fowler and Strutt (1917), and of Fabry and Buisson (1913) and others, to be due to the absorbing action of a layer of O_3 (equivalent in amount to a 3 mm. column at N.T.P.) formed in the upper atmosphere. The long series of works by Götz, Meetham and Dobson (1934) and Regener (1934) have shown that this layer extends from about 20 km., reaches a maximum concentration at 30 km., and probably does not extend much beyond 50 km. But, as we shall see presently, the principal photochemical reactions in N_2 and O_2, including ionization, are produced only by light of wave-length < 3000 A, and hence in order that a correct estimate may be made of the action of sunlight on O_2 and N_2 gas above the ozone layer, it is necessary for us to have a detailed knowledge of the emission of the sun below λ3000 A. In the absence of direct knowledge, recourse is made to extrapolation, i.e. emission below λ3000 A is supposed to be identical with that of a black body at 6800°K. The justification for such an assumption is found in the work of H. H. Plaskett[4] and Fabry that the intensity distribution in the solar spectrum in regions free from any absorption lines agrees very well with that of a black body at 6800°K. But this evidence is at best indirect, and many observers hold that solar emission in the ultraviolet is subject to a good deal of fluctuation and differs widely from that of a black body.[5]

3—THE NEGATIVE BANDS OF NITROGEN IN THE SPECTRUM OF THE NIGHT SKY

It is now possible to produce further evidence that ultra-violet emission from the sun is widely different from black-body radiation, but we shall at the outset discuss in full only *one line of evidence which does not appear to admit of any other interpretation.* This is the appearance of the earlier members of the first negative bands of nitrogen in the spectrum of the upper atmosphere when illuminated by sunlight. These bands have the wave-lengths {(0, 0)—3914}, and {(0, 1)—4278}, and on unimpeachable spectroscopic grounds they have been ascribed to N_2^+, *vide* § 6.[6]

These bands are very intense in the spectrum of the polar aurora, where they are produced by the bombardment of N_2 gas by electrons. The intensity is found to be the same as that of the green line of O, λ5577·35. But the lines are also found in the spectrum of the night sky, though so faintly that some observers have even denied their existence in the night-sky spectrum. But the issue has been cleared up by the following observation due to Slipher (1933):

"But the negative nitrogen bands typical of auroral display spectra do not accompany this chief yellow line (green) in the sky, except when auroral displays are actually present. However, these nitrogen bands, I found, could be photographed in the morning and evening skies if brief exposure were made at the moments, when the last and first traces of sunlight touch the high atmosphere. Thus the day, as it were, begins and ends with a sort of auroral flash."

The physical meaning of this observation becomes clear if we consider the genesis of the N_2^+ bands. For this purpose it is necessary to turn to fig. 1, which is the energy-level diagram of N_2 and N_2^+. We notice that the first negative bands are due to transition of the electron from a level called $A'(N\,{}^4S.N^+\,{}^3P.B\,{}^3\Sigma)$[7] to the normal level of N_2^+ called $X'(N\ {}^2D.N^+\ {}^3P.\ {}^2\Sigma_g^+)$. The energies of excitation of these two levels have been obtained from both cathode-ray bombardment and from spectroscopic analysis, both of

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[4] For detailed report on this very intricate problem, and generally on the temperature of stars, see Brill (1932); for later work, see the same, *Ergänzungsband*, **7**, but usually discussion is confined only to available radiation from stars.

[5] The opinion that the ultra-violet radiation from the sun differs widely from that of a black body at 6800°K. has been expressed by many workers, from different points of view. Petit (1935) finds, from actual measurements between λλ4100-3000, that the emission curve shows no resemblance to that of a black body.

Mulders (1935) finds that the solar emission curve (when corrected for absorption) shows a form which bears no resemblance to a black-body curve. From λ9500 to λ4100 it approximates a black-body curve at 7140°K, but between λλ4000-3000 it approximates a black body curve at 4800°K. These determinations are subject to a good deal of uncertainty, as no account is taken of absorption by O_2 and N_2 in the uppermost layers, as described in the present paper, and therefore they do not apply to the region discussed in this paper.

Speculations below λ3000. To explain terrestrial magnetic storms and aurorae, Maris and Hulburt (1929) proposed a hypothesis that the sun may, from time to time, be subjected to outbursts of ultra-violet emission localized at certain points. These flares of radiation may have 10^6 times the intensity of black-body radiation between λλ500-1000, according to the above-mentioned authors.

Gurney (1928) expresses the view that the solar radiation in the ultra-violet (near λ584·4) is in excess of black-body radiation by a factor of 10^8. In a note (Saha 1936) the present author pointed out that the flash of bands due to CO^+ and N_2^+ in the tail of comets can be explained if we suppose that the sun shoots out high energy photons and ionizes CO and N_2 in the tail in the way proposed in § 3 of this paper. In the course of a discussion, Professor H. N. Russell pointed out that once N_2 and CO are ionized, they can be maintained in excited states of N_2^+ and CO^+ by visible radiation from the sun. The subject of cometary spectra will be taken up in a subsequent paper.

[6] For photographs of N_2^+ bands in the aurora, see Slipher and Sommer (1929); see also Slipher (1933).

[7] This notation means that one N atom is in a ${}^4S$ state, the other is singly ionized and is in a ${}^3P$ state and the molecule as a whole is in a ${}^3\Sigma$ state, and so on.

which yield concordant values. As a glance at fig. 1 shows, the first ionization potential (excitation of the X′ level) is 15.55 V, and the second ionization potential (excitation of A level) is 18.68 V. But Slipher's observation shows that the A′ level of N_2^+ is produced by sunlight acting directly on the N_2 molecules of the upper atomsphere. It therefore becomes necessary to find out how these bands are produced by direct photochemical action of sunlight, without the intervention of any bombarding electron. This is furnished by the study of the absorption spectrum of N_2 by Hopfield (1930), who found a number of abosrption bands at λλ723, 694, 681, 675, 671 which pass to a continuous absorption at λ660. Mulliken (1933) shows that the most probable explanation of the origin of these bands is as follows:

$$\mathrm{N}^4\,\mathrm{S.N}\,{}^4\mathrm{S.}\,{}^1\Sigma_g \rightarrow \mathrm{N}\,{}^4\mathrm{S.N}\,2p^2ns\,{}^4\mathrm{P},$$

i.e. one of the component atoms remains unchanged. In the other atom, one electron passes to the *ns* state, thus giving rise to a number of ⁴P terms in a Rydberg series. The limit corresponds to the state of N_2^+

$$(\mathrm{N}\,{}^4\mathrm{S.N}^+\,{}^3\mathrm{P.A'B}\,{}^2\Sigma),$$

which is marked by a continuous absorption at λ660, which corresponds to the ionization of N_2 to the A level of N_2^+. What is particularly important to notice is the fact that Hopfield did not find any trace of continuous absorption at the first ionization potential of N_2, corresponding, to the X′ level.

Several investigators (for example, see Price and Collins 1930, particularly para. 2, p. 715) have subsequently found that many diatomic molecules show a similar type of strong absorption leading to one or more higher ionization potentials, *the absorption leading to the lowest ionization potential being very feeble or sometimes totally absent.*

Hopfield's experiment therefore proves that light of wave-length λ794 cannot directly ionize N_2 to the N_2^+ normal state, i.e. a quantum having an energy content of 15.55 V (X′ level), λ794, has no direct action on N_2 though the energy is sufficient for raising N_2 to the lowest state of N_2^+. But a quantum of energy content of 18.68V, λ661, can directly ionize N_2 to the A level. This supplies the clue to the interpretation of Slipher's result. Sunlight of wave-length < λ661 produces direct ionization of N_2 to the A state of N_2^+, which, being excited, emits the negative bands and reverts to the normal N_2^+ state (X). This explains the flash of negative bands at sunrise and sunset. After the withdrawal of sunlight, the excited N_2^+ ions speedily revert to the normal state, and we are left only with N_2^+ normal ions. These are incapable of radiating, and in the course of the night may be neutralized by the direct capture of an electron in different exicted states of N_2, but it is quite probable that when the colliding electrons have sufficient velocity, a number of N_2^+ (X′) ions may be further excited to the A state. This process may account for the feeble emission of negative bands during the night observed by Sommer and certain other workers.[8]

4—IONIZATION OF THE NITROGEN MOLECULE IN THE UPPER ATMOSPHERE

The above arguments therefore prove in a very conclusive manner that N_2 is ionized above a height of 200 km. directly to N_2^+ by the direct action of sunlight. It is difficult to estimate the number of N_2^+ excited molecules thus produced, without photometric measurement of the intensity of the bands, and other relevant laboratory experiments. But we obtain an idea of the number of free electrons in this region from measurement of the F_2 layer ionization. This is estimated by Appleton (1936) and others to be nearly 5×10^5 electrons per c.c., and we can assume that a fair proportion of these electrons is produced by the direct ionization of N_2 to N_2^+ by the action of ultra-violet sunlight. Apart from this evidence, the very intensity of N_2^+ bands during daylight flash, and their intensification in a sunlit aurora (Störmer 1931), is definite proof that sunlight produces considerable ionization of N_2 to N_2^+. It will now be shown that if the radiation from the sun be supposed to be the same as that given by a black body at 6500°, the number of quanta available having an energy content greater than 18.68V (excitation potential of N_2 to the A state of N_2^+) is hopelessly inadequate for the purpose. The argument is as follows:[9]

The number of quanta of frequency greater than ν, and falling normally on unit surface of the earth per sec., is given by

$$\mathcal{N}_\nu = 3 \times 10^{17}\, I_1,$$

where

$$I_1 = \int_{x_0}^{\infty} \frac{x^2}{e^x - 1}\, dx \text{ and } x = \frac{h\nu}{KT}. \tag{1}$$

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[8] The author has discussed the line of argument followed here with many workers on the field in Europe and America, in the course of his travels during 1936, but the only serious objection against it was raised in the course of a friendly conversation with Dr Wulf, of the Bureau of Soils and Agricultural Research, Washington, D. C. Dr Wulf thinks that the ionization of N_2 to N_2^+ is due to the photons having the wave-length λ794, corresponding to the first ionization potential of 15·55 V; the N_2^+ ions produced in this way further absorb the quanta representing the second negative bands of N_2, and thus raise N_2^+ to the N_2^+ excited state A′. The flash of negative bands is due to fluorescence of these excited states of N_2^+.

The mechanism of N_2^+ luminescence postulated by Dr Wulf appears unlikely, as according to the experiments of Hopfield, N_2 shows no, or extremely feeble, absorption at λ794. If we suppose that the absorption exists at all, it must be very small, hence we should have to suppose that these rays penetrate to very low depths of the atmosphere. The observational fact that N_2^+ bands are obtained at heights exceeding 200 km. and not below, shows that the photons giving rise to N_2^+ luminescence are absorbed completely by a very small amount of N_2. This can apply only to continuous absorption at λ660, corresponding to the second ionization potential.

Regarding emission of N_2^+ bands by the night sky, free from aurora, evidence appears to be positive, Dejardin (1936, p. 10). The bands are extremely faint.

[9] For further details about this calculation see Saha (1935).

For $\lambda=660$ A corresponding to 18.68e-volts, $I_1=3\times10^{-13}$, hence we have

$$\mathcal{N}_\nu=10^4. \tag{1'}$$

So the solar rays can produce only 10^1 ions of N_2^+ (A state)/sec./cm.[2] in the whole depth of the atmosphere. But according to a calculation by Chapman (1931), the total number of ions to be produced per sec. for maintaining the *total ionization* is 3×10^{10}. Of course, the total ionization is not entirely due to N_2^+, probably the greater part is due to ionization of O_2^+. But the intensity of N_2^+ bands shows that at least a substantial part, say one-tenth, is due to ionization of N_2. Hence we conclude that the solar ultra-violet light of wave-length < λ660 is about a million times more intense than that given by a black body at a temperature of 6500°K. This conclusion, *to which it is difficult to see any alternative*, brings out the necessity of investigating the ultra-violet emission of the sun with greater care than has hitherto been done. From arguments which are given elsewhere, it appears probable that if we could observe the solar spectrum outside the atmosphere of the earth, it would appear very much like those of planetary nebulae, i.e. composed of a faint continuous background superimposed with bright emission lines of H, He and He^+, Fe^+, Fe^{++}, and other elements which are abundant in the atmosphere of the sun, and which have their resonance lines in this part of the spectrum.

Bearing these points in mind, we now turn to a critical examination of the results on the night-sky spectrum and on the ionosphere.

5—Distribution of Elements in the Upper Atmosphere

A rigorous theoretical treatment of all the upper air phenomena requires a knowledge of the distribution of elements at different heights of the atmosphere, and its variation by night and day. We shall illustrate the point by an example.

In the foregoing paragraphs, we discussed in detail the the appearance of N_2^+ bands as a flash in the upper atmosphere produced by the disappearing light of the evening sky, or by the dawning light of the morning sky. Rough estimates show that the phenomenon occurs at a height of 200 km. (see Dejardin 1936, p, 10). Why does not this flash extend below? The obvious answer is that at this height solar light of wave-length < λ660 is completely absorbed by the layer of gas traversed. We have next to link up this phenomenon with the laboratory experiments dealing with the intensity of absorption of N_2 gas at wave-lengths below λ660. Supposing we find, from accurate laboratory experiments, that 1/500 cm. of N_2 at N.T.P. reduces the intensity of λ660 to $1/e$th of its value, and suppose we assume that the action of light is inappreciable when the intensity falls to 10^{-3} of its primitive value. This can be achieved by $x\times1/500$ cm. of N_2 gas at N.T.P., where $e^x=10^3$ i.e. $x=7$, and the thickness of gas is 0·014 cm. at N.T.P., i.e. we conclude that the amount N_2 gas traversed by sunlight at nearly horizontal incidence at a height of 200 km. is 0·014 cm. of N_2 at N.T.P., and hence there will be no ionization below 200 km.

At the present time our knowledge of the absorption coefficient of every ray below λ3000 in O_2 and N_2 is in an extremely unsatisfactory state, but probably this will be available before long. Knowledge of this absorption coefficient will enable us to estimate quantitatively the photochemical reactions produced in the upper atmosphere, provided we have a knowledge of the distribution of the elements at different heights. We should therefore have ready for use a table which tells us of the quantity of gas of each kind (N_2 or O_2) which lies above a height z. It is usual to express this quantity in lengths, i.e. centimetres of the gas at N.T.P., 1 cm. being equal to 2.79×10^{19} mol. On the surface of the earth the quantity is given by H, the height of the homogeneous atmosphere. At any height z, let the corresponding quantity for a gas x be given by H_z^x. Then we have $H_z^x=P_z^x/\rho_0^x$, where P_z^x is the partial pressure of the gas x at height z, and ρ_0^x is the density of the gas at N.T.P. To calculate P_z^x we take the hydrodynamical equation

$$dp=-\rho g dz. \tag{2}$$

We have omitted z and x from p and ρ for the sake of elegance. Now we have

$$p=\frac{RT}{M}\rho,$$

where M=molecular weight, R=universal gas constant. Hence

$$\frac{dp}{p}=-\frac{Mgdz}{RT} \text{ or } \log_e\frac{P_z^x}{P_0^x}=-\frac{gM_x}{R}\int_0^z\frac{dz}{T}. \tag{3}$$

The integral $\int_0^z\frac{dz}{T}$ is common for all gases. Let it be denoted by β. Then we have

$$P_z^x=P_0^x\,e^{-\frac{gMx}{R}}\,\beta\,,\ \text{and}\ H_z^x=H_0^x\,e^{-\frac{gMx}{R}}\,\beta\,, \tag{4}$$

where $H_0^x=\frac{P_0^x}{\rho_0^x}$ denotes the quantity of gas at N.T.P. which is equivalent to the whole column in the atmosphere.

An approximate (not accurate, but sufficient for the height considered by us) value of the integral is obtained if we know the total pressure at z, for considering that the mixture does not change much, we have

$$\log_e\frac{P_z}{P_0}=-\frac{gM}{R}\int_0^z\frac{dz}{T}=-\frac{gM}{R}\beta \tag{5}$$

or

$$\beta=\frac{-R}{gM}\log_e\frac{P_z}{P_0},$$

where P_z, P_0 are total pressures, and M=mean molecular weight. We have

$$H_z^x=H_0^x\left(\frac{P_z}{P_0}\right)^{\frac{M_x}{M}}. \qquad (6)$$

The calculation of the integral $\int_0^z \frac{dz}{T}$ is one of the main problems in Meteorology, but as it cannot be obtained, we have taken empirical values of (P_z/P_0) as obtained directly or in the ionosphere by radio experiments, and tried to calculate H_z^x. The procedure cannot be far wrong.

TABLE 1

Height in km.	Pressure in mm. of Hg	Amount of gas in metres	
		N_2	O_2
0	760	6445	1508
10·5	215	1724	342
20	42	386	60
30	10	94·8	12
40	2	20	2
50	10^{-1}	110 cm.	$7\times10^{-2}=7$ cm.
60	10^{-2}	11 cm.	0·57 cm.
100 E	10^{-3}	—	0·044 cm.
140 E′	—	—	—
180 F_1	—	—	—
250 F_2	10^{-6}	14×10^{-3} cm.	—

6—A General Review of the Spectra of Nitrogen and Oxygen

Recent work on spectra of the night sky and sunlit aurora prove that even up to 200-300 km., where these phenomena appear, the atmosphere consists chiefly of O_2 and N_2. Helium and hydrogen, which have sometimes been postulated to exist still require confirmation. Hydrogen appears to be definitely absent. Paneth has recently devised methods for estimating quantitatively amounts of helium at different heights.

The recent state of our knowledge of the spectrum of N_2 and N has been very fully described in a report by L. S. Mathur and P. K. Sengupta (1936),[10] and as this knowledge is important for the discussion which follows, we give a brief account of the spectra of these elements with some necessary additions, chiefly on absorption. Further, the energy-level diagram, reproduced below, will make perusal of this subject somewhat easier.

The night-sky spectrum shows the following bands due to N_2 and N_2^+:

(i) Vegard-Kaplan intercombination bands.
(ii) The first positive bands.
(iii) The second positive bands.
(iv) The first negative bands due to N_2^+.

The origin of these bands is illustrated in the energy-level diagram, fig. 1.

The figures on the *y*-axis denote the excitation potential of the different levels in V. The symbols $^4S+^2D$, etc., on the sides of the *y*-axis show the state of the atoms composing the molecule which give rise to the particular level. Thus $(^2D+^2P)$ $C^3\Pi_u$ denote that the component N atoms of the molecule are in the ^2D and ^2P states, and they give rise to a $^3\Pi_u$ term, and the excitation voltage is 10.98 V. The level X′ is the fundamental level of N_2^+, its energy value is 15.55V. The diagram also illustrates how N_2 is ionized to N_2^+ photo-chemically as mentioned in § 3. The Hopfield absorption bands raise the normal $(^4S+^4S)$ $X'\Sigma_g$ level to $(^4S+n^4P)$ levels, $n=3, 4\ldots.$, by the excitation of the electron in one of the component atoms of N_2 to the n^1P state; and when $n=\infty$, we get ionization of N_2 to N_2^+ $(N\ ^4S+N^+\ ^3P)$ A′ state. This is the excited state of N_2^+, and this reverts to the N_2^+ $(^2D+^3P)$ state X′ by radiation of the negative bands, as described on p. 255.

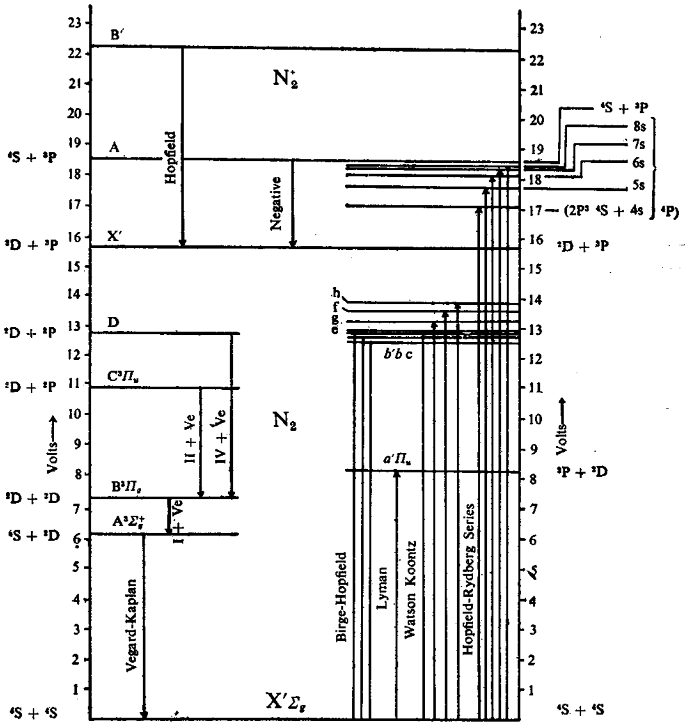

FIG. 1[11]

For further details, the original papers may be consulted.

We observe that absorption by the normal nitrogen molecule N_2 is confined to

(*a*) The Birge-Hopfield bands $N_2(^4S+^4S)$ $^1\Sigma\rightarrow N_2{}^1\Pi_u$ bands. The vibration formulae for these bands are given by

$$\nu=68962{\cdot}7+(1678{\cdot}96v'-13{\cdot}318v'^2-0{\cdot}0354v'^3)-(2345{\cdot}16v''-13{\cdot}93v''^2).$$

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[10] For a general report on the spectra of O_2 and N_2 see Sponer (1935).

[11] Reprinted from *Proc. Nat. Inst. Sci. Ind.*, **1,** 232, 1935.

These bands extend from $\lambda 1450$ to $\lambda 1226$, corresponding to $v''=0$. No quantitative estimate is available of the intensity of this absorption. It is stated by Lyman (1928) that 9 mm. of air at N.T.P. is sufficient to show this absorption. The bands were first obtained in absorption, and identified by Sponer.

The corresponding amount is attained at a height of about 60 km., but it is probably unnecessary to consider this absorption, as oxygen has far stronger absorption in this region. In fact, Ladenburg finds that 0·002 cm. of O_2 at N.T.P. reduces $\lambda 1450$ to one-half its strength, so it is clear that this radiation is almost completely absorbed above the E layer by oxygen molecules.

(*b*) The Vegard-Kaplan bands $(X'\Sigma_g \rightarrow A^3\Sigma_g^+)$. These bands are given by the formula

$$\nu = 49774{\cdot}4 + (1446{\cdot}46v' - 13{\cdot}93v'^2) - (2345{\cdot}46v'' - 14{\cdot}45v''^2),$$

and absorption by normal molecules should extend from $\lambda 2000$ towards the ultra-violet. But as the values of r for the normal and excited states are widely different ($r'=1{\cdot}29$ cm., $r''=1{\cdot}09$ cm.), transitions from $v''=0$ to some high value of v' will be more probable, according to the Franck-Condon Principle. Such bands will occur at about $\lambda 1700$.

Though no laboratory experiment has yet been done with the express intention of obtaining the absorption of Vegard-Kaplan bands, it appears that they were recorded by Hopfield (1928) some years ago. He found that with 0·06 to 19 m. of N_2 column at N.T.P., the following bands were obtained: $\lambda\lambda 1742{\cdot}4$, 1728·4, 1701·4, 1688·3, 1666·3, 1650·2. These are possibly Vegard-Kaplan absorption bands.

These wave-lengths are also strongly absorbed by O_2, but not so strongly as $\lambda 1460$. Hence it is quite plausible that by means of this absorption, a large proportion of N_2 molecules is excited to the N_2 $(N^4S+N^2D)A^3\Sigma_u^+$ stage, which is the final level of the first positive bands of N_2. It therefore appears plausible that, during daytime, a large proportion of N_2 molecules will be found in the excited state of N_2 $A^3\Sigma_u^+$, and molecules in such excited states will give rise to absorption of the first positive bands. But it is not possible to make any calculation of the proportion of such excited molecules, as all the data required for the purpose are lacking. These are (1) the intensity of solar light in the region $\lambda\lambda 2000$–1700; (2) the intensity of absorption of these bands in nitrogen gas. But the process is probably confined to over 30 km., as at this height the amount of N_2 gas is about 100 m. at N.T.P., which is the amount required for complete absorption of these bands.

As purely a tentative measure, an attempt has been made to find out whether any of the well-known N_2 band lines belonging to the first or the second positive bands, or due to N_2^+, occur amongst the unidentified lines of the telluric part of the Fraunhofer spectrum. The results, which are not very conclusive, will be communicated in a later paper.

THE NEGATIVE BANDS OF NITROGEN

No estimate is yet available of the intensity of continuous absorption of N_2 at $\lambda 661$ which is responsible for ionizing N_2 to the N_2^+ A′ state and thus giving rise to the negative bands of N_2^+ observed in the first sunlight flash of morning or evening hours. But it appears that the N_2^+ ion is a normal constituent of the upper atmosphere during daytime, and if there be a sufficient number of them, we may obtain the strongest N_2^+ bands in the Fraunhofer spectrum as telluric lines. The relevant data will be discussed elsewhere. They are also not very conclusive.

Can nitrogen be photochemically decomposed into atoms by sunlight ?

It is well known that in the case of most diatomic molecules, and particularly in the case of O_2, a continuous absorption process is known which decomposes the molecule into a normal and an excited atom. Usually no continuous absorption is known which corresponds to the dissociation of the molecule into normal atoms. For nitrogen we can expect the following process:

$$N_2(^1\Sigma_g) + h\nu = N\,^4S + N\,^2D - E_1,$$

$$N_2(^1\Sigma_g) + h\nu = N\,^4S + N\,^2P - E_2,$$

$$E_1 = D + N\,^2D - N\,^4S = 7{\cdot}32 + 2{\cdot}37 \text{ V} = 9{\cdot}69 \text{ e-volts} = 1273\text{A},$$

$$E_2 = D + N\,^2P - N\,^4S = 7{\cdot}32 + 3{\cdot}66 \text{ V} = 10{\cdot}98 \text{ e-volts} = 1124\text{A}.$$

No such continuous absorption corresponding to these processes has yet been discovered for N_2. Hopfield noted two isolated absorptions at $\lambda 1518{\cdot}02$ and $\lambda 1437{\cdot}2$. The forbidden lines of nitrogen are

$$\begin{array}{lll} ^4S\text{–}^2D = \nu & \left.\begin{array}{l} 19223 \\ 19231 \end{array}\right\} & \lambda \begin{array}{l} 5202{\cdot}1, \\ 5199{\cdot}9, \end{array} \\ ^4S\text{–}^2P = \nu & 28840 & \lambda\ 3467{\cdot}4, \\ ^2D\text{–}^2P = \nu & \left.\begin{array}{l} 9617 \\ 9606 \end{array}\right\} & \begin{array}{r} 10398{\cdot}3, \\ \lambda\ 10410{\cdot}2. \end{array} \end{array}$$

The last is in the infra-red and has not yet been observed either in the morning or the evening flash. ^4S—^2P, $\lambda 3467{\cdot}4$, is too far in the ultra-violet and has not yet been found. ^4S–^2D, $\lambda 5202$, is promising, but it is unfortunately mixed up with the (0, 2) bands of N_2^+. Sommer (Slipher and Sommer 1929) at one time identified the line observed near $\lambda 5206$ as being the ^4S–^2D line of N, but the matter needs careful reinvestigation. The discussion shows that as yet there is no definite evidence for the presence of forbidden lines of N in the night-sky spectrum, but this does not absolutely exclude the possibility of their occurrence. [Slipher (1933) has given some very strong red and infra-red bands, without indicating their origin].

OXYGEN

Oxygen is very interesting, as so far no band lines due to O_2 or O_2^+ have been traced in the spectrum of the night sky or the polar aurora. The Fraunhofer spectrum of the sun shows only the A, B...bands of oxygen, and the night-sky spectrum shows only the green line ($^1D_2$–$^1S_0$), and the red lines due to the forbidden transition $^3P_{1,2}$–$^1D_2$. From these findings the conclusion has sometimes been drawn that oxygen exists in the upper atmosphere completely in the atomic state, i.e. is dissociated completely by sunlight above a certain height into atomic oxygen.

We get to a better understanding of these facts when we first critically consider the spectra of O_2 and O_2^+, so far as they are known at the present time. Unfortunately, the knowledge, particularly beyond 1000A, is not as complete as can be desired. Whatever is known is presented in the energy-level diagram, fig. 2, and tables.

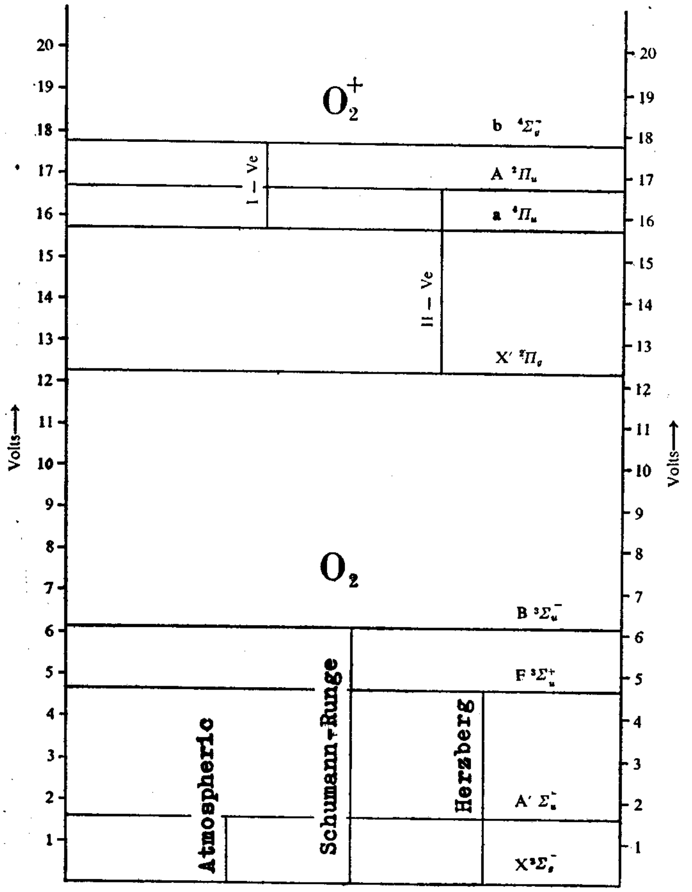

FIG. 2[12]

We observe that absorption by normal oxygen is confined to

(1) The atmospheric bands corresponding to the transition

$$X^3\Sigma_g^- \leftarrow A\Sigma_u^-.$$

These bands occur very prominently in the Fraunhofer spectrum and constitute the A, B and α bands of Fraunhofer.

(2) The Schumann-Runge bands and the continuum beyond it. Of all the absorption bands of O_2, these are the best studied. They correspond, according to Mulliken, to the transition

$$O(^3P+{}^3P)X\ {}^3\Sigma_g^- \leftarrow O(^3P+{}^1D_2)B\ {}^3\Sigma_u^-.$$

Beyond λ1750, these bands pass into continuous absorption, corresponding, as Herzberg has shown, to the photochemical decomposition of O_2 into atoms as follows:

$$O_2+h\nu=O\,^3P+O\,^1D_2.$$

This absorption extends up to λ1250A. The beginning at λ1750 corresponds to $7{\cdot}05V=D+E$, where D is the heat of dissociation of O_2 into two normal O ^3P atoms, $=5{\cdot}09V$, and E is the heat of excitation of O ^3P atom to the O $^1D_2$ state, viz. 1·96V. For the lower wave-lengths in the continuum, absorption denotes that the products of decomposition separate with some kinetic energy.

(3) A very feeble set of absorption bands, which appear to pass into a feeble continuum, has been reported by Herzberg at $\lambda\lambda$2595–2429. The continuum at λ2429 has been interpreted as giving rise to decomposition of O_2 into two normal O ^3P atoms, for λ2429 corresponds exactly to the dissociation potential of O_2, viz. 5·09V. But the intensity of this absorption is about 10^{-7} times less than that of the continuum beyond λ1750, for a column of 0·002 cm. of O_2 at N.T.P. reduces λ1460 to one-half, while 25 m. of O_2 at N.T.P. scarcely suffice to bring out the absorption of the bands at $\lambda\lambda$2595–2429. According to Table I, this absorption may occur at about 20–40 km., but as this is the ozone region which cuts off all light between $\lambda\lambda$2900–2300, we need not consider it.

The three types of absorption described above give rise to three well-known processes:

(*a*) The Schumann-Runge absorption ($X^3\Sigma_g^- \leftarrow B^3\Sigma_u^-$). This produces ozone as follows:

$$O_2+h\nu=O_2^*(O_2\ {}^3P\ O\ {}^1D_2B^3\Sigma_u^-), \tag{A}$$

where O_2^* denotes the excited state of O_2, viz. $B^3\Sigma_u^-$. The O_2^* molecule collides with a normal O_2 molecule (collision of the second kind) and dissociates it into two atoms as follows:

$$\begin{aligned} O_2+O_2^* &= O_2+O+O+(h\nu-Q) \\ &= O_3+O+(h\nu+24\text{ kcal.}-Q). \end{aligned} \tag{B}$$

(*b*) The second process indicates that one of the atoms combines with O_2 to form an O_3 molecule. This process is highly probable, as the reaction is exothermic. We have, according to careful calorimetric investigations,

$$O_2+O=O_3+24\text{ kcal.} \tag{C}$$

The energy set free is $h\nu+24-Q$, and if the wave-length used be λ2040, $h\nu=141$ kcal. Hence the energy set free is

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[12] Reprinted from *Proc. Nat. Inst. Sci. Ind.* **1,** 230, 1935.

$141+24-117=48$ kcal., and this may raise the remaining O atom to the O $^1D_2$ state, as shown below:

$$\mathrm{O}\ ^1D_2=\mathrm{O}\ ^3P+1{\cdot}96\ \mathrm{V}=\mathrm{O}\ ^3P+45\ \mathrm{kcal.} \qquad \text{(D)}$$

This O $^1D_2$ atom reacts more readily with another O_2 atom and forms a second O_3 molecule and 72 kcal. of heat is produced. Thus, as Warburg experimentally established long ago, one quantum of light $< \lambda 2040$ produces two molecules of O_3.

(*c*) Light of wave-length $> \lambda 2040$ can also convert O_2 into O_3, but as has been shown experimentally, this is a high-pressure phenomenon. It corresponds to the Herzberg absorption at $\lambda 2425$. This probably plays no part in the formation of ozone in the upper atmosphere, and in the lower atmosphere it is ineffective owing to the fact that $\lambda\lambda 3000$–2300 is cut off by ozone.

Let us now form a rough idea of the heights at which these processes take place in the upper atmosphere. *It is easy to show that the* O_3 *formation and the dissociation of* O_2 *into atoms* take place at quite different heights, and the two phenomena have no connexion with each other. According to Kreussler (see Lyman, 1928), a length of 20 cm. of O_2 reduces $\lambda 1860$ (Schumann-Runge band) to two-thirds of its intensity. So according to Table I, $\lambda 1860$ is reduced to one-fourth of its intensity at a height of 45 km. But the other wave-lengths can be completely absorbed only at lower heights. $\lambda 1930$ loses 6·2% of its intensity by the same column, so to reduce it to one-tenth its intensity, we require a column of oxygen 840 cm. in length, and this is reached at a height of about 35 km. These calculations are rather rough, but they suffice to show that the discovery of Götz, Meetham and Dobson (1934) that the O_3 layer exists at a height of 20-50 km. is in substantial agreement with the absorption data on Schumann-Runge bands. The decomposition of O_2 into O ^3P and O $^1D_2$ takes place at quite different heights, for as mentioned before, $\lambda 1460$ is reduced to half its strength by 0·002 cm. of O_2 at N.T.P. So this ray is reduced to 10^{-3} times its strength when the equivalent column is 0·014 cm., and Table I shows that this is accomplished at about 180 km., i.e., above the E region of the ionosphere. The Herzberg absorption at $\lambda 2429$ appears to be ineffective in producing any substantial dissociation of O_2 into atoms, as this wave-length is absorbed by the ozone layer above a height of 30 km., above which there is not sufficient oxygen which can be appreciably dissociated in this fashion.

IONIZATION OF O_2 TO O_2^+

Let us now examine how O_2 is photo-ionized to O_2^+. Tate and Smith (1932) have measured two ionization potentials of O_2, viz. at 12·5 and 16·1 V. Mulliken and Stevens (1933) have shown how these measurements can be reconciled with the known spectroscopic levels of O_2^+.

The known levels of O_2 are:

(1) The first negative band between $\lambda\lambda 5300$-7900 consisting of single headed bands shaded towards the red.

According to Mecke (1927) the band heads are given by

$$\nu=16592{\cdot}2+(1180{\cdot}3v'-17{\cdot}8v'^2)-(1026{\cdot}1v''-11{\cdot}1v''^2).$$

According to Mulliken and Stevens (1933) the electronic transition is

$$(\mathrm{O}^+\ ^4S.\mathrm{O}\ ^1D_2)b^4\Sigma_g^- \leftarrow (\mathrm{O}^+\ ^4S.\mathrm{O}\ ^3P)\mathrm{a}^4\Pi_u.$$

(2) The second negative bands between $\lambda\lambda 2200$-4400 consist of double bands shaded towards the red. The band heads are given by

$$\nu=38308+(887v'-13{\cdot}4v'^2)-(1859{\cdot}9v''-16{\cdot}53v''^2).$$

The electronic transition, according to Mulliken and Stevens, is

$$(\mathrm{O}^+\ ^4S.\mathrm{O}\ ^1D_2)\mathrm{A}^2\Pi_u \leftarrow (\mathrm{O}^+\ ^4S.\ \mathrm{O}\ ^1D_2)^2\Pi_g,$$

$r''=1{\cdot}14$, $r'=1{\cdot}41$, hence bands like (11, 0, 12, 0) lying between $\lambda\lambda 2100$-1975 are strong.

No intercombination between the two systems of bands is known.

The energy values of the levels are given by

Band	Ionization potential (experimental)	Spectroscopic
X $^2\Pi_g$	12·5	12·2
a $^4\Pi_u$	16·1	16·1
A $^2\Pi_u$	—	16·7
b $^4\Pi_g$	—	18·2

Recently a set of absorption experiments has been carried out by Price and Collins (1935) which show that the photoelectric ionization of O_2 to O_2^+ is effected in the same way as for N_2, i.e. there is no ionization by light of wave-length corresponding to the lowest ionization potential of 12·5 V which can ionize O_2 to the lowest state of $O_2\ ^2\Pi_g$, but they obtain a set of absorption bands (H, I, . . .) which can be formed into a Rydberg sequence coming to a limit at 130,800 cm.$^{-1}$, i.e. 16·14 V. This is identified with the a $^4\Pi_u$ state. Another set of bands passes to a continuum at 18·2 V. This is identified with $^4\Sigma_g$. A third strong ionization continuum is found at 16·7 V round about $\lambda 740$, which is provisionally identified with the production of the state A $^2\Pi_u$. There appears to be no absorption corresponding to the first observed ionization potential, viz. 12·5 e-volts. Thus it appears that the photochemically active light which can ionize O_2 to O_2^+ must have the energy equivalent to 16·20 e-volts at least, though the first ionization potential is 12·15 e-volts.

No negative bands of O_2^+ have yet been detected in the spectrum of the night sky or the aurora. Also, no photochemical process has so far been found which can be interpreted as decomposing the oxygen molecule into atoms, one of which is in the O $^1S_0$ state. In fact, our knowledge of the spectroscopy of O_2 and O_2^+ is meagre.

The value of the absorption coefficient at none of the supposed ionization continua has yet been obtained. It is stated by Price and Collins (1935) that a partial pressure of 0·01 mm. and a path of 1·5 m. (i.e. a path of 1·5 to 0·15 cm.) brings out the absorption quite clearly. According to Table I, we have this mass of oxygen at a height of about 100 km. It is therefore quite possible that the E layer ionization is produced by the ionization of O_2 to O_2^+ in the way supposed here.

The above summary of our knowledge of the spectra of O_2 and N_2 probably brings out clearly the necessity of undertaking a well-planned set of experiments on the spectroscopy of oxygen and nitrogen, particularly in the far ultra-violet, without which a satisfactory theory of the phenomena in the ionosphere, and of the luminous night-sky spectrum, is not possible.

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SUMMARY

In this paper it is shown that a satisfactory theory of Upper Air Phenomena, such as the luminous night sky, the ionization in the different layers (E, F,...), etc., must be based on a precise knowledge of the action of ultra-violet sunlight (below λ3000) on molecular oxygen and nitrogen. The knowledge which we possess at present is summarized in the present paper; and the nature of molecular ionization and excitation, and the heights at which they occur, are discussed in detail. It is shown that according to laboratory evidence available at present molecular ionization of O_2 and N_2 by photochemical action does not take place at the lowest ionization potential, but at the second ionization potential, i.e. the photon which causes ionization of O_2 and N_2 leaves the molecular ion excited. It is concluded that the knowledge we possess is rather scanty and does not enable us to start any adequate physical theory, beyond indicating barely the physical processes which cause such phenomena. But the discussion brings out the necessity of carrying out well-planned laboratory experiments on the absorption spectra of O_2 and N_2, without which it will not be possible to furnish an adequate explanation of upper air phenomena. The discussion also shows that the ultra-violet radiation from the sun differs widely from that of a black body, and in selected wave-lengths the sun must be emitting nearly a million times more photons than is given by a black body at 6500°K. This may possibly be due to the fact that the ultra-violet spectrum of the sun may consist of a continuous background of faint light on which are superposed emission lines of H, He, He^+, Fe^+, and other elements which are represented in the visible range by lines of subordinate series, or by patches of ultra-violet continuous light (near about λ500) leaking through the solar atmosphere from a much hotter region inside the photosphere, as suggested by Professor H. N. Russell.

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