6. CONCLUSION

From the above discussion and from the close agreement between the calculated percent reduction of the magnetic field and the experimental values shown in Figs. 6 and 7, it may be concluded that the reduction of the magnetic field inside and outside the tube is due to the demagnetizing effect of the free poles distributed along the whole length of the tube, or in other words, the reduction of the magnetic field in the neighborhood of the tube can be accounted for by the theory of demagnetization without introducing any other hypothesis.

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On the Existence of Atomic Nitrogen in the Upper Atmosphere of the Earth

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Evidence for the existence of atomic nitrogen in the upper atmosphere is presented. It is shown that the absence of certain lines of NI and the absence of continuous absorption which leads to the dissociation of N_2 cannot be considered conclusive evidence against the existence of atomic nitrogen. Relative densities of the E and F layers are discussed, and it is shown that observations of high density in the F layer may be compatible with the existence of atomic nitrogen. Possible transitions which produce the night sky spectrum are discussed.

PARTLY on the basis of the observed spectra of the night sky and of the aurora and partly on the basis of the absence in the laboratory of continuous absorption by the nitrogen molecule leading to dissociation $N_2+h\nu\rightarrow N+N$, the view is held by many investigators that in the upper atmosphere oxygen exists in the atomic and nitrogen in the molecular state. On this view many attempts have been made by various investigators to deal with such problems as the existence of various ionized layers, the density at different heights in the atmosphere, the excitation mechanism of the radiations of the aurora and the night sky, etc. The purpose of the present note is to present some arguments for the view that there may exist atomic nitrogen in the upper atmosphere, and to indicate the changes that this picture entails in our present view of the above-mentioned problems.

I

One of the reasons for supposing nitrogen to exist in the molecular state in the atmosphere is that while the forbidden lines $^1D-^1S$, $^3P-^1D$ of oxygen OI are the most prominent radiations in night sky and the aurora, the forbidden lines $^4S-^2P$, $^4S-^2D$ of NI are absent in these spectra. Kaplan has pointed out the possible presence of the $^4S-^2P$ line in the spectrum of the night sky.[1] While this identification, if confirmed by more observational data, would establish the existence of atomic nitrogen, it must be emphasized that the absence of this and the $^4S-^2D$ line constitutes no proof against the presence of atomic nitrogen. The transition probability of $^4S-^2P$ is of the order of 1 per second and the lifetime of the ^2P state is thus comparatively short. Any $N(^2P)$ atoms produced by dissociation by solar radiation (see Section II below) will rapidly settle down into the states ^2D and ^4S on the emission of the lines $^2D-^2P$ and $^4S-^2P$. The lifetime of the ^2D state is of the order 10^5 seconds so that the failure to observe the line $^4S-^2D$ may only mean an insufficiently large number of $N(^2D)$ atoms. Unless $N(^2P)$ are excited by proper and

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[1] J. Kaplan, Phys. Rev. **56**, 858 (1939); **57**, 249 (1940).

frequent processes in the night sky and in the aurora, there may be considerable N(^4S) and N(^2D) atoms without revealing themselves in the spectrum.

II

Perhaps the main reason for believing in the absence of atomic nitrogen in the upper atmosphere is the absence of continuous absorption by N_2 down to 600A in the ultraviolet that leads to the dissociation of the molecule. Now, according to the configuration theory, of the many theoretically possible molecular states resulting from two N atoms, the following can combine by dipole transitions with the normal state $X\,^1\Sigma_g^+$ of N_2: two $^1\Pi_u$ states from N(^2D)+N(^2D); one $^1\Sigma_u^+$ and three $^1\Pi_u$ states from N(^2D)+N(^2P); and two $^1\Sigma_u^+$ and three $^1\Pi_u$ states from N(^2P)+N(^2P). Some, if not all, of these are repulsive states so that continuous absorption by N_2 in the normal state $X\,^1\Sigma_g^+$ will lead to dissociation. Thus

$$N_2(X\,^1\Sigma_g^+)+h\nu\rightarrow N(^2P)+N(^2P)(^1\Sigma_u^+;\,^1\Pi_u), \quad (1)$$

$$N_2(X\,^1\Sigma_g^+)+h\nu\rightarrow N(^2P)+N(^2D)(^1\Sigma_u^+;\,^1\Pi_u), \quad (2)$$

$$N_2(X\,^1\Sigma_g^+)+h\nu\rightarrow N(^2D)+N(^2D)(^1\Pi_u). \quad (3)$$

That such continuous absorptions have not been observed in the laboratory may be due to the circumstance that the potential energy curves of these repulsive states rise very steeply with the decrease in internuclear distance so that, by the Franck-Condon principle, absorption will not be appreciable until the radiation frequency is very much greater than ν_0 given by $h\nu_0=D+E$, where D is the dissociation energy of the normal state $X\,^1\Sigma_g^+$ and is 7.35 volts, and E is the sum of the excitation energies of the two resulting N atoms from the ^4S state. Thus appreciable absorptions by the processes (1), (2), (3) may lie in the region beyond 500A not yet explored in the laboratory, and in the region $\lambda>600$A the absorption may be so weak that they are masked by the very strong absorptions of the Hopfield and the Worley-Jenkins bands that lead to the ionization of N_2.

Despite the situation that dissociative absorption will take place only for radiations of very short wave-length, an appreciable number of N_2 may still be dissociated since there is now strong evidence that there is a great abundance of high frequency radiations emitted by the sun.[2] They are probably due to the radiative recombinations of electrons and ionized atoms carried through the photosphere by convective transfer, and their energy density may be very much greater than that of a blackbody at ~6000°K, possibly by some high powers of 10. As shown later, a calculation of the degree of dissociation of N_2 is yet not possible on account of the lack of pertinent informations. The point, however, is that the processes (1), (2), (3) are theoretically possible provided there are radiations of sufficiently high frequency, for the existence of which there seems now to be strong astrophysical evidence.

III

Consider now briefly some of the consequences of the existence of atomic nitrogen in the upper atmosphere. On account of the smaller mass of the N atom, the dissociation of N_2 will lead to a greater density, at a given height, than that obtained on the assumption of a N_2 and O mixture. Thus estimates based on the assumption that N_2 and O are in diffusive equilibrium above ~150 km show that the air density in the F layer (~250 km) is about 1/5000 of that in the E layer.[3] However, from the observed collision frequencies by radio wave experiments, it is known that the air density in the F layer is about 1/30 of that in the E layer. This abnormally high density in the F layer may be partly due to the dissociation of N_2 into N atoms.

The dissociation of N_2 will also give rise to an ionized layer due to the ionization of the N atoms. When the variation of the degree of dissociation with height is known, it will be possible to calculate the height of this ionized layer.[4] This may contribute to a better understanding of the nature of the various ionized layers now known. Unfortunately a calculation of the variation of the degree of dissociation with height is not yet possible for reasons given later.

IV

Another observed fact connected with the problem of the ionized layers may perhaps be

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[2] Cf. A. Eddington, M. N. R. A. S. **101**, 177 (1941); **102**, 154 (1942).

[3] S. K. Mitra and H. Rakshit, Ind. J. Phys. **12**, 47 (1938); S. K. Mitra and A. K. Banerjee, *ibid.* **13**, 117 (1939).

[4] Bates, Buckingham, Massey, and Unwin, Proc. Roy. Soc. **A170**, 322 (1938).

understood on the introduction of atomic nitrogen in the upper atmosphere. The effective recombination coefficients of electrons are observed to be $\simeq 1.2\times 10^{-8}$ and 0.8×10^{-10} cm^3/sec. in the E and F layers, respectively. In the prevalent theory,[5] the electrons are removed by direct radiative recombinations with positive ions

$$n^+ + e \rightarrow n + h\nu, \quad \text{recombination coeff.} = \alpha_e,$$

and through attachment by a neutral particle forming a negative ion, and subsequent non-radiative recombinations between the positive and the negative ions, yielding two excited atoms

$$n + e \rightarrow n^- + h\nu, \quad \text{attachment coeff.} = a,$$
$$n^- + n^+ \rightarrow n' + n'', \quad \text{transfer coeff.} = \alpha_i.$$

On denoting the concentrations by simply e, n^-, n^+, and letting

$$\lambda = n^-/e,$$

then, since $e + n^- = n^+$, one has

$$(1+\lambda)(de/dt) = dn^+/dt,$$

and

$$dn^+/dt = -\alpha_e e n^+ - \alpha_i n^- n^+,$$
$$de/dt = -(\alpha_e + \lambda\alpha_i)e^2.$$

Theoretical calculations of Bates *et al.* show that for oxygen, $\alpha_e \simeq 10^{-12}$ cm^3/sec. and $\alpha_i \simeq 10^{-11}$ cm^3/sec.[5] Thus to obtain an effective recombination coefficient in agreement with the observed values above, the ratio λ must be of the order 100–1000 in the E layer and 10 in the F layer. The high concentration of negative ions in the E layer is supported by the observed variations of terrestrial magnetism and is understandable if one assumes that there oxygen atoms are abundant and, having an electron affinity of 2.2 volts, readily form O^- ions. The equilibrium ratio λ of negative ion – electron is determined by the rates of attachment above and of detachment

$$O^- + X \rightarrow OX + e, \quad \text{detachment coeff.} = d,$$

where X is a neutral particle, namely,

$$\lambda = \frac{O^-}{e} = \frac{aO}{\Sigma d_i X_i}.$$

The summation is taken over all the probable detachment processes, for example, $X = O, O_2, N_2$, etc. Now on the prevalent view of a N_2, O atmosphere, the concentration of O would increase relative to that of N_2 in passing from the E to the F layer so that a decrease of λ in passing from the E to the F layer is difficult to understand. On the other hand, on assuming N_2 to be dissociated, the ratio O/N of the concentrations of oxygen and nitrogen atoms will decrease with height. Since the N atoms are probably just as active in the detachment process but form no negative ions on account of their very small electron affinity, the value λ will accordingly decrease in passing from the E to the F layer.

Bates *et al.* have pointed out the possibility of thermal detachment in the F layer as a cause of the comparatively low concentration of negative ions. As the electron affinity of O atom is 2.2 volts, the temperature must be quite high for thermal detachment to be important. As the N_2 are mostly dissociated by radiations of frequency very much greater than ν_0 given by $h\nu_0 = D + E$ (see Section II above), the resulting atoms will possess high kinetic energies. This would result in a high temperature in the upper atmosphere, on which there seems to be general agreement among different authors but which has been ascribed to the energy of electrons in the ionization of the atoms rather than of the atoms in the dissociation of the molecules.

V

A difficulty of the prevalent view that nitrogen exists as N_2 and is hence confined to the lower strata (below ~250 km) of the atmosphere is that, according to it, the observed nitrogen bands from high aurora become difficult to understand. There does not seem to be a plausible theory that can account for the excitation of the various radiations of nitrogen, especially for the sunlit aurora that have been observed at heights as great as ~800 km and of which the negative bands of N_2^+ are particularly enhanced. The theory of Maris and Hulburt attempts to ascribe the aurora to particles sent up with great velocities to very great heights on collisions of the second kind with excited atoms or molecules in the uppermost region of the atmosphere, ionized by solar radiations, and spiraling down along the earth's magnetic lines of force toward the polar regions. It has been shown, however,

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[5] Bates, M. N. R. A. S. **100**, 25 (1939), has calculated the theoretical absorption coefficient of N atom.

recently by the writer that the mechanism suggested by these authors is entirely inadequate for explaining the aurora.[6] On our present view here, the extension of atomic nitrogen to great heights may at least provide for the presence of nitrogen molecules in the upper atmosphere by such recombination processes as

$$\mathrm{N}+\mathrm{N}\rightarrow \mathrm{N}_2+h\nu$$

(Vegard-Kaplan and other bands of N_2),

$$\mathrm{N}+\mathrm{N}^+\rightarrow \mathrm{N}_2{}^+ + h\nu$$

(first negative bands of $N_2{}^+$).

VI

Finally, on the assumption that there exist in the upper atmosphere atomic oxygen and nitrogen produced by the processes (1), (2), (3) and

$$\mathrm{O}_2(X\,{}^3\Sigma_g{}^-)+h\nu\rightarrow \mathrm{O}({}^3P)+\mathrm{O}({}^1D), \qquad (4)$$

the writer has recently proposed a theory of the excitation mechanism of the night sky spectrum.[7] The key processes are the radiative recombinations between the atoms, forming metastable molecules of N_2 and O_2:

$$\mathrm{N}({}^4S)+\mathrm{N}({}^2D)({}^3\Sigma_g{}^+;\,{}^3\Pi_g)\rightarrow \mathrm{N}_2(A\,{}^3\Sigma_u{}^+)+h\nu, \qquad (5)$$

$$\mathrm{N}({}^2D)+\mathrm{N}({}^2D)({}^3\Pi_g)\rightarrow \mathrm{N}(A\,{}^3\Sigma_u{}^+)+h\nu, \qquad (6)$$

$$\mathrm{O}({}^3P)+\mathrm{O}({}^3P)({}^3\Pi_g)\rightarrow \mathrm{O}(C\,{}^3\Sigma_u{}^+)+h\nu. \qquad (7)$$

The strong Vegard-Kaplan bands are excited by (5) and (6). Collisions among the various metastable atoms and molecules provide for the excitation of the various radiations. For example, the green and red lines of OI are excited by the processes

$$2\mathrm{O}_2(C\,{}^3\Sigma)\rightarrow \mathrm{O}_2(X\,{}^3\Sigma)+\mathrm{O}({}^3P) +\mathrm{O}({}^1S)+0.12\text{ volt}, \qquad (8)$$

$$\mathrm{O}({}^3P)+\mathrm{N}({}^2D)\rightarrow \mathrm{O}({}^1D)+\mathrm{N}({}^4S)+0.47\text{ volt}. \qquad (9)$$

A high metastability of $O_2(C\,{}^3\Sigma)$ will enable its concentration to build up and the process (8) will explain the small rise in intensity of the green line ${}^1D-{}^1S$ in the first part of the night. On the other hand, with an initially large number of $O({}^3P)$ and $N({}^2D)$ atoms produced by (1), (2), (3), (4), and their gradual depletion by recombination and other processes, the process (9) may explain the decrease of intensity of the red line ${}^3P-{}^1D$ immediately after sunset. Without assuming the presence of N atoms, the excitation of the Vegard-Kaplan bands and the other bands of N_2 seem very difficult to explain.[7]

VII

From the foregoing discussions, it seems very desirable to settle the question whether N_2 is dissociated in the upper atmosphere by calculating theoretically the degree of dissociation as a function of the pressure in the atmosphere. This would necessitate a knowledge of the radiation energy density ρ_ν of the proper wavelength, the absorption coefficient τ_ν as a function of frequency, the temperature T of the atmosphere where dissociation is being calculated, and the effect of "cycles" of such processes for the formation of the normal $N_2(X\,{}^1\Sigma_g{}^+)$ and the removal of $N({}^4S)$ as

$$\mathrm{N}({}^4S)+\mathrm{N}({}^2D)\rightarrow \mathrm{N}_2(A\,{}^3\Sigma_u{}^+)+h\nu,$$

$$\mathrm{N}_2(A\,{}^3\Sigma_u{}^+)\rightarrow \mathrm{N}_2(X\,{}^1\Sigma_g{}^+) + \text{Vegard-Kaplan bands}.$$

On ignoring the effect of such processes and considering the process (3) alone, one readily obtains the following dissociation formula

$$\frac{[\mathrm{N}]^2}{[\mathrm{N}_2]}=\frac{2g_{\mathrm{N}^2}^2}{g_{\mathrm{N}_2}hr_0{}^2}\left(\frac{MkT}{8\pi}\right)^{\frac{1}{2}}e^{-D/kT}(1-e^{-h\omega/kT})W\frac{c^3}{8\pi h}$$

$$\cdot\int_{\nu_0}^{\infty}\frac{1}{\nu}\tau_\nu\rho_\nu e^{-\tau_\nu p/2Mg}d\nu\Big/\int_{\nu_0}^{\infty}\tau_\nu e^{-h\nu/kT}\nu^2 d\nu,$$

where $[\mathrm{N}]$, $[\mathrm{N}_2]$, and the g's are the concentrations and the statistical weights of the atoms and the molecule; ω is the vibrational frequency, r_0 the nuclear separation, $2M$ the mass of the molecule $N_2(X\,{}^1\Sigma)$; W is the dilution factor and is $\sim 4\times 10^{-6}$; and p is the partial pressure of N_2 at the height where the degree of dissociation is being calculated. As $[\mathrm{N}]^2/[\mathrm{N}_2]$ is exceedingly sensitive to the values of ρ_ν, T, and τ_ν, and as these quantities are not known with any certainty, any estimate of the degree of dissociation with the use of questionable values for these quantities will be premature.

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[6] T. Y. Wu, Proc. Ind. Acad. Sci. **A18**, 345 (1943).

[7] T. Y. Wu, Proc. Ind. Acad. Sci. **A18**, 40 (1943).