EXCITATION PROCESSES IN THE NIGHT SKY
AND THE AURORA

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Introduction

Our knowledge concerning the conditions prevailing in the upper atmosphere of the earth comes mainly from the following two sources: (1) From the behaviour of the ionized layers towards radio waves and the magnetic variations, it is possible to make certain estimates of the concentrations of electrons, heavy ions and neutral particles in the different layers. In the present work, we shall not be concerned with the various aspects of these problems. Suffice it to summarize the main results as follows:

<table>
<thead>
<tr>
<th>Layer</th>
<th>Electron Density (Day)</th>
<th>Electron Density (Night)</th>
<th>Heavy Ion Density</th>
<th>Collision Frequency</th>
<th>Concentration of Neutral Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>F layer 200–300 km.</td>
<td>$3 \times 10^5$ /c.c.</td>
<td>$2 \times 10^5$ /c.c.</td>
<td>$10^5$–$10^6$ /c.c.</td>
<td>$6 \times 10^3$ /sec.</td>
<td>$10^{12}$ /c.c.</td>
</tr>
<tr>
<td>E layer 100 km.</td>
<td>$1.5 \times 10^5$ /c.c.</td>
<td>$8 \times 10^3$ /c.c.</td>
<td>$10^8$ /c.c.</td>
<td>$2 \times 10^9$ /sec.</td>
<td>$3 \times 10^{13}$ /c.c.</td>
</tr>
</tbody>
</table>

The ionization and the dissociation of the atoms and molecules are due to the ultraviolet radiations from the sun. The rather slow falling off of the electron density after sunset and the much higher concentration of heavy ions than that of electrons, are due to the small probability of recombination between electrons and positive ions and the much more frequent occurrence of attachment process of electrons to neutral atoms and molecules, the former process taking place at the rate of about $10^{-5}$ per second and the latter about 1 per second at the pressure of the E layer.

(2) From the analysis of the spectra of the night sky and the aura, it is found that in both cases the radiations consist of the forbidden lines of

1 Cf. H. S. W. Massey, *Negative Ions*, 1938, Cambridge Univ. Press (1938), pp. 89–100. Later results are unfortunately not available to the writer, but they would not affect the discussions in the following.
Excitation Processes in the Night Sky and the Aurora

[OI], the various band systems of N\(_2\) and N\(_2^+\), some weak bands of O\(_2\) and H\(_2\)O and some lines or bands of uncertain origin. There is a great difference, however, between the spectrum of the night sky and that of the aurora borealis, namely, the negative bands of N\(_2^+\) are very strong in the latter but very weak in the former, while the Vegard-Kaplan bands of N\(_2\) are very strong in the former but rather weak in the latter. In each individual band system, certain bands in certain sequences are particularly enhanced. Evidently a clear understanding of the excitation mechanisms of these radiations will contribute greatly to our knowledge of the conditions in the upper atmosphere of the earth. For convenience of the discussion, we shall summarize the main features of the spectra of the night sky and the aurora as follows:

(a) The forbidden lines of [OI].—The green line at 5577 A is by far the most intense line in the spectrum of the night sky and is also very intense in the aurora. The red lines at 6300 and 6364 A are inferior in intensity in both cases, but are still fairly strong compared with the other bands in each spectrum. In the night sky, the green line increases very slowly in intensity and reaches a maximum towards midnight after which it decreases slowly again. The red lines on the other hand have the greatest intensity immediately after sunset and fall off gradually in the night. In the sunlit aurora, the red lines are found to be greatly enhanced relative to the green one.

(b) First negative bands of N\(_2^+\).—In the aurora spectrum, the following negative bands of N\(_2^+\) are very intense:

\[
\begin{align*}
4708 \text{ A } (v' = 0 \rightarrow v'' = 2), & \quad 4278 \text{ A } (v' = 0 \rightarrow v'' = 1), & \quad 3914 \text{ A } (v' = 0 \rightarrow v'' = 0), \\
4648 \quad (1 \rightarrow 3), & \quad 4236 \quad (1 \rightarrow 2), & \quad 4199 \quad (2 \rightarrow 3),
\end{align*}
\]

The 4708, 4278 and 3914 bands have comparable or even greater intensities than the green 5577 line in the ordinary aurora, and become very much more intense than the latter in sunlit aurora. In the night sky, perhaps only the 3914 band can be identified with certainty.

(c) Vegard-Kaplan bands of N\(_2\).—In the night sky spectrum, the radiations next in intensity to the forbidden lines of [OI] are the Vegard-Kaplan bands of N\(_2\).
bands of $N_2$. The bands observed by Sommer, Cabannes and Elvey, Swings and Linke are summarized in Table I.

**Table I**

*Vegard-Kaplan Bands in the Night Sky*

<table>
<thead>
<tr>
<th>$v'$</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3598</td>
<td>3889</td>
<td>4220</td>
<td>4603</td>
<td>5062</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3425</td>
<td>3707</td>
<td>3984</td>
<td>4316</td>
<td>4719</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3501</td>
<td>3787</td>
<td>4073</td>
<td>4420</td>
<td>4827</td>
<td>5324</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3582</td>
<td>3855</td>
<td>4174</td>
<td>4543</td>
<td>4962</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3664</td>
<td>3949</td>
<td>4270</td>
<td>4650</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3742</td>
<td>4048</td>
<td>4379</td>
<td>4768</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Of these, the 4073, 4171, 4270, 4420, 4543 and 4827 bands from the levels $v' = 2$, 3, 4 are the most intense. In the aurora spectrum, some 10 stronger ones of these bands have also been identified, although they are in general very weak.

*(d) First positive bands of $N_2$.*—In the aurora spectrum, the bands observed by Vegard at 6323 and 7880 Å have been identified with the $v' = 10 \rightarrow v'' = 7$ and $v' = 7 \rightarrow v'' = 6$ transitions respectively. In the spectrum of the night sky, a number of first positive bands has been found, the more intense ones being those from the vibrational levels $v' = 7$ and 15 according to Cabannes. More recently, Elvey, Swings and Linke have identified from their own and Babcock's observations the following bands: $(4, 1), (7, 4), (8, 5), (9, 6), (10, 4), (10, 5), (11, 5), (11, 8), (12, 7), (12, 8), (13, 8), (13, 9), (14, 9), (15, 11), (16, 12)$. These are weak compared with the Vegard-Kaplan bands.

*(e) Second positive bands of $N_2$.*—In the aurora, the sequences $v'^{'} - v' = -1, 0, 1, 2, 3, 4$, with $v'$ from 0 to 5 and 6, are observed. They are weak compared with the negative bands of $N_2 +$. In the night sky, the bands of the second positive system are very weak. Cabannes found the bands 4574 Å ($v' = 1 \rightarrow v'' = 6$), 4059 Å ($v' = 0 \rightarrow v'' = 3$), 3998 Å ($v' = 1 \rightarrow v'' = 4$). On the other hand, these bands do not appear in Elvey, Swings and Linke's spectrograms. These authors found instead only the 3159 (1$\rightarrow$0) and the 3371 (0$\rightarrow$0) bands; even then the identifications are not certain since each

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of these bands can be equally well ascribed to other transitions in other band systems.

(f) Lyman-Birge-Hopfield bands of $N_2$.—The existence of bands of this system, especially those from $v' = 0$ to $v'' = 19 - 23$, has recently been made plausible by the observations and identifications of Elvey, Swings and Linke.\(^4\)

(g) Atmospheric bands of $O_2$.—The observations and analysis of Cabannes seem to suggest the existence of the A, B, a, a', a'', bands of $O_2$ at 0.76 $\mu$, 0.69 $\mu$, 0.63 $\mu$, 0.58 $\mu$, 0.54 $\mu$, corresponding to the transitions $0 \rightarrow 0$, 1$\rightarrow$0, 2$\rightarrow$0, 3$\rightarrow$0, 4$\rightarrow$0 respectively.\(^3\) On the other hand, from Babcock's and their own observations, Elvey et al. concluded that probably only the a' band is present in the spectrum of the night sky.\(^4\)

(h) Schumann-Runge bands of $O_2$.—Elvey, Swings and Linke showed from their own observations, and Kaplan from those of Gauzit, that the positions of certain ultraviolet bands in the night sky agree quite well with the transitions $v' = 0$, 1$\rightarrow$0$'' = 12 - 18$, in the Schumann-Runge system and suggested their probable presence.

(i) The yellow lines of Na.—The yellow lines of Na have been observed by Bernard, Cabannes and others at 5893 A in the spectrum of the night sky.\(^7\) They are not observed in the aurora.

(j) Water vapour bands.—The observations and analysis of Cabannes\(^3\) seem to suggest strongly the presence of the water vapour bands at 0.59 $\mu$, 0.65 $\mu$, 0.698 $\mu$, and 0.72 $\mu$. On the other hand, from their own and Babcock's observations, Elvey, Swing and Linke concluded that probably only the 0.65 $\mu$ band is present in the spectrum of the night sky and regarded the problem of water vapour bands in the night sky as unsettled.

In addition to these, there are some weaker lines or bands of uncertain origin in both the spectrum of the night sky and that of the aurora. But undoubtedly the above-mentioned radiations are the most important features in both cases.

To explain the cause of the auroae, their shapes and spectral characteristics, many theories have been proposed. A common feature of the more successful ones is that the emission of radiations of the aurora is excited by swift particles which may be directly ejected from the sun, or may be secondary particles resulting from these corpuscular rays or from ionization of the uppermost atmosphere by sudden outbursts of ultraviolet

radiations from the sun. These theories, while successful in furnishing a source of energy for excitation and explaining the forms of the aurorae, and their concentration near the poles, cannot account for the selective nature of the excitations of the various radiations, and in particular, for the enhancement of certain bands in a system. Corpuscular rays, whatever they may be, must be expected to have a certain spread in energy; and as the excitation functions of atomic and molecular transitions by electron impact do not possess sharp maxima in general, one would expect more or less non-descript rather than the highly selective excitations observed. Also the complete absence of radiations corresponding to the allowed transitions in the atoms of N, O, He and H would be difficult to understand, as the difference between the excitation potentials of these atoms and those of the observed lines and bands would be small compared with the energies available in the corpuscular rays. Hence it appears that while these theories may be correct in dealing with the large-scale features, the corpuscular rays cannot be solely responsible for the excitations of the radiations in the aurora and in the night sky.

Towards the understanding of the nature of the mechanism in the excitation processes in the upper atmosphere, considerable progress on the experimental side has been made by Kaplan by reproducing very closely the various spectral characteristics of the aurora and the night sky by running electrical discharges and afterglows under special conditions in the laboratory. Thus he found that it is possible to produce the green [OI] line, the Vegard-Kaplan bands and other bands of N₂ and N₂⁺ in various relative intensities by varying the conditions of the discharge. The production of the Vegard-Kaplan bands not only shows that the metastable N₂ (A³Σ⁺) molecules are present but suggests that they may play an important role in the excitation of the other bands. In fact it is possible to explain the enhancement of the bands from \( \nu' = 6, 7 \) and \( \nu' = 10, 11 \) in the first positive system of N₂ in an afterglow in active nitrogen as the result of collisions of the second kind \( Q_{10} \) and \( Q_9 \) in Table II. While these

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8 We believe that the absence of the He and H lines in the aurora and the night sky is no argument against the presence of He and H in the upper atmosphere, but means that the excitation condition there is not adequate for the production of the lines of He and H as well as those of N and O. In fact, there is some indication, although uncertain, for the presence of two NH bands 3371 Å (0→0) and 3360 Å (1→1) in the night sky, according to Kaplan, *Phys. Rev.*, 1939, 55, 593, and Elvey, Swings and Linke, *loc. cit.* If these identifications are correct, they would indicate the presence of atomic H in the upper atmosphere, which forms NH on combining with the N atoms.

9 Kaplan's experiments are reported in various issues of the *Physical Review* and the *Nature* from 1928 to the present day.
experiments are exceedingly valuable in throwing considerable light on the problem, one cannot immediately identify the conditions in the upper atmosphere with those in the discharge tubes. In the latter, excitations by electron impact play a rôle that cannot be ignored, while in the upper atmosphere excitations by electron impact become impotent on account of the low energies of the free electrons, unless one invokes high energy electrons in corpuscular rays, in which case one introduces the difficulty with the selective excitations discussed above. The considerable difference in pressure in the discharge tube and in the upper atmosphere is another factor that must be reckoned with, since the question whether a forbidden transition radiates or not depends on the frequency of quenching collisions, which is in turn determined by the concentration of the appropriate colliding particles. Even the walls of the discharge tube constitute a great difference from the atmosphere, since they furnish the most efficient third-body for the formation of metastable molecules on recombinations between the atoms, while a three-body collision becomes a rare event in the upper atmosphere on account of the low pressure there.

On the theoretical side, many theories have been proposed for the excitation mechanisms in the upper atmosphere, among which the one due to Chapman seems to be most favoured by many authors. According to it, the source of energy of the radiations in the night sky is the energy of dissociation of the oxygen molecules stored up during the day, and the radiations of the O atom and the N₂ molecule are excited when two O atoms recombine in their neighbourhood in a three-body collision. We shall show in the following that the frequency of occurrence of such three-body collisions is entirely much too low to account for the observed intensities of the various radiations and that the theory is inadequate in explaining the diurnal intensity variations of the most prominent radiations in the night sky. It is proposed to show that the main spectral features, especially of the night sky, can be satisfactorily understood on the view that the key processes are the formation of the metastable molecules of oxygen and nitrogen by radiative recombinations between the atoms generated during the day, and the excitation processes are then the various collisions of the second kind, of the resonance type, between the metastable molecules and atoms. It is important that any suggested mechanisms be not judged on energetic considerations alone; it is necessary to pay a closer attention to the

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10 S. Chapman, Phil. Mag., 1937, 23, 657. Most unfortunately this journal is not available either in Kun-ming or in Chungking; but from another paper by Chapman, Astrophys. Jour., 1939, 90, 309, and a paper by Cabannes, Comptes Rendus, 1939, 208, 1770, it is gathered that only dissociation of O₂ and three-body recombinations are considered.
rates at which the various processes might take place in the upper atmosphere and to see if they may account for the observed intensities of the radiations. For this a closer discussion of the probabilities of the various processes is necessary.

Theory

We shall start with an atmosphere that is composed mainly of N\textsubscript{2}, a smaller amount of O\textsubscript{2}, some rare gases and some water vapour, and assume that as the result of dissociation and ionization of the N\textsubscript{2} and O\textsubscript{2} molecules by the ultraviolet solar radiations, there are also present N and O atoms, N\textsubscript{2}\textsuperscript{+} and O\textsubscript{2}\textsuperscript{+} ions as well as N\textsuperscript{+} and O\textsuperscript{+} ions. These ions, the electrons and the negative ions formed by the attachment of electrons to neutral atoms and molecules do not play any direct rôle in the excitation processes in the theory and hence will be ignored in the following. The primary processes are:

\begin{align*}
N\textsubscript{2} (X^{1}\Sigma) + h\nu (\lambda < 1000 \text{ A}) &\rightarrow 2 \text{N} (^{2}\Pi), \quad (1) \\
N\textsubscript{2} (X^{1}\Sigma) + h\nu (\lambda < 1200 \text{ A}) &\rightarrow N (^{2}\Pi) + N (^{2}\Pi), \quad (2) \\
O\textsubscript{2} (X^{3}\Sigma) + h\nu (\lambda < 1750 \text{ A}) &\rightarrow O (^{3}\Pi) + O (^{1}\Pi), \quad (3)
\end{align*}

and to a less extent and in the lower atmosphere,

\begin{align*}
O\textsubscript{2} (X^{3}\Sigma) + h\nu (\lambda < 2400 \text{ A}) &\rightarrow 2 \text{O} (^{3}\Pi), \quad (4) \\
O\textsuperscript{3} + h\nu (\lambda < 2700 \text{ A}) &\rightarrow O\textsubscript{2} (X^{3}\Sigma) + O (^{1}\Pi). \quad (5)
\end{align*}

Positive ions may be produced by the photo-ionization of the N\textsubscript{2} and O\textsubscript{2} molecules and the atoms, by solar radiations of very short wave-length; but it is also possible that the metastable N\textsubscript{2} (A\textsuperscript{3}\Sigma) and O\textsubscript{2} (C\textsuperscript{3}\Sigma) formed from the N and the O atoms by the processes, Q\textsubscript{1}, Q\textsubscript{3}, Q\textsubscript{2}, Q\textsubscript{4} in Table II contribute greatly to the ionization by absorption of ultraviolet radiations of longer wave-length and hence of greater abundance in the solar radiations.

\begin{align*}
N\textsubscript{2} (A^{3}\Sigma) + h\nu &\rightarrow 2 \text{N}, \quad (6) \\
N\textsubscript{2} (A^{3}\Sigma) + h\nu &\rightarrow N\textsubscript{2}^{+} (X^{2}\Sigma) + e, \quad (7) \\
O\textsubscript{2} (C^{3}\Sigma) + h\nu &\rightarrow 2 \text{O}, \quad (8) \\
O\textsubscript{2} (C^{3}\Sigma) + h\nu &\rightarrow O\textsubscript{2}^{+} (X^{3}\Pi) + e. \quad (9)
\end{align*}

The ionization potentials in (7) and (9) are 9\cdot7 and 7\cdot5 volts respectively compared with the 13\cdot6 and 14\cdot5 volts respectively for the O and N atoms. It is not necessary to exclude the possibility that some dissociation and ionization are effected by agents other than ultraviolet radiations; but as we shall immediately see, on account of the low probabilities for either the radiative or the three-body recombination, the atoms produced in the day by the processes (1), (2), (3), (6) and (8) will disappear slowly enough to account for the rôle they are assumed to play in the night sky. In fact,
for this purpose alone, it is not necessary to invoke the action of agents other than the solar radiances.

On the assumption that there are present in the upper atmosphere the atoms and molecules of N and O but no radiations to remove the metastable $N_2(A^3\Sigma)$ and $O_2(C^3\Sigma)$, as it is the case after sunset, the various processes in Table II are possible. In the following we shall assess their plausibilities. The actual contribution of a given process depends of course, besides on the intrinsic probability of the process, also on the concentrations of the particles involved.

Of these processes, $Q_6$, $Q_7$, $Q_8$, $Q_9$, $Q_9''$, $Q_9'''$, $Q_9'''$, $Q_{10}$, $Q_{10}'$, $Q_{11}$, $Q_{12}$, $Q_{12}'$, $Q_{13}$, $Q_{14}$, $Q_{15}$, $Q_{16}$, $Q_{17}$ are collisions of the second kind in which the energy of electronic excitation of one particle is transferred into the energy of electronic and vibrational excitation of a molecule. In these cases, the resonance is very close since the vibrational levels are only 1/5 to 1/4 of a volt apart. In Table II the vibrational level which is excited with the energy of electronic excitation of one particle is transferred into the

| Table II |
| Excitation Processes in the Upper Atmosphere |

<table>
<thead>
<tr>
<th>Notation</th>
<th>Process</th>
<th>Radiation excited</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_1$</td>
<td>$N(\text{S}) + N(\text{S}) + X \rightarrow X + N_2(A^3\Sigma)$, $\nu$ up to 7</td>
<td>Vegard-Kaplan</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>$O(\text{P}) + O(\text{P}) + X \rightarrow X + O_2(C^3\Sigma)$</td>
<td>Herzberg bands</td>
</tr>
<tr>
<td>$Q_3$</td>
<td>$N(\text{P}) + N(\text{S}) \rightarrow N_2(A^3\Sigma) + h\nu$</td>
<td>Vegard-Kaplan</td>
</tr>
<tr>
<td>$Q_4$</td>
<td>$O(\text{P}) + O(\text{P}) \rightarrow O_2(C^3\Sigma) + h\nu$</td>
<td>Herzberg bands</td>
</tr>
<tr>
<td>$Q_5$</td>
<td>$O_2(C^3\Sigma) + O_2(C^3\Sigma) \rightarrow O_2(X^2\Sigma) + O(\text{P}) + O(\text{S}) + 0.12$</td>
<td>Red [Ol]</td>
</tr>
<tr>
<td>$Q_6$</td>
<td>$2N_2(A^3\Sigma) \rightarrow N^+_2(X^2\Sigma) + N_2(C^3\Pi)$, $\nu$ up to 5</td>
<td>2nd positive</td>
</tr>
<tr>
<td>$Q_7$</td>
<td>$N^+_2(X^2\Sigma) + O(\text{P}) \rightarrow O(\text{P}) + N_2(B^3\Pi)$, $\nu = 15$</td>
<td>1st positive</td>
</tr>
<tr>
<td>$Q_8$</td>
<td>$N_2(A^3\Sigma) + O(\text{P}) \rightarrow N_2(C^3\Pi) + N_2(a^3\Pi)$, $\nu = 9$</td>
<td>Lyman-Birge-Hopfield</td>
</tr>
<tr>
<td>$Q_9$</td>
<td>$N_2(A^3\Sigma) + N(\text{P}) \rightarrow N(\text{P}) + N_2(B^3\Pi)$, $\nu = 11$</td>
<td>1st positive</td>
</tr>
<tr>
<td>$Q_{10}$</td>
<td>$N_2(A^3\Sigma) + N(\text{P}) \rightarrow N(\text{S}) + N_2(B^3\Pi)$, $\nu = 0$</td>
<td>Lyman-Birge-Hopfield</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>$N_2(A^3\Sigma) + O_2(X^2\Sigma) \rightarrow N_2(X^3\Sigma) + O_2(B^2\Sigma)$, $\nu = 0$</td>
<td>Schumann-Runge</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>$N_2(A^3\Sigma) + O_2(X^2\Sigma) \rightarrow N_2(X^3\Sigma) + O_2(C^3\Pi)$, $\nu = 0$</td>
<td>2nd positive</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>$N_2(A^3\Sigma) + N^+_2(X^2\Sigma) \rightarrow N_2(X^3\Sigma) + N_2^+(B^2\Sigma)$, $\nu = 11$</td>
<td>1st positive</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>$N_2^+(X^2\Sigma) + N(\text{P}) \rightarrow N(\text{S}) + N^+_2(B^2\Sigma)$, $\nu = 1$</td>
<td>1st negative</td>
</tr>
<tr>
<td>$Q_{15}$</td>
<td>$N^+_2(X^2\Sigma) + O(\text{S}) \rightarrow O(P) + N^+_2(B^2\Sigma)$, $\nu = 3$</td>
<td>A, B, a bands of $O_2$</td>
</tr>
<tr>
<td>$Q_{16}$</td>
<td>$O_2(X^2\Sigma) + O(\text{P}) \rightarrow O(\text{P}) + O_2(A^3\Sigma)$, $\nu = 2$</td>
<td>$a^\prime$, $a^\prime\prime$ bands of $O_2$</td>
</tr>
<tr>
<td>$Q_{17}$</td>
<td>$O_2(X^2\Sigma) + O(\text{P}) \rightarrow O(\text{P}) + O_2(A^3\Sigma)$, $\nu = 4$</td>
<td>Red [Ol]</td>
</tr>
<tr>
<td>$Q_{18}$</td>
<td>$O(\text{P}) + N(\text{P}) \rightarrow O(\text{P}) + N(\text{S}) + 0.41$</td>
<td>Green [Ol]</td>
</tr>
<tr>
<td>$Q_{19}$</td>
<td>$O(\text{P}) + N(\text{P}) \rightarrow O(\text{P}) + N(\text{S}) + 0.16$</td>
<td>Yellow lines Na</td>
</tr>
<tr>
<td>$Q_{20}$</td>
<td>$N_2(\text{S}) + N(\text{P}) \rightarrow N_2(\text{P}) + O(\text{P}) + N(\text{S}) + 0.27$</td>
<td>Water vapour bands</td>
</tr>
<tr>
<td>$Q_{21}$</td>
<td>$N_2(\text{S}) + O(\text{P}) \rightarrow N_2(\text{P}) + O(\text{P}) + 0.14$</td>
<td>Water vapour bands</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>$N_2(X^2\Sigma^\prime) + H_2O \rightarrow N_2(X^2\Sigma^\prime) + H_2O'$</td>
<td>Water vapour bands</td>
</tr>
</tbody>
</table>
closest resonance is given. The cross-sections of the processes are, however, not solely determined by energy considerations alone. A theoretical evaluation of the cross-sections of such processes is very difficult, as they depend on the coupling between the electronic and the nuclear motions of the molecule. Some rough idea about the order of magnitude of the probabilities of such processes may be obtained from the experiments of Zemansky in which the cross-sections for the de-excitation of Hg $^3P_1 \rightarrow ^3P_0$ by energy transfer to the vibrational motion of a colliding molecule are found to be of the order of the gas kinetic values.\footnote{Zemansky, Phys. Rev., 1930, 36, 919.} The processes concerned here involve also the excitation of electronic states; their cross-sections may be smaller than the gas kinetic values when the spin rule is violated, but may be of the same order as the latter when the spin rule is satisfied. In the latter category we have $Q_7'$, $Q_7''$, $Q_8'$, $Q_{10}'$, $Q_{12}'$, $Q_{12}''$, $Q_{16}'$, $Q_{17}$.

The processes $Q_{18}$ to $Q_{22}$ involve the transfer of purely electronic energies and hence may have very large cross-sections for very close resonance. Their exact values are not known, but it is probable that they lie between $10^{-2}$ and $10^4$ times the gas kinetic values when the spin rule is satisfied and have small values when it is not.\footnote{For processes involving the transfer of electron and electronic energy, reference may be made to the experimental work of Manley and Duffendack, Phys. Rev., 1935, 47, 56, and of Duffendack and Gran, ibid., 1937, 51, 804. These show that the cross-section of a process in which a neutral atom is simultaneously ionized and excited on collision with a positive atomic ion may be as large as $10^{-4} - 10^5$ times the gas kinetic value when the resonance is close. For processes involving the transfer of electronic energy alone, there is the theoretical work of Kallmann and London, Zeits. f. phys. Chem., 1929, B 2, 220, but no experimental work seems available. It is probable that the cross-sections are of the same order as those above.} Thus of the three processes $Q_{20}$, $Q_{21}$, $Q_{22}$ for the excitation of the yellow lines of Na, $Q_{21}$ is by far the most probable both because of the small energy discrepancy and the spin rule.

The processes $Q_5$, $Q_5'$, $Q_6'$, $Q_6''$ represent the dissociation of a molecule on collision with another, the energy being furnished, not by the kinetic energy of relative motion, but by the energies of excitation of both molecules. There is involved a transfer of electronic energy to the kinetic energy of the resulting particles and for this reason the cross-sections will be large only when there is very close resonance, \textit{i.e.}, when the amount of energy to be transformed into the kinetic energy of the heavy particles is small. Thus the cross-section of $Q_5$ may be expected to be very large compared with the others since the spin rule is satisfied and the energy discrepancy is small.

Consider next the radiative processes such as $Q_4$. If the final state can combine with the quasi-state formed by the close approach of the two atoms...
by dipole transitions, the cross-sections may be estimated on general considerations at $10^{-7} - 10^{-5}$ times the gas kinetic values for slow atoms,$^{13}$ and are hence small compared with those of the resonance collisions of the second kind. That they cannot be omitted from our considerations is due to the fact that they are still the chief mechanisms for the recombination of atoms in the upper atmosphere and are the source of energy of the excitation and radiation processes in the night sky, and possibly to a certain extent in the aurora. The other recombination processes, namely, three-body collisions such as $Q_1$, have even smaller probabilities at the low pressure of the upper atmosphere. The probability of a three-body process may be expressed in terms of a cross-section for unit concentration of the third body, namely, $q \propto \pi r^2 \cdot r/\lambda$, where $r$ is the atomic dimension and $\lambda$ is the mean free path of the recombining particles for unit concentration of the third body.$^{13a}$ Obviously $\lambda$ depends on the cross-section of the energy transfer from the recombining particles to the third body. Assuming, for the optimum case, that there is resonance in this transfer so that the cross-section may be as large as $10^3$ times the gas kinetic value, one obtains for $\lambda$ a value $10^{18}$ cms. and then $q \simeq 10^{-37}$ cm.$^5$ Hence for the three-body collisions to be as frequent as the radiative recombinations, the concentration of the third body must be as high as $10^{15}$ per c.c. or greater. This value is about $10^3$ to $10^4$ times greater than the concentration at the E layer. Hence in the upper atmosphere, radiative recombinations are far more important than three-body processes, although in the lower atmosphere and in all laboratory experiments the reverse is the case.

Finally, in order that excitation collisions between metastable atoms and molecules be of any importance, it is necessary that de-excitations of the metastables by collisions with atoms and molecules be negligible. Now the latter process involves the transfer of electronic energy to the kinetic energies of the heavy particles (atoms and molecules); its probability can be calculated by means of the principle of detailed balancing from the probability of a process in which the electronic state of an atom or a molecule is excited by heavy particles in a collision of the first kind. As shown by Massey and Smith,$^{14}$ the probabilities of excitation of the $2^1P$ state of He by protons are extremely small for proton energies below 400 volts. On general considerations, one would expect the probabilities of excitation of metastable states

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$^{13}$ Cf. Massey, *Negative Ions*, pp. 32-36; 78-79. As the number of molecular states arising from two atoms in given atomic states is very large, for a given state of the molecule it is in general possible to find a quasi-state having the correct symmetry properties so as to combine with the state by dipole transitions.


(i.e., optically forbidden transitions) by heavy particles to be even smaller. The principle of detailed balancing then requires that the probabilities of the reverse processes, namely, the de-excitation of metastable states by heavy particles, be also extremely small, especially for the kinetic energies of atoms and molecules with which we are concerned in the upper atmosphere. It is because of these extremely low probabilities of de-excitations by atoms and molecules and the comparatively high concentrations of the metastables that the collision processes in Table II, which are mostly of the resonance type, assume relatively great importance in the upper atmosphere.

From the above discussions, however, it would appear that nothing quantitative can be said concerning the probabilities of the various processes in Table II. Fortunately, most of our arguments in the following do not depend very critically on the exact values of these probabilities, although a more exact knowledge about them will enable one to make closer estimates of the concentrations of the various atoms and molecules and is hence greatly to be desired.

Consider now the various radiations in the spectra of the night sky and of the aurora in the light of the processes in Table II. In the following we shall denote the concentration of the atom, say, O (1S), by [O 1S], and the number of collisions, say, O (1D) + N (3D) → O (1S) + N (4S), in unit volume per second by Q19 [O 1D] [N 4D] so that Q19 represents the cross-section of the process multiplied by the relative velocity of the colliding particles. For the three-body processes, q represents the cross-section for unit concentration of the third body.

(A) Green [OI] line: 1S → 1D

Since the green [OI] line is the most prominent line in both the spectra of the night sky and of the aurora, any theory must not fail to provide a satisfactory mechanism for the excitation of the line. From the earliest experiments of Kaplan in which the green line was excited in an afterglow in active nitrogen containing a small amount of oxygen, the suggestion was made that the 1S state is excited from the normal state 3P by the metastable atom N (3P). This explanation is now untenable since the energy available in N (P) is far short of being able to effect this excitation. Chapman and later Cabannes suggested that the various radiations of the night sky are excited by the recombinations between the oxygen atoms in the neighbourhood of another atom or molecule. For example, the green [OI] line is thought to be due to the process

\[ \text{O (3P) + O (3P) + O (3P) → O}_2 (X 3Σ) + \text{O (1S)} + 0.92 \text{ volt.} \]

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It can be shown, however, that even on making the most optimum assumption about the probability of the three-body process, the frequency of its occurrence is far too low to account for the observed intensity of the green line. Also the suggested mechanism fails to account for the observed diurnal variations in the intensity of the [OI] lines. For the same reason,

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30 According to Cabannes, Comptes Rendus, 1939, 208, 1770, who favoured Chapman's theory, the green [OI] line and the Vegard-Kaplan bands are excited by the following processes:

\[ 3\text{O}^{(3P)} \rightarrow \text{O}_2^{(X^3Σ)} + \text{O}^{(1S)} + 0.92 \text{volt} \quad (a) \]

\[ \text{O}^{(3P)} + \text{O}^{(1D)} + \text{N}_2^{(X^1Σ)} \rightarrow \text{N}_2^{(A^3Σ)} + \text{O}_2^{(X^3Σ)} + \text{O}^{(X^3Σ)} + 0.90 \text{volt} \quad (b) \]

While these processes are energetically possible, we shall show that they are far too infrequent to account for the observed intensities of the radiations and that they fail to account for the observed diurnal variations in the intensities of the radiations.

1. The probability of the process (a) is certainly very small if the energy excess 0.92 volt must be transformed into the kinetic energies of the resulting particles. It may be somewhat greater if this energy excess is retained as energy of vibrational excitation of the \( \text{O}_2^{(X^3Σ)} \) molecule. Even then, the probability must be very much smaller than the gas kinetic value since the spin rule is not satisfied in this case. Assuming, for the optimum situation, that it is of the same order as the gas kinetic value, then the cross-section \( q \) for unit concentration of the third body is \( \approx 10^{-40} \text{ cm}^2 \). With this value of \( q \), even a concentration of \( 10^{11} \text{ c.c.} \) for \( \text{O}^{(3P)} \) would generate \( \text{O}^{(1S)} \) by the process (a) only at the rate of about 1 per c.c. per second. This is too small to account for the observed intensity of the green line, which calls for some \( 10^{20} \text{ O}^{(1S)} \) per c.c. Higher concentrations for \( \text{O}^{(1D)} \) are not available above the E layer, and according to Cabannes and Dufay, the radiations of the night sky come from above the E layer.

2. Similar considerations show that no three-body processes are adequate in providing for a high enough concentration of \( \text{O}^{(1D)} \) to account for the intensities of the red [OI] lines.

3. If the green [OI] line is excited by the process (a), then as the concentration of \( \text{O}^{(3P)} \) decreases, the rate of production of \( \text{O}^{(1S)} \) would also decrease. This would mean a continual decrease, however slow, in the intensity of the green line in the night. Also, if the \( \text{O}^{(1D)} \) are supposed to be produced as the result of the emission of the green line, then on account of the longer lifetime of the \( \text{O}^{(1D)} \), the concentration of \( \text{O}^{(1D)} \) would first increase until the rate of production is balanced by the rate of disappearance by the emission of the red lines and by other quenching collisions. This would mean that the red lines increase in intensity immediately after sunset and reach a constant value shortly afterwards. But these are just opposite to the observed variations, namely: the green line increases in intensity after sunset to a maximum near midnight, and the red lines are most intense immediately after sunset and decline in intensity thereafter.

4. If the \( \text{N}_2^{(A^3Σ)} \) responsible for the emission of the Vegard-Kaplan bands are excited by the process (b), then, assuming again for the sake of argument the optimum value \( q \approx 10^{-40} \text{ cm}^2 \) for the cross-section of the process for unit concentration of the third body \( \text{N}_2^{(X^1Σ)} \), one would need a concentration of \( 10^{10} \text{ c.c.} \) for \( \text{O}^{(1D)} \), of \( 10^{11} \text{ c.c.} \) for \( \text{O}^{(3P)} \) and \( 10^{12} \text{ c.c.} \) for \( \text{N}_2^{(X^1Σ)} \) in order to produce one \( \text{N}_2^{(A^3Σ)} \) molecule per c.c. per second. Such a rate of production of \( \text{N}_2^{(A^3Σ)} \) is much too low to account for the observed total intensity of the Vegard-Kaplan bands, although the requisite concentration of \( \text{O}^{(1D)} \) is already neither provided for by any process nor consistent with the observed intensity of the red lines.

The above estimates are made on the assumption that the cross-sections for the three-body processes have the gas kinetic values. When account is taken of the fact that the cross-sections are probably very much smaller than the gas kinetic values, the inadequacy of the mechanisms such as (a) and (b) becomes even more obvious.
the suggestion that the molecule of $O_2$ is dissociated into the atoms $O\ (^3P)$ and $O\ (^1S)$ by active nitrogen,\textsuperscript{17} namely,

$$N_2\ (A\ ^3\Sigma) + N\ (^3P) + O_2\ (X\ ^3\Sigma) \rightarrow N_2\ (X\ ^1\Sigma) + N\ (^1S) + O\ (^3P) + O\ (^1S) + 0.4\ \text{volt},$$

is unsatisfactory. Here we suggest the process $Q_5$ as the main process for the production of $O\ (^1S)$. That the metastable $O_2\ (C^3\Sigma)$ should play the important intermediate rôle is not implausible if one remembers that the metastable $N_2\ (A\ ^3\Sigma)$ molecules are known to play a fundamental rôle in the upper atmosphere and the laboratory afterglow (as shown by the emission of the Vegard-Kaplan bands), and that the metastable $O_2\ (C^3\Sigma)$ bears a similar relation to processes involving the oxygen atoms and molecules as $N_2\ (A\ ^3\Sigma)$ to those of nitrogen.

From the measured intensity of the green line in the night sky, Rayleigh has estimated that it corresponds to approximately $10^8$ transitions per second in a column of the atmosphere of 1 sq. cm. base.\textsuperscript{18} This, together with the transition probability $A_{\text{green}} \approx 2$/sec,\textsuperscript{19} requires that there be at least some $10^2\ O\ (^1S)$ atoms produced per c.c. per second during the night. Assuming now that these are supplied by the process $Q_5$, we have

$$Q_5\ [O_2C^3\Sigma]^2 \geq 10^{12}/\text{sec. c.c.}$$

Then, for a value of the cross-section of $Q_5$ lying between $10^{-3} - 10^{3}$ times the gas kinetic value, we have, respectively,

$$[O_2\ C^3\Sigma] \geq 5 \times 10^7 - 5 \times 10^4/\text{c.c.}$$

for the necessary concentration of $O_2\ (C^3\Sigma)$ to maintain the excitation and emission of the green line. To show that such concentrations of $O_2\ (C^3\Sigma)$ are not impossible, we have only to remember that there is a high concentration of $O\ (^3P)$ for the production of $O_2\ (C^3\Sigma)$ by the process $Q_4$. If there are some $10^{10}\ O\ (^3P)$ atoms per c.c. in the upper atmosphere just after sunset, and if the probability of radiative recombination $Q_4$ is of the order of $10^{-6}$ per collision, then the $O_2\ (C^3\Sigma)$ are produced by $Q_4$ at a rate of $\sim 10^4$/sec. c.c. On assuming a high metastability of the $O_2\ (C^3\Sigma)$, it will take some 10 minutes to build up a concentration of $O_2\ (C^3\Sigma)$ of the order $10^8$/c.c. which is of the correct order of magnitude to account for the

\textsuperscript{17} E. W. Hewson, Rev. Mod. Phys., 1937, 9, 420.  
maintenance of the green line.* This building up of the concentration of \( \text{O}_2 (C^\text{3}\Sigma) \) by the process \( Q_4 \) may be responsible for the observed slight rise of the intensity of the green line towards midnight.\(^4\) The slight decline in the intensity of the line in the latter part of the night\(^4\) may be due to the gradual depletion of the oxygen atoms through the various recombination processes, three-body as well as radiative.

Neglecting the recombination processes compared with the other collisions, we have for the rate of change of the concentration of \( \text{O} (\text{1S}) \)

\[
\frac{d [\text{O} (\text{1S})]}{dt} = Q_6 [\text{O}_2 \text{C} (\text{3}\Sigma)]^2 + Q_{19} [\text{N} (\text{4}\text{D})] [\text{O} (\text{1D})] - \{A_{\text{green}} + A_{\text{trans}} + (Q_9 + Q_9') [\text{N}_2 \text{A} (\text{3}\Sigma)] + Q_{15} [\text{N}_2 \text{X} (\text{2}\Sigma)] + Q_{21} [\text{N}_2 \text{S}]\} [\text{O} (\text{1S})] \tag{10}
\]

where \( A_{\text{trans}} \) is the probability of the trans-auroral transition \( ^1\text{S} \rightarrow ^3\text{P} \) in \( \text{O} \text{I} \) and is 0.18/sec.\(^19\) This trans-auroral line is not observed in the night sky or the aurora since it lies just beyond the limit of transparency of the atmosphere. Now for the green line to appear, it is necessary that the rate of quenching by the various processes in (10) be not very large compared with the rate of emission of the line, i.e.,

\[
A_{\text{green}} \ll (Q_9 + Q_9') [\text{N}_2 \text{A} (\text{3}\Sigma)] + Q_{21} [\text{Na} \text{S}] + Q_{15} [\text{N}_2 \text{X} (\text{2}\Sigma)].
\]

In the night sky where the negative bands of \( \text{N}_2^+ \) are either not present or extremely weak, the last term can be neglected. A knowledge of the cross-sections of \( Q_9' \) and \( Q_{21} \) will enable us to set an upper limit to the concentrations of \( \text{N}_2 (\text{A} \text{3}\Sigma) \) and sodium atoms. Thus assuming the cross-section for \( Q_9' \) to lie between \( 10^{-2} \) and \( 10^2 \) times the gas kinetic value, one obtains for \( (\text{N}_2 \text{A} \text{3}\Sigma) \) an upper limit of \( 10^{13} \) and \( 10^9 \)/c.c. respectively. The actual concentration of \( \text{N}_2 (\text{A} \text{3}\Sigma) \), especially in the layer where the dissociation of \( \text{O}_2 \) but not that of \( \text{N}_2 \) is maximum, is probably very much smaller than

* On taking into account the loss of \( \text{O}_2 (\text{C} \text{3}\Sigma) \) through the emission of the Herzberg bands \( \text{O}_2 (\text{C} \text{3}\Sigma) \rightarrow \text{O}_2 (X \text{1}\Sigma) \) and the processes \( Q_5, Q_6' \). \( Q_{12}, Q_{12}', \) the rise of the concentration of \( \text{O}_2 (\text{C} \text{3}\Sigma) \) will be given by the equation

\[
\frac{d [\text{O}_2 \text{C} (\text{3}\Sigma)]}{dt} = k - \alpha [\text{O}_2 \text{C} (\text{3}\Sigma)] - \beta [\text{O}_2 \text{C} (\text{3}\Sigma)]^2
\]

where \( k \) stands for the constant rate of production by the process \( Q_4 \), \( \alpha \) represents the combined result of the processes \( O_2 (C^3\Sigma) \rightarrow O_2 (X^1\Sigma), Q_{12}, \) and \( Q'_{12} \), and \( \beta \) the result of \( Q_4 \) and \( Q_4' \). From this one obtains

\[
2\beta [\text{O}_2 \text{C} (\text{3}\Sigma)] = -\alpha + B \frac{1 - A e^{-ut}}{1 + A e^{-ut}},
\]

where \( B = \sqrt{4k\beta + \alpha^2} \) and \( A = (B - \alpha)/(B + \alpha) \). It is seen that the concentration of \( \text{O}_2 (\text{C} \text{3}\Sigma) \) will tend to a constant value \( (B - \alpha)/2\beta \) after a time \( t \) depending on the values of \( k, \alpha \) and \( \beta \).
As emphasized in the summary in the introduction, the red (OI) lines of the night sky differ from the green line in their diurnal intensity variations. The O (\( ^1S \)) atoms in the night sky are probably produced by the process \( Q_5 \). The O (\( ^1D \)) atoms are, in addition to the analogous but less probable process \( Q_6' \) and the result of the emission of the green line, now produced by the process \( Q_{18} \) which now assumes greater importance than \( Q_{16} \) for the excitation of \( ^1S \), since the initial rate of production of O (\( ^1D \)) by the process \( Q_{18} \) may now be very large on account of the large concentrations of O (\( ^3P \)) and N (\( ^2D \)). Assuming as before that immediately after sunset, there are some \( 10^{10} \) O (\( ^3P \)) and some \( 10^6 \) N (\( ^2D \)) atoms per c.c., if the cross-section of \( Q_{18} \) is taken to be of the order \( 10^{-8} \) times the gas kinetic value, the process \( Q_{18} \) will then produce O (\( ^1D \)) at the rate of some \( 10^4/sec. \) c.c. This is amply sufficient to account for the observed intensity of the red lines. With the depletion of the N (\( ^2D \)) by this and other processes, this rate of production of O (\( ^1D \)) would have decreased rapidly after sunset had it not been for the replenishment of O (\( ^1D \)) by the process \( Q_5' \) and the result of the emission of the green line. The result is a more gradual decrease in [O(\( ^1D \))] in the early part of the night, followed by a more or less steady value when the rate of depletion by the various processes in equation (11) becomes equal to the rate of replenishment. This may explain the observed fact that the red lines have the greatest intensity immediately after sunset.\(^4\) The different behaviour of the intensity variations of the green and the red lines is thus due to the different mechanisms for the production of the O (\( ^1S \)) and O (\( ^1D \)).

The rate of change of (O (\( ^1D \))) is, again on neglecting recombinations,

\[
\frac{d[O\,(^1D)]}{dt} = 2Q_5' [O_2C\,(^3\Sigma]^2] + Q_{18} [O\,(^3P)] [N\,(^2D)] + A_{green} [O\,(^1S)] - (A_{red} + Q_{18} [N_2A\,(^3\Sigma)] + Q_{16} [O_2X\,(^3\Sigma)] + Q_{19} [N\,(^2D)] + Q_{22} [Na\,(^2S)] \) \tag{11}
\]

where the transition probabilities \( A_{red} \) are \( 2.5 \times 10^{-3} \) and \( 7.5 \times 10^{-3} \) per second for the lines \( ^1D_2 \rightarrow ^3P_1 \) and \( ^1D_2 \rightarrow ^3P_2 \) respectively.\(^19\) The red lines

\(^20\) The value \( 10^8/c.c. \) for [N (\( ^2D \))] is based on the following estimates: Kaplan pointed out the possible appearance of the lines \( ^2D \rightarrow ^4S \) in NI with about \( 1/50 \) the intensity of the green [OI] line in Babcock's spectrum of the night sky (see C below). Since the lifetime of N (\( ^2D \)) is of the order \( 10^4 \) second, this requires that there be at least some \( 10^8 \) N (\( ^2D \)) per c.c. to account for the observed intensity.
Excitation Processes in the Night Sky and the Aurora

are here quenched by the processes $Q_8$ and $Q_{16}$. As $Q_8$ and $Q_{16}$ are probably of the same order of magnitude and as the concentration of the oxygen molecule in the normal state is certainly larger than that of the $N_2 (A^3\Sigma)$ by some powers of 10, we need only consider the quenching by $Q_{16}$. The condition for the red line to appear is hence

$$A_{\text{red}} \ll Q_{16} [O_2X^3\Sigma].$$

Assuming that the cross-section for $Q_{16}$ is $10^{-2}$ to $10^2$ times the gas kinetic value, one finds that for the red lines to appear, $(O_2X^3\Sigma)$ must not be very much greater than $10^{10}$ and $10^6$/c.c. respectively. Even the value $10^{10}$/c.c. is too low for the E layer where the concentration of O$_2$ is probably of the order $10^{11} - 10^{12}$/c.c. The above condition is more readily satisfied in the higher altitudes. This may be connected with the observed enhancement of the red lines in the sunlit aurorae which are situated in very much higher altitudes ($300 - 800$ km.) than the ordinary aurorae (100 km), although the enhancement may also be due to the production of O ($^1D$) by the photodissociation process (3).

Finally we may remark in passing that the great difference in the relative intensity of the green and the red lines in the night sky and in the nebulæ is not a matter of the difference in the gas pressures in the two cases alone. From equations (10) and (11), it is seen that were it not for the quenching collisions, the red lines would have been more intense than the green since any excitation of O ($^1S$) by $Q_5$ would contribute to the intensity of the red lines on emission of the green line. That the red lines are weaker than the green is probably due to the more effective quenching of the former by $Q_{16}$ (exciting at the same time the A, B, a bands of oxygen) than that of the latter by the process $O_2 (X^3\Sigma) + O (^1S) \rightarrow O_3 (A^3\Sigma) + O (^1D)$, since here the spin rule is violated. On the other hand, the extremely low pressure in the nebulae renders quenching collisions of any kind unimportant, and the intensities of the green and the red lines are determined essentially by the relative frequencies of excitations of $^1S$ and $^1D$. That the red lines are far more intense than the green line in the nebulae is to be explained by the predominance of electrons having energies enough to excite $^1D$ but not $^1S$. In fact, from the relative intensities of the red and the green lines and the theoretical excitation cross-sections of these states by electron impact, it has been possible to obtain very reasonable values for the temperatures of the nebulæ.

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(C) Forbidden lines of \([NI]\) \(^2D\rightarrow^4S\)

The situation with the forbidden lines of NI can be expected to be similar to that with OI. The lines \(^2P\rightarrow^2D\) have transition probabilities of the order 1/sec.; they lie in the infra-red \(1.04 \mu\) and hence have not been observed. The lines \(^2D\rightarrow^4S\) have the small transition probabilities of the order \(10^{-5}\)/sec. Kaplan has recently succeeded in observing both the \(^2D\rightarrow^4S\) and the \(^2P\rightarrow^4S\) lines in afterglows in nitrogen under moderately high pressure, and has pointed out the probable appearance of \(^2D\rightarrow^4S\) in Babcock's spectrogram of the night sky with an intensity about \(1/50\) that of the green [OI] line.\(^{22}\) If this identification is correct, we may consider the equations

\[
\frac{d [N^2P]}{dt} = Q^5 [N^2A^3\Sigma]^2 - \{A (^2P\rightarrow^2D) + A (^2P\rightarrow^4S) + (Q_9 + Q_9') [N^2A^3\Sigma] + Q_{14} [N^2X^2\Sigma]\} [N^2P],
\]

\[
\frac{d [N^2D]}{dt} = 2 Q^6' [N^2A^3\Sigma]^2 + A (^2P\rightarrow^2D) [N^2P] - \{A (^2D\rightarrow^4S) + (Q_{10} + Q_{10}') [N^2A^3\Sigma] + Q_{17} [O^2X^3\Sigma] + Q_{18} [O^3P] + Q_{19} [O^1D] + Q_{20} [Na^3S]\} [N^2D],
\]

in which recombination processes have again been omitted. The initial concentrations of \(N (^2P)\) and \(N (^2D)\) immediately after sunset may be very large, especially at the level where the dissociation of \(N_2\) is most intense. The large value of \(A (^2P\rightarrow^2D)\), however, reduced \((N^2P)\) rapidly to a low value so that the more or less steady but small concentration during the night is determined by the rate of the process \(Q^5\), which may be much smaller than the corresponding process \(Q^6\) in the case of the excitation of \(O (^1S)\) on account of the very much larger energy discrepancy (1.3 volt vs. 0.12 volt). On the other hand, the small value \(A (^2D\rightarrow^4S)\) can be consistent with a considerably higher value of \([N^2D]\). This may be the reason why the nebular \(^2D\rightarrow^4S\) can be observed while the trans-auroral \(^2P\rightarrow^4S\) at 3466 A with a much greater transition probability cannot.\(^{23}\)

(D) Negative bands of \(N^2+ N^2+: (B^3\Sigma)\rightarrow N^2+ (X^2\Sigma)\)

Once we have assumed the generation of \(N^2+\) by solar radiations by such process as (7), it is not necessary to assume other modes of generation during the night when one remembers the low rate of loss of \(N^2+\) by recombination processes. In fact, that the \(N^2+\) bands are greatly enhanced

\(^{22}\) J. Kaplan, Phys. Rev., 1939, 56, 858; 1940, 57, 249.

relative to the green [OI] line in sunlit auroræ\textsuperscript{24} and that the $N_2^+$ bands in the night sky increase in intensity when the last trace of sun light touches the uppermost part of the atmosphere in the evening and when the first trace of sun light reaches the top of the atmosphere at the dawn\textsuperscript{25} are consistent with the view that the $N_2^+$ are produced by solar radiations. It is true that the very much greater intensity of the $N_2^+$ bands in the auroræ than in the night sky cannot be explained without additional hypotheses about the auroræ. But granting a higher concentration of $N_2^+$ in the aurora, one can then understand why the $N_2^+$ bands are strong and the Vegard-Kaplan bands are weak in the aurora and conversely in the night sky; for the $N_2^+$ bands excited by the process $Q_{14}$ are at the expense of the metastable $N_2(A^3\Sigma)$, thus quenching the Vegard-Kaplan bands (see below on Vegard-Kaplan bands).

As summarized in the introduction, the strongest $N_2^+$ bands in the aurora and the night sky are the $\nu' - \nu'' = 0 - 0; 0 - 1; 0 - 2; 1 - 2; 1 - 3; 2 - 3$ bands. The strong enhancement of transitions from $\nu' = 0, 1, 2$ may be ascribed to the excitation processes $Q_{14}$ and $Q_{15}$. The enhancement of the $N_2^+$ bands in sunlit aurora and sunlit atmosphere is also consistent with this view since the concentrations of N ($^2P$) and O ($^3S$) generated by sun light by the processes (1), (2), (3) and possibly also (6) and (8) will be high in the sunlit regions. The transition $\nu' = 11 \rightarrow \nu'' = 13$ has a wavelength 4233.5 Å for the band centre so that its head falls just on top of the 4236 (1→2) bands. Also the $\nu' = 12 \rightarrow \nu'' = 13$ band has the wavelength 3915 Å and may contribute partly to the great intensity of the 3914 (0→0) band. This may perhaps account for the excitation of the $N_2^+$ bands by $N_2(A^3\Sigma)$.

(E) Second positive bands: $N_2(C^3\Pi) \rightarrow N_2(B^3\Pi)$

The only plausible processes for the excitation of the second positive system of $N_2$ are $Q_6$ and $Q_{12}$. The equation for $[N_2(C^3\Pi)]$ is

$$\frac{d [N_2C^3\Pi]}{dt} = Q_6 [N_2A^3\Sigma]^2 + Q_{12} [N_2A^3\Sigma] [O_2C^3\Sigma] - \lambda_{2nd} [N_2C^3\Pi] = 0. \quad (14)$$

Here no quenching collisions need be considered. The process $Q_{12}$ will be able to excite $\nu' = 0$ of $C^3\Pi$ only when the $N_2(A^3\Sigma)$ is initially in a state $\nu = 1$ (see end of G) below, while the 10550 cm.$^{-1}$ energy available in the process $Q_6$ can either all go into the excitation of $N_2(B^3\Pi)$, or be divided

\textsuperscript{24} C. Störmer, Zeits. f. Geophys., 1929, 5, 185.
\textsuperscript{25} V. M. Slipher, Monthly Notices, R.A.S., 1933, 93, 657.
between the vibrational motions of the two resulting molecules. In the first case, the bands from $v' = 0$ will be enhanced; in the second case, all bands up to $v' = 5$ can be excited, with perhaps some enhancement of $v' = 1, 2$. As seen from the summary in the introduction, these are in general agreement with the observed facts.

(F) First positive bands: $N_2 (B^3Π) \rightarrow N_2 (A^3Σ)$

The first positive bands are the characteristic feature of the night sky, the aurora and the afterglow in nitrogen. In the afterglow, Kaplan has succeeded in exciting the $v' - v'' = 3$ sequence with intensity maxima corresponding to $v' = 10$ and $v' = 6$. These enhancements have been explained as due to the processes $Q_9$ and $Q_{10}$. In the aurora, Vegard observed the bands $v' = 10 \rightarrow v'' = 7$ at 6323 A. and $v' = 7 \rightarrow v'' = 6$ at 7880 A. These seem to indicate the processes $Q_9$ and $Q_{10}$. In the night sky, bands from very high vibrational levels such as $v' = 15, 16$ have been found. These excitations are furnished by the processes $Q_7, Q_8$ and $Q_{12}'$. These together with $Q_9$ and $Q_{10}$ may account for the excitation of bands from $v' = 4$ to $v' = 15$ or higher observed in the night sky by Cabannes and Elvey, Swings and Linke.

(G) Vegard-Kaplan bands

The equation for the rate of change of [N$_2$A$^3Σ$] is

$$\frac{d [N_2A^3Σ]}{dt} = Q_1 [N^4S]^2 [X] + Q_3 [N^4S]^2 - \left\{ A_{v,K} + (Q_6 + 2Q_6' + 2Q_6'') [N_2A^3Σ] + Q_7 [O^4S] + Q_9 [N^2P] + Q_10 [N^2D] + Q_{11} [O_2X^3Σ] + Q_{13} [N_2^+X^2Σ] \right\} [N_2A^3Σ]$$

As the Vegard-Kaplan bands arise from transitions violating the selection rule for the multiplicity, they have small transition probabilities. Accordingly they will be emitted only if

$$A_{v,K} \ll (Q_6 + 2Q_6' + 2Q_6'') [N_2A^3Σ] + Q_7 [O^4S] + Q_9 [N^2P] + Q_{10'} [N^2D] + Q_{11} [O_2X^3Σ] + Q_{13} [N_2^+X^2Σ].$$

Thus the emission of these bands requires a low [N$_2^+X^2Σ$] and of course the absence of ultraviolet radiations that may destroy the N$_2$ (A$^3Σ$) by

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26 This "complementary" nature of the negative bands of N$_2^+$ and the Vegard-Kaplan bands is true not only of the aurora and the night sky, but seems to be true also in the discharge tube. In the afterglow produced by a feeble discharge, Kaplan (Pub. Astron. Soc. Pacif., 1935, 47, 257), found that the Vegard-Kaplan bands are enhanced relative to the second positive bands while the N$_2^+$ bands are absent. On the other hand, when the N$_2^+$ bands are strong, the Vegard-Kaplan bands are not found (Kaplan, Phys. Rev., 1932, 42, 807).
the processes (6) and (7). This is in agreement with the fact that in the
sunlit aurora where the $N_2^+$ bands are strong and hence $[N_2^+X^2\Sigma]$ high, the
Vegard-Kaplan bands are weak, while in the night sky where the $N_2^+$ bands
are weak, the Vegard-Kaplan bands are strong.

It is observed that the blue radiations of the night sky reach a
maximum intensity immediately after midnight,\textsuperscript{27} like the green [OI] line.
Now the strongest radiations in the blue region are the 4171 and 4425 bands
of the Vegard-Kaplan system. A rise of intensity of these bands in the
first part of the night may be due to the same cause as that for the green
line, namely, the building up of the concentration of the metastable $N_2(A^3\Sigma)$
by the processes $Q_1$ and $Q_3$. Its decline in the second part of the night
can be ascribed to the gradual depletion of the N atoms.

In the night sky, Vegard-Kaplan bands from all levels $v'$ up to 7 are
observed, the bands from $v' = 2, 3, 4$ being particularly enhanced. It is of
course not possible to say anything about the populations of the different
levels of the $N_2(A^3\Sigma)$ resulting from the radiative process $Q_3$. But those
produced by the process $Q_1$ may be in any state $v'$ up to 7 since the energy
available in the process is 1.2 volt. There may be a preponderance of
levels $v' = 2, 3, 4$ corresponding to the division of this energy between the
two resulting molecules $N_2(A^3\Sigma)$ and $N_2(X^1\Sigma)$. Also the large number
of $N_2(A^3\Sigma)$ molecules resulting from the emission of the first positive bands
$v' = 6, 7 \rightarrow v'' = 3, 4$ would enhance the Vegard-Kaplan bands from $v' = 3, 4$.

In discussing the enhancement of certain bands in a system involving
allowed transitions, it is necessary only to consider the levels excited with
close resonance since the lifetimes of these states are so short that a redistri-
bution by collisions can be neglected. With the Vegard-Kaplan bands,
on account of the long lifetime of the metastable state $A^3\Sigma$, it is necessary
to consider the effect of collisions between the $N_2(A^3\Sigma)$ molecules and other
particles. It is known, however, both experimentally and theoretically that
the probability of energy transfer between the vibrational motion of a mole-
cule and the translational motion of an atom or a molecule is very small,
of the order $10^{-7} - 10^{-6}$ per collision.\textsuperscript{28} As the collision frequency of an
atom or a molecule with other molecules is of the order $10^9$ per second at the
pressure of the E layer, it is clear that de-excitation of vibrational excitation
by collisions is unimportant. This persistence of vibrational excitation
accounts for the emission of Vegard-Kaplan bands from rather high
levels $v$.

(H) Lyman-Birge-Hopfield Bands: \( N_2 (a \: ^1\Pi) \rightarrow N_2 (X \: ^1\Sigma) \)

The existence of these bands, especially those from \( v' = 0 \) to \( v'' = 19 - 23 \), has recently been made plausible by the observations and identifications of Elvey, Swings and Linke.\(^4\) It is suggested here that this system of bands is excited from the metastable \( N_2 (A \: ^3\Sigma) \) by the metastable \( N (^2D), N (^2P) \) and \( O (^3S) \) by the processes \( Q_{10}', Q_{9}', Q_{7}' \) respectively. While \( N (^2P) \) and \( O (^1S) \) can excite the vibrational levels \( v' = 6 \) and \( 9 \) respectively, \( N (^2D) \) excites \( v' = 0 \) with almost exact resonance (energy discrepancy \( \approx 1/400 \) of a volt). This may account for the enhancement of the bands \( 3378 (0 \rightarrow 19), \ 3834 (0 \rightarrow 21), \ 4420 (0 \rightarrow 23) \). The possible appearance of bands from \( v' = 10 \) or higher may arise from excitations by \( O (^1S) \) of \( N_2 (A \: ^3\Sigma) \) initially in the vibrational levels \( v = 1, 2 \) or \( 3 \). That this is possible is seen from the foregoing discussion of the persistence of vibrational excitation.

The equation for the rate of change of \( [N_2 a \: ^1\Pi] \) is

\[
d [N_2 a \: ^1\Pi] \frac{dt}{dt} = \{Q_{7}' [O \: ^1S] + Q_{9}' [N \: ^2P] + Q_{10}' [N \: ^2D] \} [N_2 A \: ^3\Sigma] - A_{LBH}[N_2 a \: ^1\Pi] = 0. \tag{16}
\]

Again no quenching collisions need be considered here.

(I) Atmospheric bands of \( O_2 \): \( O_2 (A \: ^3\Sigma) \rightarrow O_1 (X \: ^3\Sigma) \)

If the existence of the "A", "B", "a", "a'", "a"" bands of \( O_2 \) corresponding to the transitions \( 0 \rightarrow 0, 1 \rightarrow 0, 2 \rightarrow 0, 3 \rightarrow 0, 4 \rightarrow 0 \) respectively in the night sky is established, then a mechanism for the excitation of the first three is provided by the process \( Q_{16} \) and one for the last two by \( Q_{17} \). These processes are responsible for the partial quenching of the "nebular" lines in \([OI]\) and \([NI]\) respectively.

(J) Schumann-Runge bands of \( O_2 \): \( O_2 (B \: ^3\Sigma) \rightarrow O_2 (X \: ^3\Sigma) \)

The observations of Dufay, Gauzit, Elvey, Swings and Linke suggest very strongly the presence of the Schumann-Runge bands in the night sky, especially those from the levels \( v' = 0 \) and \( 1 \). A mechanism for the excitation of these bands is provided by the process \( Q_{11} \) whose cross-section may not be small since the energy discrepancy for excitation of \( v' = 0 \) is only \( 1/20 \) of a volt.

(K) Na lines: \( ^2S \rightarrow ^2P \)

The yellow lines of sodium have been observed in the night sky and various aspects of the problem concerning it have been discussed by a number of authors. Chapman suggested the process \( Q_{22} \) for the excitation mechanism and accounted for the energy deficiency of 0.14 volt by means
of the kinetic energy of the particles.\textsuperscript{29} The fraction, however, of atoms having this kinetic energy is very small unless the temperature of the atmosphere has a value above 1000° K., for which there does not seem to be very strong evidence (see foot-note 30 below). On the other hand, the process $Q_{20}$ is energetically more probable, and on account of the smaller transition probabilities $A (^2D \rightarrow ^4S)$ than those for the red [OI] lines, the concentration of $N (^2D)$ may be greater than that of $O (^1D)$. The process $Q_{21}$ has an even higher cross-section since the resonance is closer and the spin rule is satisfied. This may make up for the low concentration of $O (^1S)$ and has to be taken into account in assessing the relative importance of the various processes for the excitation of the Na lines. More information concerning the variations of the intensity of the Na lines with time and altitude is necessary for a proper understanding of the problem of atmospheric sodium.

\textit{(L) Water vapour bands}

According to Cabannes, the water vapour bands at 0·59 $\mu$, 0·65 $\mu$, 0·698 $\mu$, 0·72 $\mu$ corresponding to $4 v_1 + v_3$, $3 v_1 + v_2 + v_3$, $v_1 + 3 v_3$, $3 v_1 + v_3$ respectively are present in the spectrum of the night sky, and possibly also in the aurora.\textsuperscript{8} These bands, if their existence is established, are interesting in that they differ from all the other radiations in being pure vibration-rotational bands. The most effective modes of excitation would be a collision of the first kind with another atom or molecule, or a collision of the second kind with a molecule in a vibrationally excited state. The probability of the first collision is extremely small, and the fraction of particles having a kinetic energy of the order of 1 volt must be exceedingly small. On the other hand, molecules in highly vibrationally excited states [such as $v = 13, 14, 15$ in $N_2 (X 1\Sigma)$ as the result of the Vegard-Kaplan transitions] may be fairly abundant, and it is possible that these molecules are responsible for the excitation of the water vapour bands by a resonance process.

The existence of these high combination, and hence weak, water vapour bands in the night sky would indicate appreciable concentration of water vapour in the upper atmosphere. As water vapour plays the most important part in the problem of radiative equilibrium of the earth's atmosphere, it would be desirable to have some measurements of the absolute intensities

\textsuperscript{29} S. Chapman, \textit{Astrophys. Jour.}, 1939, 90, 309. The mechanism $NaO + O \rightarrow Na + O_2$ suggested there for the maintenance of free Na atoms in the presence of oxygen has to be considered not only from the point of view of energies, but also together with the fact that the process involves an activation energy approximately equal to the dissociation energy of NaO. At the temperature of the upper atmosphere, such a process will be exceedingly improbable.
and some theoretical estimates of the transition probabilities of these bands so that one may estimate the concentration of water vapour, and hence the temperature, of the upper atmosphere.\footnote{30}

\textit{(M) Other radiations}

It seems to be generally agreed that in the spectra of the night sky and the aurora, there are no atomic lines other than the lines of [OI] and possibly the $^2\text{D} \rightarrow ^2\text{S}$ of [NI].\footnote{31} The absence of the atomic lines of N, O as well as H and other rare gases is now understandable since the energies available for excitation in the metastable atoms and molecules of nitrogen and oxygen do not exceed 6\,1 volts. In fact, the strong point of the proposed mechanisms here is that they provide a reasonable process for each of the radiations observed and at the same time allow satisfactorily for the absence of others that are not observed.

Concerning the possible presence of bands from such molecules as NO, NH, CH and CN, the observational material is still too meagre to warrant any discussion. In any case, the bands, if they are definitely confirmed, are so weak and so scanty that these molecules must be very rare in the upper atmosphere. The absence or scarcity of NO alone perhaps

\footnote{30} It seems that no accurate knowledge concerning the temperature of the upper atmosphere of the earth is available. Vegard (quoted in Rosseland's \textit{Theoretical Astrophysics}, Oxford Univ. Press, 1936, pp. 234-37) has estimated the temperature of the aurora from the intensity distribution in the unresolved 4278 A. band of $\text{N}_2^+$ and found a value 70° C. This can only be a rough estimate on account of the low dispersion of the spectrum. [The formula on p. 234 for the intensity of a rotational line in a band, namely, $I (j \rightarrow j + 1) \propto (2j + 1) \exp. (- E_j/kT)$, is slightly in error as it does not take into account the factor depending on the transition probability of the line. The correct expression is $(j + 1) \exp. (- E_j/kT)$. More recently, from the $R$ branch of the 4278 band, Vegard and Tonsberg, \textit{Geofys. Pub.}, 1938, 12, 3, obtain a temperature of $- 35° C$. In any case, the temperature so determined will represent the temperature of the atmosphere only if the excitation process does not greatly change the distribution in the rotational states, for example, if the bands are excited by electron impact. On the other hand, if the bands are excited by collisions of the second kind with heavy particles, the temperature parameter determined from the intensity distribution in a band may differ from the thermal temperature in a way depending on the probability of energy transfer to and from the rotational motion in such collisions.

On the basis of the theory of intensities of electronic transitions and the intensity distribution in the negative bands of $\text{N}_2^+$ and the positive bands of $\text{N}_2$, Rosseland and Steensholt (quoted in Rosseland's book, p. 244) have also calculated the temperature of the aurora and found values of the order 2000°-3000° K. As emphasized by Rosseland, these values must not be taken to mean the temperature of the atmosphere since the bands are assumed to have been excited by swift particles not in thermal equilibrium with the atmosphere. On our view here, the bands are excited by collisions of the second kind. The intensity distribution in a band system depends then only on the resonance mechanism and has nothing to do with the temperature of the atmosphere at all.

\footnote{31} For the aurora spectrum, M. Nicolet, \textit{Ann. d'Astrophys.}, 1938, 1, 381; for the night sky, Elvey, Swings and Linke, \textit{Astrophys. J.}, 1941, 93, 337.
Excitation Processes in the Night Sky and the Aurora

needs some consideration, in view of the abundance of the N and O atoms. This is probably because of the fact that the layers of maximum dissociation of the nitrogen and the oxygen molecules, and hence the layers of maximum concentration of the N and O atoms, are different. Thus while a concentration of O atoms of $10^{10}$/c.c. will lead to a recombination into O$_2$ at a rate of $10^4$/sec. c.c., the presence of N atoms at the same layer with a concentration $10^6$/c.c. will lead to the formation of only 1 NO per sec. per c.c.

**Concluding Remarks**

To sum up, then, it is seen from the present theory that the various emission processes take place at the expense of the energies of excitation of the metastable atoms and molecules of N and O, and these metastable atoms and molecules are constantly replenished by the recombinations of the atoms generated by photo-dissociation during the day. It is interesting to note that the various processes do not all proceed in one direction alone, with a consequent rapid depletion of the metastable atoms or molecules. Rather many of these processes form cycles so that continual excitation and emission of the various radiations are possible. The overall result of all the processes is, of course, the recombinations of the atoms into molecules. For example, from equations (12), (13), (15), (16) and the following ones

$$
\frac{d}{dt} [N^4S] = \{Q_6'' [N_2A ^3Σ] + (Q_6 + Q_9') [N^2P] + (Q_{10} + Q_{10'}) [N^2D] \} [N_2A ^3Σ] + \{Q_{17} [O_2X ^3Σ] + Q_{18} [O^3P] + Q_{18} (O^3D) + A (3D→4S) \} [N^2D] + Q_{14} [N_2X ^2Σ] [N^2P] - 2 (Q_1 [X] + Q_a) [N^4S]^2,
$$

$$
\frac{d}{dt} [N_2X ^1Σ] = \{(Q_6 + Q_6' + Q_6'') [N_2A ^3Σ] + Q_{13} [N_2X ^2Σ] + A_{v, x} \} [N_2A ^3Σ] + A_{LBH} [N_2a ^1Π],
$$

we have, as we expect,

$$
\frac{d}{dt} \{[N^4S] + [N ^3D] + [N ^3P] + 2 [N_2X ^1Σ] + 2 [N_2A ^3Σ] \} = 0.
$$

As $\frac{d}{dt} [N_2X ^3Σ]$ must be positive since in the absence of sunlight no collision process can lift the N$_2$ molecule from the normal state or dissociate it, and as $\frac{d}{dt} [N_2A ^3Σ]$ must be $\leq 0$ in the steady (or very slowly varying) state during the night when the intensity of the Vegard-Kaplan bands does not vary greatly, it follows that

$$
\frac{d}{dt} \{[N^4S] + [N ^3D] + [N ^3P] \} < 0,
$$

i.e., the net result of the various processes is a steady decrease in the concentrations of the atoms. Entirely similar result holds for the processes
FIG. 1. Energy levels involved in the collisional excitations and radiative transitions in the night sky and the aurora.
involving the oxygen atoms and molecules. The O atoms disappear either through the radiative processes of the type $Q_4$ or through three-body processes of the type $Q_2$, followed by processes $Q_5$, $Q_{12}$ and others, ending eventually in the normal state $O_2(X^2Σ)$. The various processes and their interrelations are rendered clear by the diagrams in Figs. 1 and 2.

Finally we need only add that the rates of the various processes of excitation and radiation depend either directly or indirectly on the rates of supply of the metastable $N_2(A^3Σ)$ and $O_2(C^3Σ)$ molecules, which in turn depend on the rates of recombination of the atoms. As these recombinations are the bottle-neck of the various processes, we need only consider them in order to see if the supply of atoms at sunset will last through the
night. That they will last is seen from our estimate of the rate of recombination of the O atoms in connection with the discussion of the green [OI] line.

Summary

It is shown that the main features in the selective emission spectra of the night sky and the aurora, namely, the forbidden [OI] lines, the various systems of bands of N$_2^+$ and N$_3$ and O$_2$, and in particular, the enhancement of certain lines and bands relative to others and the diurnal variations of the intensity of certain lines in the night sky, can be satisfactorily explained on the view that all the excitation and quenching processes in the upper atmosphere are collisions of the second kind, of the resonance type, between the metastable atoms and molecules of nitrogen and oxygen. The metastable atoms are generated in the night by collisions between the metastable molecules; the latter are in turn formed by the recombinations of the normal atoms which are produced by photo-dissociation of the molecules during the day. A strong argument for the theory is that, not only the observed radiations are provided with reasonable excitation processes, but the absence of other atomic lines N, O, H and the rare gases is automatically accounted for by the maximum energy available for the excitations in these metastables, which is only 6.1 volts (the energy of N$_2$ [A $^3Σ$]). It is suggested that these processes in Table II are the microscopic processes responsible for the observed spectra, while such large-scale features as the shapes of the aurorae and seasonal variations in the intensities, etc., may have to be explained by further hypotheses.