

Role of Ozone in the Sodium and Hydroxyl Nightglow

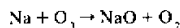
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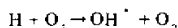
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ABSTRACT

One-dimensional photochemical diffusion model which includes oxygen-hydrogen-sodium atmosphere has been used to examine the relation between sodium and hydroxyl nightglow and the role of ozone in it. It is found that both emissions can be obtained on the basis of photochemistry. The following reactions



and



play key role in sodium and hydroxyl emission respectively. Further it is found that variations in both emissions are controlled by the variation in the concentration of ozone.

I. INTRODUCTION

In the last four decades many studies have been carried out to examine the sodium airglow (Chapman, 1939; Bates and Nicolette, 1952; Chamberlain, 1956; Hunter, 1967; Mitra, 1974; Simovich et al., 1979; Kirchoff, et al., 1981; etc.) and hydroxyl airglow (Bates, 1954; Balif and Venkateshwaramn, 1963; Hunt, 1971; Evans and Llewellyn, 1972; Morrels and Magie, 1977; Jones et al., 1985 etc.). Their studies concluded that photochemical reactions are the main source of energy for the nighttime excitation of both sodium and hydroxyl radicals. Present study is some sort of simultaneous study of Na' and OH* nightglows with help of one-dimensional photochemical diffusion model and mainly to study the role of ozone in the photochemistry of these airglows.

II. MODEL

Oxygen-Hydrogen-Sodium atmosphere is considered for the study of Na' and OH* nightglow. Important photochemical reactions concerning these two emissions are presented in Table 1. The general form of one-dimensional photochemical diffusive model used for this study is as follows:

$$\frac{\partial Y_i}{\partial t} = P_i - Q_i \cdot Y_i - \frac{\partial}{\partial z} \left\{ \left[Y_i \right] \left[\frac{1}{Y_i} \right] \cdot \frac{\partial Y_i}{\partial z} + \frac{1}{T} \frac{\partial T}{\partial z} (K + E) + \left(\frac{K}{H_a} + \frac{E}{H_i} \right) \right\}, \quad (1)$$

where

Y_i —Concentration of *i*th constituent;

P_i —Photochemical Production of *i*th constituent;

Q_i —Photochemical Loss of *i*th constituent;

T —Atmospheric temperature;

K & E —Eddy and molecular diffusion coefficient respectively;

H_a & H_i —Scale heights of atmosphere and i th constituent respectively.

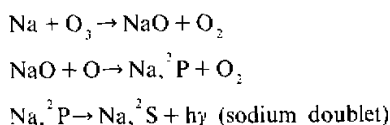
This model incorporates 17 constituents viz. O_3 , O_2 , $O_2(^1\Delta_g)$, $O(^3P)$, $O(^1D)$, $O(^1S)$, OH , OH^* , HO_2 , H_2O , H , H_2 , H_2O_2 , $Na(^2P)$, NaO , NaH , NaO_2 . This major input parameters to this model are solar fluxes, absorption cross sections, reaction rate coefficients, eddy and molecular diffusion coefficients. The details of computational technique, boundary and initial conditions and data used is same as our previous paper (Hingane, 1984).

III. RESULTS

The results obtained from the above model are presented as follow:

1. Sodium D-line Emission

Chapman (1939) has defined chemistry of sodium nightglow in a simple way as: Sodium oxide is produced through the oxidation of ground state sodium ($Na, ^2S_1$) by O_3 and then this oxide gives rise to excited sodium in 2P state by reduction with atomic oxygen. Excited sodium ($Na, ^2P$) while coming to ground state emits D-lines at wavelength 5890 and 5896 which is known as sodium doublet. This can be summerized as :



There are also other mechanisms which give excited sodium. However, in the preliminary calculation it is found that they are not playing dominating role. In the above Chapman mechanism, sodium oxide is found to play central role towards the emission of sodium D-lines in nightglows. Therefore, its formation and destruction processes are examined critically .

(1) Sodium oxide

Computation of reaction rate at different altitude shows that in the production of NaO,

$$K_{54}[NaO_2][O] > K_{51}[Na][O][M] \quad (2)$$

and it is further noted that

$$K_{51}[Na][O_3] > K_{54}[NaO_2][O] + K_{53}[Na][O][M], \quad (3)$$

when $h > 78$ km

therefore reaction R_{51} i.e. Chapman reaction completely predominate above 78 km and is a major one even below this height. Similarly in the loss reaction it is found that three body reaction i.e. R_{56} is unimportant at all the altitudes of interest. It is also seen that

$$K_{52}[O] > K_{57}[O_3] \quad \text{— When } h > 80 \text{ km} \quad (4)$$

and $K_{52}[O] < K_{57}[O_3]$ — When $h < 75$ km. (5)

These two inequalities result due to rapid decrease of atomic oxygen during night below 80

km. For the sake of simplicity of understanding, the concentration of NaO obtained from steady state model is presented in Fig.1. Other compounds of sodium like NaO₂ and NaH are found relatively insignificant as compared with NaO for the emission of sodium doublet.

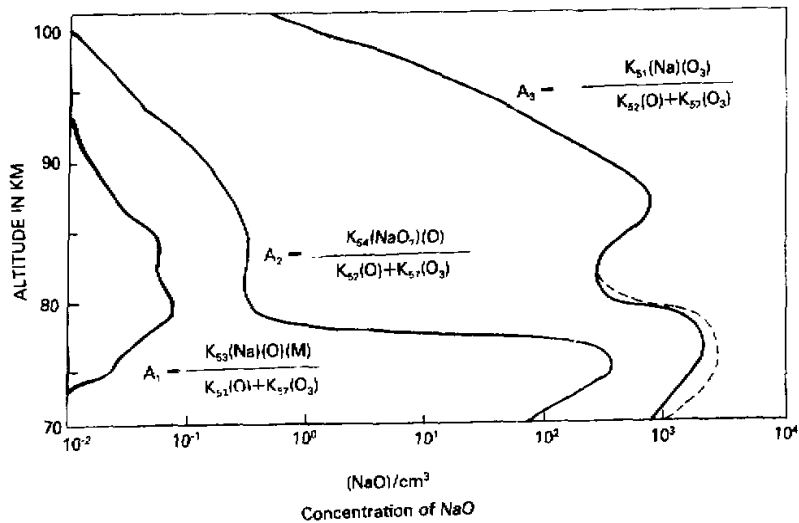


Fig.1. Concentration of sodium oxide resulting through different production processes (Dotted curve represents total concentration).

(2) Production rate of excited sodium (Na, ²P) and total intensity of emission

From Table 1, it can be seen that reactions R₅₂, R₆₀, R₆₁, and R₆₂ are to give rise to the excited sodium. These excitation mechanisms are respectively suggested by Chapman (1939), Battes and Nicolet (1950), Bates (1954) and Shrivastava and Shukla (1970). The production rate of Na(²P) based upon these reaction is

$$\frac{d}{dt}(\text{Na}, ^2\text{P}) = K_{52}[\text{NaO}][\text{O}] + K_{60}[\text{NaH}][\text{O}] + K_{61}[\text{NaH}][\text{H}] + K_{62}[\text{NaH}][\text{OH}] \tag{6}$$

The contribution of each reaction to the total production rate of excited sodium is presented in Fig.2. It can easily be seen that first term on the right hand side of above Eq.(6), outweighs all the other terms at all heights, therefore production rate of (Na, ²P) can simply be written as

$$\frac{d}{dt}(\text{Na}, ^2\text{P}) = K_{52}[\text{NaO}][\text{O}]. \tag{7}$$

Then the total intensity of sodium nightglow have been computed using the standard formula as

$$I_{Na} = 10^{-6} \cdot q \int_{h_1}^{h_2} K_{52} [NaO][O] dh, \tag{8}$$

where q is the quantum efficiency and is taken equal to unity. h_1 and h_2 are the lower and upper limits which we have taken at 60 and 100 km respectively. This equation gives value of total intensity of sodium D-lines about 45 R which is comparable with the observed value of 87 R (Chiplonkar and Tillu, 1967).

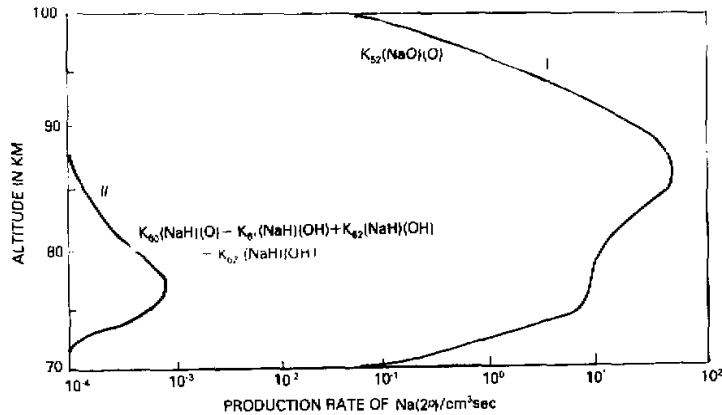


Fig.2. Production rate of $(Na,^2P)$ due to different processes.

2. Hydroxyl Night Airglow

Hydroxyl bands are the most intense emission in the D region of the atmosphere. It is extensively studied experimentally as well as theoretically and is generally accepted that reaction of hydrogen with ozone is the major source of hydroxyl emission. Hydroxyl radical gets excited upto the 9th vibrational level through $H-O_3$ mechanism. The production rate due to $H_2O + O \rightarrow OH^*$ ($v < 5$) is quite negligible and hence the rate of production of OH^* is taken as

$$\frac{d}{dt} (OH^*) = K_{20} [H][O_3]. \tag{9}$$

The production rate of OH^* with altitude is shown in Fig.3. From this the total intensity of emission is obtained as

$$I_{OH} = 10^{-6} \cdot q \int_{h_1}^{h_2} K_{20} [H][O_3] dh, \tag{10}$$

where q is assigned for the number of emitted quanta in $H-O_3$ reaction which is taken equal to 4.8 photons / reaction (see Evans and Llewellyn, 1972). Lower and upper limit of integration (i.e. h_1 and h_2) is the same as used in Eq. (8). It gives total intensity of emission at midnight equal to 6.5 MR, which is comparable with observed values. The peak emission appears at about 85 km. Total value of intensity and altitude of appearance of peak is comparable with that of experimental one.

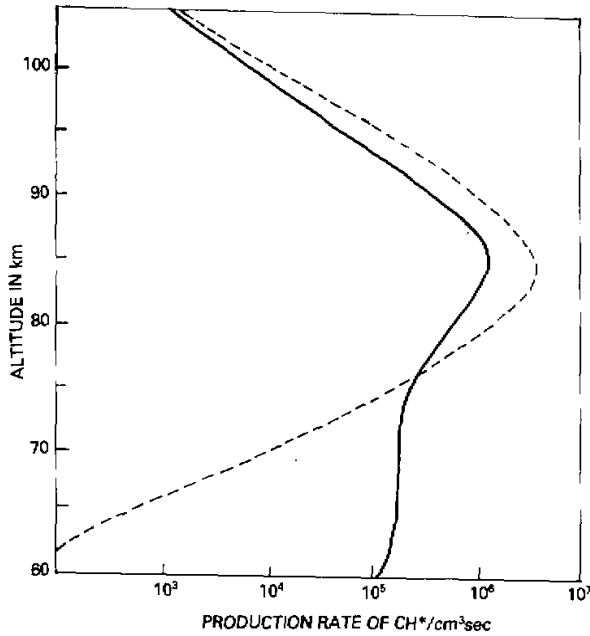


Fig.3. Production rate of OH^* (Dotted curve is midnight value and continuous curve is presunset value).

IV. DISCUSSION

In the preceding section, production rate of excited sodium is obtained in Eq. (7) as

$$P_1 = K_{52}[\text{NaO}][\text{O}],$$

assuming steady and static state; density of NaO can be estimated as follows:

$$[\text{NaO}] = \frac{K_{51}[\text{NaO}][\text{O}_3]}{K_{52}[\text{O}] + K_{57}[\text{O}_3]} \quad (11)$$

Second term in the denominator of Eq. (11) can be neglected safely because it does not play any significant role except around 75 km altitude whereas maximum production rate of $(\text{Na}, {}^2\text{P})$ is around 85 km. Hence equation(11) can be written as

$$[\text{NaO}] = \frac{K_{51}[\text{Na}][\text{O}_3]}{K_{52}[\text{O}]} \quad (12)$$

Substituting Eq.(12) into Eq. (7) we get production rate of $\text{Na}({}^2\text{P})$ as:

$$\frac{d(\text{Na}, {}^2\text{P})}{dt} = K_{51}[\text{Na}][\text{O}_3]. \quad (13)$$

Therefore total intensity can be obtained as

$$I = 10^{-6} \cdot q \int_{h_1}^{h_2} K_{51}[\text{Na}][\text{O}_3] dh. \quad (14)$$

It can be seen from Eq.(14) that temporal variation of sodium D-lines emission depends up on the temporal variables of ozone and ground state sodium ($\text{Na}, ^2\text{S}$). The sodium and its compounds in the upper atmosphere are trace constituents and hence the effect of their variation on the other constituents of oxygen-hydrogen atmosphere are not significant. On the contrary, small change in concentration of O-H constituents, for example in ozone, makes a large difference in the variation of sodium and its compounds. In Eq. (14), K_{s1} is constant and the concentration of ground state sodium also remains almost constant throughout the night. It is thus clear that the rate of change of sodium emission is associated with the rate of change of ozone concentration during night, i.e. nocturnal variation of sodium D-lines emission follows the ozone variation. Fig.4 depicts this relation.

Further the second but very small peak of O_3 and peak emission of sodium appears at about 85 km altitude and the qualitative shapes of altitude variation are also in good agreement in that limited region.

Similarly it can be shown that temporal variation of hydroxyl nightglow depends mostly on that of O_3 .

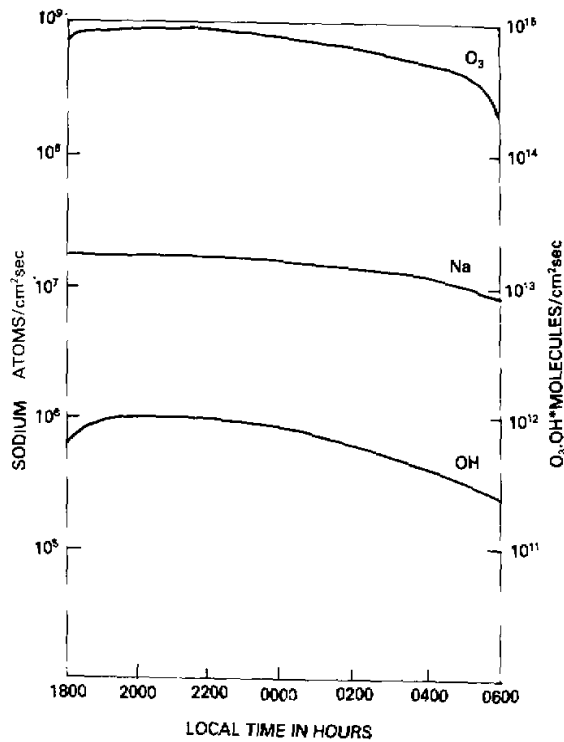


Fig.4. Nocturnal variation of Na^2P , OH^1 and O_3 .

V. CONCLUSION

One dimensional photochemical diffusive model is used to understand the relation between sodium and hydroxyl nightglow and hence the role of ozone in these airglows. From the above study the following conclusion can be drawn.

1. Both emissions can be obtained on the basis of photochemistry.
2. Maximum emission of both nightglow appears around 85 km where second but small peak of O_3 also appears.
3. Intensity of sodium and hydroxyl emission decreases gradually throughout the night. Nocturnal and altitude variation of both these emissions follow the variation of O_3 concentration faithfully.
4. During night, the ratios of I_{\max} / I_{\min} are expected to be 2.5 for Na' and 3.7 for OH' whereas that of $O_3(\max) / O_3(\min)$ is 2.9.

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Table 1 (a). Chemical Reactions Incorporated in the Present Model

No.	Reactions	Rate Coefficient
R ₁	O+O+M → O ₂ +M	$K_1 = (2.87 \pm 0.3) \times 10^{-14} \exp(710 \pm 175 / T)$
R ₂	O+O ₂ +M → O ₃ +M	$K_{2a} = 1.0 \times 10^{-34} \exp(104 / RT)$ $K_{2b} = 1.1 \times 10^{-34} \exp(500 / T)$ (for stratosphere)
R ₃	O+O ₃ → 2O ₂	$K_3 = 1.3 \times 10^{-11} \exp(-2200 / T)$
R ₄	O+O+O → O ¹ S+O ₂	$K_4 = 4.8 \times 10^{-11}$
R ₅	O(¹ S) _r → O(¹ D)+hν	$K_5 = 1.4 \times 10^0$
R ₆	O(¹ S)+O ₂ → O+O ₂	$K_6 = 4.9 \times 10^{-2} \exp(-850 \pm 100)$
R ₇	O(¹ D)+M → O+M	$K_7 = 5 \times 10^{-11}$
R ₈	O(¹ D) _r → O+hν	$K_8 = 1 \times 10^{-2}$
R ₉	O(¹ D)+O ₂ → O ₂ +O	$K_9 = 5 \times 10^{-11}$
R ₁₀	O ₂ (¹ Δ _g)+O ₁ → 2O ₂ +O	$K_{10} = 2.5 \times 10^{-7}$
R ₁₁	O ₂ (¹ Δ _g) _r → O ₂ +hν	$K_{11} = 8.5 \times 10^{-2}$
R ₁₂	O ₂ (¹ Δ _g) → O ₂ +hν	$K_{12} = 2.8 \times 10^{-4}$
R ₁₃	(¹ Δ _g)+M → O ₂ +M	$K_{13} = 10^{-20}$
R ₁₄	O ₂ (¹ Δ _g)+O ₁ → 2O ₂ +O	$K_{14} = 3.2 \times 10^{-15}$
R ₁₅	O ₂ (¹ D)+O → O ₂ +O	$K_{15} = 3 \times 10^{-11}$
R ₁₆	O(¹ D)+H ₂ O → 2OH	$K_{16} = 3 \times 10^{-11}$
R ₁₇	O(¹ S)+H ₂ O → 2OH	$K_{17} = 7 \pm 3.5 \times 10^{-11}$
R ₁₈	O ₂ (¹ Δ _g)+O ₂ → 2O ₂	$K_{18} = 2.2 \times 10^{-18}$
R ₁₉	O(¹ S)+O(¹ P) → 2O	$K_{19} = 7.5 \times 10^{-12}$
R ₂₀	H+O ₃ → OH+O ₂	$K_{20} = 1.5 \times 10^{-11} \exp(-200 / T)$
R ₂₁	OH+O → H+O ₂	$K_{21} = 5.0 \times 10^{-11}$
R ₂₂	HO ₂ +O → OH+O ₂	$K_{22} = 3 \times 10^{-12} (T)^{-2}$
R ₂₃	H+O ₂ +M → HO ₂ +M	$K_{23} = 1.9 \times 10^{-12} \exp(236 / T)$
R ₂₄	OH+O ₂ → HO ₂ +O ₂	$K_{24} = 1.3 \times 10^{-12} \exp(-950 / T)$
R ₂₅	HO ₂ +O ₁ → OH+2O ₂	$K_{25} = 3.3 \times 10^{-14} \exp(-1000 / T)$
R ₂₆	OH+OH → H ₂ O+O	$K_{26} = 1 \times 10^{-11} \exp(-550 / T)$
R ₂₇	HO ₂ +HO ₂ → H ₂ O+O	$K_{27} = \exp(-500 / T)$
R ₂₈	H+H+M → H ₂ +M	$K_{28} = 2 \times 10^{-12} \times (273 / T)^{0.81}$
R _{29a}	H+HO ₂ → H ₂ +O ₂	$K_{29a} = 1 \times 10^{-11}$
R _{29b}	H+HO ₂ → 2OH+O ₂	$K_{29b} = 2.8 \times 10^{-10} \exp(1000 / T)$
R ₃₀	H+OH → H ₂ O	$K_{30} = 1.4 \times 10^{-14} \times T \cdot \exp(-3500 / T)$
R ₃₁	OH+H ₂ O ₂ → H ₂ O+HO ₂	$K_{31} = 4 \times 10^{-12} \exp(-600 / T)$
R ₃₂	H ₂ O ₂ +O → H ₂ O+O ₂	$K_{32} = 1.5 \times 10^{-13} \exp(-3000 / T)$
R ₃₃	OH+HO ₂ → H ₂ O+O ₂	$K_{33} = 2 \times 10^{-10}$
R ₃₄	H+H ₂ O ₂ → H ₂ +HO ₂	$K_{34} = 1 \times 10^{-11}$
R ₃₅	H ₂ +O(¹ D) → H+OH	$K_{35} = 2.1 \times 10^{-11} \exp(-9400 / RT)$
R ₃₆	H ₂ +O(¹ D) → H+OH	$K_{36} = 1.9 \times 10^{-10}$
R ₃₇	H ₂ +OH → H+H ₂ O	$K_{37} = 6.8 \times 10^{-14} \exp(-650 / T) 50T300K$

Continue Table I(a).

No.	Reactions	Rate Coefficient
R ₃₈	OH+OH+M → H ₂ O ₂ +M	K ₃₈ = 3 × 10 ⁻³⁰
R ₃₉	H+OH+M → H ₂ O+M	K ₃₉ = 6.1 × 10 ⁻²⁶ T ⁻²
R ₄₀	OH' → OH+hγ	K ₄₀ = 15.2
R ₄₁	OH' + O ₂ → OH+O ₂	K ₄₁ = 1.0 × 10 ⁻¹⁴
R ₄₂	H+O ₂ → OH' + O	K ₄₂ = 4.25 × 10 ⁻¹²
R ₄₃	OH' + OH' → H ₂ O+O	K ₄₃ = 3 × 10 ⁻¹¹
R ₄₄	O(¹ D)+O ₁ → 2O ₂	K ₄₄ = 10 ⁻¹¹
R ₄₅	O(¹ S)+O → O+O	K ₄₅ = 7.5 × 10 ⁻¹²
R ₄₆	H+OH+M → HO ₂ +M	K ₄₆ = 1.4 × 10 ⁻⁵
R ₄₇	H+O+M → OH+M	K ₄₇ = 8 × 10 ⁻¹³
R ₄₈	OH+O ₂ → HO ₂ +O ₂	K ₄₈ = 6.8 × 10 ⁻¹⁴
R ₄₉	OH' + N ₂ → OH+N ₂	K ₄₉ = 3.6 × 10 ⁻¹⁵
R ₅₀	OH+O(¹ S) → 2OH	K ₅₀ = (71 ± 3.5) × 10 ⁻¹¹
R ₅₁	Na+O ₃ → NaO+O ₂	K ₅₁ = 3.0 × 10 ⁻¹¹
R ₅₂	NaO+O → Na(² P)+O ₂	K ₅₂ = 2 × 10 ⁻¹²
R ₅₃	Na+O+M → NaO+M	K ₅₃ = 7 × 10 ⁻¹³
R ₅₄	NaO ₂ +O → NaO+O ₂	K ₅₄ = 9.3 × 10 ⁻¹²
R ₅₅	Na+O ₂ +M → NaO ₂ +M	K ₅₅ = 2 × 10 ⁻¹³
R ₅₆	NaO+O+M → NaO ₂ +M	K ₅₆ = 8 × 10 ⁻³⁰
R ₅₇	NaO+O ₂ → Na+2O ₂	K ₅₇ = 3 × 10 ⁻¹²
R ₅₈	NaO ₂ +H → NaH+O ₂	K ₅₈ = 3 × 10 ⁻¹²
R ₅₉	Na+H+M → NaH+M	K ₅₉ = 4.0 × 10 ⁻³²
R ₆₀	NaH+H → Na(² P)+H ₂	K ₆₀ = 4.5 × 10 ⁻¹⁷
R ₆₁	NaH+O → Na(² P)+OH	K ₆₁ = 1.7 × 10 ⁻⁸
R ₆₂	NaH+OH → Na(² P)+H ₂ O	K ₆₂ = 2.1 × 10 ⁻¹⁶

Note: i) for three-body mechanism units are cm⁻⁶s⁻¹ . ii) for two-body mechanism units are cm⁻³s⁻¹ .

Table I(b). Photodissociation Processes

J ₁	O ₂ + hγ → O(¹ D) + O(¹ P)	(1351 < λ < 1754)
J ₂	O ₂ + hγ → O(³ P) + O(¹ P)	(1750 < λ < 2431)
J ₃	O ₃ + hγ → O(¹ D) + O ₂ (¹ Δ _g)	(1980 < λ < 2560)
J ₄	O ₃ + hγ → O(³ D) + O ₂ (¹ Δ _g)	(2560 < λ < 3125)
J ₅	H ₂ O + hγ → OH + H	(1Lym < λ < 2857)
J ₆	H ₂ O ₂ + hγ → OH + OH	(1887 < λ < 2857)
J ₇	HO ₂ + hγ → OH + O(³ P)	(1887 < λ < 2857)

