Depletion of ozone and its effect on night airglow intensity of Na 5893 Å at Srinagar and Halley Bay

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The paper presents the effect of O₃ depletion on night airglow emission of Na 5893 Å line at Srinagar (34°N, 74.8°E), India and Halley Bay (76°S, 27°W), a British Antarctic survey station. Calculations based on chemical kinetics reveal that the airglow intensity of Na 5893 Å line is also affected due to ozone decline. The nature of yearly and seasonal variation of intensity of Na 5893 Å line for the above two stations are shown and compared. It is shown that the rate of decrease of yearly intensity of Na 5893 Å line is comparatively more at Halley Bay due to dramatic decrease of Antarctic O₃ concentration. During Antarctic spring time, stratospheric ozone is depleted dramatically at Antarctic region because of very low temperature (−80°C), elevated concentration of atomic chlorine and chlorine oxides, low abundances of nitrogen oxides and large appearance of polar stratospheric clouds (PSCs).

Keywords: Ozone depletion, Airglow emissions, Excitation mechanism, Intensity.

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1 Introduction

In a dark moonless night away from city light, a certain amount of light is observed to come from space. Excluding the light from stars, zodical belt, galaxy and that scattered by atmospheric particles, the remaining light of about 40% is produced by the self luminescence of atmospheric atoms and molecules and it is called airglow¹. There are three types of airglow – day, twilight and night airglow. During daytime atmospheric atoms, molecules and ions are excited by absorbing solar energy. Afterwards, they come down to the ground state and emit energy in the form of light which is called day airglow. During twilight, ions, atoms and molecules are partly excited by absorbing solar energy and partly by different collisional processes. But at nighttime, only collisional processes are responsible. There are several airglow emission lines, e.g. oxygen airglow (O 5577 Å, O 6300 Å); hydroxyl airglow [OH (9,4), (8,3),(6,2),(5,1)]; lithium airglow and sodium airglow lines.

Ozone, though a very minor atmospheric constituent, plays an important role to control the chemical kinetics of troposphere, stratosphere and mesosphere. The global ozone assessment confirms that ozone is declining everywhere with smaller amount². But Farman et al.³ first reported that dramatic decrease of ozone concentration takes place at Antarctica during spring time causing an ozone hole. Conventionally it is assumed that there is an ozone hole when the ozone abundance is ≤ 220 Dobson units (DU) (1DU=0.001 atm cm) in a specific geographic place⁴. The 1997 monthly averaged column ozone from the total ozone mapping spectrometer (TOMS) is up to 25 DU lower than the TOMS climatological mean (1979-1996) and up to 20 DU below the previous record low values⁵. Kerr⁶ reported that the 1998 Antarctic ozone hole is the biggest one ever observed. Average area of ozone hole was 25.3 ×10⁶ km² in September and 20.6 × 10⁶ km² in October 1998. The area of Antarctic ozone hole (area of O₃ < 220 DU) increased steadily from 1979 to 1998 and the 2000 ozone hole was the largest on record⁶. Averaged area of the Antarctic ozone hole, determined by the area enclosed by the 220 DU total ozone contour, increased⁹ from 2.6×10⁶ km² to 25.8×10⁶ km² for the month of September and from 2.7×10⁶ km² to 16.7×10⁶ km² for the month of October, during 1982-2003. Several theories have been proposed for the Antarctic ozone hole. Chemical, dynamical and natural theories are mainly important and are explained in an earlier publication¹⁰. If ozone hole is created at any place in the atmosphere, O₃ concentration also decreases in other regions due to atmospheric diffusion and circulation¹¹.
The excitation mechanism of sodium airglow line indicates that the intensity of Na 5893Å line is affected with the depletion of ozone. From the excitation mechanism of Na 5893 Å, the volume emission rate of Na 5893Å is calculated. From the volume emission rate curve, the intensity of Na 5893Å is calculated. Following this process, the intensity of the same line for the two stations namely, Srinagar (34°N, 74.8°E) and Halley Bay (76°S, 27°W), is calculated for other years, considering the depletion of O₃. The nature of variations of the intensity of Na 5893Å line is compared for the above stations.

Ions, atoms and molecules are not visible to us. From the nature of variation of intensity of airglow emission line which is related to O₃ concentration, one can estimate and identify the variation of number density of different types of ions, atoms and molecules. In this paper, the variation of airglow intensity of Na 5893Å has been calculated for the above stations and compared the nature of variations due to ozone fluctuations. This process may be continued for other stations also.

2 Excitation mechanism
Chapman first discussed the photochemistry of Na. The excitation mechanism is as follows:

\[
\text{NaO}^* + O \rightarrow \text{Na}^*(2^P) + O_2
\]

\[
\text{Na}^*(2^P) \rightarrow \text{Na} (2^S) + h \nu \text{(5893Å)}
\]

where asterisk sign indicates excited state. NaO* may be produced by other way:

\[
\text{Na} + O + M \rightarrow \text{Na}^* + \text{O}_2 + M \quad \ldots (1)
\]

\[
\text{Na} + \text{O}_2 + M \rightarrow \text{Na}^* + \text{O}_2 + M \quad \ldots (2)
\]

\[
\text{NaO}_2 + O \rightarrow \text{NaO}^* + \text{O}_2 \quad \ldots (3)
\]

\[
\text{Na} + \text{O}_3 \rightarrow \text{NaO}^* + \text{O}_2 \quad \ldots (4)
\]

where, M represents a third body required to carry away excess energy and momentum; \( K_1, K_2, K_3, K_4 \) and \( K_5 \) are the rate co-efficients having numerical values of \( 4 \times 10^{-11} \text{cm}^3\text{s}^{-1}, 7 \times 10^{-33} \text{cm}^6\text{s}^{-1}, 2 \times 10^{-33} \text{cm}^6\text{s}^{-1}, 1 \times 10^{-11} \text{cm}^3\text{s}^{-1} \) and \( 6.56 \times 10^{-12} \text{cm}^3\text{s}^{-1} \), respectively. Ghosh and Midya showed that the volume emission rate of Reaction (4) at 90 km is greater than those of Reactions (1) and (2). Thus, it may be concluded that O₃ plays an important role for the emission of 5893Å line. The volume emission rate of NaO* by Reaction (4) is given by

\[
n (\text{NaO}^*) = K_5 n (\text{Na}) n (\text{O}_3)
\]

Ignoring the quenching terms, the rate of production of Na* is

\[
n(\text{Na}^*) = K_1 n(\text{NaO}^*) \times n(\text{O})
\]

\[
n(\text{Na}^*) = K_1 K_5 n(\text{Na}) n(\text{O}) n(\text{O}_3)
\]

Using the number densities of Na, O and O₃, the volume emission rates of \( n(\text{Na}^*) \) for different altitudes are calculated and shown in Fig. 1(a). Intensity is then calculated from the volume emission rate curve with the help of the following equation:

\[
\text{Intensity} = \frac{1}{2} \times \text{layer thickness} \times \text{peak volume emission rate}
\]

Nighttime \( n(\text{Na}) \) is taken from rader laser data of Gibson and Sandford, \( n(\text{O}_3) \) and \( n(\text{O}) \) are taken from Krassovsky and Jacchia, respectively. The total column ozone (TCO) and number densities from the altitude 16 km to 100 km are measured by total ozone mapping spectrometer (TOMS) and upper atmosphere satellite (UARS) halogen occultation experiment (HALOE), respectively.

3 Calculations and results
The intensity of 5893Å line is calculated with the help of Eq. (6) and it is 161.84 R, which fairly agrees with accepted value. Equation (5) clearly reveals that the volume emission rate of Na is directly proportional to the concentrations of Na, atomic oxygen and ozone. The concentration of ozone in stratosphere varies in considerable amount from month to month as well as from year to year. This variation of ozone may influence the mesospheric altitudinal concentration of ozone. From the recent study on the inter-annual changes of dynamical structure in the lower stratosphere and contemporaneous changes of ozone observed by TOMS, Salby et al. also reported that inter-annual changes of ozone in lower stratosphere is accompanied by coherent changes in the upper stratosphere and mesosphere. Percentage of ozone fluctuation for each year is calculated from the mean of yearly mean concentration of ozone during the period 1979 -1998. The effect of variation of ozone is considered in the calculation of volume emission rate and intensity of Na, assuming that concentrations of Na and atomic oxygen remain constant. Ozone
concentrations at Halley Bay and Srinagar are obtained from the website http://jwocky.gsfc.nasa.gov.

In 1979, the percentages of ozone variation at Srinagar and Halley Bay are found to be 3.77 and 15.04, respectively. Altitudinal concentrations of ozone and consequently the volume emission rates and intensities of Na for the year 1979 also increased at the same rates at Srinagar and Halley Bay, respectively. Global volume emission rates of Na 5893Å at different altitude are calculated by Eq.(5) with the help of measured altitudinal concentrations of Na, O and O₃.

Altitudinal concentrations of O₃ at Srinagar and Halley Bay are calculated from global altitudinal concentration of ozone and found to be elevated by 3.77% and 15.04%, respectively, for the year 1979. Then volume emission rates of Na 5893Å for above stations are calculated with the help of Eq.(5). Table1 shows the number densities of Na, O and O₃, calculated number densities of O₃ and volume emission rates of Na at Srinagar and Halley Bay for different altitudes for the year 1979. The altitudinal variations of volume emission rates of Na 5893Å at Srinagar and Halley Bay are shown in Fig. 1[(b) and (c)]. The nature of variation of volume emission rates of Na 5893Å is similar for Halley Bay, Srinagar and Global due to the similar nature of the altitudinal variation of ozone at the above stations. The intensities of Na 5893Å for the stations Srinagar and Halley Bay are calculated using Eq.(6) for the year 1979 and its values become 167.94 R(Rayleigh) and 186.18 R, respectively.

Following this process, the intensities of 5893Å line for different years are calculated theoretically for
the stations Srinagar and Halley Bay from 1979 to 1998 and are shown in Table 2. The variations of intensities at Srinagar and Halley Bay are shown in Fig. 2[(a) and (b)] for the period 1979 - 1998. The yearly intensity of Na 5893Å is found to decrease continuously at Srinagar and Halley Bay from 1979 to 1998, because the yearly concentration of ozone is continuously decreasing at above stations for the same period. It is clear from Fig.2 that the rate of decrease of intensities of Na 5893 Å line for Srinagar and Halley Bay are 0.3933R and 2.4038R per year, respectively. The excitation mechanism clearly reveals that the volume emission rate of Na* is directly proportional to the concentration of O3. So, intensity of Na 5893Å line will be governed by the concentration of O3. If concentration of O3 decreases, the intensity of Na 5893 Å line will also decrease. Since the rate of decrease of O3 at Srinagar is less than that at Halley Bay, the rate of yearly decrease of Na intensity at Srinagar will be less than that at Halley Bay, which has been shown in the present result. The drastic decrease in intensity at Halley Bay is due to the dramatic decrease of ozone at Halley Bay.

The intensities of Na 5893Å line are calculated theoretically for different months in a year with the

<table>
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<tr>
<th>Year</th>
<th>Mean O3 (DU) at Srinagar</th>
<th>%O3 variation from mean at Srinagar</th>
<th>Mean O3 (DU) at Halley Bay</th>
<th>%O3 variation from mean at Halley Bay</th>
<th>Volume emission rate of Na 5893Å at Srinagar</th>
<th>Volume emission rate of Na 5893Å at Halley Bay</th>
<th>Intensity of Na 5893Å at Srinagar</th>
<th>Intensity of Na 5893Å at Halley Bay</th>
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<tr>
<td>1979</td>
<td>300.49</td>
<td>3.77</td>
<td>303.73</td>
<td>15.04</td>
<td>24.00</td>
<td>26.59</td>
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Fig. 2—Yearly variations of intensity of Na 5893Å line (a) at Srinagar (34°N, 74.8°E) and (b) at Halley Bay (76°S, 27°W)
help of ozone depletion for corresponding months of the period 1979-1998, for Srinagar and Halley Bay. The variation of intensity of Na 5893Å line for the above two stations for different months are shown in Fig. 3[(a) and (b)]. It is clear from Fig.3 that maximum intensity occurs for the month of February-March and minimum intensity occurs for the month of October-November at Srinagar. But in case of Halley Bay, maximum intensity occurs during the month of December and minimum occurs for the month of October. Intensity gradually increases from the month of January, attains its maximum for the month of February-March, then gradually decreases and attains its minimum value for the months of October- November at Srinagar due to similar nature of variation of ozone at Srinagar. But for Halley Bay maximum ozone concentration occurs for the month of December and January, then gradually decreases, attains minimum for the month of October and then gradually increases. The minimum intensity during the month of October at Halley Bay is due to the dramatic decrease in ozone concentration at Halley Bay during spring time because of special atmospheric climatic condition prevailing there at Antarctica during that time. The special atmospheric conditions of Antarctica are as follows:

(i) During Antarctic spring, temperature becomes very low (~80°C).
(ii) Concentrations of Cl and oxides of chlorine are elevated.
(iii) Concentrations of oxides of nitrogen becomes low and
(iv) Large amount of polar stratospheric clouds appear.

These are supported by several expeditions.

4 Summary
The intensity of Na 5893Å at Halley Bay (76°S, 27°W) is comparatively higher than that at Srinagar(34°N, 74.8°E) in 1979 due to its higher percentage increase of ozone from its mean value. The rate of yearly decrease in intensity is greater at Halley Bay compared to Srinagar due to larger loss of yearly mean ozone concentration from 1979 to 1998. The intensity of Na 5893Å at Halley Bay during a year achieves a minimum value for the months of October and November due to the minimum ozone concentration for the above months at Antarctica.

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