

## Observations of NO<sub>2</sub> and O<sub>3</sub> during Thunderstorm Activity Using Visible Spectroscopy

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### ABSTRACT

Simultaneous observations for the total column densities of NO<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O were carried on using the portable Spectrometer (438–450 nm and 400–450 nm) and the visible Spectrometer (544.4–628 nm) during premonsoon thunderstorms and embedded hail storm activity at Pune (18°32'N & 73°51'E), India. These observations confirm the fact that there is an increase in O<sub>3</sub> and NO<sub>2</sub> column densities during thunderstorms. The increase in O<sub>3</sub> was observed following onset of thunderstorm, while the increase in NO<sub>2</sub> was observed only after the thunder flashes occur. This implies that the production mechanisms for O<sub>3</sub> and NO<sub>2</sub> in thunderstorm are different. The observed column density of NO<sub>2</sub> value ( $1$  to  $3 \times 10^{17}$  molecules  $\cdot$  cm<sup>-2</sup>) during thunderstorm activity is 10 to 30 times higher than the value ( $1 \times 10^{16}$  molecules  $\cdot$  cm<sup>-2</sup>) of a normal day total column density. The spectrometric observations and observations of thunder flashes by electric field meter showed that  $6.4 \times 10^{25}$  molecules / flash of NO<sub>2</sub> are produced. The increased total column density of ozone during thunderstorm period is 1.2 times higher than normal (clear) day ozone concentration. The multiple scattering in the clouds is estimated from H<sub>2</sub>O and O<sub>2</sub> absorption bands in the visible spectral region. Considering this effect the calculated amount of ozone added in the global atmosphere due to thunderstorm activity is 0.26 to 0.52 DU, and the annual production of ozone due to thunderstorm activity is of the order of  $4.02 \times 10^{37}$  molecules / year. The annual NO<sub>2</sub> production may be of the order of  $2.02 \times 10^{35}$  molecules / year.

**Key words:** Visible Spectroscopy, Thunderstorm, Ozone production, NO<sub>2</sub> production, Atmospheric electricity, Lightning flashes, Multiple scattering factor

### 1. INTRODUCTION

Ozone production and destruction processes are very much important for the study of sensitive issues such as ozone depletion and green house warming. The possible modification of the atmospheric composition by natural processes like thunderstorm has attracted considerable interest in recent years. The increase in ozone concentration during thunderstorm activity has been reported by various workers (Dobson et al. 1945; Dufay 1949; Vassy 1965, 1957; Shlanta and Moore 1972; Clarke and Griffing, 1985; Dickerson et al., 1987; Franzblau, 1993).

Noxon (1976), observed increase in NO<sub>2</sub> with optical spectrometers during thunderstorm. The insitu observations of Dickerson et al., (1987) also reported increased NO<sub>2</sub> and O<sub>3</sub> concentrations during thunderstorm. Drapcho et al. (1983) estimated from their observations that a lightning flash produced  $4 \times 10^{26}$  molecules of NO<sub>x</sub> with an uncertainty of one fourth to twice the amount. Using Barringer correlation (spectrometer) (COSPEC) Franzblau (1993) carried out the observations of nitrogen dioxide during lightning. They used this COSPEC system in such a way that the system could "see" the entire cylinder of NO<sub>2</sub> and the entire cylinder of NO<sub>2</sub> passes through the view of COSPEC. From their observations they have estimated that  $4$  to  $10 \times 10^{25}$  molecules / flash of NO<sub>2</sub> are yielded after normalizing to flashes at sea level.

## II. OBSERVATIONS AND ANALYSIS

Observations of  $O_3$ ,  $NO_2$  and  $H_2O$  were carried out in the campus of Indian Institute of Tropical Meteorology, Pune ( $18^{\circ}32'N$  &  $73^{\circ}51'E$ ). By using (1) Visible spectrometer and (2) Portable spectrometers on three periods (I) 5 May 1989, (II) 28 May and 2 June 1991, and (III) 7,9 June 1993. During these periods active thunderstorms are noticed. The detailed specifications of the spectrometers are given in Londhe et al. (1989) and Bose (1993).

## III. EXPERIMENTAL SET UP

Measurements of total column densities of  $NO_2$ ,  $O_3$  and  $H_2O$  were made using a portable spectrometer and a visible spectrometer. The details of these instruments and experimental set up were given in earlier papers by Londhe et al. (1990), and Bhone et al. (1992). Out of the three periods simultaneous observations by using both these spectrometers were taken only during period II. The precautions taken in the present experiments are described briefly as follows.

1. The plain mirror is used to divert the zenith sky radiations towards the spectrometer.
2. Baffles are used to avoid the interference of the radiations other than zenith sky radiations.

## IV. ANALYSIS OF VISIBLE SPECTROMETER DATA

The visible spectrometer controlled by personal computer was operated during 28 May and 2 June 1991 in the spectral region 544.6 to 628 nm for the observations of  $O_3$  and  $H_2O$ . The spectral region was scanned within 12 seconds with 1 nm resolution and the data recorded on the 360 KB floppy disks. Three hundred sample points were selected from the ratio of zenith sky spectra during thunderstorm activity and the noon time spectra of same day for retrieving  $O_3$  and  $H_2O$  concentrations. The  $O_3$  absorption cross sections were adopted from (Amoruso et al., 1990; Griggs, 1968; Vigroux, 1953) and are shown in Fig. 1. The absorption cross sections given by Griggs (1968), and Amoruso et al., (1990) were used for deriving  $O_3$  densities. The Amoruso et al. (1990) absorption cross section curve was used after extrapolating as shown by the dotted line in Fig. 1, with these cross sections better matching with the observed ratio curves being observed. The pseudo  $H_2O$  absorption cross sections are deduced from the ratio of noon time solar spectra, with thin clouds and with clear sky as shown in Fig. 2. The pseudo absorption cross sections are deduced from the ratio of noon time solar spectra, with thin clouds and clear sky as shown in Fig. 2. The pseudo absorption cross sections were compared with the absorption cross sections of  $H_2O$  at three different wavelengths (Miyachu, 1985) and good correlation was observed, hence the pseudo absorption cross sections derived may safely be used to eliminate the effect of  $H_2O$  absorption from observations. The typical ratio spectra in visible region is shown in Fig. 3, and the absorption features of  $O_3$  and  $H_2O$  are clearly seen in the ratio spectra. The absorption cross sections of  $H_2O$  and  $O_3$  are used to retrieve the  $O_3$  and  $H_2O$  slant column densities from the ratio spectra as discussed by various workers (Solomon et al., 1987; Bhone et al., 1992). The measurement accuracy increases by increasing the number of sample points. The typical absorption depth in the yellow spectral region (544.4 to 628 nm) is of the order of 5 to 40 percent and the standard deviation of the calculated and the observed spectra is of the order of  $\pm 0.5$  to  $\pm 3$  percent. The experiment of calculating absorption structures by imposing noise on it shows that the noise of the order of 0.5% to 3% on 5% to 40% absorption depth can introduce error of the order of less than 0.5% in the retrieved concentration of  $O_3$ .

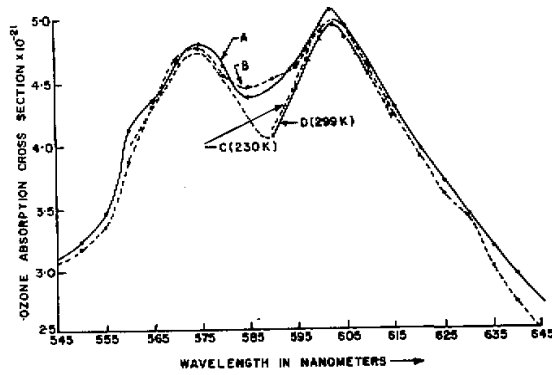


Fig. 1. Absorption cross section of  $O_3$ . i. A—Griggs (1968) ii. B—Vigroux (1953) iii. C and D—Amoruso et al. (1990) at 230 K and 299 K. The portion shown by dotted line of the curve D is extra-plotted.

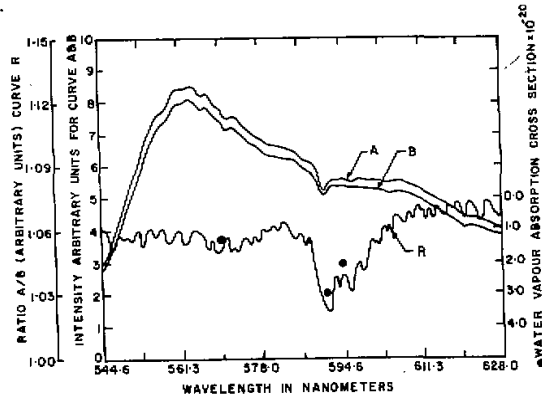


Fig. 2. Pseudo absorption cross section of water vapour deduced from the ratio of the solar spectra. A is the solar spectra with thin clouds, B is the solar spectra without clouds and R is the ratio spectra (A / B). The absorption cross section of water vapour for three different wavelengths by Miyauchi (1985) is shown by circled stars.

#### V. ANALYSIS OF PORTABLE SPECTROMETER DATA

The portable spectrometer was operated during 5 May 1989, 28 May and 2 June 1991 in the spectral region 430 to 450 nm for the observations of  $O_3$ ,  $NO_2$  and  $H_2O$ . The spectral region was scanned within 60 seconds with 0.4 nm resolution and the data recorded on the 6 channels chart recorder. The noon time zenith sky spectrum taken on the same day before thunderstorm activity is used as reference spectrum. The diurnal pattern of convective activity is such that we can take reference spectra at 12 hrs IST (which was clear sky condition), the cloudiness start appearing around 15 hrs IST. The ratio of the zenith sky spectra during thunderstorm activities and reference spectra gives the ratio spectra. The Fraunhofer absorption features and spectral distribution of solar spectra and the instrument functions are eliminated in the ratio spectra as the scattered radiation of the sun are observed with the same

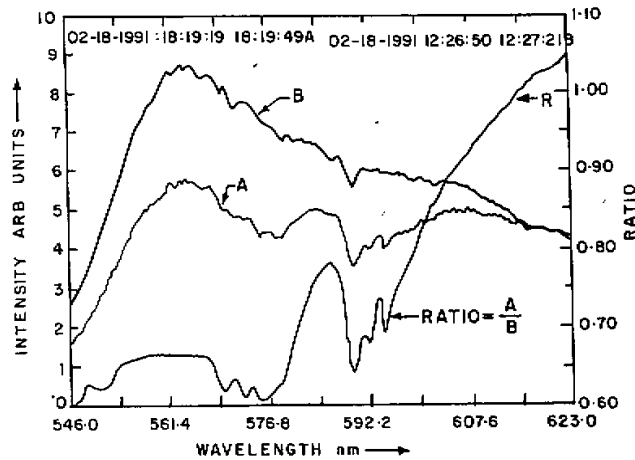


Fig. 3. Typical ratio spectra of the visible spectrometer. Where B is the noon time zenith sky spectra at 12.26.50 hrs IST, and A is the evening time zenith sky spectra at 18.19.19 hrs IST on 18 Feb. 1991 and R is the ratio spectra.

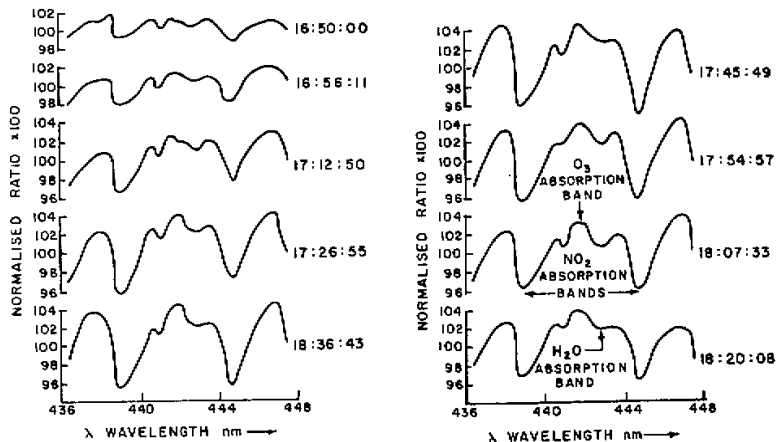


Fig. 4. Normalized ratio spectra of 28 May 1991, thunderstorm activity. The absorption features of  $\text{NO}_2$ ,  $\text{O}_3$  and water vapour are clearly seen in the ratio spectra and the depth of absorption increases with the advancement of thunderstorm.

instrument at noon time and during the time of thunderstorm. Hence only the absorption features of  $\text{NO}_2$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}$  are seen in the ratio spectra as shown in Fig. 4. The variation in absorption structures during the thunderstorm can be seen in the same figure, as thunderstorm advances, the depth of absorption increases. Twenty wavelengths are selected from the Fraunhofer structure of the spectra and the absorption cross sections for the particular wavelengths are adopted from Solomon et al. (1987) for  $\text{NO}_2$  and  $\text{O}_3$ , Johnson and McKenzie, (1984) for  $\text{H}_2\text{O}$ . Fig. 5 shows the absorption cross sections for  $\text{NO}_2$  and  $\text{O}_3$  in the violet

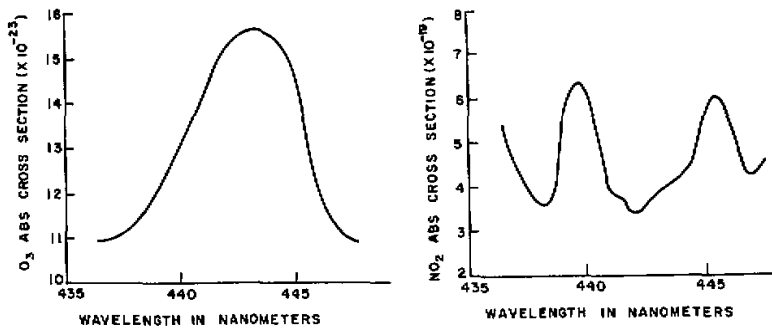


Fig. 5. Absorption cross section of  $\text{NO}_2$  and  $\text{O}_3$  in the violet spectral region by Solomon et al., 1987.

spectral region. The matrix inversion technique is used to retrieve the contribution of individual species i.e.  $\text{NO}_2$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}$  in the violet spectral region is not very diagnostic hence visible spectral region was also used for monitoring  $\text{O}_3$  simultaneously.

#### VI. RESULTS

The results of above observations are presented below. During thunderstorms on 5 May 1989, the observations of  $\text{NO}_2$  and  $\text{O}_3$  along with simultaneous measurement of electrical field using radio active probe were carried out using portable spectrometer. The slant column densities of  $\text{NO}_2$  and  $\text{O}_3$  were derived as discussed in the above section.

The number of flashes per minute and  $\text{NO}_2$  slant column density are plotted as shown in Fig. 6. The observations were started at 15:40 Indian Standard Time when the thunderstorm activity was overhead. The figure clearly shows the difference in maxima of  $\text{NO}_2$  slant column density curve and number of flashes per minute curve. The discontinuity in the data is due to the power failure during observations. During these observations the time constant of electric field meter was of the order of 3 seconds. Hence the expected overlapping of the flashes were corrected by the optical observations recorded simultaneously by the portable spectrometer with time constant of the order of 0.1 sec, but the optical observations were only possible when the thunder clouds were in the field of view of the monochromator. It was observed that actual number of flashes observed by optical method are approximately two times higher than the flashes observed by electric field meter. This correction was considered for deriving the  $\text{NO}_2$  production per flash from the observed  $\text{NO}_2$  slant column densities.

The variations of  $\text{NO}_2$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}$  observed on 28 May 1991 and 2 June 1991 during thunderstorm hours are shown in Fig. 7 and Fig. 8. It is observed that (Fig. 8) the increase in  $\text{NO}_2$  concentration was started only after the beginning of thunder flashes (16.55 IST) but increasing  $\text{O}_3$  concentration was started at the beginning of the thunderstorm (15.59 IST).

#### VII. CONFIRMATION OF OBSERVATIONS

The observations of  $\text{NO}_2$  and  $\text{O}_3$  production during thunderstorms activity are confirmed by taking observations in wider spectral region at 0.4 nm resolution from 400 nm to 450 nm with visible spectrometer on 7,9 June 1993. The absorption cross-sections for  $\text{NO}_2$  and  $\text{O}_3$  for this spectral region are adopted from Solomon et al. (1987). Fig. 9 and Fig.

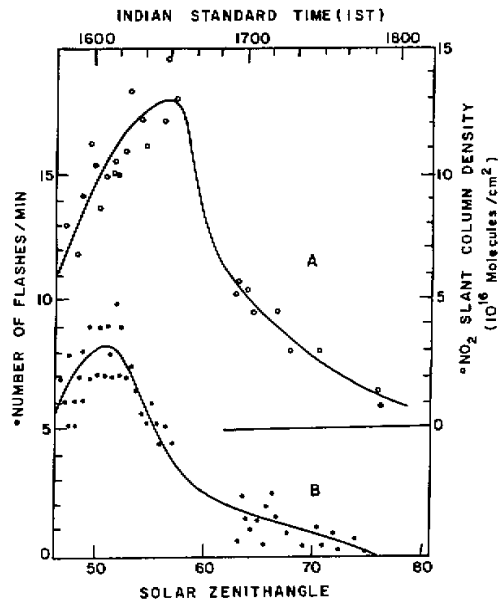


Fig. 6. Comparison of  $\text{NO}_2$  slant column density (A) observed by portable spectrometer and the number of flashes per minute observed by Electric field meter (B) during thunderstorm activity on 5 May 1989. The time difference between two maxima is of the order of 20 minutes. The discontinuity in data is due to power failure during observations.

10 show these observations on 7, 9 June 1993 premonsoon thunderstorm activity. On 7 June 1993 observations one side of the thunderstorm active cloud was passed overhead the observational sight. The storm moved east-west direction of the observation sight. This observation had also showed the increase in  $\text{NO}_2$  and  $\text{O}_3$  during thunderstorm activity. During 9 June 1993 observations (Fig. 10) the observational field of view was in between two thunderstorms moving in the east-west direction. The spectrometer was looking at zenith sky where the thin clouds were moving in the east-west direction. For these thin clouds the thunder activity was not observed. Drizzle was also observed during these observations. The increase in  $\text{NO}_2$  and  $\text{O}_3$  concentrations during these observations indicates the mixing processes during thunderstorm activity. On the same day, the twilight observations were also carried out. These twilight observations also showed the enhancement of  $\text{NO}_2$  and  $\text{O}_3$  slant column density compared to clear day twilight observations. This may be due to continuing thunderstorm activity in the vicinity of observational sight after the sunset.

The airmass factor was changing during the observations and this was mainly due to change in solar zenith angle and multiple scattering inside the cloud. This changing airmass factor is taken into account by calculating multiple scattering factor from simultaneous observations of  $\text{H}_2\text{O}$  and  $\text{O}_2$ .

#### VIII. MULTIPLE SCATTERING FACTOR

During these type of observations the solar radiation is scattered through clouds, hence multiple scattering is expected before the radiation reaching the spectrometer. Due to this

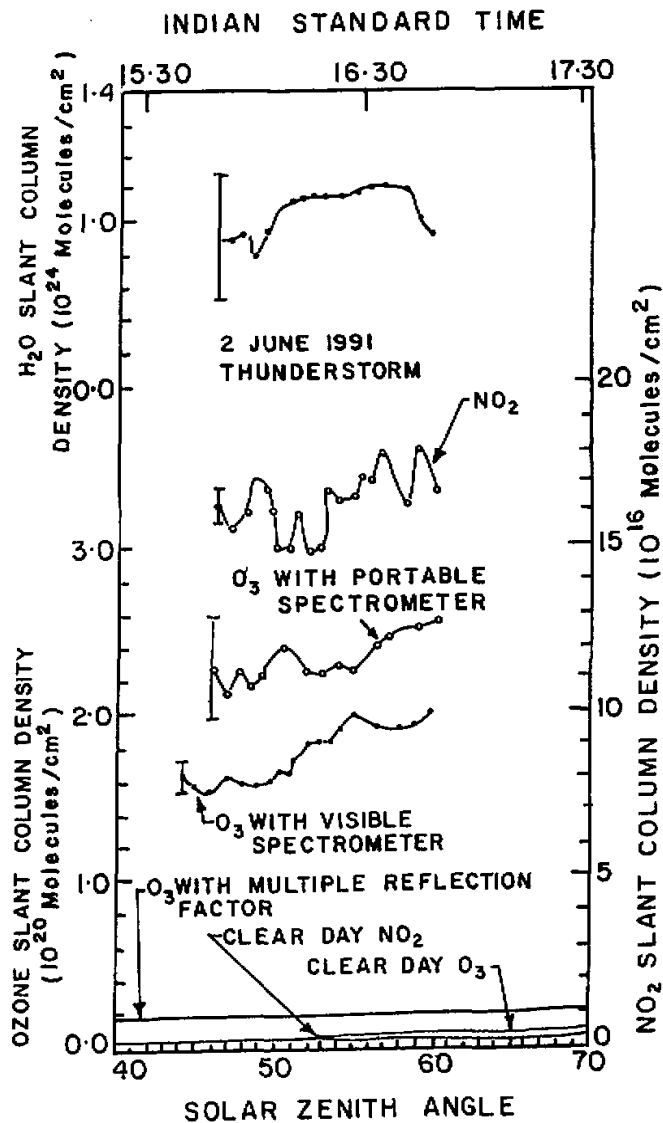


Fig. 7. The observed slant column density of NO<sub>2</sub>, O<sub>3</sub> and water vapour during thunderstorm activity on 2 June 1991 by portable and visible spectrometer. The clear day O<sub>3</sub>, NO<sub>2</sub> slant column density and the O<sub>3</sub> slant column density with multiple scattering factor are also plotted for comparison.

multiple scattering, the observed NO<sub>2</sub> and O<sub>3</sub> concentration is not the real concentration but an apparent one. To calculate the actual concentration, the multiple scattering factor is deduced from the absorption bands of the known species like a H<sub>2</sub>O and O<sub>2</sub>. These absorption

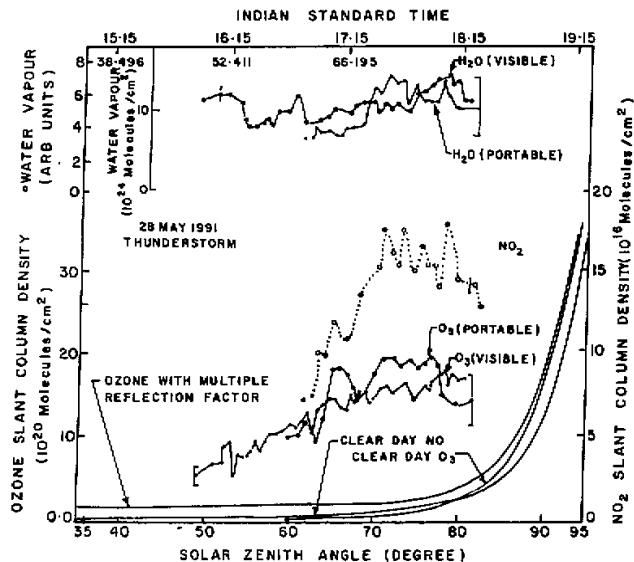


Fig. 8. A plot of  $\text{NO}_2$ ,  $\text{O}_3$  and water vapour slant column densities during thunderstorm on 28 May 1991 by Portable and Visible Spectrometers. The clear day  $\text{O}_3$  and  $\text{NO}_2$  slant column densities as well as  $\text{O}_3$  slant column densities calculated by considering multiple scattering factor are also plotted for comparison. The enhanced slant column densities of  $\text{O}_3$  were observed from the beginning of the thunderstorm activity but  $\text{NO}_2$  slant column densities were enhanced after the occurrence of thunder flashes.

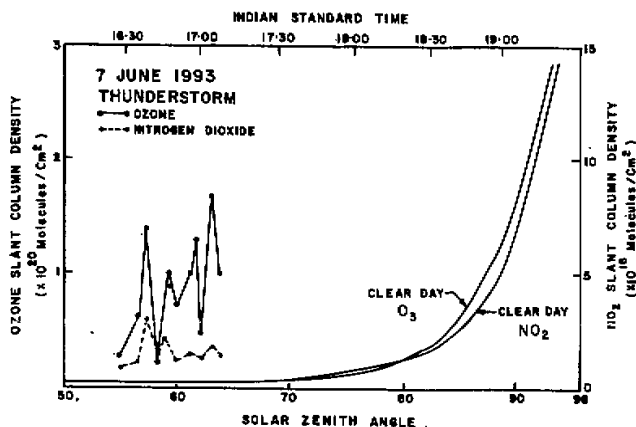


Fig. 9. The observed slant column densities of  $\text{NO}_2$  and  $\text{O}_3$  on 7 June 1993 obtained with data collected by visible spectrometer in the fractal region 400–450 nm. Thin cloud at zenith was in field of view of spectrometer. Two thunderclouds were separated by this thin cloud. The observed increase of  $\text{NO}_2$  and  $\text{O}_3$  densities may be due to mixing processes of thunderstorm activity.

features were taken into consideration for deriving the  $\text{O}_3$  concentration. The total column density of  $\text{H}_2\text{O}$  that can be accommodated in a column upto 15 km is about  $1 \times 10^{23}$  mole-



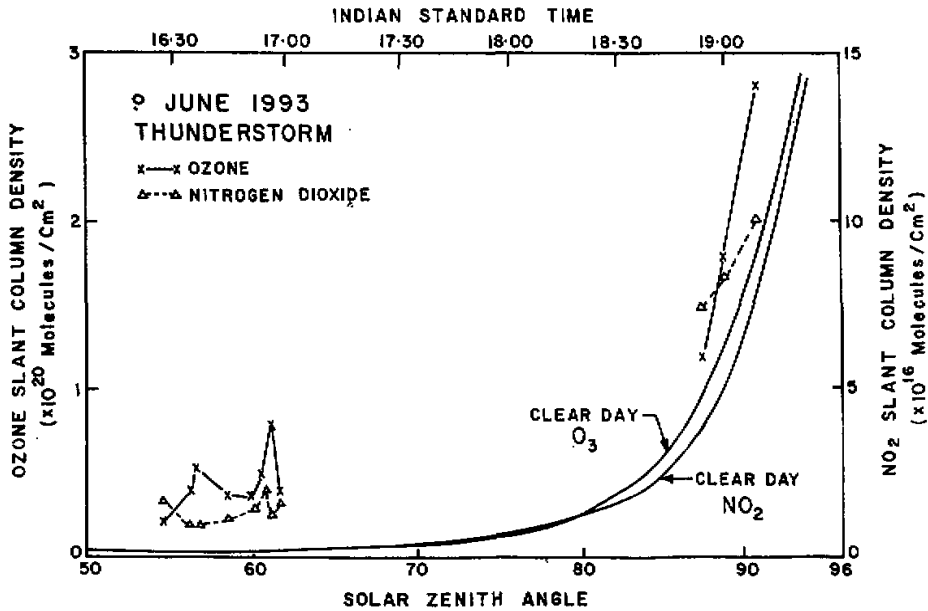


Fig. 10. The slant column densities of  $\text{NO}_2$  and  $\text{O}_3$  observed on 9 June 1993 during passage of the thundercloud partly (overhead) in the field of view of spectrometer. The twilight observations also showed increase in slant column densities of  $\text{NO}_2$  and  $\text{O}_3$  (see text).

cules/cm<sup>2</sup>. However, the observed columnar density of  $\text{H}_2\text{O}$  is  $10 \times 10^{23}$  molecules/cm<sup>2</sup>. Hence  $\approx 10$  times higher densities are observed due to multiple scattering. The similar multiple scattering factor was also observed from  $\text{O}_2$  absorption bands near 762.1 nm. This factor is similar to airmass factor during clear sky conditions.

The water vapour concentration observed by both the spectrometers is shown in the Fig. 7 and Fig. 8. The value of water vapour column density is  $1 \times 10^{24}$  Molecules/cm<sup>2</sup>. Both spectrometer derived values of  $\text{H}_2\text{O}$  are comparable, though the observational error is more for the portable spectrometer.

#### IX. PRODUCTION OF $\text{NO}_2$

The  $\text{NO}_2$  observed at a particular instance may be given by

$$D_2 = FP + D_1 K \quad (1)$$

where  $D_1$  &  $D_2$  are the  $\text{NO}_2$  concentration at time  $t_1$  and  $t_2$

$F$  is number of flashes observed in the time interval  $(t_2 - t_1)$

$P$  is  $\text{NO}_2$  produced per flash and

$K$  is constant which depends upon the time interval  $(t_2 - t_1)$  taken during calculations.

From two curves A and B in Fig. 6, numbers of simultaneous equations can be generated for a constant time interval  $t_2 - t_1$ . In the present case for 10 minutes interval, 90 simultaneous equations were generated. These simultaneous equations were solved by matrix inversion method and the value of  $p$  i.e.  $\text{NO}_2$  produced per flash and  $k$  the constant were derived. The value of constant is approximately 0.5 when the time interval of 10 minutes is considered. This indicates that the  $\text{NO}_2$  remains in the atmospheric for some time. The photochemical

time constant of  $\text{NO}_2$  during noon time is 100 seconds and during night time it is around 25 minutes (Shimazaki(1984)). The photochemical time constant of  $\text{NO}_2$  during thunderstorm activity will be around few minutes to 25 minutes. However the time difference between two peaks is of the order of 20 minutes. This may be due to the other chemical processes or cloud movements. It is observed that  $6 \times 10^{14}$  molecules/cm<sup>2</sup>/flash of  $\text{NO}_2$  is distributed throughout the cloud area by various processes. Hence the total  $\text{NO}_2$  produced per flash is the product of cloud area and  $\text{NO}_2$  column density as observed by the portable spectrometer. Considering normal cloud area of  $5 \times 5$  km<sup>2</sup>, total  $\text{NO}_2$  produced per flash is  $15 \times 10^{25}$  molecules/flash (i.e.  $7.5 \times 10^{25}$  molecules/stroke when 2 strokes/flash are considered according to Sisterson and Liaw (1990)). The number may be modified after considering the types of flashes i.e. from cloud to ground flashes or inter cloud flashes as follows.

We can calculate the number of effective observed strokes by our method of observations for 100 flashes. We can assume 30 per cent of the thunderstorm flashes are observed due to cloud to ground flashes for tropical station like our observational sight (Uman (1969)). The  $\text{NO}_2$  produced from these flashes will be observed due to direct absorption and the multiple scattering factor for these observations can be assumed as one. The effective number of strokes observed by our method of observations for these flashes can be equal to number of flashes  $\times$  strokes/flash  $\times$  multiple scattering factor i.e.  $30 \times 4$  (strokes/flash)  $\times$  1. For cloud to ground flashes, the mean strokes/flash is assumed as 4 (Uman (1969)). Hence effective  $\text{NO}_2$  observing strokes due to cloud to ground strokes is 120.70 flashes out of 100 flashes are due to inter cloud flashes. Generally for inter cloud flashes 1 stroke/flash is observed (Uman (1969)) and the multiple scattering factor for these  $\text{NO}_2$  molecules may be assumed as 5. For total cloud top of 15 km the multiple scattering factor observed by our method is 10 and the inter cloud flashes can occur at one half to two third of the cloud height (Sisterson and Liaw (1990)), hence the multiple scattering 5 is assumed in this case. The effective observable strokes by inter cloud flashes by our method is  $70 \times 1 \times 5 = 350$ . Hence, the total observable strokes for  $\text{NO}_2$  by our method is  $120 + 350 = 470$ . In previous calculations we have assumed 200 strokes for 100 flashes (Sisterson and Liaw (1990)). However, the total  $\text{NO}_2$  observed for 100 flashes is equivalent to 470 observable strokes. Taking into account this factor the  $\text{NO}_2$  production per stroke is of the order of  $3.2 \times 10^{25}$  molecules/strokes and (i.e.  $6.4 \times 10^{25}$  molecules/flash).

The hail storm on 28 May 1991 was observed with the portable spectrometer and visible spectrometer around 48° solar zenith angle. Measurable  $\text{NO}_2$  was observed only around 65° solar zenith angle as shown in Fig. 8, which was the beginning of thunder flashes and  $\text{NO}_2$  was increased with the thunderstorm activity, but sufficient ozone was present in the cloud before the beginning of thunder flashes as shown in the same figure. The ozone concentrations observed by both the spectrometers are comparable.

The ozone and  $\text{NO}_2$  slant column densities observed by the same method during clear sky condition are also given in the same figure for comparison. As the solar zenith angle increases the optical path also increases hence higher concentration is observed at higher zenith angle. The method of calculating enhancement factor and slant column density is discussed in detail by Solomon et al., (1987) and Bhone et al., (1992) and hence not repeated here. For the present observations multiple scattering factor is equivalent to the enhancement factor which is used for clear sky conditions.

#### X. OZONE PRODUCTION DURING THUNDERSTORM

After subtracting the normal day ozone which can be observed during clear sky, the additional amount of ozone observed during thunderstorm by our system is  $= 1 \times 10^{20}$  mole-

cules / cm<sup>2</sup>.

$$\text{Actual ozone increase } (O_1) = \frac{\text{Observed increase in ozone}}{\text{Multiple scattering factor}}$$

hence =  $1 \times 10^{19}$  Molecules / cm<sup>2</sup> increase in O<sub>3</sub> was observed during thunderstorm activity. The ozone produced in a thunderstorm can be given as:

$$\text{Ozone produced / storm} = \text{Cloud area} \times \text{Increase in O}_3 \text{ density during storm}$$

Hence it is assumed that ozone produced may remain in cloud volume only. However, it is observed that ozone produced can be transported to cloud free region near cloud. Assuming  $5 \times 5 \text{ km}^2$  cloud area ozone produced per storm is

$$\begin{aligned} &= 5 \times 10^5 \times 5 \times 10^5 \times 1 \times 10^{19} \\ &= 2.5 \times 10^{30} \text{ Molecules / storm} \end{aligned}$$

The ozone produced is destroyed by various photochemical processes hence the increase in ozone at equilibrium during thunderstorm may be given as

$$I_0 = nCA(T_0 + T_S), \quad (2)$$

where  $I_0$  = increase in ozone at equilibrium,

$n$  = No. of storms / sec. (i.e. 0.5 storms / sec.) (Viemeister, 1961),

$C$  = Column density of ozone due to thunderstorm

(i.e.  $1 \times 10^{19}$  Molecules / cm<sup>2</sup>),

$A$  = Area of cloud (i.e.  $5 \text{ km} \times 5 \text{ km}$ ),

$T_0$  = daytime photochemical life time of ozone (= 30 min = 1800 sec.) (Shimazaki, 1984).

Hence  $I_0 = (0.5) (1 \times 10^{19}) (25 \times 10^{10}) (3.600) \times 10^3 = 0.45 \times 10^{34}$  Molecules. Therefore  $0.45 \times 10^{34}$  Molecules of ozone are present in the atmosphere at any time due to thunderstorm.

This ozone is mixed in the atmosphere by various atmospheric processes such as diffusion, circulation, transport etc. Hence the additional ozone in the atmosphere due to thunderstorm can be given by

$$A_0 = \frac{I_0}{A_E}, \quad (3)$$

where  $A_0$  is the ozone added in the atmosphere due to thunderstorm.

$I_0$  is the increased O<sub>3</sub> present in atmosphere / due to thunderstorm at equilibrium,

$A_E$  is the Area of the earth =  $5.4457 \times 10^8 \text{ cm}^2$ .

It is found that  $0.0826 \times 10^{26}$  Molecules / cm<sup>2</sup> (0.0328 D.U.) of ozone is added to the atmosphere due to thunderstorm. Considering large photochemical lifetime of O<sub>3</sub> during night time, approximately 0.066 D.U. of ozone may be added in atmosphere. However in case of ozone, the increase is also observed in the vicinity of thunderstorm (Clarke and Griffing, 1985) hence we can consider double the area of thunderstorm for the calculation. The electrified clouds can also produce ozone and its life time may be assumed two times more than thunderstorm life time. Hence the total addition of O<sub>3</sub> in global atmosphere may be = 0.262 to 0.525 DU due to thunderstorm. This amount is negligible compared to the total production of ozone. The annual ozone production may be given by

$$O_A = N \times I_0, \quad (4)$$

where  $O_A$  = Annual O<sub>3</sub> production due to thunderstorm activity,

$N$  = No. of thunderstorm / year (i.e.  $44000 \times 365$ ) (Viemeister, 1961) and  $I_0$  = Actual in-

crease in  $O_3$  due to thunderstorm, (i.e.  $2.5 \times 10^{30}$  molecules / storm).

It is found that  $4.02 \times 10^{37}$  Molecules/year of  $O_3$  are produced by thunderstorm activity. If the observed ozone is distributed homogeneously throughout the height of thundercloud (i.e. upto 15 km for Pune), then the ozone concentration observed maybe of the order 250 ppb. i.e. ozone concentration during thunderstorm activity may reach up to 250 ppb.

Our results of  $NO_2$  and  $O_3$  observations compared with other investigators and plausible contribution by different production mechanisms are discussed below.

#### XI. DISCUSSION

The comparison of observations for increase in ozone during thunderstorm activity by other workers and by us is given below.

Our observation of ozone showed value of concentration about 250 ppb during thunderstorm activity. The following observations also corroborate our ozone observations as discussed below.

i) The observations by Dobson et al.,(1945), on a cloudy sky, when the thunderstorms passed near by overhead in succession produced maximum ozone of 0.40 to 0.45 cm thickness. Ozone measurement before and after the storm indicated a clear air value of approximately 0.25 cm. Thus the total ozone in the vicinity of thunderstorm by Dobson et al., (1945), is approximately two times compared to the clear air ozone value. The ozone added to the atmosphere due to thunderstorm is of the order 0.15 to 0.20 cm, if this amount of ozone is distributed uniformly in the column of 10 km height, (approximate height of thunder-cloud) then the ozone density in this column would be of the order 150 to 200 ppb.

ii) The slit spectrograph observations by Dufay, (1949), obtained by exposing the spectrograph to several flashes in a thunderstorm were used to derive ozone. Dufay (1949), using previously determined characteristic curve for his plate, measured the rate of decrease in the transmitted intensity through a cut off region of 400 nm, and assuming this absorption was due to ozone, he calculated a reduced  $O_3$  thickness of 0.3 cm. He observed intracloud as well as cloud to ground flashes simultaneously. This represents the amount of  $O_3$  existing in the path between the spectrograph and the several flashes that produced the spectrum. If this amount is distributed between the flashes and observer (i.e. = 7 km) then the increase in ozone concentration due to thunderstorm may be of the order 430 ppb.

iii) Clarke and Griffing (1985), observed anomalously large short term ozone concentrations on several occasions by aircraft. During an experiment on 5 Aug. 1980 near the vicinity of thunderstorm Clarke and Griffing (1985) observed ozone spikes of about 500 ppb in less than 30 seconds when traversed by aircraft. (travelled distance was less than 2 km). They have attributed these spikes as ozone production by chemical reactions activated by lightning associated with thunderstorm.

iv) Sisterson and Liaw (1990) suggested that the occasional high  $O_3$  concentration observed in and near thunderstorms do not appear to be explained by either lightning or corona processes. They suggested that the high  $O_3$  reading may be due to corona discharge by  $O_3$  sensors and another possibility of stratospheric intrusion via very large thunderstorms. Our present observations and the observations by others (Dobson, 1945) suggest that there is high concentration of ozone in thunderstorm and the stratospheric intrusion is also taken into account as the total column density is measured by our method.

#### XII. BEGINNING OF $O_3$ AND $NO_2$ PRODUCTION

Fig. 8 shows the simultaneous observations of  $NO_2$  and  $O_3$  during 28 May 1991 thunder-

storm activity. Enhanced ozone was observed at the beginning of the thunderstorm activity ( $\approx 15.59$  hrs IST). However the enhanced  $\text{NO}_2$  was only observed at beginning of thunder flashes i.e. around 16.55 hrs IST. This indicates the different production processes of  $\text{NO}_2$  and  $\text{O}_3$  during thunderstorm activity.

In most of the cases Vassy (1965, 1957) also found that the increase in ozone began before the first near by lightning and the ozone concentration returned to the fine weather value soon after the end of the storm. Vassy concluded that lightning and stratospheric air were not the primary sources of the ozone perturbation found beneath the thunderstorm. This indicates that there is production of  $\text{O}_3$  by electrical processes other than thunder flash activity also.

### XIII. OZONE PRODUCTION PROCESSES

The ozone production during the thunderstorm activity may be due to following different processes.

(i) Ozone production due to lightning flash, (ii) Point discharge processes at ground surface, (iii) Pollution transport from the ground and (iv) Electric corona discharge processes, or discharge processes inside the thundercloud.

Our estimation of ozone concentration in thundercloud region is of the order of 250 ppb and the annual production of  $\text{O}_3$  is around  $4 \times 10^{37}$  molecules/year. The above different processes may contribute for the observed  $\text{O}_3$  enhancement. For the sake of simplicity the electric discharge at ground during thunderstorm is called point discharge process and the electric discharge inside cloud is called corona discharge or discharge only.

#### 1. Ozone Production Due to Lightning Flash

For confirming the production of  $\text{O}_3$  by thunder flash, the cloud to ground flash observations will be more suitable. As the cloud volume where ozone production due to other processes will not be in the field of view. These types of observations are discussed below.

The slitless spectrograph observations by Salanave, (1962) in UV region of a single cloud to ground flash that occurred a distance of 0.85 km from the spectrograph was analysed by Orville (1967) and derived ozone concentration. The value was one order greater than the clear air tropospheric value. He was not able to determine whether the enhanced ozone was localized in a mantle around the lightning channel or distributed in the air between the spectrograph and the channel. Salanave (1970) used slitless spectrograph and ultra violet source to measure ozone after storms and found that the thunderstorm activity increased the post storm concentration of ozone near ground level by a factor less than 3 and suggested that his strong cut off in lightning spectra was predominantly due to a region of high concentration of ozone around the discharge channel. These observations are for the amount of ozone present between cloud to ground flash and the observer. This indicates that the amount of ozone produced due to flash is lower by a factor of 2 compared to observations of flashes through cloud. Hence we can conclude that along with thunder flash production there is also other mechanism for the production of ozone in the thunder cloud.

According to Griffing (1977),  $3 \times 10^{26}$  ozone molecules per lightning flash are produced and an average worldwide rate of 100 cloud to ground lightning flashes per second, may obtain  $9.5 \times 10^{35}$  molecules of ozone per year.

#### 2. Point Discharge Process at Ground

Shlanta and Moore (1972) observed short duration increase in the concentration of atmospheric ozone beneath active New Mexican thunderstorms in the vicinity of an exposed

and grounded sharp metal rod. They observed 6.4 times more ozone concentration due to lightning induced emission of negative charges during thunderstorm compared to fine weather concentration. The longer duration increase in the atmospheric ozone to about 1.5 times the prestorm concentration was found above a collection of natural grass points when overhead clouds were electrified with a net positive charge.

According to Peyroux and Lapeyer (1982) estimation the point discharge at ground can produce is  $15 \text{ Tg O}_3 \text{ r}^{-1}$  i.e.  $1.9 \times 10^{35}$  molecules / year. The cloud base to ground point discharge processes are specially due to pointed objects on earth surface.

### 3. Pollution Transport from Ground

Dickerson et al. (1987) reported the aircraft observations of various chemical species like carbon monoxide, hydrocarbons, ozone and reactive nitrogen compounds. They observed that the concentrations of these species were much greater in the cut off region of the storm up to 11 km in altitude than in surrounding air. They concluded that thunderstorm may transfer local air pollution problems in to regional or global atmospheric chemistry problems. The observed values of Dickerson (1987) are 40–90 ppb ozone during thunderstorm. These values are 3 to 4 times less than the value obtained by our observations. The comparison of such observations with large numbers of in situ observations by different techniques may be helpful for deriving definite conclusions. However the observation sight like our station where the air pollution is very low the contribution due to this process will be less.

### 4. Electric Corona Discharge Process or Discharge Process inside the Cloud

Shlanta and Moore (1972) also concluded that the ozone is produced by point discharge from the surfaces of water droplets under intense electric field and their processes may account for some of the ozone concentration observed in the thunderstorm. Their balloon observations inside thunder cloud showed the ozone concentration 80 to 200 ppb at 3 to 5 km altitude region.

Electric corona production of  $\text{O}_3$  by cloud electrical activities is highly uncertain (Dickerson, 1987), this will only be possible if  $\text{NO}_2$  and  $\text{O}_3$  in enriched region do not mix. The corona of ice particles and precipitation elements at any particular instant may increase local  $\text{O}_3$  concentration values up to 200 ppb. The values larger than this value may be due to the other cases. Plausible estimation of the total ozone observed during thunderstorm is given in conclusions.

## XIV. $\text{NO}_2$ PRODUCTION PROCESS

As discussed in the  $\text{NO}_2$  production section, our observations and estimation showed that the  $6.4 \times 10^{25}$  molecules / flash ( $3.2 \times 10^{25}$  molecules / stroke)  $\text{NO}_2$  molecules are produced. Considering 100 flashes / second (Sisterson and Liaw 1990), the annual  $\text{NO}_2$  production is of the order of  $2.02 \times 10^{35}$  molecules / year. This estimation is towards lower side compared to estimation by Noxon (1976), Griffing (1977) and Drapcho et al. (1983). Although this value is very close to the theoretical calculations and laboratory experiments by various workers, more observations are required for definite conclusions.

Our observations also showed that the  $\text{NO}_2$  increase was observed after the beginning of thunder flashes. The  $\text{NO}$  produced after thunder flash may be converted into  $\text{NO}_2$ . For this reaction  $\text{O}_3$  is required which is also enhanced during thunderstorm activity. From these observations we may say that the thunder flashes are major contributor for  $\text{NO}_2$  production during thunderstorm activity.

## XV. CONCLUSION

Our results indicate an increase in ozone and nitrogen dioxide concentration during thunderstorm activity. They also suggest that production mechanisms are different for  $O_3$  and  $NO_2$ . The multiple scattering factor consideration are essential to derive the concentrations of  $NO_2$  and  $O_3$  when the observations are taken by passive technique in presence of clouds like thunderstorms.

The observed  $O_3$  concentration in the thunderstorm region may reach up to 250 ppb. Global distribution of  $O_3$  showed that 0.26 to 0.52 Dobson unit of  $O_3$  may be added to the total  $O_3$  in the atmosphere due to thunderstorm (which is negligible compared to total ozone observed).

According to above discussion we can roughly estimate the contributing different ozone production processes during thunderstorm activity as follows.

1. *The Ozone Production Due to Lightning Flash*

The ozone production by this process is  $= 9.5 \times 10^{35}$  molecules of ozone per year. The contribution by this process may be approximately 2 to 3 percent of the total ozone.

2. *Point Discharge Processes at Ground*

The ozone production due to point discharge process is  $\approx 1.9 \times 10^{35}$  molecules / year. The contribution by this process is approximately 0.5 percent of the total ozone.

3. *Pollution Discharge Processes at Ground*

This may contribute up to  $\approx 0$  to 30 percent of observed  $O_3$  during thunderstorm activity. However this effect will be local one and for less polluted station like Pune this contribution will be negligible.

4. *Corona Discharge or Discharge Processes inside Cloud*

Considering the nature of electric fields present inside the thunderstorm this process appears to be higher contributor (i.e. = 70 to 98 percent) for the production of ozone during thunderstorm activity. At any location of thunderstorm this process will always present.

The observed  $NO_2$  concentration during thunderstorms may reach up to 20 to 40 ppb and  $NO_2$  produced per flash may be of the order  $6.4 \times 10^{25}$  molecules / flash. The amount production of  $NO_2$  is  $2.02 \times 10^{35}$  molecules / year. The major  $NO_2$  production process is lightning flash activity.

Simultaneous observations of electrical parameters,  $NO_2$ ,  $O_3$  and other gases during the thunderstorm may give better understanding regarding the production mechanism, and distribution during thunderstorm.

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