

## NEAR SIMULTANEOUS MEASUREMENTS OF NO<sub>2</sub> AND NO<sub>3</sub> OVER TROPICS BY GROUND-BASED ABSORPTION SPECTROSCOPY

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### Abstract

The present study concentrates on measurements of NO<sub>2</sub> and NO<sub>3</sub>. NO<sub>2</sub> has been measured during twilight period using zenith sky absorption spectrometric technique in the 436 to 448 nm region. NO<sub>3</sub> has been measured during night time using direct moon as a source of light in the 655 to 667 nm region. These measurements have been taken at low latitude station, Ahmedabad ( 23°N, 76°E ), India for the past two years.

### Introduction

NO<sub>x</sub> group of species plays an important role in the chemical reactions that control the distribution of O<sub>3</sub> in the stratosphere. The variabilities of NO and NO<sub>2</sub> are known to some extent, those of NO<sub>3</sub> are in considerable darkness. First observation of NO<sub>3</sub> was taken by Noxon et al. ( 1978 ), who used a scanning spectrometer and moon as a light source above the Fritz Peak Observatory ( 40°N ) in April 1978. The same spectral feature has been used to study stratospheric NO<sub>3</sub> by several authors ( Sanders et al., 1987; Solomon et al., 1989a,b ). However, these observations are not sufficient to draw a clear picture of the global NO<sub>3</sub> variability. A number of observations have been taken on the NO<sub>2</sub> content of the stratosphere by using ground-based, balloon-borne and space craft techniques ( Syed and Harrison, 1980; McKenzie et al. 1982; Mount et al., 1987; Pommereau et al., 1988; Johnston et al. 1992). But most of these observations are of mid- and high latitude zones. Satellite observations are available for low latitude zone; but those are not yet fully validated due to the lack of enough observations in this region. The distribution and variability of this species in the low latitude northern hemisphere, however, are not properly known. We have, therefore, initiated measurements of NO<sub>2</sub> and NO<sub>3</sub> over Ahmedabad, a low latitude station. The measurements reported here will contribute significantly to the global data base of minor neutral constituents.

### Experiment

The details of experimental set-up has been described in the companion paper(Lal & Chakrabarty).

### Methodology

Using the property that NO<sub>3</sub> has strong absorption at 662 nm, and NO<sub>2</sub> has strong absorption at 439.5 nm, NO<sub>2</sub> and NO<sub>3</sub> column abundances have been measured. Since the concentration of NO<sub>3</sub> is very low during daytime, its abundance has been measured during night time only. The technique of NO<sub>2</sub> measurement has been described by Noxon (1979), Harrison (1979) and Syed and Harrison (1980). The analysis of NO<sub>3</sub> has been done by using matrix inversion technique. For NO<sub>2</sub> measurements, the background spectrum has been obtained at minimum possible solar zenith angle. Superficially, twilight and background spectra appear similar owing to the presence of strong Fraunhofer structure in the incident sunlight. By taking their ratio, the Fraunhofer structure is removed. After this is done, absorption by NO<sub>2</sub> becomes apparent owing to the much longer path during twilight period. This ratio spectrum has been used for the calculation of NO<sub>2</sub> abundance using five point method as given by Harrison (1979).

For NO<sub>3</sub> measurements, direct solar spectrum at 80° solar zenith angle has been used as a background spectrum. All the observations have been taken at higher lunar zenith angle during night time. Besides NO<sub>3</sub> absorption, aerosol and Rayleigh scattering, and absorption due to H<sub>2</sub>O and O<sub>3</sub> are also present. These have been removed in the manner described by Solomon et al. (1989). With this residual spectrum, using least square technique, column abundance of NO<sub>3</sub> had been calculated.

### Results and discussions

Fig. 1 shows an example of the solar spectra taken during morning and noontime. These spectra contains Fraunhofer structure and absorption due to atmospheric species. Morning spectrum has been divided by the noon time spectrum to remove the Fraunhofer component

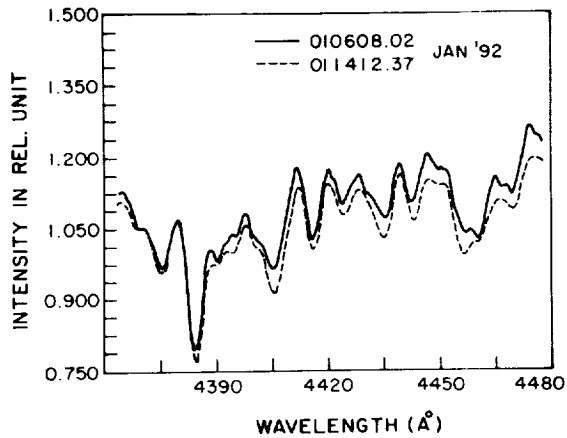


Figure 1. Zenith sky spectrum at 0802 hrs and 1237 hrs IST in the month of January.

present in it.

Fig. 2 shows an example of the ratio of the twilight to noontime spectra. In this spectrum, Fraunhofer component should have been absent. But, in some cases the fluctuations in the ratio spectrum still remain. This is the Ring component. To remove this Ring contribution, we have taken the running average of ratio spectrum. The ratio spectrum thus obtained has the contribution of aerosols and Rayleigh scattering. To remove this component we have subtracted the ratio spectrum from a straight line parallel to the slope of the ratio spectrum. From the resultant residual spectrum, the slant column density of  $\text{NO}_2$  and  $\text{O}_3$  have been calculated using the method given by Harrison (1979). It may be mentioned here that in this method, only those wavelengths have been selected which have minimum contribution of Ring component. To calibrate the instrument,  $\text{NO}_2$  cell spectrum has been scanned using artificial light source in 436 to 448 nm region, which shows good correlation with the residual spectrum obtained from the atmosphere.

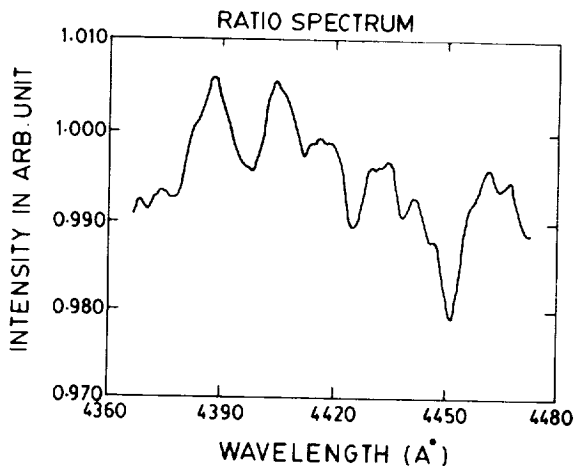


Figure 2. Ratio of twilight time and noon time spectra.

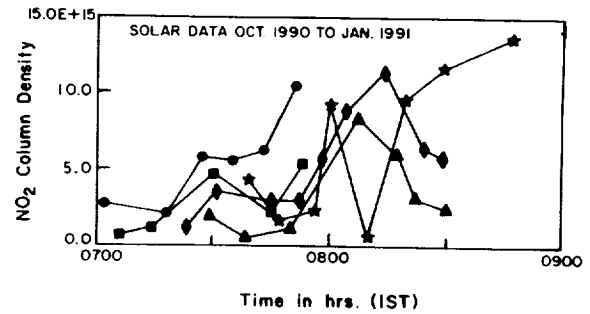


Figure 3. Increase of  $\text{NO}_2$  vertical column density after sunrise.

Fig. 3 shows the vertical column density of  $\text{NO}_2$  versus time for winter 1990-91. An increase in the value of  $\text{NO}_2$  as the sun rises is clearly discernible. This is due to the formation of  $\text{NO}_2$  by the photodissociation of  $\text{N}_2\text{O}_5$  after sunrise.

Fig. 4 shows the plot of morning and evening vertical column abundances obtained during the period December 1990 to March 1992. After September 1991, the values of  $\text{NO}_2$  appear to be slightly higher than those obtained in the earlier months. It may be mentioned here that Mt. Pinatubo erupted in June 1991 and it disturbed the aerosol distribution of the earth's atmosphere. After volcanic eruption, no alteration was made in the instrumental set-up. The interference due to additional aerosols on the retrieval process of  $\text{NO}_2$  is minimum, as explained by Harrison (1979). We do not understand why their increase in  $\text{NO}_2$ . This could be due to the increase in value of albedo below aerosols layer which causes increase in the production rate of  $\text{NO}_2$  compare to that before eruption period. The volcanic effect was more pronounced in the sunset period data compared to the sunrise period data. Contrary to our values,  $\text{NO}_2$  column density observed by

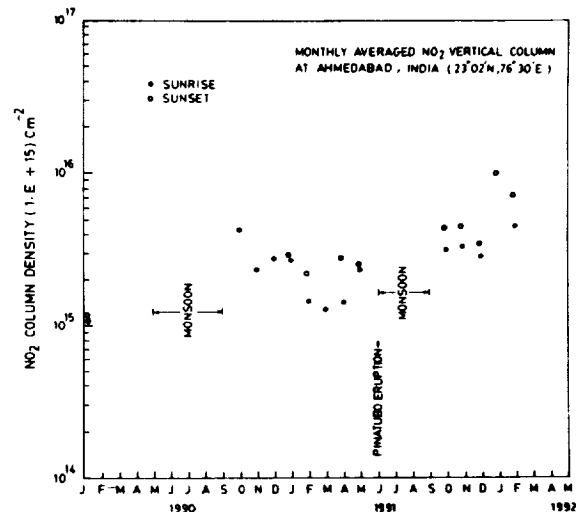


Figure 4. A plot of  $\text{NO}_2$  vertical column density over the years.

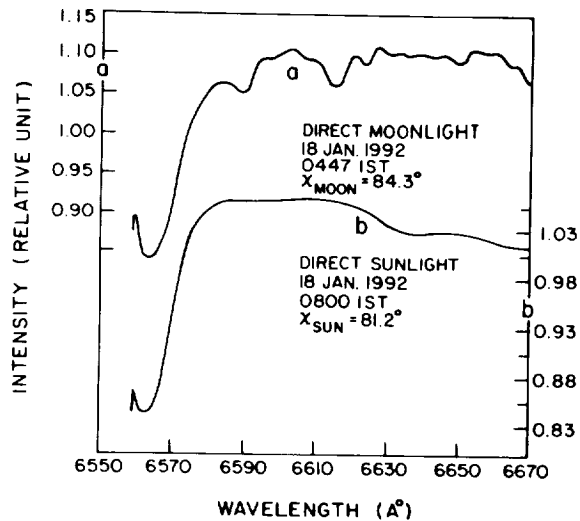


Figure 5. Direct solar and lunar spectra for large zenith angle.

similar technique at New Zealand (45°S, 170°E) shows decreasing trend after Pinatubo volcanic eruption. Before June 1991, the monthly vertical column abundance of  $\text{NO}_2$  has been found to be in the range of  $1.5 \times 10^{15} \text{ cm}^{-2}$ . From September 1991 (in the post eruption period of Mt. Pinatubo)  $\text{NO}_2$  values have been seen to increase, in February 1992, the  $\text{NO}_2$  values are  $\sim 10^{16} \text{ cm}^{-2}$ .

Fig. 5a shows the background direct solar spectrum and Fig. 5b shows the observed direct lunar spectrum between 655 and 667 nm. Except  $\text{H}_\alpha$  at 656.3 nm, there is very little solar Fraunhofer structure in the

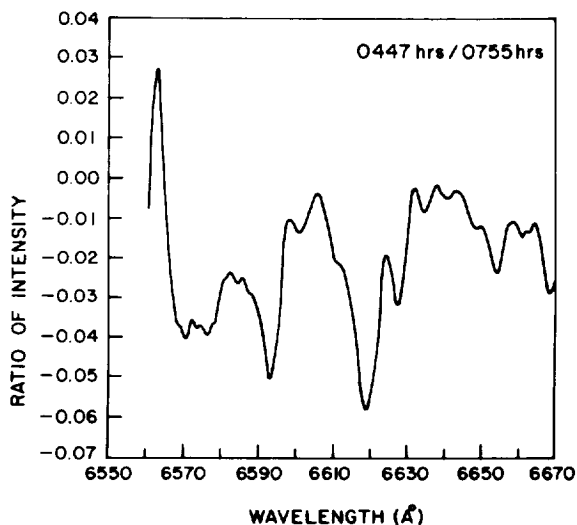


Figure 6. Residual absorption spectrum for 655 to 667 nm.

wavelength region used, thus the absorption feature due to  $\text{NO}_3$  and  $\text{H}_2\text{O}$  can clearly be seen in the raw spectrum. After taking the ratio of observed to the background spectrum, ratio spectrum has been obtained. Since aerosol and Rayleigh scattering is also present in this wavelength region (i.e., 655 to 667 nm), a slope in the ratio spectrum has been observed. Subtracting the ratio spectrum from a straight line parallel to the slope of the ratio spectrum, residual absorption spectrum has been observed.

Fig. 6 shows the residual absorption spectrum obtained in the region 655 to 667 nm region. This spectrum contains absorption due to  $\text{NO}_3$  and water vapour.  $\text{NO}_3$  has maximum absorption at 662 nm which can clearly be seen in the residual spectrum as a prominent dip. Water vapour has also absorption at 659 nm region, which can be seen as a less pronounced dip compared to the  $\text{NO}_3$ . Besides this absorption feature, the Balmer-alpha feature is also seen in the residual absorption spectrum at 656.3 nm region. To verify the absorption feature of  $\text{NO}_3$ , observations have also been taken in the 617 to 629 nm region in which  $\text{NO}_3$  has maximum absorption at 623 nm.

Fig. 7 shows the slant column abundance of  $\text{NO}_3$  vs. lunar zenith angle observed on different nights. It is to be noted that the slant column density of  $\text{NO}_3$  decreases as the lunar zenith angle increases. This is due to the modulation of aureole scattered flux at higher lunar zenith angle. The higher values of  $\text{NO}_3$  observed over Ahmedabad could be due to the tropospheric contribution from the industrial production, biomass burning in the tropics and  $\text{NO}_x$  species transported from Kuwaiti oil fires. Interestingly,  $\text{NO}_2$  values measured simultaneously are also higher than the earlier measurements.

Fig. 8 shows the vertical column density of  $\text{NO}_3$  against time observed on different nights. It is to be seen from this figure that after sunset  $\text{NO}_3$

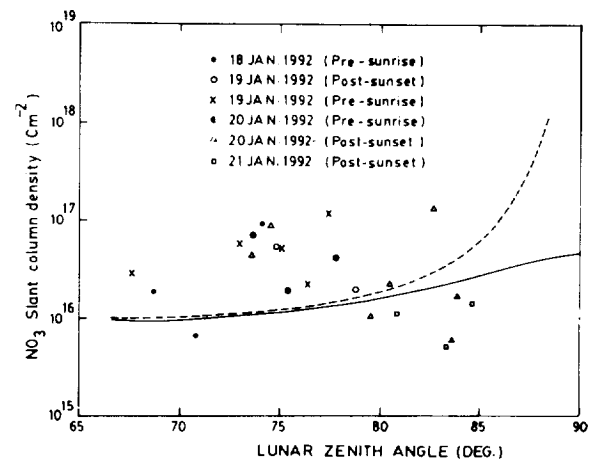


Figure 7. Slant column abundance of  $\text{NO}_3$  vs lunar zenith angle.

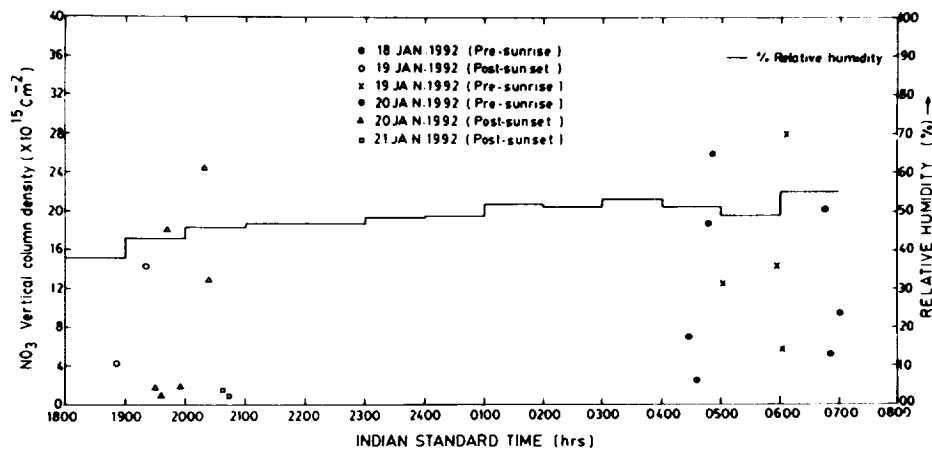


Figure 8. Vertical column abundance of  $\text{NO}_3$  against time, Relative humidity is shown by continuous line.

increases. This is in agreement with the results of Platt et al. (1981). Few observations have also been taken before sunrise, where  $\text{NO}_3$  shows a decrease in column density as one approaches sunrise. Surface relative humidity during the night has also been plotted in Fig. 8 which shows a positive correlation with  $\text{NO}_3$  as observed by Platt et al. (1981). Our measured values of  $\text{NO}_3$  lie between 1 and  $20 \times 10^{15} \text{ cm}^{-2}$ .

#### Conclusion

In this paper we have presented results of  $\text{NO}_2$  and  $\text{NO}_3$  measurements by a ground-based visible absorption spectroscopy technique. Measurements have been made at a low latitude northern hemispheric station, Ahmedabad ( $23^\circ\text{N}$ ,  $76^\circ\text{E}$ ), India. Several interesting results have been obtained. The monthly vertical column abundance of  $\text{NO}_2$  has been found to be in the range of  $1.5 \times 10^{15} \text{ cm}^{-2}$ . An increase in the value of  $\text{NO}_2$  was found after Pinatubo volcanic eruption.  $\text{NO}_3$  values have also been observed during the night time. Its values varies from 1 to  $20 \times 10^{15} \text{ cm}^{-2}$ . This suggest that tropospheric contribution of  $\text{NO}_3$  is very high at our observation site.

#### References

Greenblatt, G.D., J.J. Orlando, J.B. Burkholder and A.R. Ravishankara, 1990 : Absorption measurements of oxygen between 330 and 1140 nm, *J. Geophys. Res.*, 95, 18577-18583.  
 Harrison, A. W., 1979 : Mid-summer stratospheric  $\text{NO}_2$  at latitude  $45^\circ\text{S}$ , *Can. J. Phys.*, 57, 1110-1117.  
 Johnston, P.V., R.L. McKenzie, J.G. Keys and W.A. Matthews, 1992 : Observations of depleted stratospheric  $\text{NO}_2$  following the Pinatubo volcanic eruption, *Geophys. Res. Lett.*, 19, 211-213.  
 McKenzie, R.L., and P.V. Johnston, 1982 : Seasonal variations in stratospheric  $\text{NO}_2$  at  $45^\circ\text{S}$ .

*Geophys. Res. Lett.*, 9, 1255-1258.  
 Mount, G.H., R.W. Sanders, A.L. Schmeltekopf, and S. Solomon, 1987 : Visible spectroscopy at McMurdo station, Antarctica, 1. Overview and daily variations of  $\text{NO}_2$  and  $\text{O}_3$ , *Austral spring*, 1986, *J. Geophys. Res.*, 92, 8320-8328.  
 Norton, R.B., and J.F. Noxon, 1986 : Dependence of stratospheric  $\text{NO}_3$  upon latitude and season, *J. Geophys. Res.*, 91, 5323-5330.  
 Noxon, J.F., R.B. Norton and W.R. Henderson, 1978 : Observation of Atmospheric  $\text{NO}_3$ , *Geophys. Res. Lett.*, 5, 675-678.  
 Noxon, J.F., E.C. Whipple, Jr., and R.S. Hyde, 1979 : Stratospheric  $\text{NO}_2$ , 1. Observational method and behaviour at mid-latitude, 84, 5047-5064.  
 Pommereau, J.P., and F. Goutail, 1988 :  $\text{O}_3$  and  $\text{NO}_2$  ground-based measurements by visible spectrometry during Arctic winter and spring 1988, *Geophys. Res. Lett.*, 15, 891-894.  
 Platt, U., D. Perner, J. Schroder, C. Kersler and A. Toennissen, 1981 : The diurnal variation of  $\text{NO}_3$ , *J. Geophys. Res.*, 86, 11, 965-11,970.  
 Sanders, R.W., S. Solomon, G.H. Mount, M.W. Bates and A.L. Schmeltekopf, 1987 : Visible spectroscopy at McMurdo station, Antarctica, 3, Observations of  $\text{NO}_3$ , *J. Geophys. Res.*, 92, 8339-8342.  
 Solomon, S., H.L. Miller, J.P. Smith, R.W. Sanders, G.H. Mount, A.L. Schmeltekopf and J.F. Noxon, 1989 : Atmospheric  $\text{NO}_3$ , 1. Measurement technique and the annual cycle at  $40^\circ\text{N}$ , *J. Geophys. Res.*, 94, 11,041-11,048, 1989.  
 Syed, M.Q., and A.W. Harrison, 1980 : Ground based observations of stratospheric nitrogen dioxide, 58, 788-802.