

Seasonal and solar activity variation of NO₂ over Ahmedabad

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Nitrogen dioxide, NO₂, has strong absorption signatures in 436-448 nm region. Using this property, column density of this species has been determined at Ahmedabad, a low latitude station. Absorption spectrum has been measured by a ground-based spectroscopy technique during twilight period. Scattered zenith sunlight has been used as the source of light. The twilight slant column density (SCD) values have been found to be $\sim 10^{17}$ cm⁻². A summer maximum and a winter minimum, and a decreasing trend of NO₂ with an increase of solar activity level are seen. These results have been compared with the UARS and GOME satellite values.

Keywords: Nitrogen dioxide, Nitrogen dioxide column density, Absorption spectrum; Sunlight absorption

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1 Introduction

During the past two-and-a-half decade considerable attention has been paid to the stratosphere, because of the concern that man-made pollutants are altering its composition leading to depletion of ozone in the atmosphere. A large volume of work exists which establishes the role of different minor constituents present in the stratosphere for depletion of ozone. They are mainly some compounds of nitrogen, hydrogen and halogens. Nitrogen dioxide is one among the compounds of nitrogen. It plays an important role in the chemical reactions that control the distribution of ozone in the stratosphere.

Column amount of NO₂ has been measured by ground-based UV visible spectrometer since the work of Brewer *et al.*¹ and Noxon². They used the property that NO₂ possesses a highly structured absorption spectrum in this region. Pioneering work in this direction has been done by two groups, one in Boulder (40°N, 109°W) in the northern hemisphere³ and another at Lauder (45°S, 170°E), New Zealand in the southern hemisphere⁴. Some work has also been done by a French group⁵ and a Japanese group⁶. According to Harder and Brault⁷, the 410-450 nm region is one of the best in the visible region of the electromagnetic spectrum for making atmospheric measurements of NO₂.

A number of observations have been taken on the NO₂ content of the stratosphere by using ground-

based, balloon-borne and space craft techniques. These observations are mostly for mid- and high-latitude zones. For low-latitude zone, observations are sparse. Satellite observations are available for low-latitude zone; but these are not yet fully validated due to the lack of enough observations in this region. The variability of this species in the low-latitude northern hemisphere is also not properly known. In India the first measurements of NO₂ content were made by Bhonde *et al.*⁸ during 1990 at Pune (18°N, 73°E) and Lal *et al.*⁹ during 1989-90 at Ahmedabad (23°N, 72°E). Recently Meena *et al.*¹⁰ have reported results of some more measurements made at Pune during 2000-2001. In this paper results of NO₂ content measurements made at Ahmedabad, by visible absorption spectroscopy technique from January 1996 to May 2000 have been presented. Seasonal and solar activity variations of NO₂ column amounts have also been studied. In addition, the results have been compared with the GOME and UARS satellite data.

2 Methodology

In the 435-450 nm spectral region, NO₂ has strong absorption signatures at 439.5, 445.0 and 448 nm. In the same region, there are strong absorption signatures due to O₃, H₂O and O₄ at 443.5, 442.7 and 446.7 nm, respectively. Thus by measuring the absorption spectrum in 435-450 nm range, it is possible to determine the column density of NO₂ as

well as O₃, H₂O and O₄. The absorption of the scattered sunlight from the zenith sky in the 436-448 nm range has been measured during the period 1996-2000. From these measurements the column densities of H₂O, NO₂, O₃, and O₄ have been derived. The algorithms to derive these densities from the absorption measurements are different for different species. Earlier¹¹, H₂O column density derived from these measurements has been reported. In this paper NO₂ column density derived from these measurements is being presented.

3 Experimental description

The intensity of the scattered sunlight from the zenith sky in the 436-448 nm range has been measured. The schematic diagram of the experimental set-up has been shown earlier (see Fig. 2 of Ref. 11). The essential components are described here again in brief. Scattered radiation from zenith falls on a plane mirror mounted at 45° to the horizontal axis of the optical system. The radiation after reflection from the plane mirror falls on the entrance slit of a monochromator. The wavelength-dispersing element of this monochromator is a plane diffraction grating. A resolution of 0.4 nm has been used by keeping the entrance and exit slit width equal to 0.04 mm. The grating is rotated by an in-built stepper motor. At a particular angle it allows only one wavelength to pass through, depending upon the resolution of the instrument. A R732 Hamamatsu photomultiplier tube has been used as a detector. A laboratory made converter has been used in DC mode with variable gain. The current DC mode has been converted into voltage DC mode. A lock-in-amplifier (Stanford Research System Model SR530) has been used for enhancing the signal-to-noise ratio. The output of the amplifier has been fed to a computer through an A/D (PCL-205) card. This PCB was able to record in 5 V range. The analog signal voltage was digitized with 12-bit accuracy. The details are given in Ref. 11.

4 Observation

Observations were taken during the evening twilight period for solar zenith angle of about 90°. At that time the radiation coming from the sun travels a longer path through the atmosphere; thus the signature of the absorption will be large. The measured signal includes contribution from Fraunhofer absorption lines also. To remove the Fraunhofer component, observations were also taken during noontime. By taking the ratio of the evening to noon spectra, the

ratio spectrum has been made free, to a large extent, from the contribution due to Fraunhofer lines. Both forward and backward scanning were done. Twelve scanning were done in 3 min. Then the average of these 12 spectra was taken. This process also nullifies the scintillating effect of the earth's atmosphere.

5 Theoretical details

Let $I_n(\lambda)$ and $I_t(\lambda)$ be the observed intensities during noontime and during twilight time conditions at wavelength λ . Then we define:

$$R(\lambda) = \log_e[I_t(\lambda)/I_n(\lambda)] \quad \dots(1)$$

The details of the theory to be used for the determination of NO₂ density has already been described in Ref. 11. The equation which has been used in the present work is as follows:

$$R(\lambda) = -a_1(\lambda).[M_1]-a_2(\lambda).[M_2]-a_3(\lambda).[M_3]-a_4(\lambda).[M_4] - A/\lambda^4 - B/\lambda \quad \dots(2)$$

where, $a_1(\lambda)$, $a_2(\lambda)$, $a_3(\lambda)$ and $a_4(\lambda)$ are absorption cross-sections of O₃, NO₂, H₂O and O₄, respectively at wavelength λ ; A and B are constants associated with Rayleigh scattering and aerosol scattering and $[M_1]$, $[M_2]$, $[M_3]$ and $[M_4]$ are slant column densities of O₃, NO₂, H₂O and O₄, respectively. In Eq. (2), $R(\lambda)$ is the measured quantity; $a_1(\lambda)$, $a_2(\lambda)$, $a_3(\lambda)$ and $a_4(\lambda)$ are known from laboratory measurements and $[M_1]$, $[M_2]$, $[M_3]$, $[M_4]$, A and B are six unknowns. The values of $a_1(\lambda)$ and $a_2(\lambda)$ are taken from Harrison¹², those of $a_3(\lambda)$ are taken from Harder and Brault⁷ and $a_4(\lambda)$ from Greenblatt *et al*¹³. We have 512 values of $R(\lambda)$, which will form 512 linear equations. In actual calculations there are 487 linear equations, because observed spectra are smoothed by 25 points running average. These equations are transformed into a 6 × 6 matrix by the method of least squares. Then by matrix inversion method the values of six unknowns are calculated.

6 Results and discussion

Using Eq. (2), the slant column density values of NO₂ from January 1996 to May 2000 have been calculated. These values are shown in Fig. 1. In this figure the averaged value and the maximum and minimum values for each month are shown. There are about 20 observations in one month. The graph shows that the slant column density of NO₂ is ~10¹⁷ cm⁻². A large scatter is noticed in the values of NO₂. This could be due to the fact that during one day several

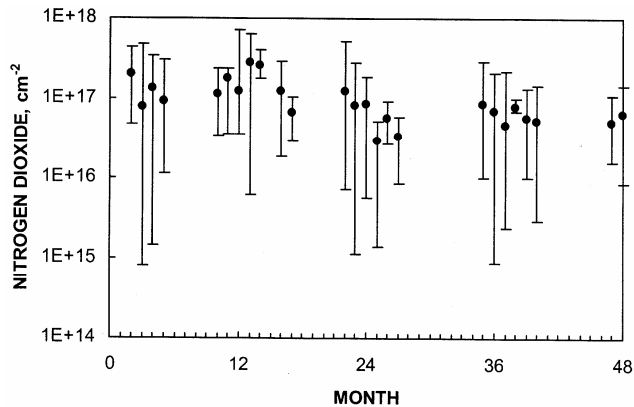


Fig. 1—Nitrogen dioxide slant column density of the present work from January 1996 to May 2000

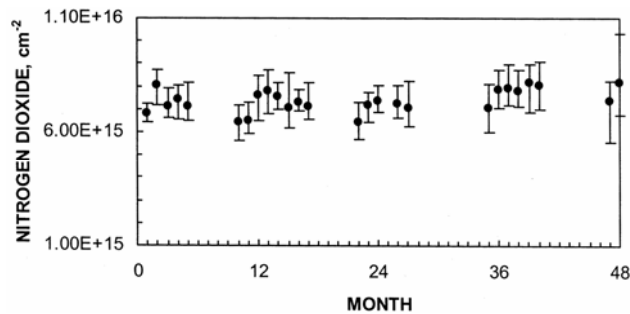


Fig. 2—GOME satellite vertical column density of nitrogen dioxide from January 1996 to May 2000

observations were taken from 80° to 90° solar zenith angle. Also contribution due to tropospheric pollution is possible. Meena *et al.*¹⁰ found VCD (vertical column density) to be $1\text{--}10 \times 10^{15} \text{ cm}^{-2}$. In Fig. 2, GOME VCD data from ERS-2 satellite for the same period has been shown. They are $\sim 7 \times 10^{15} \text{ cm}^{-2}$. GOME data have been obtained from web site <ftp://g0dps01u.ecs.nasa.gov/>. In Fig. 3 VCD values of UARS for the same period have been shown. They are about $3.5 \times 10^{15} \text{ cm}^{-2}$. UARS data have been obtained from web site <http://disc.gsfc.nasa.gov>. A comparison of Figs 2 and 3 shows that GOME satellite values are about a factor of 2 higher than the UARS values. It may be mentioned here that GOME satellite values are for the solar zenith angle range $16\text{--}45^\circ$ near noontime in 200 km range grid, whereas UARS values are for the sunset time and are in $\pm 5^\circ$ latitude and $\pm 15^\circ$ longitude range grid with respect to Ahmedabad coordinates. It may be mentioned here that according to NO_2 theory, the near noontime and the sunset values should not differ much.

It may be noticed that GOME satellite and UARS data do not show much scatter as has been seen in our

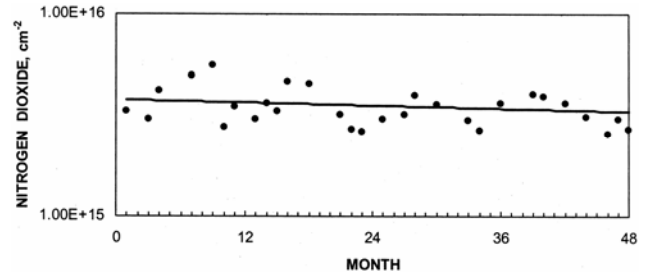


Fig. 3 — UARS vertical column density of nitrogen dioxide from January 1996 to May 2000

data. This is due to the heavy smoothening of the data. It may further be mentioned that in the UARS data very often tropospheric contribution has been observed. UARS data are in the form of VMR (volume mixing ratio) from about 10 to 50 km. From this data set VCD has been obtained by integrating these values over altitude. However, while integrating these values, the tropospheric altitude has been excluded. If we take tropospheric contribution into consideration, then scatter in UARS data is also seen as in our results. More recently, Preston *et al.*¹⁴ have demonstrated that removing the tropospheric contribution eliminates the large-scale scatter. Another thing we would like to mention here is that in the UARS data, in one month, there are two to three days observation only, whereas in our case, there are observations of about 20 days. So the scatter in our data could be due to day-to-day variation also.

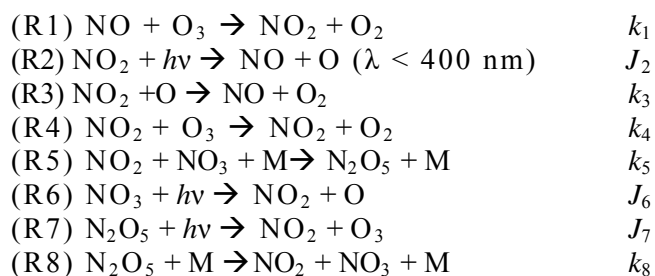
Our NO_2 densities are SCD values. To compare our NO_2 densities with those of GOME and UARS, we have to divide our values by the air mass factor (AMF). Air mass factor is the ratio of slant column density and vertical column density. The vertical column density of a gas is its column density for 0° solar zenith angle (χ). For $\chi < 75^\circ$, $\text{AMF} = \sec \chi$. For $\chi > 75^\circ$, $\text{AMF} \neq \sec \chi$. For such values of χ , the radius of curvature of the earth becomes important. If we assume that NO_2 density decreases exponentially with increase of height like N_2 or O_2 , then the value of AMF becomes ~ 10 . But in reality NO_2 density increases with height, becomes the maximum between 30 and 35 km and then decreases. The value of AMF will be different if the height of this maximum is varied in calculation. For this type of height profile, calculation is done by dividing the atmosphere in a number of slabs and assuming some concentration in each slab.

Calculations have been done by different authors taking the thickness of the slab from 5 to 6 km and concentration in the slab $\sim 10^{16} \text{ cm}^{-2}$. In addition, some

have considered single and some others multiple scattering. Some have considered twilight chemistry and some others ignored it. For a mid-latitude station, Kerr *et al.*¹⁵ and Noxon *et al.*¹⁶ have given values as 19.4 and 25.2, respectively. McKenjie *et al.*⁴ taking NO₂ vertical profile of Lauder, have given values between 16 and 17 with and without chemistry of NO₂. Perliski and Solomon¹⁷ have given a value of 20 for stratosphere and more than 1 for the troposphere for 90° solar zenith angle. More recently, for a mid-latitude station, Aberdeen, Preston *et al.*¹⁴ have given the value of AMF as 15.7. For Pune, recently, Meena *et al.*¹⁰ have given the value of AMF as 20. Thus there are several uncertainties in the calculation of AMF value and hence there is no consensus about the value of AMF for NO₂ around 90° zenith angle. Taking into consideration the AMF value of Pune (= 20 as given by Meena *et al.*¹⁰) and the value for monotonic decrease of NO₂ with the height (= 10), we have taken the value of AMF for 90° zenith angle for Ahmedabad equal to 15.

Now if we divide our SCD values by 15, our values come close to the GOME values but still a factor of 2 higher than the UARS values. This implies that satellite values have to be treated with caution. To retrieve satellite values from the telemetry signal, several assumptions are made. Over the years these are validated. As for example, UARS data shown in this paper are the 19th version.

The present NO₂ values of Fig. 1 have been shown again in Fig. 4. In the same figure the values of 10.7 cm solar flux for the same period have also been shown. The density of NO₂ appears to decrease with the increase of solar activity level. This feature is also seen in UARS data. To explain this feature we take a simple chemistry of NO₂ used by us earlier¹⁸. It contains the following chemical reactions:



Using the above reactions, the continuity equation of NO₂ with time at a particular height can be written as:

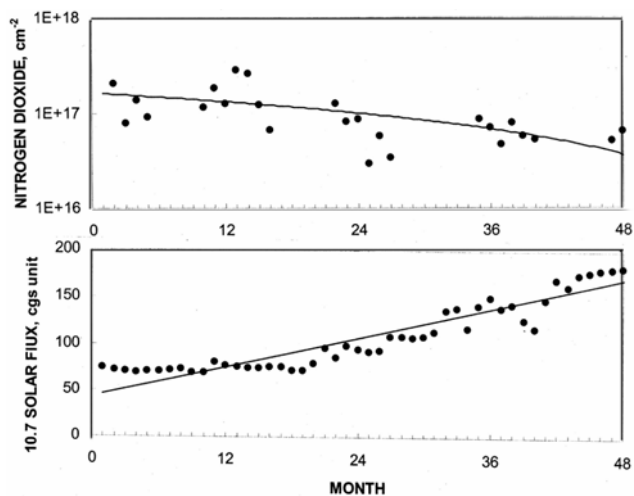


Fig. 4—Nitrogen dioxide slant column density of the present work and 10.7 cm solar flux from January 1996 to May 2000

$$\frac{d[\text{NO}_2]}{dt} = k_1.[\text{NO}].[O_3] + J_6.[\text{NO}_3] + k_8.[\text{N}_2\text{O}_5].[M] + J_7.[\text{N}_2\text{O}_5] - J_2.[\text{NO}_2] - k_3.[O].[NO_2] - k_4.[O_3].[NO_2] - k_5.[\text{NO}_3].[NO_2] \quad \dots (3)$$

During daytime, the density values of NO₃ and N₂O₅ are negligible. Then Eq. (3) for a steady state condition can be written as:

$$[\text{NO}_2] = k_1.[\text{NO}].[O_3] / (J_2 + k_3.[O] + k_4.[O_3]) \quad \dots (4)$$

In Eq. (4), in the denominator, predominant term is *J*₂. Solar flux has been reported to increase from low to high solar activity condition by different amounts in different wavelength ranges (de Toma *et al.*¹⁹). It is not properly known by what amount the intensity of radiation of λ < 400 nm increases with the increase of solar activity level. We assume that the intensity of this radiation is proportional to 10.7 cm solar flux. From Fig. 4, it appears that 10.7 cm solar flux increases by a factor of 4. If there is an increase in the intensity of radiation of λ < 400 nm by this amount, and if [O] and [O₃] do not change with change of solar activity level, then, as per Eq. (4), NO₂ should decrease by a factor of ~4 with the increase of solar activity, though the actual chemistry may be more complex.

In Fig. 5 we have shown the seasonal variation of NO₂ for the period 1996-2000. The features to be noticed from this figure are summer maximum and winter minimum. Meena *et al.*¹⁰ have also found that density of NO₂ is maximum during summer months and minimum during winter months at Pune. Both Lauder and Boulder groups have found similar features at mid-latitude stations.

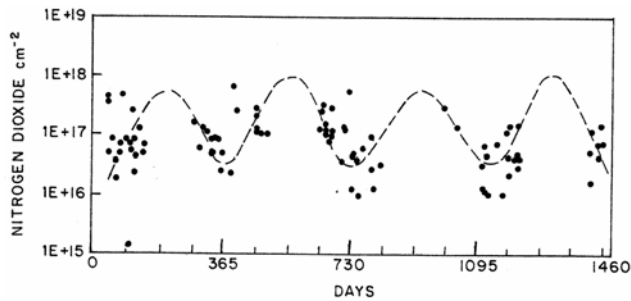


Fig. 5—Seasonal variation of nitrogen dioxide slant column density of the present work from January 1996 to May 2000

The density of NO_2 column is strongly affected by the length of night and hence its value in the sunrise period. During nighttime the loss of NO_2 is mainly through reactions R4 and R5 and if NO_3 is considered to be in steady state during nighttime (which is reasonable), then NO_2 nighttime variation can be expressed by:

$$d[\text{NO}_2]/dt = -2.k_4.[\text{O}_3].[\text{NO}_2] \quad \dots (5)$$

which gives

$$[\text{NO}_2]_{\text{sr}} = [\text{NO}_2]_{\text{ss}} . \exp(-2.k_4.[\text{O}_3].\Delta t) \quad \dots (6)$$

where sr and ss stand for sunrise and sunset times and Δt represents length of the night. Since length of the night, Δt , in summer is smaller than that in winter, during summer the destruction of NO_2 during nighttime will be less than that during winter. As a result, the summer $[\text{NO}_2]_{\text{sr}}$ values will be larger than the winter $[\text{NO}_2]_{\text{sr}}$ values. This is also understandable from Eq. (6).

5 Conclusion

A ground-based visible absorption spectroscopy technique has been used to measure column density of NO_2 at a low latitude station, Ahmedabad. The twilight slant column density for $\chi \approx 90^\circ$ comes to $\sim 10^{17} \text{cm}^{-2}$. Scatter in the data is noticed. There could be tropospheric contamination. Summer maxima and winter minima and a decreasing trend with an increase of solar activity level of nitrogen dioxide content have also been seen. If air mass factor is taken as 15, then our values come close to GOME satellite values.

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References

- 1 Brewer A W, McElroy C T & Kerr J B, Nitrogen dioxide concentrations in the atmosphere, *Nature (UK)*, 246 (1973) 129.
- 2 Noxon J F, Nitrogen dioxide in the stratosphere and troposphere measured by ground-based absorption spectroscopy, *Science (USA)*, 189 (1975) 547.
- 3 Solomon S, Schmeltekopf A L & Sanders R W, On the interpretation of zenith sky absorption measurements, *J Geophys Res (USA)*, 92 (1987) 8311.
- 4 McKenzie R L, Johnston P V, McElroy C T, Kerr J B & Solomon S, Altitude distributions of stratospheric constituents from ground-based measurements at twilight, *J Geophys Res (USA)*, 96 (1991) 15499.
- 5 Pommereau J P & Goutail F, Stratospheric O_3 and NO_2 observations at the southern polar circle in summer and fall 1988, *Geophys Res Lett (USA)*, 15 (1988) 895.
- 6 Shibasaki K, Iwagami N & Ogawa T, Stratospheric nitrogen dioxide observed by ground-based and balloon-borne techniques at Syowa station, *Geophys Res Lett (USA)*, 13 (1986) 1268.
- 7 Harder J W & Brault J W, Atmospheric measurements of water vapour in the 442-nm region, *J Geophys Res (USA)*, 102 (1997) 6245.
- 8 Bhonde S D, Mehra P, Bose S, Londhe A L & Jadhav D B, Simultaneous measurements of low latitude NO_2 and O_3 from zenith sky observations in visible region, *Indian J Radio Space Phys*, 21 (1992) 18.
- 9 Lal M, Chakrabarty D K, Sidhu J S, Das S R & Verma S D, Some results of ground-based measurements of atmospheric NO_2 at Ahmedabad by visible absorption spectroscopy, *Indian J Radio Space Phys*, 22 (1993) 108.
- 10 Meena G S, Jadhav D B & Bhosale C S, Total column density variations of NO_2 and O_3 by automatic visible spectroscopy over Pune, India, *Curr Sci (India)*, 85 (2003) 171.
- 11 Chakrabarty D K, Patel S, Vala P & Iyer K N, Column density of atmospheric water vapour over Ahmedabad; *Indian J Radio Space Phys*, 32 (2003) 301.
- 12 Harrison A W, Mid-summer stratospheric NO_2 at latitude 45°S , *Can J Phys (Canada)*, 57 (1979) 1110.
- 13 Greenblatt G D, Orlando J J, Burkholder J B & Ravishankara A R, Absorption measurements of oxygen between 330 and 1140 nm, *J Geophys Res (USA)*, 95 (1990) 18577.
- 14 Preston K E, Fish D J, Roscoe H K & Jones R L, Accurate derivation of total and stratospheric columns of NO_2 from ground-based zenith-sky measurements, *J Atmos Chem (Netherlands)*, 30 (1998) 163.
- 15 Kerr J B, Evans W F J & McConnell J C, The effect of NO_2 changes on the tangent ray NO_2 measurements, *Geophys Res Lett (USA)*, 4 (1977) 577.
- 16 Noxon J F, Whipple E C Jr. & Hyde R S, Stratospheric NO_2 observational method and behaviour at mid-latitude, *J Geophys Res (USA)*, 84 (1979) 5047.
- 17 Preliski L M & Solomon S, On the evaluation of air mass factors for atmospheric near-ultraviolet and visible absorption spectroscopy, *J Geophys Res (USA)*, 98 (1993) 10363.
- 18 Chakrabarty D K, Peshin S K, Srivastav S K, Shah N C & Pandya K V, Further evidence of total ozone variation during solar eclipse of 1995, *J Geophys Res (USA)*, 106 (2001) 3213.
- 19 de Toma G, White O R, Chapman G A & Walton S R, Solar irradiance variability—progress in measurement and empirical analysis, *Adv Space Res (UK)*, 34(2) (2004) 237.