Reports

Nitrogen Dioxide in the Stratosphere and Troposphere Measured by Ground-Based Absorption Spectroscopy

Abstract. *The NO_2 abundance in the stratosphere has been determined from ground-based spectra of the rising and setting sun and moon and of the twilight sky near 4500 angstroms. The spectra were taken at the Fritz Peak Observatory, at an altitude of 3 kilometers in the Colorado mountains. Separation of the stratospheric contribution requires observations at a relatively unpolluted site; direct measurement of the tropospheric absorption in the Colorado mountains often yields an upper limit on the tropospheric mixing ratio of 0.1 part per billion. The stratospheric NO_2 abundance is two to three times greater at night than during the day and increases significantly during the course of a sunlit day; these changes are related to photolytic decomposition of NO_2 and N_2O_5 in the daytime stratosphere. Absorption by NO_3 was sought but not found; the results set an upper limit of 2 percent on the nighttime abundance ratio of NO_3 to NO_2 in the stratosphere.*

A pronounced structure in the absorption spectrum of NO_2 near 4500 Å was used to determine the total daytime atmospheric content of NO_2 by Brewer *et al.* (*1*), who also measured the stratospheric content separately from an aircraft. They used a modified Dobson ozone spectrophotometer recording at three wavelengths of maximum and minimum absorption. As pointed out by Johnston (*2*), use of the ratio of solar intensities at such wavelengths to determine the NO_2 abundance can present difficulties, since the ratio in the absence of NO_2 must be known very accurately.

We have pursued the problem by making complete spectral scans in the region 4350 to 4500 Å. With the full spectrum the identification of the absorber is unambiguous, and by making measurements under a variety of conditions it is possible to separately determine the tropospheric and stratospheric NO_2 abundances from ground-based measurements alone. The observations reveal a diurnal variation of NO_2 in the stratosphere and set a very small upper limit on the NO_2 density in the unpolluted troposphere. We have also searched in nighttime and twilight spectra for absorption by NO_3, which is reported to have a sharp maximum of $\sim 4 \times 10^{-18}$ cm^2 at 6630 Å (*3*). Several measurements at sunset and moonset failed to yield definite absorption and set an upper limit of 2×10^{14} cm^{-2} on the vertical column abundance of NO_3. The NO_2 measurements, as described below, yielded $\sim 10^{16}$ cm^{-2} for the nighttime NO_2 abundance in the stratosphere; hence we infer an upper limit of 2 percent on the ratio of NO_3 to NO_2 in the nighttime stratosphere.

The spectrum was scanned at 5 Å resolution between 4370 and 4470 Å with an Ebert spectrometer at the Fritz Peak Observatory, located at an altitude of 3 km a few kilometers east of the continental divide in Colorado. Solar spectra were obtained as a function of air mass using a diffuse scattering screen; with the moon as a source it was necessary to direct moonlight onto the slit with a mirror. We also secured spectra of the zenith sky in the twilight period. To study the tropospheric NO_2 absorption we used as a source several powerful incandescent lamps situated about 12 km from the observatory. The observations were usually reduced to absorption per unit air mass (AM), the reduction factor being the ratio of total atmospheric abundance along the line of sight to that in the zenith.

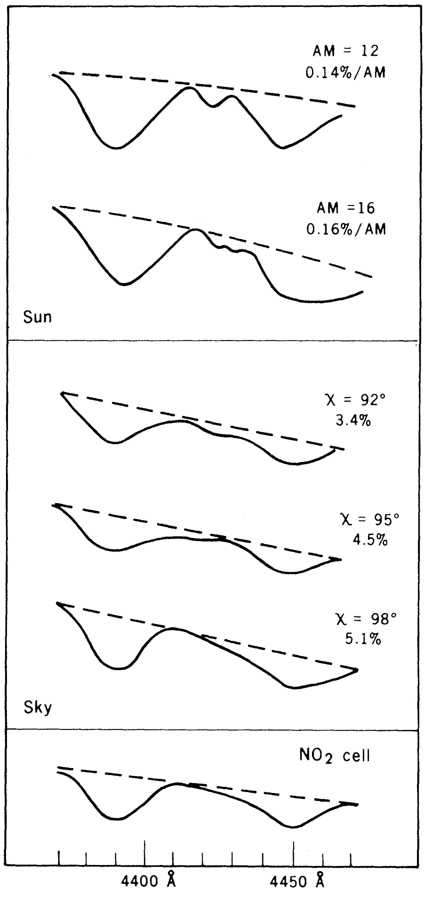

Fig. 1. Spectra of the sun and twilight zenith sky compared with a laboratory spectrum of NO_2; the ordinate scales vary. The air mass (AM) and absorption per unit air mass at 4390 Å are shown for the solar spectra; the solar zenith angle (χ) and measured absorption are for the twilight sky. Each spectrum is an average of three 1-minute scans. The dashed lines connect regions of minimum absorption; the total absorption by NO_2 at 4390 Å is close to twice the adjacent minimum values. By "absorption" we mean the intensity difference between the solid and dashed line divided by the intensity at the dashed line, all at 4390 Å. For the 2.5-cm-thick cell the absorption defined in this way was about 13 percent with an NO_2 pressure of 5 torr.

In principle, spectra obtained with an intervening atmosphere should be compared with a spectrum of the sun (or moon) obtained above the atmosphere. In practice, we used as a control spectrum the average of a number of spectra obtained at 1.3 AM on different days with the sun as a source. The absorption by atmospheric NO_2 in the control spectrum is always negligible compared with that in spectra of the sun or moon near the horizon (or in the twilight sky.

A control spectrum is necessary since the solar spectrum is densely packed with Fraunhofer structure in this region; the magnitude of this structure is about 10 percent of the total intensity even at 5 Å resolution. Except for the direct tropospheric observations, where the background was a flat continuum, our measurements were always converted to a ratio of the observed to the control spectrum. A laboratory absorption spectrum of NO_2 obtained with the same spectrometer was used for the absolute determination of atmospheric NO_2 abundance; our absorption coefficient was in good agreement with earlier results (*3*). For the measurements involving spectral ratios absorption at 4300 Å of 0.3 percent or greater could be detected; the sensitivity was about 10 times better for the tropospheric measurements because the integration times were longer and it was not necessary to take a ratio.

Figure 1 shows spectra of the sun before

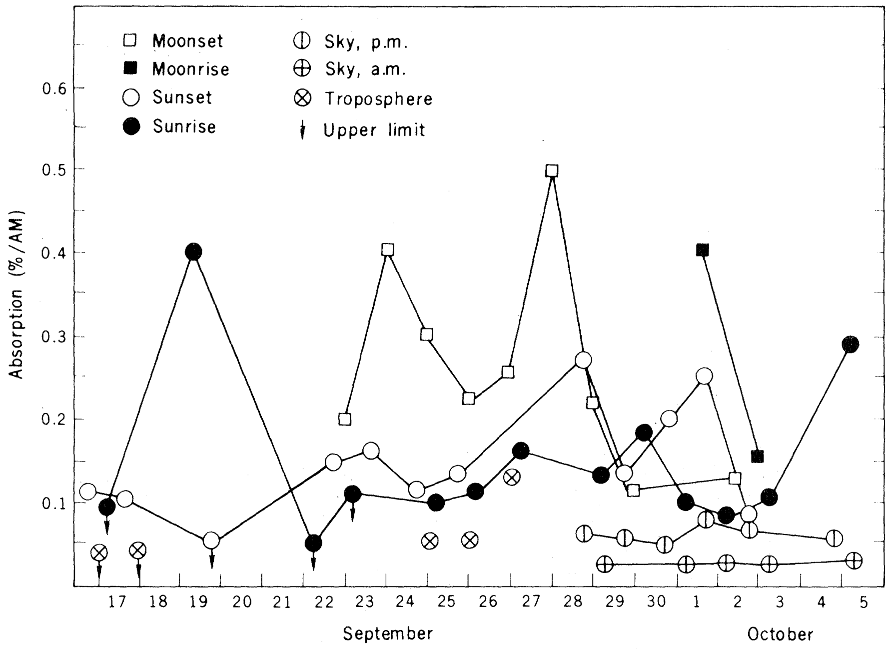

Fig. 2. Absorption due to NO_2 expressed as percentage per unit air mass at 4390 Å. The spectra were obtained with a variety of sources in the fall of 1974, as explained in the text.

sunset and the zenith sky after sunset, as well as a laboratory NO_2 spectrum. The sun and sky spectra are ratios of the observed spectra to the control solar spectrum and do not have a common ordinate scale. Their close resemblance to the spectrum of pure NO_2 makes it clear that NO_2 is primarily responsible for the observed atmospheric absorption. The feature at 4425 Å in the upper solar spectrum in Fig. 1 is due to absorption by water vapor. Curcio *et al.* (*4*) report three water vapor lines near 4425 Å and four more in the range 4447 to 4464 Å, including one at 4447 Å which falls within one of the spectral channels of Brewer *et al.* (*1*). We looked for an effect of water vapor absorption in spectra of the sun taken on cloudy, humid days and found no discernible effect at the 4390 Å feature used in our study.

The solar and lunar spectra provide a direct measure of the total number of NO_2 molecules along the line of sight. Absorption per unit air mass gives the vertical column abundance; the conversion factor is 3.3×10^{15} cm^{-2} for 0.1 percent absorption. The sky spectra are not as simply interpreted, and we can only present a preliminary discussion of them at present. At 4500 Å a ray that grazes the surface of the earth and passes through the entire atmosphere suffers an extinction of $\sim 10^8$ as a result of Rayleigh scattering. Rays that pass the terminator at higher altitude suffer a rapidly decreasing extinction; for those at 20 km the extinction factor is only 4. If multiple scattering is ignored, the sky spectra for solar zenith angle $\chi \gtrsim 90°$ reflect only absorption by NO_2 located above about 20 km near the terminator. In a single scattering approximation the zenith sky brightness is proportional to the integral over height of the ratio of atmospheric density to the extinction factor. This ratio has its maximum value for rays that pass the terminator at 20 km and its half-maximum value for rays at 15 and 30 km. For rays at and below 10 km the ratio is less than 2 percent of the maximum value. Thus, the sky spectra are heavily weighted toward NO_2 in the altitude range 15 to 30 km above the terminator and so give at least an approximate measure of the amount of NO_2 in that region. With multiple scattering there will be some contribution to the total absorption from rays that have passed through the terminator region below 15 km, so the use of sky spectra to infer the stratospheric NO_2 abundance may lead to an overestimate if the troposphere is heavily polluted. The density of NO_2 in the troposphere is usually very low at our observing site, and we expect that the inclusion of multiple scattering effects in our calculations will confirm our hypothesis that sky spectra provide information about stratospheric NO_2 alone. Even so, the total measured absorption is not simply related to the total vertical column abundance in the stratosphere, but depends on how the total abundance is distributed with altitude between 15 and 30 km. Assuming that the mixing ratio is constant in this altitude range, the effective air mass factor in the sky measurements increases from ~ 40 at sunset ($\chi = 90°$) to ~ 80 for $\chi > 95°$. The effective air mass is less if the mixing ratio increases with altitude, as it probably does; the effective air mass varies inversely as the square root of the scale height of NO_2. However, since the total absorption in the sky spectra does not significantly increase for $\chi > 95°$, use of these air mass factors will underestimate the vertical column abundance between 15 and 30 km by less than a factor of 2.

The spectra shown in Fig. 1 indicate that the total column abundance of NO_2 near sunset was about 5×10^{15} cm^{-2} and the stratospheric abundance (between ~ 15 and 30 km) was roughly half this value, based on air mass factors appropriate to a mixing ratio independent of height.

We also obtained NO_2 absorption spectra over a 12-km horizontal path through the troposphere at 3 km above sea level. At a time when an east wind blew polluted air from the Denver area (~ 50 km away) into the mountains, we observed a mixing ratio of ~ 10 parts per billion (ppb). Under the more customary circumstance of a westerly wind we usually found an upper limit of 0.1 ppb; Salt Lake City, ~ 500 km to the west, is the only major source of anthropogenic NO_2 in this direction for many hundreds of kilometers. Except at the end points the optical path remained between 200 and 300 m above ground densely covered with evergreen trees.

In Fig. 2 we collect the results of a number of measurements made over a 3-week period in the fall of 1974. The solar and lunar measurements were made with the source at elevation angles corresponding to a range of 5 to 15 AM. In all cases each rising or setting source was measured several times over this air mass range and gave values for the absorption per unit air mass that usually agreed within 20 percent. The sky spectra generally spanned the range from $\chi = 90°$ to 98° and yielded similar internal agreement when reduced to absorption per unit air mass. In two spectra, taken at sunrise and moonrise during the week preceding the measurements shown in Fig. 2, the absorption per unit air mass varied considerably (up to 0.5 percent/AM). This was during a period when high tropospheric abundance was directly measured, and we suspect that the large and varying absorption must have been due to anthropogenic NO_2 from Denver. The two high sunrise measurements in Fig. 2 doubtless arise from the same cause.

To show the tropospheric results in Fig. 2 in the same units as the other results, we reduced the observed absorption to what would have been seen with a 7-km path. Assuming that tropospheric NO_2 is well mixed, at least above 3 km, the results in Fig. 2 correspond to the tropospheric component of the total absorption that would be seen with the sun or moon as the source. Measured tropospheric mixing ratios generally did not exceed 0.1 ppb, except on 15–16 September (10 ppb) and on 26–27

September (~0.15 ppb). Reported tropospheric NO_2 abundances, obtained by chemical means, suggest very much larger mixing ratios for "clean background air": ~2 ppb in the central United States and ~0.5 ppb in the tropics (*5*). While there is not necessarily any conflict between our results and other values, we emphasize that the natural level of NO_2 can be much lower than has been reported. Measurements by Briehl *et al.* (*6*) in the altitude range 8 to 12 km over the Pacific show mixing ratios for NO below 0.05 ppb, which imply a comparably low mixing ratio for NO_2.

Figure 2 makes it clear that there is considerable day-to-day variation in the column abundance of NO_2; since the lunar measurements are certainly dominated by stratospheric NO_2, there must be considerable variation in the latter. Apart from the variations, an important conclusion follows from a comparison of the lunar and solar measurements in Fig. 2. The mean value of the lunar results between 22 and 29 September is ~0.3 percent/AM; on many of the same nights the tropospheric contribution to the total absorption is $\leqslant 0.05$ percent/AM, and we conclude that more than 80 percent of the total measured NO_2 must have been in the stratosphere. As far as we know, this is the first measurement of stratospheric NO_2 at night. During the same period the total NO_2 abundance at sunrise and sunset averaged about half of that at moonset; the lunar and solar measurements show some tendency to follow each other from day to day. The results indicate that the stratospheric NO_2 abundance at night exceeded that in the daytime by a factor that is at least 2 and could be as large as 4. If we assume that the daytime tropospheric absorption was ~0.05 percent/AM, the mean daytime stratospheric contribution was ~0.1 percent/AM, corresponding to an NO_2 column abundance of $\sim 3 \times 10^{15}$ cm^{-2}. The results of Brewer *et al.* (*1*), as interpreted by Johnston (*2*), give $\sim 3 \times 10^{15}$ cm^{-2} above 12 km, and the infrared measurements from balloon reported by Ackerman *et al.* (*7*) suggest a similar daytime stratospheric abundance. From our lunar spectra (mean absorption, ~0.3 percent/AM) we infer a nighttime stratospheric abundance close to 10^{16} cm^{-2}; the nearly threefold increase at night is primarily the result of photolytic conversion of NO_2 to NO in the daytime stratosphere. Ackerman's infrared measurements suggest an approximately equal abundance of NO and NO_2 in the daytime stratosphere. Brewer *et al.* (*1*) reported an attempt to obtain lunar nighttime measurements; their results suggested that there was no appreciable difference in total atmospheric NO_2 between day and night, but their spectra show more contamination with tropospheric absorption than ours (*8*). Theoretical calculations (*2*) suggest a day-to-night change similar to what we infer.

Figure 2 also shows a systematically greater total atmospheric NO_2 content at sunset than at sunrise; the sky measurements show the same trend. The latter primarily reflect the behavior of stratospheric NO_2, and the increase during the day presumably reflects the slow photolytic decomposition of such compounds as N_2O_5, which slowly build up at night (*2, 9*). The observations from aircraft by Brewer *et al.* also show this effect. We do not claim that the difference between the solar and sky absorption in the period 28 September to 4 October is all due to tropospheric NO_2. The difference is generally somewhat greater than would be expected from the mean measured tropospheric absorption (~0.05 percent/AM), almost certainly because the sky spectra tend to underweight the total stratospheric NO_2 abundance by as much as a factor of 2. Nevertheless, the sky spectra should provide a ready means for monitoring the stratospheric abundance. They should also permit some exploration of its horizonal variation over distances up to ~1000 km, since the terminator travels this distance over the range $\chi = 90°$ to ~100°, beyond which the twilight sky intensity fades into the night sky background.

Our results suggest that spectral scanning provides a simple and reliable means for monitoring the stratospheric NO_2 abundance at locations where the troposphere is relatively clean. Since there is a major need for global information on both the stratospheric and tropospheric NO_2 abundance, we emphasize the potential power of the ground-based method, utilizing absorption in the visible, as a means toward satisfying this need.

Since the original submission of this report we have performed similar measurements extending up to 70°N, using a spectrometer on board a U.S. Air Force jet aircraft. The observations were principally of the zenith sky after sunset and revealed a major decline in stratospheric NO_2 abundance between 40° and 50°N during the period December 1974 through February 1975. When referred to $\chi = 95°$ the upper limit on the absorption at 4390 Å was less than 0.4 percent north of 50° compared with the typical value of 5 percent shown in Fig. 2 at 40°. By April 1975 the latitude variation was greatly reduced; the typical absorption at 4390 Å was then 1.5 percent in the latitude range 50° to 65°.

A pronounced winter decrease in stratospheric NO_2 thus exists north of 45°, even where the sun is above the horizon for several hours during each day. A few direct solar observations at 53°N in January 1975 confirmed the sky measurements and showed the total atmospheric NO_2 abundance to be less than 10^{15} cm^{-2} at sunset, compared with an average value of 5×10^{15} cm^{-2} for the corresponding measurements shown in Fig. 2. The low abundance of NO_2 at high latitude during the winter may possibly reflect a shift in the daytime equilibrium mixture toward nitrogen oxides, such as N_2O_5, which are effectively screened from photolysis by ozone itself for low solar elevation. On one occasion, however, in February 1975, sky measurements showed ~1.5 percent absorption at $\chi = 95°$ over a 2° zone of latitude centered at 65°N; this was the only occasion before April when absorption was detected north of 50° above the 0.4 percent limit.

J. F. NOXON

Fritz Peak Observatory, Aeronomy
Laboratory, National Oceanic and
Atmospheric Administration,
Environmental Research Laboratories,
Boulder, Colorado 80302

References and Notes

→ A. W. Brewer, C. T. McElroy, J. B. Kerr, *Nature (Lond.)* **246**, 129 (1973).
2. H. S. Johnston, in *Proceedings of the Third Conference on the CIAP Program*, A. J. Broderick and T. M. Hard, Eds. (Department of Transportation, Washington, D.C., 1974).
→ ______ and R. Graham, *Can. J. Chem.* **52**, 1415 (1974).
4. J. A. Curcio, L. F. Drummeter, T. E. Cosden, *Nav. Res. Lab. Rep. 4669* (1955).
5. R. S. Breeding *et al.*, *J. Geophys. Res.* **78**, 7057 (1973).
6. D. Briehl, E. Hilsenrath, B. A. Ridley, H. I. Schiff, *J. Am. Meteorol. Soc.*, in press.
7. M. Ackerman, J. C. Fontanella, D. Frimout, A. Girard, N. Louisnard, C. Muller, *Planet. Space Sci.*, in press.
8. Brewer *et al.* [A. W. Brewer, C. T. McElroy, J. B. Kerr, in *Proceedings of the Third Conference on the CIAP Program*, A. J. Broderick and T. M. Hard, Eds. (Department of Transportation, Washington, D.C., 1974)] recently presented a revised version of their original report (*1*). Their sky measurements for $\chi \geqslant 90°$ imply NO_2 absorption equivalent to an abundance of $\sim 10^{17}$ cm^{-2} at $\chi = 90°$. Their sunrise and sunset solar measurements from an aircraft at 12 km are consistent with a vertical column abundance of $\sim 3 \times 10^{15}$ cm^{-2} above ~10 km. These results are similar to those we present here. However, they report a large NO_2 abundance in the lower troposphere near sunrise and sunset from their ground-based solar measurements, as well as a major midday maximum in stratospheric NO_2 (their noon abundance of 3.5×10^{-3} atm cm corresponds to an absorption at 4390 Å of more than 3 percent/AM), which we do not observe. We find no difference greater than 0.3 percent/AM in our solar and lunar spectra obtained in the range 1.5 to 5 AM at 4390 Å. Our observations thus imply a midday upper limit on the column abundance little greater than what we measure near sunset. It seems important to consider the possible effect of water vapor absorption in interpreting the observations of Brewer *et al.*, particularly those made at ground level in eastern Canada, where there seems to be large absorption in their measurements.
9. P. Crutzen, *J. Geophys. Res.* **76**, 7311 (1971).
10. I thank P. Crutzen for calling attention to the importance of visible NO_2 absorption, E. Marovich and W. Henderson for essential contributions to the observational program, and D. Murcray for pointing out the existence of water vapor absorption near 4400 Å. I also thank the Ionospheric Dynamics Branch of the Air Force Cambridge Research Laboratory for the opportunity to perform the aircraft observations and J. G. Moore for his help in carrying them out, and I appreciate discussions on the latitude effect with P. Crutzen and I. Isaksen.

3 December 1974; revised 7 February 1975