

SIMULTANEOUS MEASUREMENTS OF NO AND NO₂ IN THE STRATOSPHERE, AND THE PARTITIONING OF ODD-NITROGEN SPECIES

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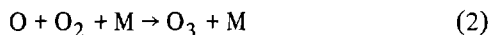
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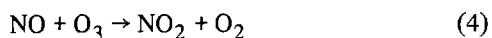
ABSTRACT: The recording of infrared solar spectra at sunset from a balloon gondola at 38 km altitude has led to the determination of the vertical distributions of stratospheric NO and NO₂. The measured NO₂-to-NO ratio indicates the limited validity of sunset observations of these two species. This determination of NO_x levels, in conjunction with other data available on HNO₃, allows a better definition of the partitioning of the odd-nitrogen species in the low stratosphere.

Research on the stratosphere has remained rather academic until recently. In 1971, it was assumed (Johnston, 1971) that the projected increase in oxides of nitrogen from aircraft flying in the stratosphere could reduce the ozone shield by about a factor of 2, thus permitting the harsh radiation below 300 nanometers to permeate the lower atmosphere, and consequently endangering life at the earth's surface. The interest of aeronautical industries and of governmental agencies in the problem has changed the level of activity in stratospheric research. The emphasis of this research has become measuring and modeling the natural stratosphere for the prediction of possible modifications.

Ozone is formed from atomic oxygen resulting from the dissociation of molecular oxygen by solar ultraviolet radiation,



An ozone reduction would result from increased scavenging of odd-oxygen atoms in a catalytic set of reactions involving increased nitric oxide and nitrogen dioxide, as follows:



It is currently accepted that nitric oxide is formed in the stratosphere by reaction of nitrous oxide which originates from biological activity at

ground level. Since odd-nitrogen molecules apparently do not build up continuously, a removal mechanism by nitric acid rain-out has been suggested.

Three years of experimental work have only transformed our ignorance of the real natural abundance of NO, NO₂, and HNO₃ in the stratosphere into a preliminary knowledge. It is time, however, to assess the available results and to compare them with theoretical predictions.

NITRIC OXIDE

Detection of nitric oxide in the stratosphere has been reported by various authors (Toth et al., 1973; Ridley et al., 1973; Girard et al., 1973). Vertical distributions of this constituent have been derived by absorption spectrometry using the sun as a source (Ackerman et al., 1973, 1975) and by chemiluminescence with O₃ (Ridley et al., 1974). After sunset, reaction (4) should transform nitric oxide into nitrogen dioxide. Nitric oxide has been observed (Patel et al., 1974) to reappear after sunrise, due to the photodissociation process



which regenerates atomic oxygen, making it available for ozone formation by reaction (2). Chemiluminescence has also been used on board high-flying aircraft (Loewenstein et al., 1974) to measure stratospheric NO. This method indicates large variations at 18 and 20 km over a period of several months (Savage et al., 1974).

The concentration of nitric oxide has also been determined in the mesosphere and in the lower thermosphere.

Most of the experimental NO concentration data are illustrated in Figure 1. They indicate higher number densities in the stratosphere than in the mesosphere, suggesting different production regimes, as was postulated on theoretical grounds (Nicolet, 1971). A steep decrease is observed below 30 km, and possibly an increase in the vicinity of the tropopause, below which no observation is available. The abundance of NO is, however, known (Ackerman et al., 1974; Ridley et al., 1974; Savage et al., 1974) to vary with

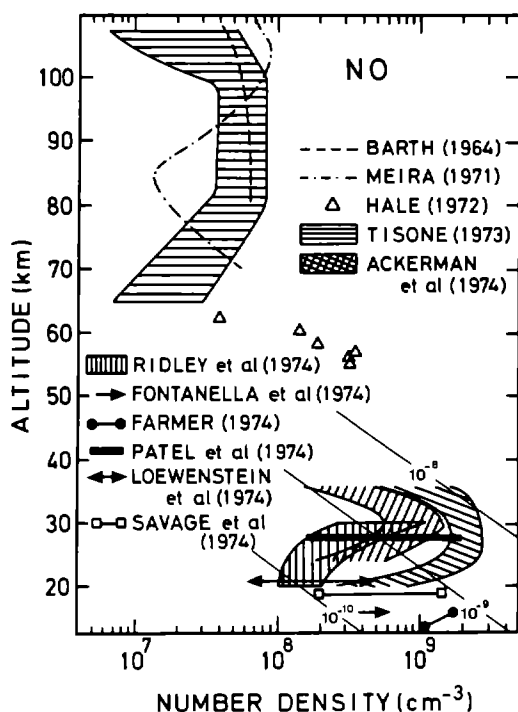


Figure 1. Measured nitric oxide number densities versus altitude in the chemosphere. In the stratosphere, Ackerman et al. (1974) have reported two very different vertical profiles, measured on May 14, 1973 (low) and on May 13, 1974 (high). Patel et al. (1974) have observed the NO variation at sunrise to be more than one order of magnitude. The variation of NO in the vicinity of 20 km altitude over a few days, reported by Savage et al. (1974), is also illustrated. Constant volume mixing ratios are roughly indicated by the straight lines marked 10^{-8} , 10^{-9} and 10^{-10} .

time and location. Loewenstein et al. (1975) have simultaneously measured NO and O_3 at two altitudes over a wide latitude range. In the troposphere over tropical areas (as indicated by low ozone number densities) they observed an NO bulge with values as high as $1.8 \times 10^9 \text{ cm}^{-3}$ at 18.3 km. At 21.3 km, it can be seen from their O_3 abundances that the data were gathered in the stratosphere at all latitudes (5° to 75° north), and NO values were generally larger there except over tropical areas where the bulge was reduced.

The nitric oxide observations at 19 km made by Savage et al. (1974) from November 1973 to June 1974, from 75° to 120° west and from 33° to 49° north, indicate a sudden NO increase of a factor of 7, leading to a high value of $1.4 \times 10^9 \text{ cm}^{-3}$ persisting until the end of May. This should probably be attributed to transport by motion of air masses, since the difference is too large to be accounted for by ozone fluctuations' changing the NO_2/NO ratio by reactions (4) and (5). It is thus not astonishing that two vertical distributions observed (Ackerman et al., 1974) by means of the same instrumentation under the same experimental conditions, but separated by almost exactly one year, exhibit a difference of a factor of 2 to 10 at 24 km, as shown by Figure 1. The meteorological situations shown in Figure 2 were very different at the two dates at the observation sites (44° north; -1° to 3° west). These situations were rather typical for the period preceding the experiments; namely, low pressures reached lower latitudes in May 1974 than in May 1973. It might also be interesting to notice that soundings made over Arosa showed a very different behavior of the ozone layer below the peak during the first experiment (May 14, 1973) and the second experiment (May 13, 1974), as shown in Figure 3. A well-marked tropospheric air-injection process into the stratosphere was taking place from 10 to 18 km in the second case; a well-marked variability also existed from 22 to 28 km, as illustrated in Figure 3b.

There are, however, too few measurements of nitric oxide at present for us to attempt quantitative evaluations of the observed variations. However, these variations are real, and their interpretations obviously require the simultaneous observation of several parameters, including minor constituents and dynamic processes, on a synoptic basis of reasonable extent.

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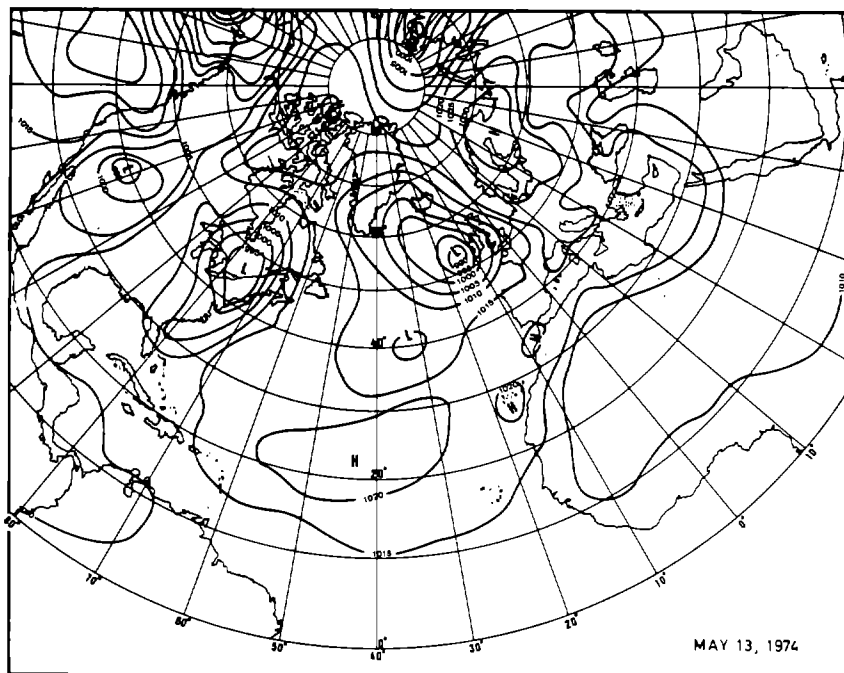
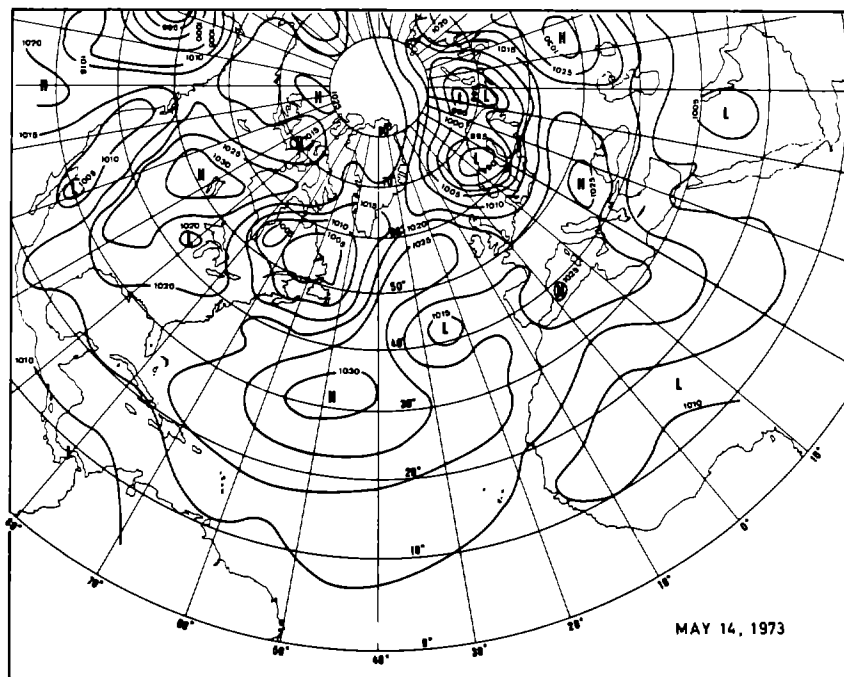


Figure 2. Surface-pressure maps at the dates of the NO measurements reported by Ackerman et al. (1974). Low pressures were extending more towards lower latitudes on May 14, 1974 (Figure 2a) than in the case of May 13, 1973 (Figure 2b). These situations were rather characteristic of the two periods.

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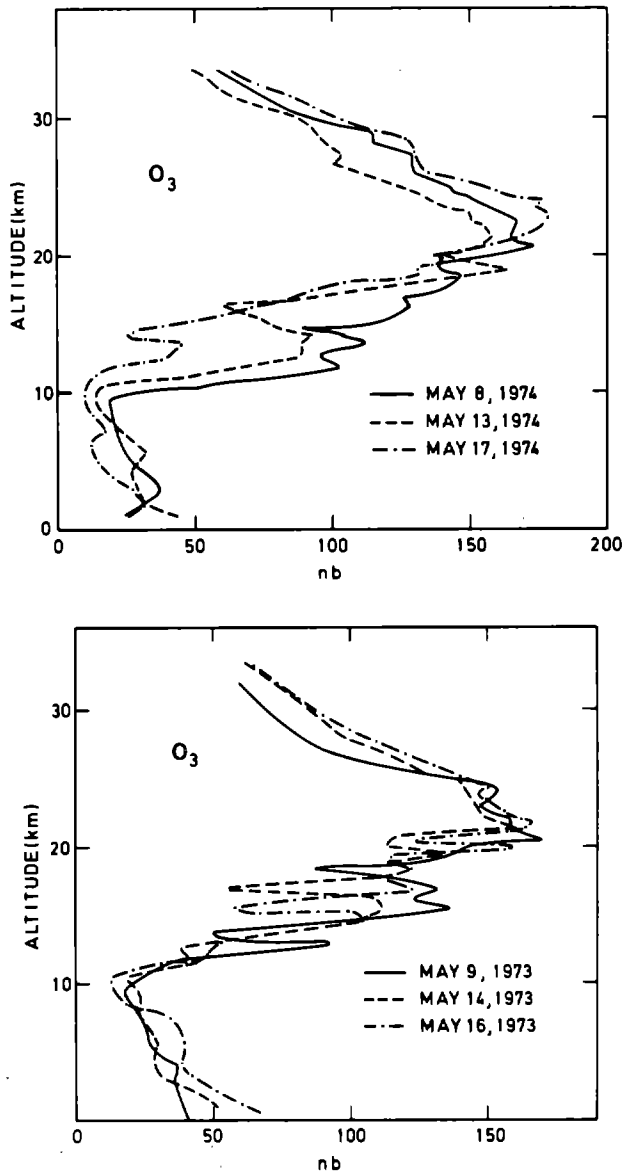


Figure 3. Ozone partial pressure versus altitude over Switzerland at the two periods of NO observations by Ackerman et al. (1974). In 1973 (a) ozone appears to vary from day to day at random, while in 1974 (b) a trend is observed in the ozone below 18 km; an organized decrease occurs from May 8 to May 17.

NITROGEN DIOXIDE

The observations of nitrogen dioxide number densities available for the troposphere and for the stratosphere are plotted in Figure 4. Chemical analyses (Moore, 1974; Nash, 1974;

Georgii and Jost, 1964) of air samples performed from ground level up to 6 km altitude, as well as remote spectrometry (Brewer et al., 1973), have been used in the troposphere to determine NO_2 . The experimental values are spread over almost two orders of magnitude. Measurements of supposedly unpolluted ground-level air indicate values that differ by more than a factor of 100. Georgii and Jost (1964) conclude from their measurements made on board aircraft that tropospheric NO_2 originates partly from biological activity in soils. The latter source would explain why the values observed in summer are higher than those observed in winter. The enrichment in N^{14} observed (Moore, 1974) for tropospheric NO_2 could be due to the biological contribution. A significant variability of tropospheric NO_2 seems to be firmly established, as well as the influence of human activities. Robinson and Robbins (1971) propose a latitudinal variation (4 ppb over tropical and temperate land areas, 0.5 ppb over polar land areas and oceans).

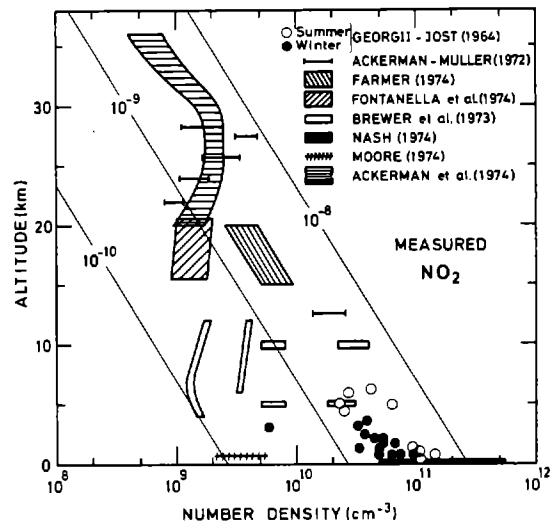


Figure 4. Number densities of nitrogen dioxide versus altitude measured by means of ground-based and aircraft- and balloon-borne instruments. Constant volume mixing ratios are roughly indicated by the straight lines marked 10^{-8} , 10^{-9} , and 10^{-10} .

The abundance of NO_2 in the stratosphere is known from infrared remote spectrometry (Ackerman and Muller, 1972, 1973; Farmer, 1974; Ackerman et al., 1974; Fontanella et al., 1974) performed from balloon gondolas and

from aircraft. As is the case for NO, the few determinations are also at mid-latitudes, limiting the possible comparison with theoretical models at roughly 45° north which could be representative of average conditions.

Several models have yielded NO and NO₂ vertical distributions for average conditions and even for specific latitudes and seasons. Some of the results are illustrated in Figure 5. Models in which various sets of possible vertical distributions are proposed can hardly be compared with experimental results. In one of the cases represented in Figure 5 (Levy, 1973) a tropospheric abundance of NO₂ was assumed in order to deduce other parameters. At 30 km altitude the modeling data are consistent with each other and with experimental results. The situation is different at lower altitudes. It should be pointed out that the various models considered give NO₂

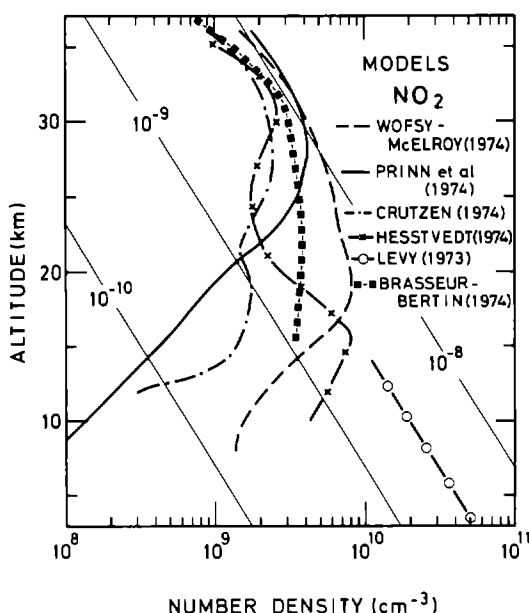


Figure 5. Theoretically evaluated NO₂ number densities versus altitude. Only models yielding unique distributions have been used. Where various latitudes have been considered, only the numbers for 45° latitude are shown. Levy (1973) did not compute NO₂ but introduced a distribution to compute other parameters. Constant volume mixing ratios are represented by straight lines marked 10⁻⁸, 10⁻⁹, and 10⁻¹⁰.

values at 30 km that agree within a factor of two, whereas values at 15 km spread over a factor of twenty. Does this mean a weak coupling between the two altitudes? Particularly in the tropopause region, values used or deduced in models are spread over two orders of magnitude, even where it does not seem to have been the authors' intention to demonstrate a variability. Models can produce double and single peaks in the vertical distributions, but only the latter situation has been observed.

Due to the short characteristic time (≈ 100 sec) for interconversion of NO into NO₂ and of NO₂ into NO in daylight through reactions (4), (5), and (3), the last one being negligible in the low stratosphere, the balance between these two oxides of nitrogen can better be represented by their sum, currently called NO_x. This can be evaluated from experimental NO₂ and NO data available from ground level up to 36 km, by

$$\text{NO}_x = \text{NO}_2 \left(\frac{1+R}{R} \right) = \text{NO} (1+R)$$

$$\text{where } R = \frac{k_4 [\text{O}_3]}{J_5 + k_3 [\text{O}]}$$

R has been evaluated by several authors, and measured once. The various values are represented versus altitude in Figure 6. From the curve given by Brasseur and Nicolet (1973) (which best agrees with the experimental data at the altitudes where they can be compared), and from the NO₂ and NO measurements shown in Figure 1 and in Figure 4, a possible envelope of NO_x values has been derived; it is shown in Figure 7. It will be discussed later. The measured values of R are strikingly smaller than those deduced in models. This could be attributed to an underestimate of J₅, which has always been computed without taking Rayleigh scattering into account. As already pointed out (Ackerman, 1974), diffuse radiation can in some cases contribute as much to photodissociation as direct solar radiation, yet only the latter has been considered in models up to now.

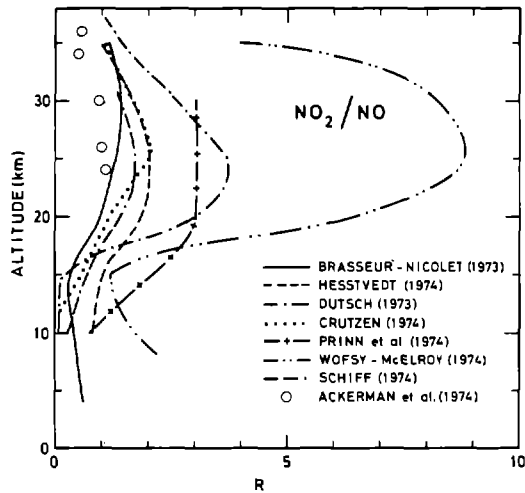


Figure 6. NO_2/NO ratios versus altitude computed in various models. The circles represent measurements taken at low solar elevation that have nonetheless been considered by the authors to represent daytime values.

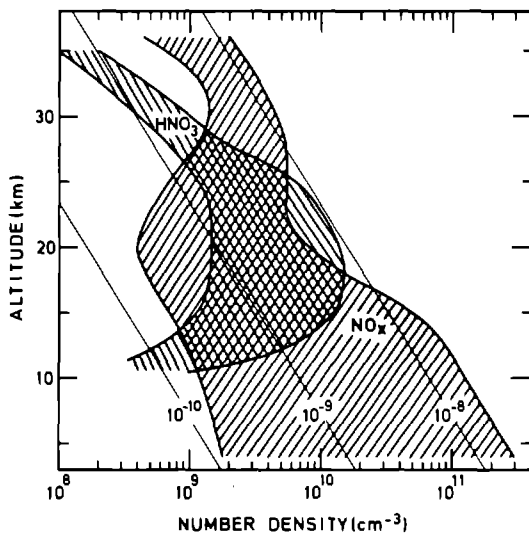


Figure 7. Envelopes including the available data on NO_x ($\text{NO} + \text{NO}_2$) and on HNO_3 . Constant volume mixing ratios are roughly represented by the straight lines marked 10^{-8} , 10^{-9} and 10^{-10} .

NITRIC ACID

Absorption spectra have led to the detection (Murcray et al., 1969) of HNO_3 in the stratosphere, and to several determinations of its profile. A rather large number of measurements make this odd-nitrogen molecule the most

measured in the stratosphere of the three that are considered here. High-resolution absorption spectroscopy performed from ground level (Vigroux, 1973) has indicated (on the basis of the narrowness of the observed lines) that HNO_3 is more in the upper than in the lower layers of the atmosphere. By means of aircraft-borne emission spectroscopy (Harries, 1974), a sharp increase in nitric acid has been observed above the tropopause. The same method used at shorter wavelengths, on board balloon gondolas (Murcray et al., 1974), has yielded vertical distributions of the abundance of nitric acid in the stratosphere at various latitudes. The chemical analysis of in-situ-collected samples (Lazrus and Gandrud, 1974) has also demonstrated the variability of nitric acid with time and latitude, with higher values towards the pole than towards the equator. The concentrations obtained by this method tend to be the lowest, particularly at low altitudes, while absorption spectroscopy from aircraft (Fontanella et al., 1974) has a tendency to give higher concentrations, and so do some interpretations of emission measurements (Fried and Weinman, 1970).

No optical measurement seems to have been reported for HNO_3 in tropospheric air. We have used spectra taken by absorption spectrometry during balloon ascents, and published by Murcray et al. (1969), to evaluate one tropospheric upper limit corresponding to a volume mixing ratio smaller than 10^{-10} . The result is shown in Figure 8 with envelopes representing the data obtained by means of the various methods at various times and locations. All results are included in the broad envelope illustrated in Figure 7.

Examples of theoretically deduced vertical distributions of HNO_3 are shown in Figure 9. Values given for altitudes higher than 15 km represent the experiments rather well, while below 12 km theory appears to overestimate abundances of HNO_3 .

DISCUSSION

Nitric acid is known, like any very polar molecule, such as HCl , to have an extremely low activity in dilute aqueous solutions. On the other hand, Warneck (1974) has shown that the time constant for collisions of trace constituents with

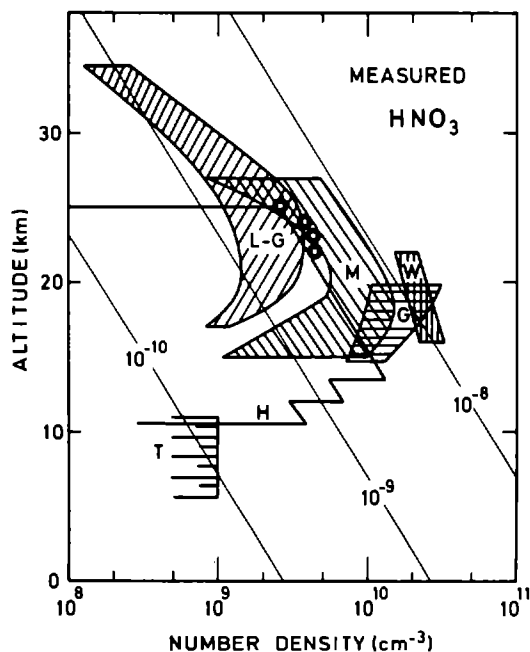


Figure 8. Envelopes representing the measured nitric acid number densities versus altitude. L-G corresponds to the data of Lazrus and Gandrud (1974), M to those of Murcray et al. (1974), G to those of Fontanella et al. (1974), W to those of Fried and Weinman (1970) and H to those of Harries (1974). The values represented by the circles and by the upper limit marked T have been evaluated by the present author on the basis of the atmospheric experiments of Murcray et al. (1969) and of the laboratory data published by Fontanella et al. (1974). Constant volume mixing ratios are roughly illustrated by the straight lines marked 10^{-8} , 10^{-9} , and 10^{-10} .

cloud elements is less than five seconds. These considerations would explain a low concentration of HNO_3 in the tropospheric gas phase. They have not been taken into account in models where rain-out times longer than a few days have been introduced to represent the evacuation of odd nitrogen from the stratosphere to the troposphere. They might, however, improve the agreement between theory and experiment in the region of the tropopause and below. This would probably need adjustments to maintain the computed concentrations of NO_2 at the level indicated by the observations, requiring other sources of odd nitrogen in the low stratosphere.

NO_x obviously presents an important variability with time in the stratosphere. Seasonal

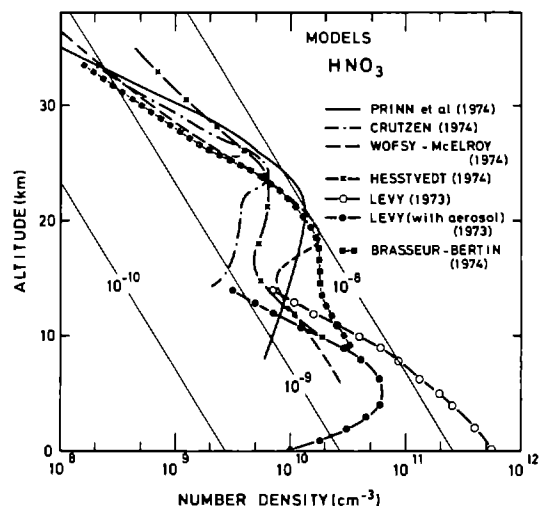


Figure 9. Theoretically evaluated HNO_3 number densities versus altitude. Only models yielding unique distributions have been used. Where various latitudes were considered, only the numbers for 45° are shown.

variations have been considered in models, as well as the possibility (Ruderman and Chamberlain, 1975) of the interpretation of the apparent correlation of ozone variation with the eleven-year cycle of solar activity in terms of the effect of nitrogen-oxides modulation by cosmic rays. Even if doubts have been cast on the significance of such correlations (London and Oltmans, 1973), such investigations are very interesting. There is, however, no conclusive demonstration of the direct role of oxides of nitrogen as an intermediate in these phenomena that would allow firm assessments (Johnston, 1974) to be made of the possible effects of stratospheric aircraft on ozone. Large variations of NO have been observed, as described in a previous section. The NO abundances observed by Ackerman et al. in May 1973 and in May 1974 differ markedly. Total ozone data for the two months are shown in Figure 10. In May 1973, total ozone appears to vary from day to day randomly around mean values which are larger at high latitudes. The latitudinal variation is also present in May 1974, but a pronounced decrease of 10 to 20% appears over one week. The observations indicate the occurrence of a well-organized modification of large geographic extent, from at least 51° north to 39° north, including the area of high NO observations. The

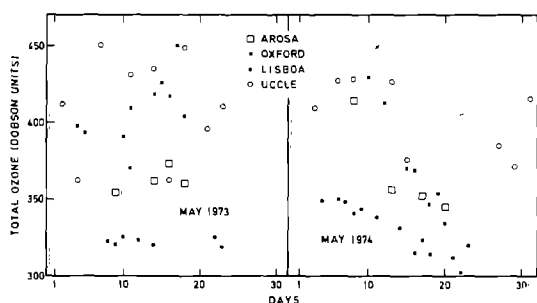


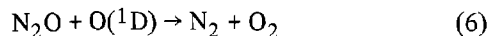
Figure 10. Total ozone versus time measured over various European stations in May 1973 and in May 1974. In this latter case, the beginning of the summer minimum occurs while May 1973 is still in the spring maximum.

decrease in total ozone is suggested to be due to the replacement of ozone-rich air below 20 km by ozone-poor air. This suggestion stems from the vertical profiles observed over Switzerland which were shown in Figure 3. The umkehr observations made over Lisbon show the same trend, which is not unusual near the end of the ozone spring maximum at this station (Figueira, 1973) — namely, during the total-ozone minimum in the month of May 1974, levels 2 and 3 (12 and 16.5 km) exhibit minimum values, while maximum values for the whole month are observed at levels 5, 6, and 7 corresponding respectively to 25, 30, and 35 km.

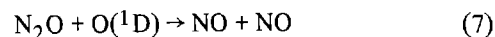
The ozone reduction below 20 km, which is responsible for the reduction in total ozone, cannot be attributed to NO_x chemistry, since the currently accepted atomic-oxygen content at these altitudes implies a characteristic reaction time longer than a year. It should also be remarked that this ozone decrease in the lower stratosphere occurred concurrently with an increase in the middle stratosphere. All these observations suggest that the variability with time of total ozone, that could be related in this case with NO_x on the basis of chemical interactions in a simple correlation, was actually entirely under the control of transport processes.

Determinations of tropospheric NO_2 indicate a wide range of NO_x values, tentatively illustrated in Figure 7. Low values are usually thought to be characteristic of unpolluted air and are much smaller than those used in models (Levy, 1973; Chameides and Walker, 1974). The

reduction of NO_x in these models would reduce the production of HNO_3 that has been considered by Warneck (1974) as being too high in comparison with the observed global precipitation of nitric acid in rain. On the other hand, high values of NO_x concentrations, suggested by the observations of Georgii and Jost (1964), who have indicated a seasonal variation (summer values higher than winter ones) that could hardly be explained on the basis of human activities, could have consequences for the stratosphere. They could lead to injections of tropospheric NO_x into the stratosphere when its mixing ratio at the stratospheric heights is smaller than that in the troposphere. This could be supported by the isotopic composition of HNO_3 observed between 21 and 27 km (Moore, 1974), which shows about the same $\text{N}^{14}/\text{N}^{15}$ ratio as for standard N_2 . If stratospheric HNO_3 is all derived from N_2O having a marked N^{15} enrichment, this should also appear in nitric acid as a product of NO_x , provided that the reactions



and



have no differential isotopic effects. This is a reasonable assumption that should, of course, be checked experimentally to allow a firm interpretation of the stratospheric isotopic measurements.

Considering the replacement time (Danielson, 1968) of stratospheric air by tropospheric air and the high HNO_3 amounts derived by absorption spectrometry (Fontanella et al., 1974), a downward flux of nitric acid larger than $5 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ should be accepted. Such a flux would imply another source of odd stratospheric nitrogen besides reaction (7), whose odd-nitrogen production has been estimated as $(0.29-1.5) \times 10^8$, $(0.25-0.65) \times 10^8$, $(0.5-1.3) \times 10^8$, and $(0.8-1.0) \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ by Crutzen (1974), Wofsy and McElroy (1974), Brasseur and Nicolet (1973), and Isaksen (1973), respectively.

On the other hand, the low HNO_3 values of Figure 7 would imply, given the same interchange time between tropospheric and stratospheric air, a flux equal to $.8 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$. The average value, $(2.9 \pm 2.1) \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$,

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shows clearly that the actual uncertainty in the HNO_3 measurements is unsatisfactory. If it were admitted that HNO_3 abundances derived from in-situ sampling were systematically too low, and if, on the basis of such an argument, they were rejected, an average flux value of $(3 \pm 2) \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ would be derived, which would exclude several of the theoretical values. An additional source of stratospheric odd nitrogen would have to be introduced, particularly if the absolute quantum yield for the formation of $\text{O}(^1\text{D})$ in O_3 photolysis, the value of which has always been assumed (Welge, 1974), is in fact smaller than currently accepted.

CONCLUSION

Measurements of the chemically related odd-nitrogen molecules in the atmosphere appear to be particularly good tests for models designed to predict the possible modifications of the stratosphere under natural and artificial constraints. Measurements are at present too sparse to provide a thorough check. However, they indicate possibilities of improving the evaluation of vertical distributions and temporal variations of NO_x and HNO_3 that are required for the lower stratosphere and for the troposphere. In particular, diffuse as well as direct solar radiation should be taken into account when certain photodissociation rates are evaluated in models.

Fundamental matters, such as the sources and fate of odd nitrogen above the *average* tropopause height as well as in the troposphere, seem to require further high-priority investigations. Quasi-horizontal transport should be considered in more detail, since it can lead to injection of tropospheric NO_x -rich air from the tropics into the middle-latitude stratosphere over periods of time that are short (Piaget, 1971) compared with the conversion time of NO_x into HNO_3 . This could be a partial cause of the short time and small scale of observed NO_x variations, and could represent an additional natural source of stratospheric odd nitrogen. Certain experimental methods have contributed most of the available information. Their use should be intensified. But the use of other methods has perhaps not been emphasized enough up to now.

As far as the prediction of a possible reduction of ozone by a factor of two is

concerned, some models now predict that it could be 1% for a similar fleet of stratospheric aircraft. Present models can, however, scarcely describe the variations of the natural stratosphere.

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REFERENCES

- Ackerman, M. and C. Muller (1972), "Stratospheric nitrogen dioxide from infrared absorption spectra," *Nature* **240**, 300-301.
- Ackerman, M. and C. Muller (1973), "Stratospheric methane and nitrogen dioxide from infrared spectra," *Pure Appl. Geophys.* **106-108**, 1325-1335.
- Ackerman, M., D. Frimout, C. Muller, D. Nevejans, J.-C. Fontanella, A. Girard and N. Louisnard (1973), "Stratospheric nitric oxide from infrared spectra," *Nature* **245**, 205-206.
- Ackerman, M. (1974), "Solar ultraviolet flux below 50 kilometers," *Can. J. Chem.* **52**, 1505-1509.
- Ackerman, M., J.-C. Fontanella, D. Frimout, A. Girard, N. Louisnard and C. Muller (1975), "Simultaneous measurements of NO and NO_2 in the stratosphere," *Planet. Space Sci.* **23**, 651-660.
- Barth, C.A. (1964), "Rocket measurement of the nitric oxide dayglow," *J. Geophys. Res.* **69**, 3301-3303.
- Brasseur, G. and M. Bertin (1974), "Un modèle bi-dimensionnel de la stratosphère," in *Proceedings of the Anglo-French Symposium on the Effects of Stratospheric Aircraft* (Oxford), pub. British Meteorological Office, XXIV-1.
- Brasseur, G. and M. Nicolet (1973), "Chemospheric processes of nitric oxide in the mesosphere and stratosphere," *Planet. Space Sci.* **21**, 939-961.
- Brewer, A.W., C.T. McElroy, and J.B. Kerr (1973), "Nitrogen dioxide concentrations in the atmosphere," *Nature* **246**, 129-133.
- Chameides, W. and J.C.G. Walker (1973), "A photochemical theory of tropospheric ozone," *J. Geophys. Res.* **78**, 8751-8760.

ACKERMAN

- Crutzen, P. (1974), "A review of upper atmospheric photochemistry," *Can. J. Chem.* **52**, 1569-1581.
- Danielsen, E.F. (1968), "Stratospheric-tropospheric exchange based on radioactivity, ozone and potential vorticity," *J. Atm. Sci.* **25**, 502-518.
- Dütsch, H.U. (1973), "Recent developments in photochemistry of atmospheric ozone," *Pure Appl. Geophys.* **106-108**, 1361-1384.
- Farmer, C.B. (1974), "Infrared measurements of stratospheric composition," *Can. J. Chem.* **52**, 1544-1559.
- Figueira, M.F. (1973), "Atmospheric ozone and flow field variations over Lisbon," *Pure Appl. Geophys.* **106-108**, 1586-1599.
- Fontanella, J.-C., A. Girard, L. Gramont and N. Louisnard (1974), "Vertical distribution of NO, NO₂ and HNO₃ as derived from stratospheric absorption infrared spectra," in *Proceedings of the Third Conference on CIAP* (Cambridge, Mass.), U.S. Department of Transportation, DOT-TSC-OST-74-15, 217-233; and *Appl. Opt.* **14**, 825 (1975).
- Fried, P.M. and J.A. Weinman (1970), "Vertical distribution of HNO₃ vapor in the stratosphere," *Bull. Amer. Meteorol. Soc.* **51**, 1006.
- Georgii, J.-W. and D. Jost (1964), "Untersuchung über die Verteilung von Spurengasen in der freien Atmosphäre," *Pure Appl. Geophys.* **59**, 217-224.
- Girard, A., J.-C. Fontanella and L. Gramont (1973), "Détection de l'oxyde azotique dans la stratosphère," *C.R. Acad. Sci. Paris* **276**, 845.
- Hale, L.C. (1972), as discussed in M.B. McElroy (1972), "Conference Summary," in *Proceedings of the Survey Conference, Climatic Impact Assessment Program*, Dept. of Transportation, DOT-TSC-OST-72-13, on pp. 262 and 266.
- Harries, J.E., D.G. Moss and N.R. Swann (1974), "H₂O, O₃, N₂O and HNO₃ in the arctic stratosphere," *Nature* **250**, 475-476.
- Hesstvedt, E. (1974), "Reduction of stratospheric ozone from high-flying aircraft, studied in a two-dimensional photochemical model with transport," *Can. J. Chem.* **52**, 1592-1598.
- Johnston, H. (1971), "Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust," *Science* **173**, 517-522.
- Johnston, H.S. (1974), "Photochemistry in the stratosphere with applications to supersonic transports," *Acta Astronaut.* **1**, 135-156.
- Lazrus, A.L. and B.W. Gandrud (1974), "Distribution of stratospheric nitric acid vapor," *J. Atm. Sci.* **31**, 1102-1108.
- Levy, H. II (1973), "Photochemistry of minor constituents in the troposphere," *Planet. Space Sci.* **21**, 575-591.
- London, J. and S. Oltmans (1973), "Further studies of ozone and sunspots," *Pure Appl. Geophys.* **106-108**, 1302-1307.
- Loewenstein, M. and H.F. Savage (1975), "Latitudinal measurements of NO and O₃ in the lower stratosphere from 5.5° to 82° North," in this volume.
- Loewenstein, M., J.P. Paddock, I.G. Poppoff and H.F. Savage (1974), "NO and O₃ measurements in the lower stratosphere from a U-2 aircraft," *Nature* **249**, 817-818.
- Loewenstein, M., H.F. Savage, and R.C. Whitten (1975), "Seasonal variations of NO and O₃ at altitudes of 18.3 and 21.3 km," in this volume.
- Meira, L.G., Jr. (1971), "Rocket measurements of upper atmospheric nitric oxide and their consequences to the lower ionosphere," *J. Geophys. Res.* **76**, 202-212.
- Moore, H. (1974), "Isotopic measurement of atmospheric nitrogen compounds," *Tellus* **26**, 169-174.
- Murcray, D.G., T.G. Kyle, F.H. Murcray and W.J. Williams (1968), "Nitric acid and nitric oxide in the lower stratosphere," *Nature* **218**, 78-79.
- Murcray, D.G., F.H. Murcray, W.J. Williams, T.G. Kyle and A. Goldman (1969), "Variation of the infrared solar spectrum between 700 cm⁻¹ and 2240 cm⁻¹ with altitude," *Appl. Opt.* **6**, 2519-2536.
- Murcray, D.G., A. Goldman, W.J. Williams, F.H. Murcray, J.N. Brooks, R.N. Stocker and D.E. Snider (1974), "Stratospheric mixing ratio profiles of several trace gases as determined from balloonborne infrared spectrometers," in *Proceedings of the International Conference on Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations* (Melbourne), pub. IAMAP, 292-306.
- Nash, T. (1974), "Nitrous acid in the atmosphere and laboratory experiments on its photolysis," *Tellus* **26**, 175-179.
- Nicolet, M. (1971), "Aeronomic reactions of hydrogen and ozone," in *Mesospheric Models and Related Experiments*, ed. G. Fiocco, Reidel Pub., Dordrecht, 1-15.

ACKERMAN

- Patel, C.K.N., E.G. Burkhardt and C.A. Lambert (1974), "Spectroscopic measurements of stratospheric nitric oxide and water vapor," *Science* **184**, 1173-1176.
- Piaget, A. (1971), "Utilisation de l'ozone atmosphérique comme traceur des échanges entre la troposphère et la stratosphère," *Veröffentlichungen der Schweizerischen Meteorologischen Zentralanstalt*, Zürich, **21**, 1-71.
- Prinn, R.G., F.N. Alyea, D.M. Cunnold and A. Katz (1974), "The distribution of odd nitrogen and odd hydrogen in the natural and perturbed stratosphere," in *Preprints of the Second International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere* (San Diego), pub. AMS, 180-186.
- Ridley, B.A., H.I. Schiff, A.W. Shaw, L. Bates, L.C. Howlett, H. Levaux, L.R. Megill and T.E. Ashenfelter (1973), "Measurements in-situ of nitric oxide in the stratosphere between 17.4 and 22.9 km," *Nature* **245**, 310-311.
- Ridley, B.A., H.I. Schiff, A. Shaw and L.R. Megill (1974), "In-situ measurements of NO in the stratosphere using chemiluminescence," in *Proceedings of the Third Conference on CIAP* (Cambridge, Mass.), Department of Transportation, DOT-TSC-OST-74-15, 193-196.
- Robinson, E. and R.C. Robbins (1971), "Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants," *Amer. Petrol. Inst.*, Washington D.C., 77 pp.
- Ruderman, M.A. and J.W. Chamberlain (1975), "Origin of the sunspot modulation of ozone: Its implications for stratospheric NO injection," *Planet. Space Sci.* **23**, 247.
- Savage, H.E., M. Loewenstein and R.C. Whitten (1974), "In-situ measurements of NO and O₃ in the lower stratosphere," in *Preprints of the Second International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere* (San Diego), pub. AMS, 5-10.
- Schiff, H.I. (1974), "Measurements of NO, NO₂ and HNO₃ in the stratosphere," *Can. J. Chem.* **52**, 1536-1543.
- Tisone, G.C. (1973), "Measurements of NO densities during sunrise at Kauai," *J. Geophys. Res.* **78**, 746-750.
- Toth, R.A., C.B. Farmer, R.A. Schindler, O.F. Raper and P.W. Schaper (1973), "Detection of nitric oxide in the lower stratosphere," *Nature Phys. Sci.* **244**, 7-8.
- Vigroux, E. (1973), "High resolution analysis of the sun's radiation received at the ground from 9μ to 11.6μ," *Pure Appl. Geophys.* **106-108**, 1336-1340.
- Warneck, P. (1974), "On the role of OH and HO₂ radicals in the troposphere," *Tellus* **26**, 39-46.
- Welge, K.H. (1974), "Photolysis of O_x, HO_x, CO_x and SO_x compounds," *Can. J. Chem.* **52**, 1424-1435.
- Wofsy, S.C. and M.B. McElroy (1974), "HO_x, NO_x and ClO_x: Their role in atmospheric photochemistry," *Can. J. Chem.* **52**, 1582-1591.