CONFERENCE ON THE UPPER ATMOSPHERE

A portion of the contents of this issue of the JOURNAL OF THE ATMOSPHERIC SCIENCES is devoted to studies of our upper atmosphere—the stratosphere, mesosphere, and thermosphere. Most of these papers, but not all, are based on presentations in more or less similar form made at the Conference on the Upper Atmosphere, 30 September–4 October 1974, in Atlanta, Ga., organized by the Committee on the Upper Atmosphere of the American Meteorological Society.

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NO, NO$_2$ and HNO$_3$ below 35 km in the Atmosphere

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ABSTRACT

Experimental data on NO, NO$_2$ and HNO$_3$ in the atmosphere are reviewed. The low abundance of nitric acid in the tropospheric gas phase is emphasized, as well as the high variability of NO$_x$ in the low stratosphere and in the troposphere. Some model-predicted distributions of these odd-nitrogen molecules are presented. Areas of agreement and of disagreement between theory and experiment are indicated.

1. Introduction

Stratospheric research has remained rather academic until recently. In 1971 it was assumed (Johnston, 1971) that the projected increase in the oxides of nitrogen from aircraft flying in the stratosphere could reduce the ozone shield by about a factor of 2, thus permitting increased ultraviolet radiation below 300 nm to reach the lower atmosphere, and consequently endanger life at the earth surface. The interest of aircraft industries and governmental agencies in the problem has changed the level of activity in stratospheric research. Increased emphasis has been put on measuring and modeling the natural stratosphere in order to be able to predict possible modifications.

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

$$O_2 + h\nu \rightarrow O + O, \qquad (1)$$

$$O + O_2 + M \rightarrow O_3 + M. \qquad (2)$$
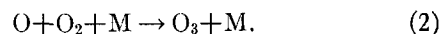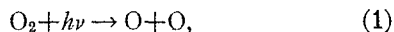
Ozone reduction would result in more scavenging of odd-oxygen atoms in a catalytic set of reactions involving increased nitric oxide and nitrogen dioxide:

$$NO_2 + O \rightarrow NO + O_2, \qquad (3)$$

$$NO + O_3 \rightarrow NO_2 + O_2. \qquad (4)$$
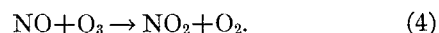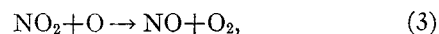
It is currently accepted that nitric oxide is formed in the stratosphere by reaction of nitrous oxide originating from biological activity at ground level. Since odd-nitrogen molecules have not continued to build up, a removal mechanism has been suggested, based on nitric acid rainout.

Three years of experimental work have yielded only preliminary knowledge of the real natural abundance of NO, NO$_2$ and HNO$_3$ in the stratosphere. It is time to summarize the available results and to compare them with theoretical predictions.
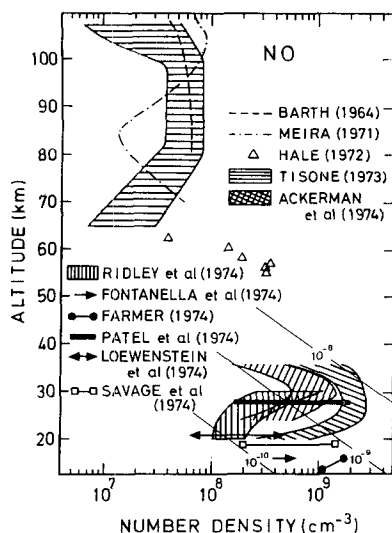
FIG. 1. Height profiles of measured nitric oxide number densities in the chemosphere. In the stratosphere, Ackerman *et al.* (1974) have reported two very different vertical profiles, one on 14 May 1973 (low) and the other on 13 May 1974 (high). Patel *et al.* (1974) have observed NO variations at sunrise of more than one order of magnitude. The variation of NO in the vicinity of 20 km 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}.

2. 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, 1974) and by chemiluminescence with O_3 (Ridley *et al.*, 1974). After sunset, reaction (4) should transform nitric oxide that has been observed (Patel *et al.*, 1974) to appear after sunrise by the photodissociation process

$$NO_2 + h\nu \rightarrow NO + O, \qquad (5)$$
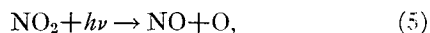
regenerating atomic oxygen available for ozone formation by reaction (2). Chemiluminescence has also been used on high-flying aircraft (Lowenstein *et al.*, 1974) to measure stratospheric NO. This method indicates large variations at 18 and 20 km over a period of several months (Savage *et al.*, 1974).

Nitric oxide has also been determined in the mesosphere and in the lower thermosphere.

Most of the experimental data are illustrated in Fig. 1. They indicate higher number densities in the stratosphere than in the mesosphere, suggesting different production regimes as 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 observations are available. Most of the measurements have been obtained at mid-latitudes so that the possible meridional variation of

NO can only be conjectured. Its abundance is known, however, to vary with time and location (Ackerman *et al.*, 1974; Ridley *et al.*, 1974; Savage *et al.*, 1974).

The nitric oxide observations made at 19 km by Savage *et al.* (1974) over the period from November 1973 to June 1974 from 75° to 120°W and from 33° to 49°N indicate an NO concentration increase of a factor of 7, reaching a value of 1.4×10^9 cm^{-3} which persisted until the end of May. This was most probably due to horizontal transport by air motion since the variation is too large to be accounted for by ozone fluctuations that would change the NO_2/NO ratio by reactions (4) and (5). It is thus not surprising to find two vertical distributions (see Fig. 1), each observed (Ackerman *et al.*, 1974) with the same instrumentation under the same experimental conditions but separated by almost exactly one year, which exhibit a difference of a factor of 2–10 at 24 km. The meteorological situations shown in Figs. 2a and 2b were quite different for the two observations, each at 44°N, 1°–3°W. The surface synoptic maps were rather typical for the period preceding the experiments, with low pressures reaching lower latitudes in May 1974 than in May 1973. It might also be interesting to notice (see Figs. 3a and 3b) that the soundings made over Arosa showed that the ozone layer below the peak changed significantly from the period of the first experiment (9–16 May 1973) to that of the second (8–17 May 1974). Tropospheric air was clearly being injected into the stratosphere in the second case from 10 to 18 km; in addition there was a marked layer of variability from 22 to 28 km.

However there are too few measurements of nitric oxide at present to attempt quantitative evaluations of the observed variations. Their interpretation obviously requires the simultaneous observation of several parameters including minor constituents and dynamic processes on a synoptic basis of reasonable extent.

3. Nitrogen dioxide

Observations of available nitrogen dioxide number densities for the troposphere and for the stratosphere are plotted in Fig. 4. Chemical analysis (Moore, 1974; Nash, 1974; Georgii and Jost, 1964) of air samples from ground level up to 6 km and 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 supposed unpolluted ground level air indicate values that could differ by factors of more than 100. Georgii and Jost (1964) conclude from their aircraft measurements that tropospheric NO_2 originates partly from biological activity in soils; the latter source would explain why values observed in summer are higher than those observed in winter. The observed enrichment in N^{14} (Moore, 1974) for tropospheric NO_2 could be due to the biological contribution. An important variability of tropospheric NO_2 seems to be firmly
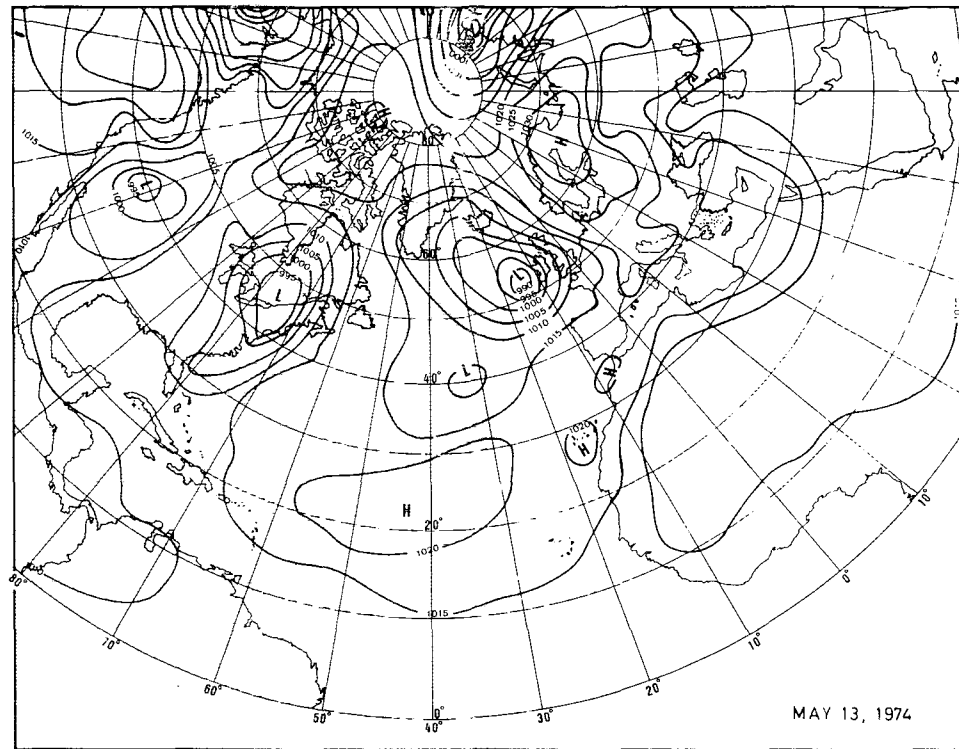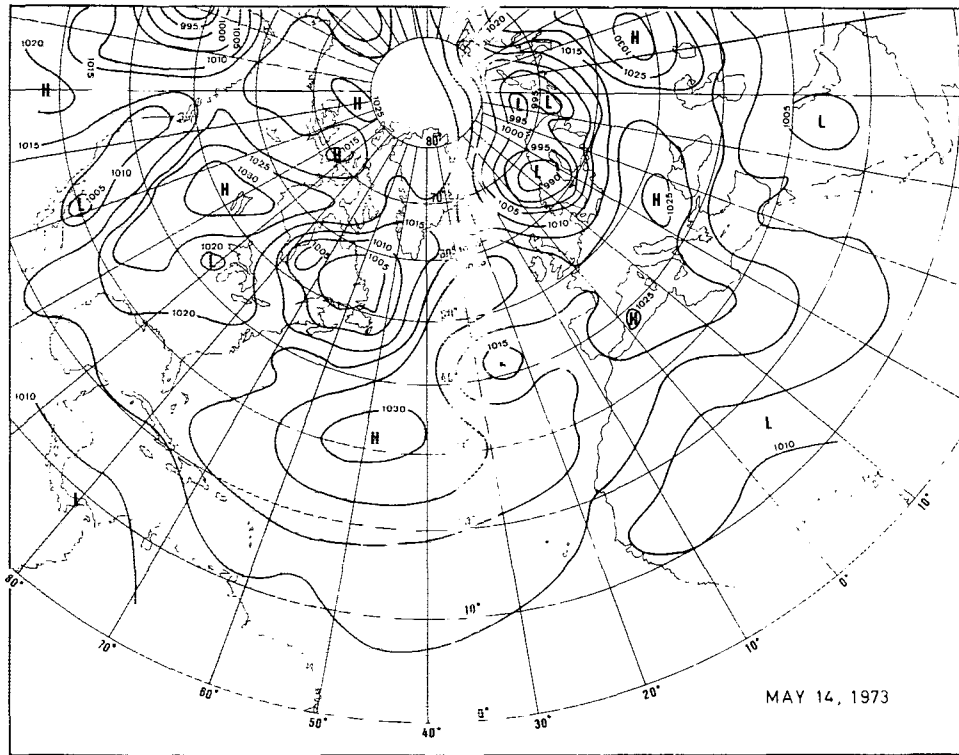
FIG. 2. Surface pressure maps for the two dates of the NO measurements reported by Ackerman *et al.* (1974). Low pressures were extending toward lower latitudes on 14 May, 1974 (Fig. 2a) than in the case of 13 May 1973 (Fig. 2b). These situations were rather characteristic of the two periods.
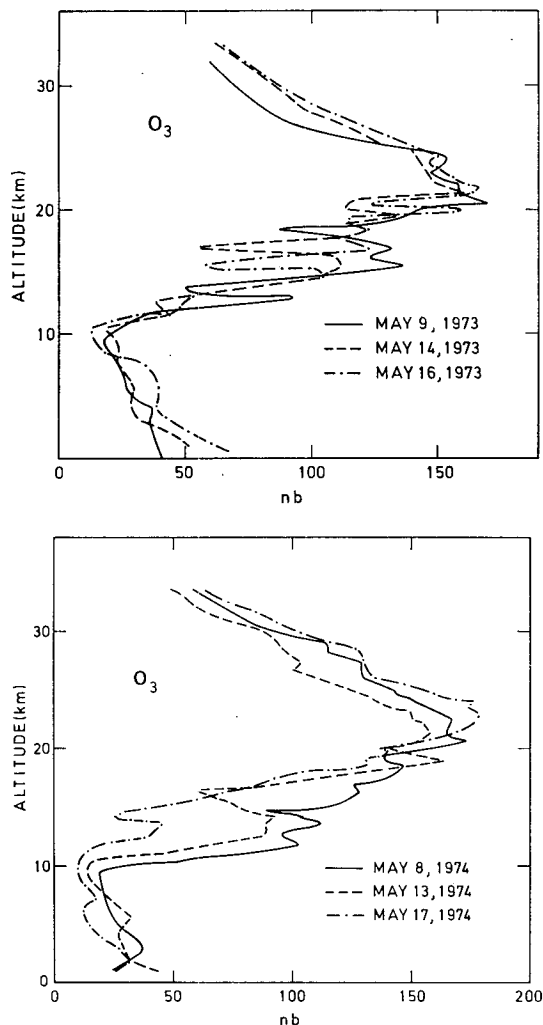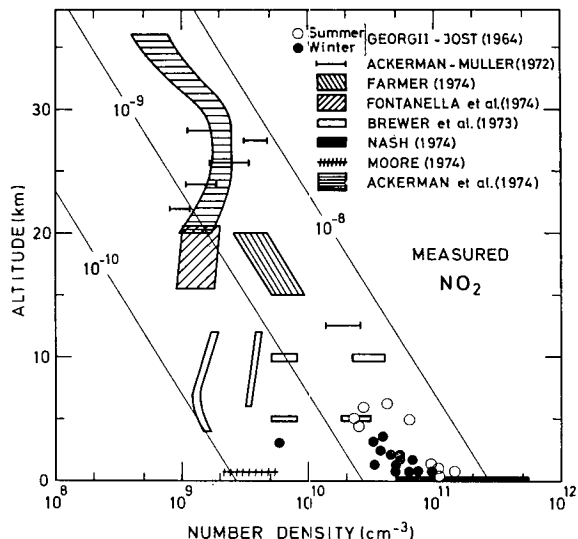
Fig. 4. Height profiles of nitrogen dioxide number densities measured by means of ground-based, aircraft and balloon-borne instruments. Constant volume mixing ratios are roughly indicated by the straight lines marked 10^{-8}, 10^{-9} and 10^{-10}.

possible vertical distributions are proposed can hardly be compared with experimental results. In one case represented in Fig. 5 (Levy, 1973) a tropospheric abundance of NO_2 was assumed to be due to the effect of other parameters. Modeling data are consistent with each other and with experimental results at 30 km altitude; the situation is different, however, at lower altitudes. It should be pointed out that the various
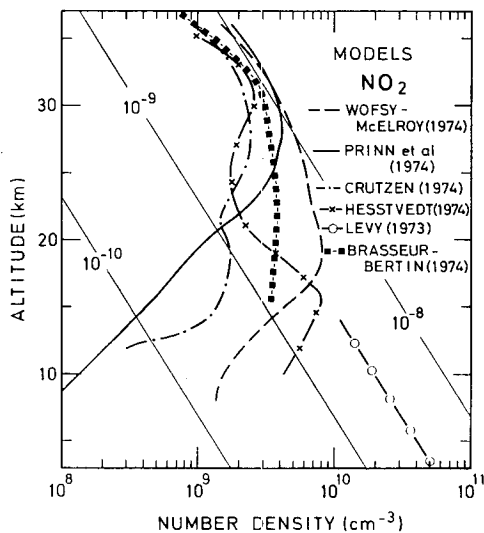

Fig. 5. Theoretically evaluated NO_2 number densities versus altitude, where only models yielding unique distributions have been used. When various latitudes have been considered, values for 45° latitude are represented. Levy (1973) did not compute NO_2 but introduced a distribution to compute other parameters. Constant volume mixing ratios are represented by straight lines marked 10^{-8}, 10^{-9} and 10^{-10}.

Fig. 3. Height profiles of ozone partial pressure over Switzerland for the two NO observation periods (Ackerman et al., 1974). In 1973 ozone appears to vary from day to day at random, while in 1974 a trend is observed below 18 km; an organized decrease occurs from 8 to 17 May.

established as well as the influence of human activities. Robinson and Robins (1971) propose a latitudinal variation (4 ppb over tropic and temperate land areas, 0.5 ppb over polar land areas and oceans).

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 available determinations are also at mid-latitudes limiting the possible comparison with theoretical models to roughly 45°N which could be representative of average conditions.

Several models have yielded NO and NO_2 vertical distributions for average conditions and even for specific latitudes and seasons. Some of the results are illustrated in Fig. 5. Models where various sets of

models considered give NO_2 values at 30 km that agree within a factor of 2, while values at 15 km are spread over a factor of 20. Does this mean a weak coupling between the two altitudes? Particularly in the tropopause region, values deduced in models are spread over two orders of magnitude even if it does not seem to have been the authors' intention to represent such variability aspects. 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 s) for converting NO to NO_2 and NO_2 to NO in daylight through reactions (4), (5) and (3), the latter being negligible in the low stratosphere, the balance of these two oxides of nitrogen can better be represented by their sum, currently called NO_x. This can be evaluated from experimental NO_2 and NO data available from ground level up to 36 km by

$$NO_x = NO_2\left(\frac{1+R}{R}\right) = NO(1+R),$$

where

$$R = \frac{k_4[O_3]}{J_5 + k_3[O]}.$$

The ratio R has been evaluated by several authors, and measured once—results are shown as altitude profiles in Fig. 6. From the curve given by Brasseur and Nicolet (1973) which best represents the experimental data at the altitudes where comparison is possible, and from the NO_2 and NO measurements shown in Fig. 1 and in Fig. 4, a possible envelope of NO_x values has been evaluated and is given in Fig. 7. It will be discussed later.

4. Nitric acid

Absorption spectra have led to the detection (Murcray et al., 1968) of HNO_3 in the stratosphere and to several determinations. 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 abundant in the upper than in the lower layers of the atmosphere. Aircraft emission spectroscopy (Harries et al., 1974) has revealed a sharp increase of nitric acid above the tropopause. The same method at shorter wavelengths on 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 toward the pole than toward the equator. The results obtained by this method tend
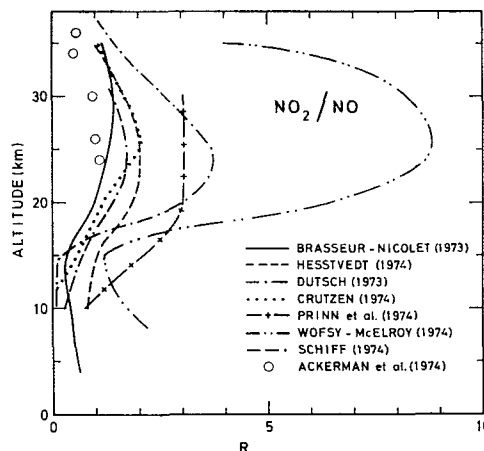

Fig. 6. Height profiles of NO_2/NO ratios computed in various models. The circles represent measurements taken at low solar elevation but that have been considered by the authors to represent daytime values.

to be the lowest, particularly at low altitudes, while absorption spectroscopy from aircraft (Fontanella et al., 1974) has a tendency to give the highest concentrations as well as some interpretations of emission measurements (Fried and Weinman, 1970).

No optical measurement seems to have been reported for HNO_3 in the troposphere. 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 less than 10^{-10}. The result is shown in Fig. 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 Fig. 7.
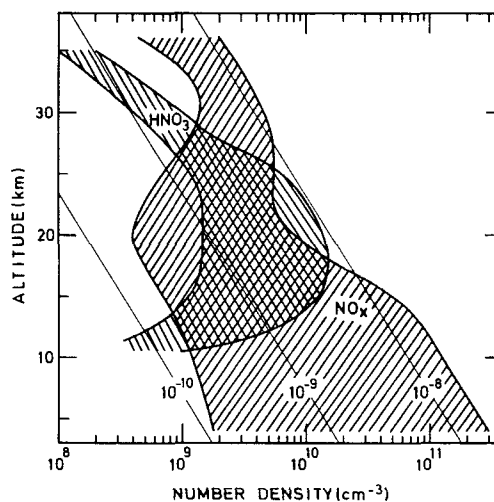

Fig. 7. Envelopes including the available data on NO_x(NO + NO_2) and on HNO_3. Constant volume mixing ratios are roughly represented by the straight lines marked 10^{-8}, 10^{-9} and 10^{-10}.
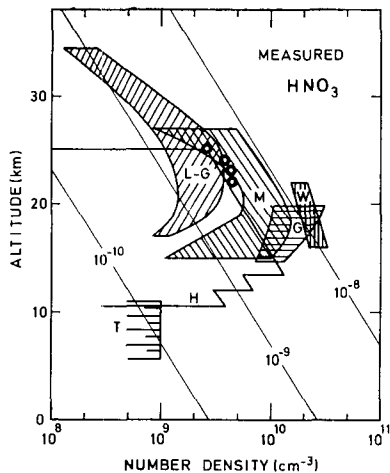
Fig. 8. Envelopes representing the measured height profiles of nitric acid number densities. L-G corresponds to the data of Lazrus and Gandrud (1974), M to those of Murcray et al. (1974), G to those of Fontanella et al. (1974), W to those of Fried and Weinman (1970), and H to those of Harries et al. (1974). The values represented by the circles and by the upper limit marked T have been evaluated 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}.

Examples of theoretically deduced vertical distributions of HNO_3 are shown in Fig. 9. Values for altitudes higher than 15 km are in good agreement with observations while below 12 km, the theory appears to give HNO_3 abundances which are too high.

5. Discussion

Nitric acid, like other very polar molecules such as HCl, is known to have an extremely low activity in dilute aqueous solutions. On the other hand, Warneck
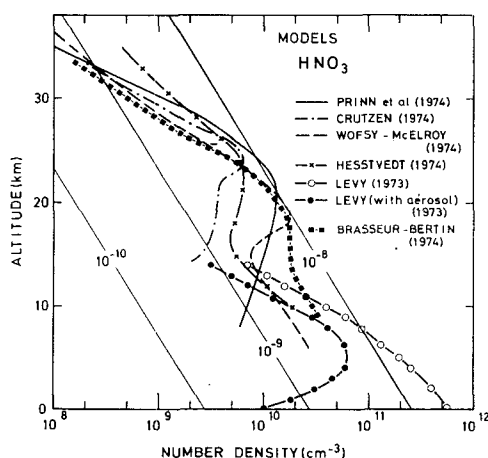

Fig. 9. Theoretically evaluated HNO_3 number densities height profiles, where only models yielding unique distributions have been used. When various latitudes were considered, the numbers for 45° have been represented.

(1974) has shown that the time constant for collisions of trace constituents with cloud elements is shorter than 5 s. 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 rainout times of the order of a few days have been introduced to represent the evacuation of odd nitrogen from the stratosphere to the troposphere. They would, however, possibly improve agreement between theory and experiment in the region of the tropopause and below. This would probably require 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.

There is obviously an important time variability of NO_x in the stratosphere. Seasonal variations have been considered in models as well as the possibility (Ruderman and Chamberlain, 1974) of interpretating the apparent correlation of ozone variation with the 11-year cycle of solar activity in terms of the effect of nitrogen oxide 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 convincing demonstration of the possible direct role of nitrogen oxides as an intermediate agent in these phenomena that would allow us to make firm assessments now (Johnston, 1974) about the possible effects of stratospheric aircraft on ozone. As noted earlier, large variations of NO have been observed. The NO abundances observed by Ackerman et al. in May of 1973 and 1974 differ markedly. Total ozone data for the two months are shown in Fig. 10. In May 1973, total ozone appears to vary from day to day randomly around mean values larger at high latitudes than currently observed. The latitudinal variation is also present in May 1974, but a well-pronounced decrease of 10–20% appears over one week. The observations indicate the occurrence of a well-organized modification of large geographic extent from at least 51° to 39°N, including the area of high NO observations. It is suggested that the decrease in total ozone is due to the replacement of ozone-rich air below 20 km by ozone-poor air. This suggestion stems from the observed vertical profiles observed over Switzerland and shown in Fig. 3a and 3b. Umkehr observations made over Lisbon near the end of the ozone spring maximum at this station (Figueira, 1973) and at other times during the year show the same trend, namely, during the minimum of total ozone 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 (25, 30 and 35 km).

The ozone reduction below 20 km 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 larger than a year. It should also be remarked
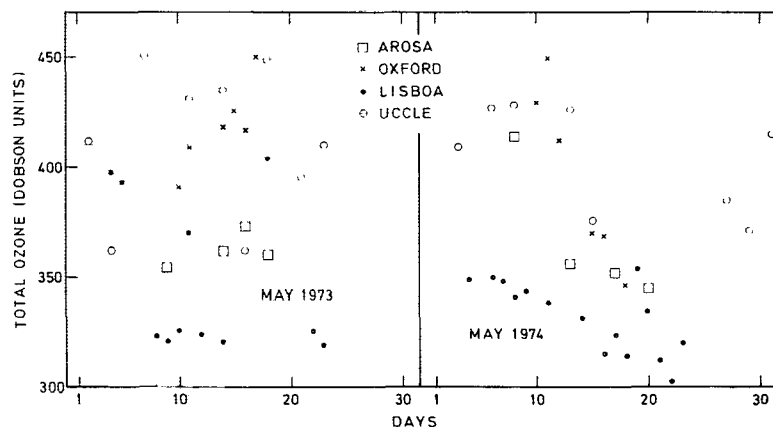
Fig. 10. Total ozone versus time measured over various European stations in May 1973 and in May 1974. The beginning of the summer minimum occurs in this latter case while May 1973 is still in the spring maximum.

that an ozone decrease in the lower stratosphere occurred concurrently with an increase at higher altitudes. All these observations suggest that the time variability of total ozone, which could quite simply be related in this case with NO_x on the basis of chemical interactions, was entirely under the control of transport processes.

Determinations of tropospheric NO_2 indicate a wide range of NO_x values tentatively illustrated in Fig. 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, 1973). The reduction of NO_x in these models would reduce the production of HNO_3 that has been considered as being too high by Warneck (1974) on the basis of 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 who have indicated a seasonal variation (summer values higher than those observed in winter) 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 stratospheric heights is smaller than in the troposphere. This could be supported by the isotopic composition of HNO_3 observed between 21 and 27 km (Moore, 1974) showing about the same N^{14}/N^{15} ratio as for standard N_2. If stratospheric HNO_3 were all derived from N_2O that shows a marked N^{15} enrichment, this should also appear in nitric acid as a product of NO_x, provided that reactions

$$N_2O + O^1D \rightarrow N_2 + O_2 \qquad (6)$$

$$N_2O + O^1D \rightarrow NO + NO \qquad (7)$$
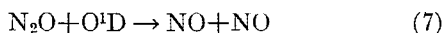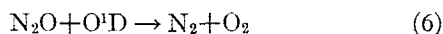
have no differential isotopic effects. This could be a reasonable assumption that should of course be checked to allow a definite interpretation of the stratospheric isotopic measurements.

If we consider the replacement time (Danielsen 1968) of stratospheric air by tropospheric air and the high HNO_3 amounts derived by absorption spectrometry (Fontanella et al., 1974), we arrive at a downward flux of nitric acid larger than 5×10^8 cm^{-2} s^{-1}. This would imply that a source of odd stratospheric nitrogen other than that from (7) has led to the odd nitrogen productions of $(0.29-1.5) \times 10^8$, $(0.25-0.65) \times 10^8$, $(0.5-1.3) \times 10^8$ and $(0.8-1.0) \times 10^8$ cm^{-2} s^{-1}, respectively, proposed by Crutzen (1974), Wofsy and McElroy (1974), Brasseur and Nicolet (1973) and Isaksen (1973).

On the other hand, the low HNO_3 values of Fig. 8 would imply, on the basis of the same interchange time between tropospheric and stratospheric air, a flux equal to 0.8×10^8 cm^{-2} s^{-1}. The average value $(2.9 \pm 2.1) \times 10^8$ cm^{-2} s^{-1} shows clearly that the actual uncertainty of the HNO_3 measurements is unsatisfactory. If it was 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 $(3 \pm 2) \times 10^8$ cm^{-2} s^{-1} would be derived (excluding several theoretical values). An additional source of odd stratospheric nitrogen would have to be introduced, particularly if a first measurement showed that the absolute quantum yield for the formation of O^1D by the O_3 photolysis, the value of which has always been assumed (Welge, 1974), is in fact smaller than currently accepted.

6. Conclusion

Measurements of the chemically related odd nitrogen molecules in the atmosphere appear to be a particularly good test 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 particularly required for the lower stratosphere and for the troposphere.

Further investigation is essential if we are to understand such fundamentals as the sources and sinks of odd nitrogen above the *average* tropopause height and in the troposphere. To date, certain experimental methods have contributed the most to the gathering of the available information, and their use should be intensified; it may also be that others should be reevaluated.

As far as the prediction of a possible reduction of ozone by a factor of 2 is concerned, some models now predict a reduction by only 1% for the same fleet of stratospheric aircraft. And none of the present models can be used for natural stratosphere forecasts.

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