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Fig. 1   Values of the ratio $[HNO_3]/[NO_2]$ derived from the NPL results[3] (solid line and solid error bars), compared with similar data due to Evans *et al.*[2] (broken line and broken error bar), and with the results of theoretical calculations using one-dimensional models[1] (hatched area).

Ratio of HNO₃ to NO₂ concentrations in daytime stratosphere

A RECENT NASA report[1] discussed the relative amounts of nitric acid and nitrogen dioxide present in the stratosphere, and pointed out that the values of the ratio $[HNO_3]/[NO_2]$ measured by Evans *et al.*[2] are, in fact, considerably lower than the values predicted theoretically using the latest values for rate constants and photodissociation coefficients for the appropriate reactions. This letter reports independent determinations of the $[HNO_3]/[NO_2]$ ratio which apparently support the measured values[2] at levels above 25 km, but which are nearer the calculated values below this level.
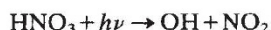
The ratio of $[HNO_3]$ to $[NO_2]$ is determined[1], in conditions of photochemical equilibrium (that is, with no transport) by the relationship

$$\frac{[HNO_3]}{[NO_2]} = \frac{k_a \cdot [OH] \cdot [M]}{J_{HNO_3} + k_b \cdot [OH]} \tag{1}$$

where k_x denotes the reaction rate for reaction $x = a$ or b, where

$$OH + NO_2 + M \rightarrow HNO_3 + M \tag{a}$$

$$OH + HNO_3 \rightarrow H_2O + NO_3 \tag{b}$$
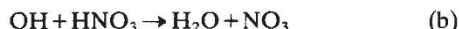
and where J_{HNO_3} denotes the photodissociation coefficient for the reaction

$$HNO_3 + h\nu \rightarrow OH + NO_2$$

The ratio depends on the concentration of the hydroxyl radical present, $[OH]$, and it has been suggested[1] that the good agreement which Evans *et al.* found between their measurements and their one-dimensional model calculations was a result of a fortuitous calculated value of $[OH]$. More recent reaction rates lead to disagreement between theory and experiment[1]. Simultaneous sub-millimetre spectroscopic studies of HNO_3, NO_2 and H_2O have provided experimental data[3] to help resolve the question of the $[HNO_3]/[NO_2]$ balance. These results, which were taken during local noon on 24 September 1974 at a latitude of 44 °N, have been re-analysed here to provide values of this ratio. The methods used to measure the concentrations are described in ref. 3.

The results of this re-analysis are presented in Fig. 1. The values of the ratio $[HNO_3]/[NO_2]$ are found to range monotonically from ~3.6 at 23 km to ~0.18 at 32 km. Also shown are the results of Evans *et al.*[2] and those of several one-dimensional model calculations[1] (the shaded area represents the range of results obtained with different models rather than any assessment of uncertainty). Between ~25 and 33 km, the agreement between our values and those of Evans is very good, but below 25 km our results lie closer to the theoretical values.

In a detailed comparison of the two sets of data it must be remembered that the NPL results were obtained during local noon. The Canadian results[2], however, were obtained at a later local time: the HNO_3 data were obtained in late afternoon at
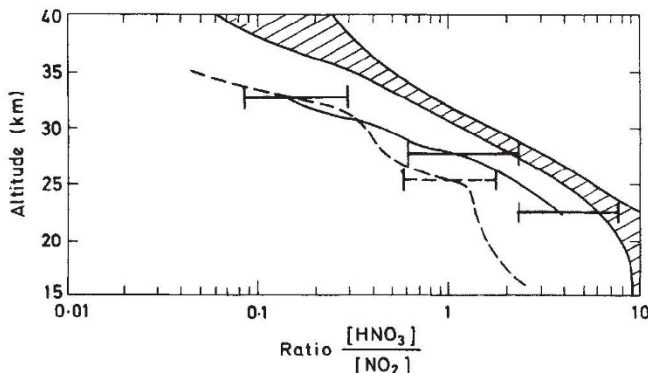
solar zenith angles of 75° to 84°, and the NO_2 data during the subsequent sunset, that is at solar zenith angles of 90° plus. The main concern might be the effects on the ratio $[HNO_3]/[NO_2]$ due to diurnal variabilities, but relatively little change occurs in $[NO_2]$ or $[HNO_3]$ between midday and the onset of sunset, although the amount of NO_2 can, of course, increase by ~two-fold during a sunset due to reformation of NO_2 from NO (ref. 4). Thus the time difference for the Canadian NO_2 measurements[2] could affect the comparison with theory and with the present results, although without further information on the exact time relative to sunset of the NO_2 measurements, we cannot conclude what that effect might be. This difficulty does not exist, of course, for the results reported here.

Uncertainties in our $[HNO_3]$ and $[NO_2]$ data were ± 25% and ±35% respectively[1], so that the uncertainties in the ratio lie between +90% and −45%. Similar uncertainties are quoted by Evans *et al.*[2] and must be borne in mind when making the comparisons between the experimental and theoretical results. However, given the close similarity of our experimental results with those of Evans *et al.*, at least above 25 km, we conclude that these new results confirm a significant disagreement between the results from one-dimensional atmospheric models and measured values for the profile of the $[HNO_3]/[NO_2]$ ratio above this level. Below 25 km the new results lie close to the calculated values. The full significance of the differences between observations and theory cannot, however, be fully evaluated without a clearer idea of the uncertainties in the results of the model calculations. Clearly, simultaneous measurements of HNO_3, NO_2 and OH will be required to fully test the model predictions.

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Uniform distribution of BeO particles in Be casting produced in rocket free fall

CAST beryllium is coarse-grained and, consequently, brittle. Much hot working is required to refine the grain structure of a cast beryllium ingot before good ductility is developed. Attempts at grain refining with for example, ultrasonics in the melt and stirring of the melt, have been unsuccessful. Research