

## The diurnal variation of hydrogen, nitrogen, and chlorine radicals: implications for the heterogeneous production of $\text{HNO}_2$

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**Abstract.** In situ measurements of hydrogen, nitrogen, and chlorine radicals obtained through sunrise and sunset in the lower stratosphere during SPADE are compared to results from a photochemical model constrained by observed concentrations of radical precursors and environmental conditions. Models allowing for heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  on sulfate aerosols agree with measured concentrations of NO,  $\text{NO}_2$ , and ClO throughout the day, but fail to account for high concentrations of OH and  $\text{HO}_2$  observed near sunrise and sunset. The morning burst of [OH] and [ $\text{HO}_2$ ] coincides with the rise of [NO] from photolysis of  $\text{NO}_2$ , suggesting a new source of  $\text{HO}_x$  that photolyzes in the near UV (350 to 400 nm) spectral region. A model that allows for the heterogeneous production of  $\text{HNO}_2$  results in an excellent simulation of the diurnal variations of [OH] and [ $\text{HO}_2$ ].

### Introduction

Data collected during the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE) provide a unique opportunity to study the diurnal variation of hydrogen, nitrogen, and chlorine radicals in the lower stratosphere. Flight tracks were designed, using a high resolution meteorological forecast model, to sample air with nearly uniform concentrations of precursors of free radicals through sunrise and sunset on successive days. In

this paper we compute the 24 hour variation of [OH], [ $\text{HO}_2$ ], [NO], [ $\text{NO}_2$ ], and [ClO] using a photochemical model constrained with measured values of pressure, temperature, aerosol surface area, concentrations of radical precursors ( $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NO}_y$ , and  $\text{Cl}_y$  inferred from  $\text{CCl}_3\text{F}$  and  $\text{CO}_2$ ), total column ozone, and planetary albedo. Comparison of calculated and observed concentrations of radicals at different times throughout a daily cycle provides a rigorous test of our current understanding of photochemical processes that regulate the abundance of radicals.

### Theory and Observation

We focus on flights of the ER-2 from Moffett Field, CA (37.4°N) on 11 May 1993 (930511) and 12 May 1993 (930512) at ~19 km altitude (~65 mbar). Concentrations of  $\text{N}_2\text{O}$  and  $\text{O}_3$  were nearly uniform from before sunrise on 930511 and from mid-afternoon through sunset on 930512 (Figure 1). Air parcels with values of [ $\text{N}_2\text{O}$ ] between 240 and 260 parts per billion (ppb) and pressure between 64.5 and 69.5 mbar were selected for analysis in this study.

Inputs to the photochemical model are given in Table 1. Concentrations correspond to the mean of measured values for selected air parcels, except for [ $\text{NO}_y$ ] and [ $\text{CH}_4$ ] which were estimated using correlations with [ $\text{N}_2\text{O}$ ] from other flights during SPADE. Concentrations of inorganic chlorine ( $\text{Cl}_y$ ) were computed from in situ measurements of halogenated source gases and [ $\text{CO}_2$ ] [Woodbridge et al., 1994]. Total column ozone and ultraviolet albedo were specified from observations by the Total Ozone Mapping Spectrometer (TOMS).

Reaction rates and absorption cross sections from DeMore et al. [1992] were used, except for extrapolation to longer wavelengths of cross sections for  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_2$ , and  $\text{HNO}_4$ . A reaction probability of 0.1 was used for the heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  [DeMore et al., 1992]. The heterogeneous hydrolysis of  $\text{ClONO}_2$  was included, but has a negligible effect on model results at the temperature (214.5 K) of these observations. Photolysis rates were calculated using a radiative transfer model that accounts for Rayleigh and aerosol scattering [Prather, 1981] using vertical profiles for [ $\text{O}_3$ ] from a climatology scaled to match the total column measured by TOMS, and vertical profiles for temperature and aerosol extinction from the National Meteorological Center and the Stratospheric Aerosol and Gas Experiment II, respectively.

We assumed that each species reached a balance between production and loss, over 24 hours, for the temperature, pressure, and

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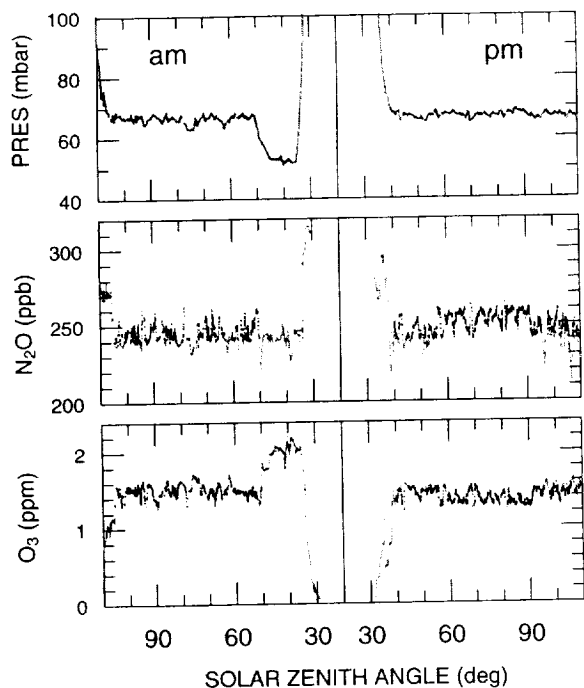
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**Figure 1.** Measurements of pressure,  $[\text{N}_2\text{O}]$ , and  $[\text{O}_3]$  obtained during ER-2 flights 930511 and 930512 plotted as a function of solar zenith angle ("am" and "pm" distinguish observations obtained before and after local noon, respectively). Dark points indicate air parcels, with pressure between 64.5 and 69.5 mbar and  $[\text{N}_2\text{O}]$  between 240 and 260 ppbv, selected for analysis.

latitude at which an air parcel was sampled. Since winds were weak during May, the flow was primarily zonal, and photochemical time constants are short, we expect *on average* relatively small deviations from steady state. Further details are provided by Salawitch et al. [1994].

Model results and observations are shown in Figure 2. Calculations neglecting heterogeneous chemistry underestimate  $[\text{OH}]$ ,  $[\text{HO}_2]$ , and  $[\text{ClO}]$  and overestimate  $[\text{NO}]$  and  $[\text{NO}_2]$  by large amounts. For the lowest solar zenith angles (SZA), a model allowing for the heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  on sulfate aerosols (*JPL-Het*, Figure 2) simulates the concentration of all radicals to within the uncertainty of measurement ( $2\sigma$  measurement uncertainties, including random and systematic effects, are estimated to be 30% for  $[\text{OH}]$ , 40% for  $[\text{HO}_2]$ , 20% for  $[\text{NO}]$ , 25% for  $[\text{NO}_2]$ , and 25% for  $[\text{ClO}]$ ). However, this model fails to account for the early morning rise and late afternoon decay observed for  $\text{HO}_x$  ( $[\text{OH}] + [\text{HO}_2]$ ) [Wennberg et al., 1994].

The time dependence of the model:measurement ratios for  $[\text{NO}]$ ,  $[\text{ClO}]$  and  $[\text{OH}]$  is illustrated in Figure 3. To evaluate the significance of these comparisons, we assume:

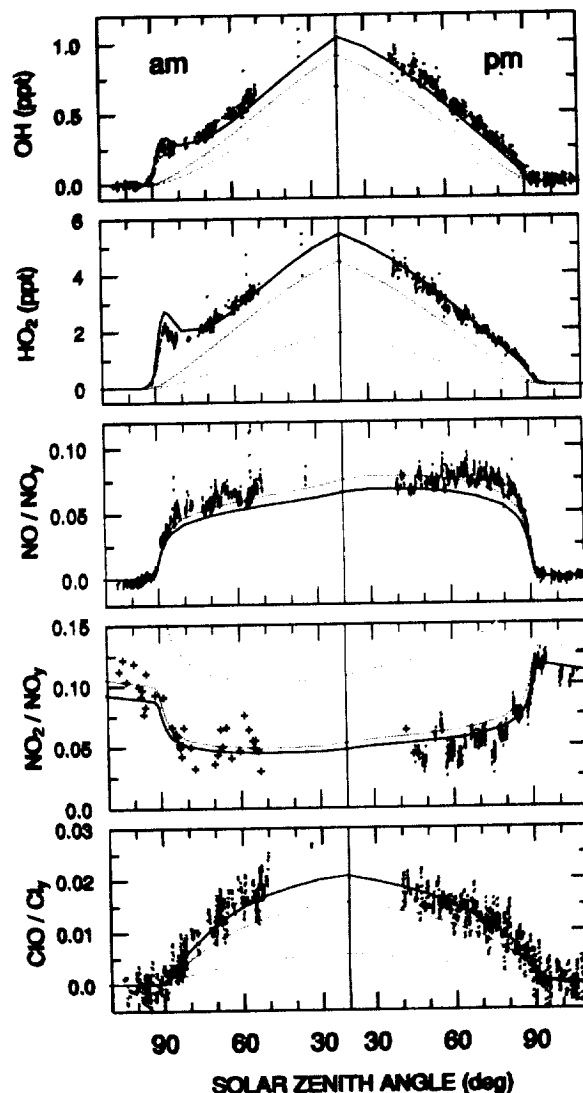
$$[\text{X}]_{\text{ATM}} = S[\text{X}]_{\text{MEAS}} + Z + P \quad (1)$$

where  $[\text{X}]_{\text{ATM}}$  and  $[\text{X}]_{\text{MEAS}}$  represent the actual and measured concentrations of species X, and S, Z and P represent the systematic

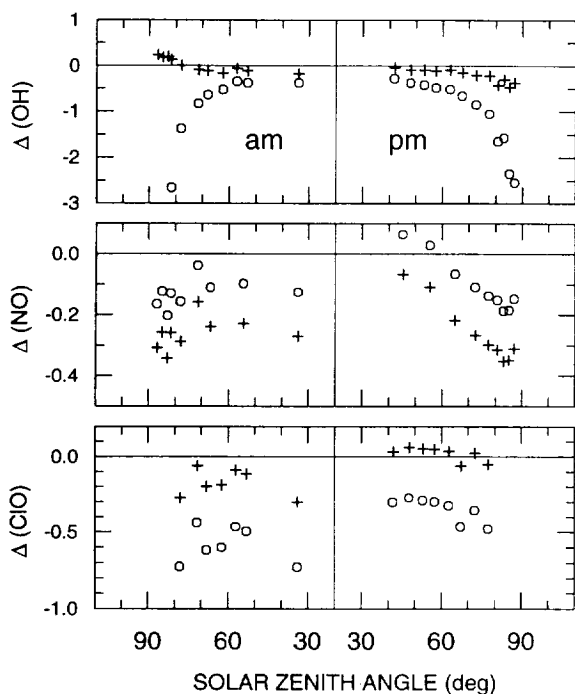
**Table 1.** Model inputs

Latitude	37.9°N	$\text{O}_3$	1.4 ppmv
Temperature	214.5 K	$\text{H}_2\text{O}$	4.4 ppmv
Pressure	66.9 mbar	$\text{CH}_4$	1.5 ppmv
Column $\text{O}_3$	353 DU	$\text{NO}_y$	5.0 ppbv
UV Reflectivity	0.34	$\text{Cl}_y$	1.2 ppbv
Surface Area	$6.0 \times 10^{-8} \text{ cm}^{-1}$		

error, zero artifact, and precision of the measurement, respectively. Nighttime observations of radicals that disappear in the dark can be used to estimate Z. The short term variability of the observations, given the nearly uniform concentration of precursors, can be used to estimate P. The ratios in Figure 3 are restricted to times when measured concentrations exceed Z+P by a factor of 3. In this case the ratios should differ from unity by a



**Figure 2.** Measurements (dots) of  $[\text{OH}]$ ,  $[\text{HO}_2]$ ,  $[\text{NO}]$ ,  $[\text{NO}_2]$  (crosses and dots represent data from the JPL and NOAA instruments, respectively), and  $[\text{ClO}]$  during ER-2 flights of 930511 and 930512, for selected air parcels illustrated in Figure 1, plotted as a function of solar zenith angle. Model simulations using rates and cross sections from DeMore et al. [1992]: neglecting all heterogeneous processes (*JPL-Gas*, blue dotted line); including heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  (*JPL-Het*, blue solid line); and same as *JPL-Het* except allowing for updated absorption cross sections for  $\text{HNO}_3$  and quantum yields of  $\text{O}(^1\text{D})$  and the heterogeneous production of  $\text{HNO}_2$  (*Model B*; red line). Measurements of  $[\text{ClO}]$  and  $[\text{NO}]$  (obtained every 16 and 1 seconds, respectively) have been smoothed using a 1 minute median filter.  $[\text{NO}]$ ,  $[\text{NO}_2]$ , and  $[\text{ClO}]$  have been divided by  $[\text{NO}_y]$  and  $[\text{Cl}_y]$  to account for slight variations in the abundance of radical precursors. Values of  $[\text{NO}]/[\text{NO}_y]$  calculated using *JPL-Gas* ( $\sim 0.18$  at mid-day) have been omitted to emphasize comparisons for the heterogeneous models.



**Figure 3.** The ratio  $\Delta(X) \equiv ([X]_{\text{MODEL}} - [X]_{\text{MEAS}}) / [X]_{\text{MODEL}}$ , where  $[X]_{\text{MODEL}}$  and  $[X]_{\text{MEAS}}$  represent modeled and measured concentrations of species  $X$ , for the *JPL-Het* (circles) and *Model B* (crosses) simulations. Ratios have been averaged into SZA bins. The ratio is displayed only when  $[X]_{\text{MEAS}} > 3 \times (Z+P)$  (see text).

constant amount,  $S$ , if the model describes properly the response of radical concentrations to changes in solar illumination.

Differences between calculated and observed  $[\text{NO}]$  and  $[\text{ClO}]$  during early morning are close to the uncertainty of measurement, and show no trend with SZA (Figure 3), demonstrating that the variation of photolysis rates for  $\text{NO}_2$  and  $\text{ClONO}_2$  with solar illumination is calculated reasonably well. It is unclear if the trend with SZA between calculated and observed  $[\text{NO}]$  during late afternoon is real, or what process is responsible. However, the trend with SZA of the model-measurement ratio for  $[\text{OH}]$  (Figure 3) exceeds the measurement uncertainty by large amounts, illustrating the existence of a source of  $\text{HO}_x$  during early morning and late afternoon not accounted for by the *JPL-Het* model.

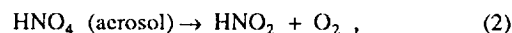
The largest sources of  $\text{HO}_x$  at low SZA are reactions of  $\text{O}(^1\text{D})$  with  $\text{H}_2\text{O}$  and  $\text{CH}_4$ , and photolysis of  $\text{HNO}_3$ . Peak production of  $\text{O}(^1\text{D})$  from photolysis of  $\text{O}_3$  and peak photolysis of  $\text{HNO}_3$  occur at wavelengths near 305 nm; at high SZA, solar radiation for this spectral region does not penetrate to ER-2 altitudes. The abruptness of the morning rise of  $[\text{HO}_x]$  and its coincidence with the rise of  $[\text{NO}]$  suggests that the missing source of  $\text{HO}_x$  is due to rapid photolysis of a gas at wavelengths longer than 320 nm, the spectral region of peak photolysis of  $\text{NO}_2$ . Significant production of  $\text{O}(^1\text{D})$  at these wavelengths can be ruled out based on the analysis of Michelsen et al. [1994].

Wennberg et al. [1994] suggested that photolysis of  $\text{HNO}_2$  (which is rapid and peaks at wavelengths near 370 nm) or a molecule with similar photolytic behavior is responsible for the missing source of  $\text{HO}_x$ . To match the morning rise of  $[\text{HO}_x]$  requires  $[\text{HNO}_2] \approx 10$  parts per trillion (pptv). However,  $[\text{HNO}_2]$  calculated for sunrise using the *JPL-Het* model (the primary sinks and sources of  $\text{HNO}_2$  are photolysis and the three body reaction of

$\text{OH}$  and  $\text{NO}$ , respectively) is too low, 0.04 pptv, to provide an appreciable source of  $\text{HO}_x$ .

Heterogeneous processes have been suggested to explain production of  $\text{HNO}_2$  in the troposphere [Notholt et al., 1992] and environmental chambers [Pitts et al., 1985]. Most of these studies have focused on reactions involving  $\text{NO}_x$  and  $\text{H}_2\text{O}$ . Production of  $\text{HNO}_2$  in the stratosphere by a heterogeneous reaction involving  $\text{NO}_2$  could explain the rise of  $[\text{HO}_x]$  at sunrise, following photolysis of  $\text{HNO}_2$  formed throughout the night. However, this process would have to be slow to limit production of  $\text{HNO}_2$  during the night to  $\sim 10$  pptv, and therefore would be unable to produce enough  $\text{HNO}_2$  during the day to account for the discrepancy between modeled and measured  $[\text{HO}_x]$  at late afternoon. Production of  $\text{HNO}_2$  by a rapid reaction of a non-radical species with an abundance comparable to  $[\text{HO}_x]$  is required to explain both the morning and afternoon discrepancies. Two possible candidates,  $\text{H}_2\text{O}_2$  and  $\text{CH}_2\text{O}$ , have production rates too slow to provide appreciable amounts of  $\text{HO}_x$  during late afternoon.

Wennberg et al. [1994] proposed heterogeneous decomposition of  $\text{HNO}_4$ ,



as a possible source of  $\text{HNO}_2$  sufficient to account for the source of  $\text{HO}_x$  at high SZA. In aqueous solutions  $\text{HNO}_4$  undergoes unimolecular dissociation producing  $\text{HNO}_2$  and  $\text{O}_2$  [Logager and Schested, 1993; Kenley et al., 1981]. The slow rate constant measured in these studies, for a temperature of 300 K, suggests this mechanism is too slow to explain the atmospheric observations unless the Henry's Law coefficient for  $\text{HNO}_4$  is extremely large.  $\text{HNO}_4$  has been observed to stick to ice surfaces with high efficiency, but without becoming chemically active [Z. Li, R. R. Friedl, and S. P. Sander, in preparation, 1994]. However, Zhu et al. [1994] suggested heterogeneous decomposition of  $\text{HNO}_4$  was the source of  $\text{HNO}_2$  in their laboratory chamber. We are unaware of any studies of the chemistry of  $\text{HNO}_4$  on sulfuric acid.

We examine the consequence of the heterogeneous production of  $\text{HNO}_2$  using *Model B*, identical to the *JPL-Het* model, except allowing for: heterogeneous decomposition of  $\text{HNO}_4$  on sulfate aerosols to form  $\text{HNO}_2$  with a reaction probability of 0.2; quantum yields of  $\text{O}(^1\text{D})$  from photolysis of  $\text{O}_3$   $\sim 25\%$  larger than recommended values [Michelsen et al., 1994]; and measurements of the temperature-dependent absorption cross section for  $\text{HNO}_3$  [Burkholder et al., 1993] that result in a 20% reduction in the photolysis rate of  $\text{HNO}_3$  at 220 K. Different photolysis rates for  $\text{O}_3$  and  $\text{HNO}_3$  used in *Model B* result in a decrease in calculated  $[\text{NO}_x]$ , an increase in  $[\text{ClO}]$ , and negligible change in calculated  $[\text{HO}_x]$  since variations induced by each change cancel. This model results in an excellent simulation of the latitudinal variation of radicals observed during SPADE [Salawitch et al., 1994].

Agreement between theory and observation for  $[\text{OH}]$  and  $[\text{HO}_2]$  is improved dramatically using *Model B* (Figures 2 and 3). Calculated concentrations of  $\text{HNO}_2$  at night (12 pptv) are sufficient to produce a large source of  $\text{HO}_x$  at sunrise. The supply of  $\text{HO}_x$  from photolysis of  $\text{HNO}_2$  is almost exhausted prior to the onset of significant production from  $\text{O}(^1\text{D})$ , resulting in a local maximum in  $[\text{HO}_x]$  during early morning. The rate of decay of  $[\text{HO}_x]$  during late afternoon is reduced because  $\text{HO}_x$  that is converted to  $\text{HNO}_4$  at midday is recycled by reaction (2) and subsequent photolysis of  $\text{HNO}_2$ .

Measurements of  $[\text{HNO}_4]$  and  $[\text{HNO}_2]$  in the lower stratosphere would greatly aid our understanding of processes governing the diurnal variation of  $[\text{HO}_x]$ . Profiles of  $[\text{HNO}_4]$  have been

obtained in the lower stratosphere from a weak Q-branch absorption feature near  $803\text{ cm}^{-1}$  recorded by the Atmospheric Trace Molecule Spectroscopy Experiment during May, 1985 [Russell et al., 1988]. However, measured  $[\text{HNO}_4]$  has large uncertainties due to limited laboratory data for the temperature dependence of the absorption coefficient of  $\text{HNO}_4$  and is consistent with values calculated by models that both include or ignore reaction (2), which results in nearly a factor of 2 reduction in calculated  $[\text{HNO}_4]$  for 20 km, at sunrise. We are unaware of any stratospheric measurements of  $[\text{HNO}_2]$ .

## Conclusions

Models that include heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  on sulfate aerosols provide an excellent description of the variation with solar illumination of observed concentrations of nitrogen oxide and chlorine radicals in the lower stratosphere. A model that allows also for the heterogeneous production of  $\text{HNO}_2$  reproduces key features of  $[\text{HO}_x]$  observed during SPADE: the burst at sunrise coincident with the appearance of elevated  $[\text{NO}]$ , the local maximum during early morning, and the slow afternoon decay. Observations of the diurnal variation of radicals during SPADE shown here suggest that rates for chemical loss of  $\text{O}_3$  by cycles involving  $\text{HO}_x$  are probably more rapid than previously believed [Wennberg et al., 1994].

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