

## In Situ Measurements of OH and HO<sub>2</sub> in the Upper Troposphere and Stratosphere

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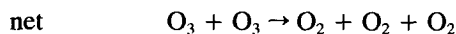
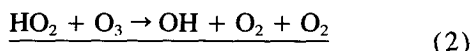
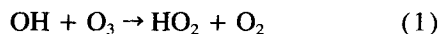
### ABSTRACT

Recent aircraft and balloon borne measurements of OH and HO<sub>2</sub> are reviewed. The authors demonstrate the ability of the laser-induced fluorescence technique to provide accurate, high signal to noise ratio measurements of OH throughout the upper troposphere and stratosphere. HO<sub>2</sub> is measured as OH after gas phase chemical titration with nitric oxide. The addition of the HO<sub>2</sub> measurement capability to the suite of instruments aboard the NASA ER-2 aircraft has provided a wealth of new information about the processes that determine the concentration of ozone in the lower stratosphere. These simultaneous, in situ measurements provide a unique test of our understanding of the mechanisms that control the odd-hydrogen chemistry of the lower atmosphere.

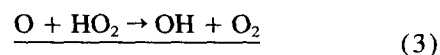
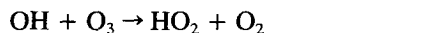
### 1. Introduction

The column density of ozone (O<sub>3</sub>) is determined by both photochemical and dynamical processes. Ozone is produced primarily in the tropical and subtropical stratosphere through the photolysis of molecular oxygen. The O<sub>3</sub> is transported to higher latitudes and removed through free radical catalysis. Removal is generally slow (time-scales approaching 1–2 years) except in polar regions, where elevated chlorine monoxide concentrations can reduce the O<sub>3</sub> lifetime to a few weeks, and in the upper stratosphere where the partitioning between O<sub>3</sub> and atomic oxygen shifts toward the latter.

As was recognized as early as 1950, reactions of hydrogen radicals (HO<sub>x</sub> ≡ H + OH + HO<sub>2</sub>) are central to the photochemistry of stratospheric O<sub>3</sub> (Bates and Nicolet 1950). These radicals directly catalyze the removal of ozone in the lower stratosphere through the reactions



and in the middle and upper stratosphere (Hampson 1964; Hunt 1966) by



Ozone is also removed by halogen and odd-nitrogen radicals, and reactions involving OH play an important role in determining the concentrations of the catalytically active ClO and NO<sub>2</sub> radicals.

This paper details measurements of OH and HO<sub>2</sub> made over the last decade by our research group. We focus on recent results from a new instrument that makes measurements of OH and HO<sub>2</sub> from the NASA ER-2 research aircraft. This instrument is discussed in detail elsewhere (Wennberg et al. 1994a). Briefly, air is brought into the nose of the aircraft through a flow system designed to provide boundary layer free sampling (Fig. 1). The OH is measured by laser-induced fluorescence (LIF) employing the Q<sub>1</sub>(2) and Q<sub>21</sub>(2) rotational lines of the A<sup>2</sup>Σ<sup>+</sup> (v = 1) ← X<sup>2</sup>Π (v = 0) electronic transition near 282 nm. Collisions with air quench the vibration of the excited state, and red-shifted fluorescence (309 nm) is observed. The laser light is produced by a high pulse-repetition-rate dye laser powered by diode-pumped Nd<sup>3+</sup>:YLF lasers (Fig. 2). The laser subsystem was designed into a space of less than 0.2 m<sup>3</sup> and weighs less than 40 kg. Fluorescence from OH, determined by tuning the laser frequency on and off resonance, is approximately proportional to the OH mixing ratio due to the efficient electronic quenching of the excited state by air. Measurement of the Stokes–Raman transition of N<sub>2</sub> at 302 nm during laboratory calibration and flight is used to monitor changes in the sensitivity of the experiment. HO<sub>2</sub> is measured after chemical conversion to OH by the fast gas phase reaction with NO. Variable concentrations of NO and variable reaction times are used to ensure the efficacy of this titration, which is complicated by the formation of HONO. The instrument runs autonomously—operation is controlled by the ER-2 pilot with a single on/off switch.

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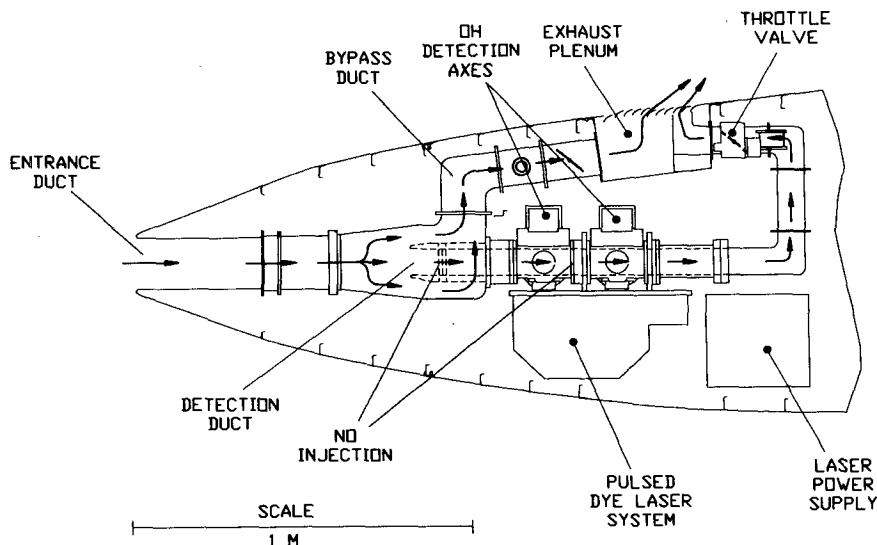


FIG. 1. Airflow through the HO<sub>x</sub> instrument mounted in the nose of the NASA ER-2 research aircraft. A double-ducted design provides the ability to vary the flow rates through the instrument while maintaining "wall less" sampling. The hydroxy radical is measured at two locations by laser-induced fluorescence; HO<sub>2</sub> is converted to OH by reaction with added nitric oxide (NO); NO is added to the flow in one of two locations, either before or in between the two OH detection axes.

Calibration of the instrument at low temperature (240 K) and high pressure (100 torr) has recently been performed. The OH concentrations are accurate to 30 percent ( $2\sigma$ ). Absolute uncertainty for HO<sub>2</sub>, which includes the uncertainty in the calibration of the instrument to OH, is approximately 40%. With the addition of a second NO injector between the two detection axes in early 1994 (see Fig. 2), OH and HO<sub>2</sub> concentrations are now measured simultaneously and with fast time response. This capability is demonstrated in Fig. 3. During ER-2 flights it is not uncommon for the aircraft to sample its own exhaust (after performing a tight turn, for instance). During these wake crossings, elevated concentrations of NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O vapor are encountered (Fahey et al. 1994). As discussed by Fahey et al., the measurements provide a direct measurement of the NO<sub>x</sub> emission rate of the ER-2 and thus provide a test of combustion models that are being used to predict how stratospheric aircraft will change the concentration of odd nitrogen compounds. HO<sub>x</sub> concentrations are also highly elevated during these events: OH concentrations are typically elevated by a factor of 2 to 3. As discussed by Hanisco et al. (1995, personal communication), these HO<sub>x</sub> measurements allow an inference of the emission rate of HO<sub>x</sub> by the ER-2.

The odd-hydrogen measurements made aboard the ER-2 are part of a much larger database that includes simultaneous measurements of most of the species thought to control the concentration of ozone in the lower stratosphere. The instrumentation for OH and HO<sub>2</sub> were added to the ER-2 platform for the Stratospheric Photochemistry, Aerosols, and Dynamics Ex-

pedition (SPADE), staged out of the NASA Ames Research Center, Mountain View, California. The entire dataset [Table 1 lists the measurements made and the principle investigator(s)] is available on CD-ROM (Hathaway et al. 1994). SPADE was designed to address the question of how emissions of nitrogen oxides from supersonic commercial aviation might affect the concentration of stratospheric ozone. The HO<sub>x</sub> instrument is presently involved in an ER-2 campaign (ASHOE/MAESA) studying the formation of the ozone hole above Antarctica.

## 2. A survey of recent results

### a. The vertical profile of OH

Shown in Fig. 4 is the vertical profile of OH in the stratosphere and upper troposphere. The data above 22 km was taken by a LIF balloonborne experiment designed and built by our research group (Stimpfle et al. 1990). The solid symbols are data taken near midday [shown in bold are the solar zenith angles (SZA) at the beginning and end of each measurement profile]. The open symbols are data taken at high SZA in the afternoon. The SZA dependence increases at lower altitudes due, primarily, to the increasing attenuation of ultraviolet radiation. At low solar zenith angles, a local minimum in the OH mixing ratio is observed at the tropopause. The SPADE measurements demonstrated that at a given altitude and SZA the OH mixing ratio is remarkably invariant with respect to latitude in the lower stratosphere (Wennberg et al. 1994b). This is a

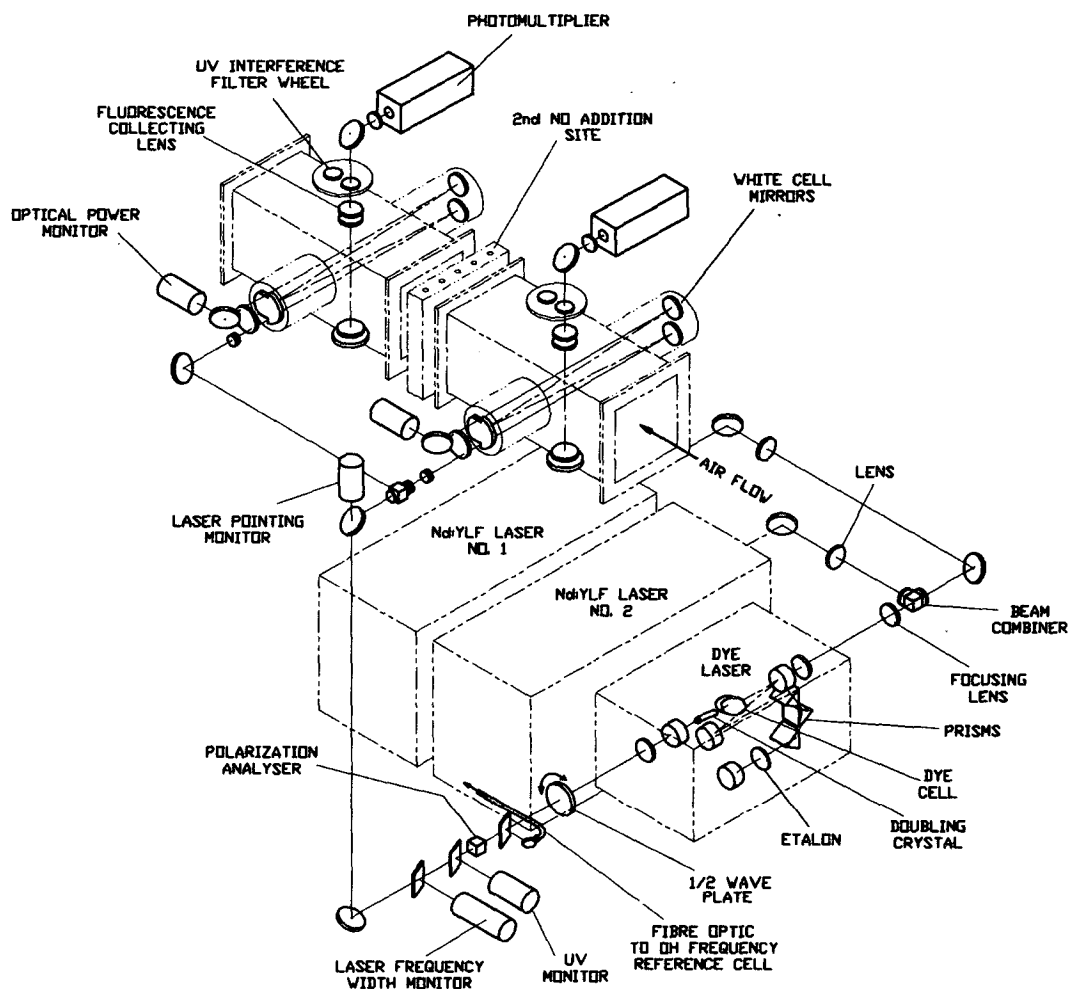


FIG. 2. Schematic of the laser system and detection axes. Two frequency-doubled, diode-pumped Nd:YLF lasers are used to power a dye laser. The dye laser fundamental (564 nm) is intracavity doubled to 282-nm resonant with one of the transitions in the A–X band of OH. A series of coupling optics are used to steer the UV laser light to the two detection axes. A white cell is used to increase the laser fluence. The hydroxyl radical is excited to the first vibrationally excited level of the A electronic state. Collisions quench the vibration, and fluorescence from the ground vibrational level is observed (310 nm) using filtered photomultipliers. The responsivity of the instrument is checked periodically by exchanging the 310-nm interference filter for a filter centered at 302 nm, where Raman scattering of nitrogen is observed.

result of the coincidental balancing of variations in the OH production and removal rates in response to variations in  $O_3$  and the odd-nitrogen species.

*b. The diurnal dependence of the odd-hydrogen radicals in the lower stratosphere*

During SPADE, an effort was made to observe the diurnal dependence of the free-radical concentrations. Figure 5, taken from Salawitch et al. (1994), shows OH and  $HO_2$  measurements for two flights plotted versus SZA. Measurements of many long-lived tracers demonstrate that the air sampled on these two days was chemically similar. Also shown is the prediction of the radical concentrations from a photochemical

model. In this model, the concentrations of the radicals are calculated using the measured concentrations of long-lived species (lifetimes  $> 1$  week—such as  $O_3$ ,  $H_2O$ , and aerosol surface area) and meteorological variables (such as temperature and pressure). Photolysis rates are calculated in a radiation model that employs satellite measurements to constrain the distribution of ozone above the airplane. Three calculations are displayed. The dashed line is a model that neglects the heterogeneous hydrolysis of  $N_2O_5$  occurring on sulfate aerosols. This reaction converts the nighttime reservoir of  $NO_x$  to nitric acid, greatly reducing the predicted concentrations of NO and  $NO_2$  in the lower stratosphere. Hydroxyl radicals and  $HO_2$  are considerably underpredicted by this

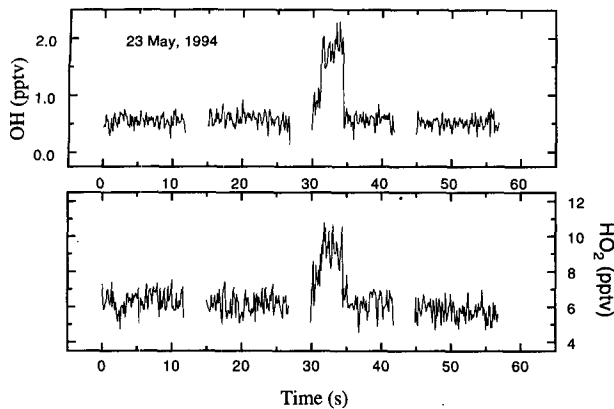


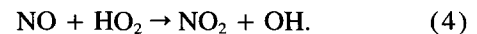
FIG. 3. Hydroxyl and HO<sub>2</sub> radical measurements during a crossing of the ER-2 exhaust wake. After executing a turn, the ER-2 intercepted its own exhaust wake. The OH and HO<sub>2</sub> concentrations are elevated dramatically during this event. This figure demonstrates the high signal to noise ratio and fast time response of the HO<sub>2</sub> instrument. Precision is better than 0.1 ppt at a sampling rate of 4 Hz.

model. Standard chemistry, including known heterogeneous processes as specified by the Jet Propulsion Laboratory (JPL) compendium (DeMore et al. 1992, hereafter referred to as JPL 92), also underpredicts the observed concentrations of OH and HO<sub>2</sub> (dark line). Disagreement is small at low zenith angles, well within the instrumental uncertainty, but increases rapidly near sunrise and sunset. A few changes to the chemical kinetic database provide for a much better match (gray line). These changes include increasing the quantum efficiency of O(<sup>1</sup>D) yields from ozone photolysis (Michelsen et al. 1994), and the addition of a heterogeneous process converting pernitric acid, HNO<sub>4</sub>, to the readily photolyzed nitrous acid, HONO. Testing of these mech-

anisms requires further laboratory investigations. It is clear, however, that simultaneous, precise measurements of radicals and the species controlling their concentrations offer a powerful technique for testing our understanding of atmospheric photochemistry. These measurements demonstrate that there is an additional source of HO<sub>x</sub> that is not accounted for in our current models. This emphasizes the role that high precision and stable calibration play in interpreting in situ data; gradients rather than absolute differences can be used to elucidate mechanistic information.

### c. Variations in the ratio of OH to HO<sub>2</sub>

Measurements of the ratio of OH to HO<sub>2</sub> provide a unique test of our understanding of HO<sub>x</sub> chemistry. Throughout most of the stratosphere, the partitioning is determined by i) reactions (1), (2), and (3)—the processes that remove stratospheric ozone, and ii) by the important reaction that couples the odd-hydrogen and odd-nitrogen families:



Measurements reported by Stimpfle et al. (1990) in the middle stratosphere and interpreted by Wennberg et al. (1990) demonstrated that the measured ratio could be modeled, using this small reaction set and an estimate of the NO profile, to within the combined uncertainties of the measurements and reaction rate constants. During SPADE, measurements of all species thought to be important in determining the HO<sub>x</sub> partitioning were made. The extensive dataset allows us to rigorously test this chemistry; large gradients in the concentration of NO were sampled at constant values of O<sub>3</sub>, and vice versa. The measurements were reported by Cohen et al. (1994) and demonstrate that our un-

TABLE 1. Measurements made from the ER-2 during SPADE.

Measurement	Investigator(s) and institution
Pressure, temperature, winds	Chan and Bowen—NASA Ames
CO <sub>2</sub>	Boering, Daube and Wofsy—Harvard University
	Toohy—University of California at Irvine
	Keeling—Scripps Institution of Oceanography
O <sub>3</sub>	Proffitt—NOAA (National Oceanic and Atmospheric Administration)
	Margitan—JPL (Jet Propulsion Laboratory)
H <sub>2</sub> O	Weinstock, Dessler, Hintsa, and Anderson—Harvard University
H <sub>2</sub> O	Kelly—NOAA
ClO/BrO	Stimpfle, Koplow, Judah, and Anderson—Harvard University
OH/HO <sub>2</sub>	Wennberg, Cohen, and Anderson—Harvard University
N <sub>2</sub> O	Loewenstein and Podolske—NASA Ames
N <sub>2</sub> O/HCl/NO <sub>2</sub> /CH <sub>4</sub>	Webster and May—JPL
CFC-11/CFC-113/CH <sub>4</sub> /CO	Elkins, Fahey, and Dutton—NOAA
NO/NO <sub>x</sub> /NO <sub>2</sub>	Fahey, Woodbridge, Keim, and Gao—NOAA
Aerosols (number, size, and surface area)	Dye and Baumgardner—National Center for Atmospheric Research
	Ferry—NASA Ames
Aerosols (number, size, and surface area)	Wilson, Jonsson, and Brock—University of Denver
UV/visible radiation	McElroy—Environment Canada

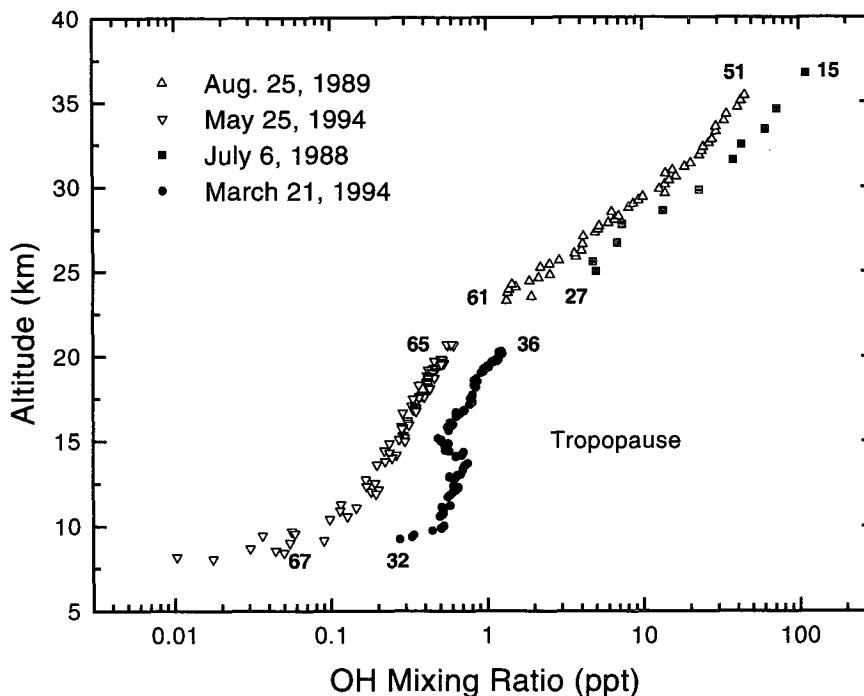


FIG. 4. Altitude profile of OH. The mixing ratio of OH is plotted versus altitude for four profiles. High-altitude measurements were made from a balloonborne experiment, while the lower altitudes were sampled by the NASA ER-2 aircraft. Shown at the beginning and end of each profile is the solar zenith angle (SZA). The dependence of OH on SZA increases lower in the atmosphere due to the increasing attenuation of the ultraviolet solar radiation that is required to produce the odd-hydrogen radicals.

derstanding of the chemical reactions controlling the partitioning of OH and HO<sub>2</sub> is complete and accurate. Figure 6, taken from Cohen et al., shows the change in the ratio of OH to HO<sub>2</sub> in response to variations in O<sub>3</sub> at a constant NO concentration. The dotted line is the expected ratio using rate constants from JPL 92 and the measured concentrations of O<sub>3</sub>, NO, ClO, and BrO. Dashed lines are calculations at the JPL 92 1- $\sigma$  uncertainty limits for the rate of OH + O<sub>3</sub> (reaction 1). Solid lines are the same for HO<sub>2</sub> + O<sub>3</sub> (reaction 2). In Fig. 7, the measured and modeled ratios are shown as a function of the concentration of NO at fixed O<sub>3</sub>. The dotted line is for the recommended values of the rate constants. Dashed lines are calculations at the JPL 92 error limits for the rate of HO<sub>2</sub> + NO (reaction 4). Solid lines correspond to the 1- $\sigma$  uncertainty in the measured NO.

This result demonstrates that our understanding of the rate constants that determine the efficiency of catalytic removal of O<sub>3</sub> by HO<sub>x</sub> are defined accurately, more accurately than suggested by JPL 92. The ratio of the rate of reaction (2) to reaction (4) determines how the rate of ozone removal by HO<sub>x</sub> will vary in response to changes in NO<sub>x</sub>. As discussed below, this addresses a question central to our understanding of the photochemistry of the lower stratosphere.

#### d. The removal of lower stratospheric ozone by free radicals

Beginning in the early 1970s, models have been used to assess the potential impact on stratospheric O<sub>3</sub> of various perturbations in the concentrations of trace gases. Most notably, efforts have been made to predict the effect on O<sub>3</sub> due to changes in the atmospheric burden of chlorofluorocarbons, nitrous oxide, methane, carbon dioxide, and emissions of nitrogen oxides from stratospheric aircraft. Changes in the column concentration of O<sub>3</sub> can occur as a result of dynamical, radiative, and chemical effects. Unfortunately, the predictions of these models have not been stable. For instance, the predictions for the change in [O<sub>3</sub>] due to the NO<sub>x</sub> effluent from a hypothetical fleet of supersonic aircraft have oscillated over the last 20 years—including changes in sign. These changes have resulted from improved understanding of the chemistry and dynamics of the stratosphere. In 1990, the consensus of atmospheric modelers was that a fleet of such aircraft would result in an approximately 10% reduction in O<sub>3</sub>; 10 years earlier it was thought that a slight enhancement in O<sub>3</sub> was probable. Within the last 3 years the consensus has once again shifted, and now such aircraft are predicted to only slightly affect O<sub>3</sub> concentrations, and

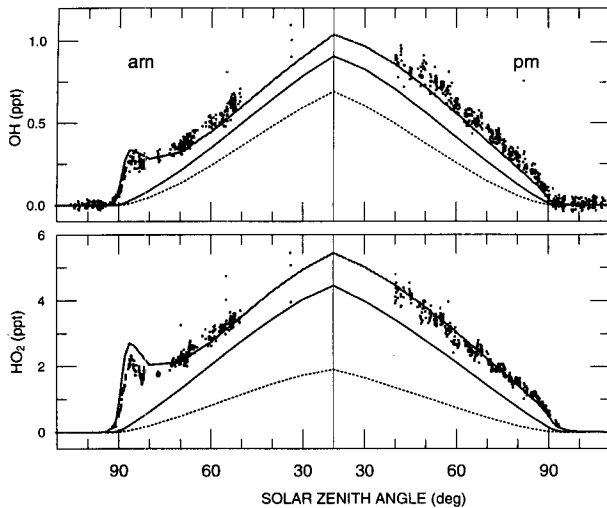
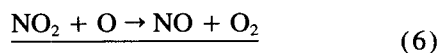
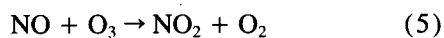


FIG. 5. Diurnal variation of OH and HO<sub>2</sub> observed near 18-km altitude on 11–12 May 1993 during the SPADE experiment (taken from Salawitch et al. 1994). Results from a photochemical model are also displayed. A model that neglects heterogeneous chemistry occurring on sulfuric acid aerosols (dashed line) underestimates OH and HO<sub>2</sub> by large amounts. Low SZA measurements are described within the experimental uncertainty by a model that includes the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> (dark line). This model, however, also underestimates the HO<sub>2</sub> concentrations at high SZAs. A model that includes a speculated heterogeneous reaction producing HONO (gray line) accurately describes the observations throughout the day.

some models suggest that O<sub>3</sub> levels will increase slightly (Weissenstein et al. 1993). In these recent models, small decreases in the ozone concentration in the middle stratosphere are offset by small increases in the lower stratosphere.

The lack of stability in the model predictions reflects the nonlinear response of O<sub>3</sub> removal rates to changes in [NO<sub>x</sub>]. Throughout the last decade, models of stratospheric chemistry uniformly predicted that the catalytic removal of ozone in the middle and lower-middle stratosphere (17–40 km) was dominated by the reaction set



Under these conditions, increases in NO and NO<sub>2</sub> concentrations lead directly to enhanced ozone removal rates and thus reduced ozone concentrations. During the last few years, however, heterogeneous chemistry in the lower stratosphere has been demonstrated to play an important role in determining the concentrations of NO and NO<sub>2</sub> (Fahey et al. 1993). The addition of this chemistry to models resulted in the drastically different predictions for the relative importance of the various catalytic cycles that destroy ozone (McElroy et al. 1992).

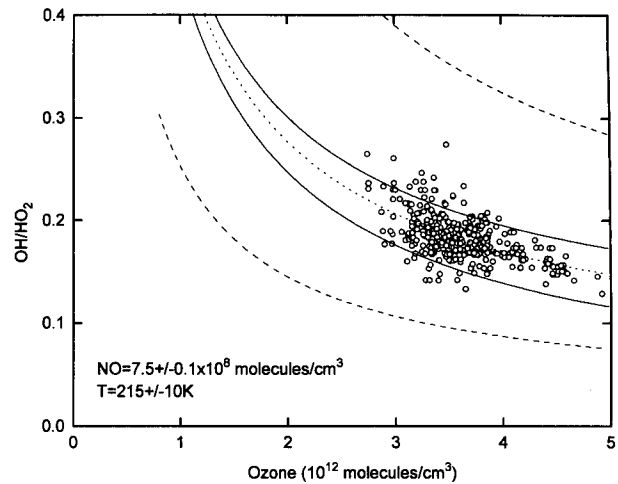


FIG. 6. Measured (o) and modeled ratio of OH to HO<sub>2</sub> versus simultaneously measured [O<sub>3</sub>] at constant [NO] (taken from Cohen et al. 1994). The dotted line is a calculation of the ratio using the JPL 92 rates and measured concentrations of O<sub>3</sub>, NO, ClO, and BrO. Dashed lines are calculations at the JPL 92 1-σ error limits for the rate of the reaction of OH with O<sub>3</sub> (Reaction 1). Solid lines are the same for the reaction of HO<sub>2</sub> with O<sub>3</sub> (Reaction 2).

The SPADE measurements allowed the first quantitative analysis of the radical-catalyzed removal of lower stratospheric O<sub>3</sub> constrained by measurements of free radical concentrations from each of the important chemical families: HO<sub>x</sub>, ClO<sub>x</sub>, BrO<sub>x</sub>, and NO<sub>x</sub> (Wennberg et al. 1994b). As shown in Fig. 8, ozone removal was dominated by the odd-hydrogen and halogen chemistry in May 1992 at all altitudes at and below the

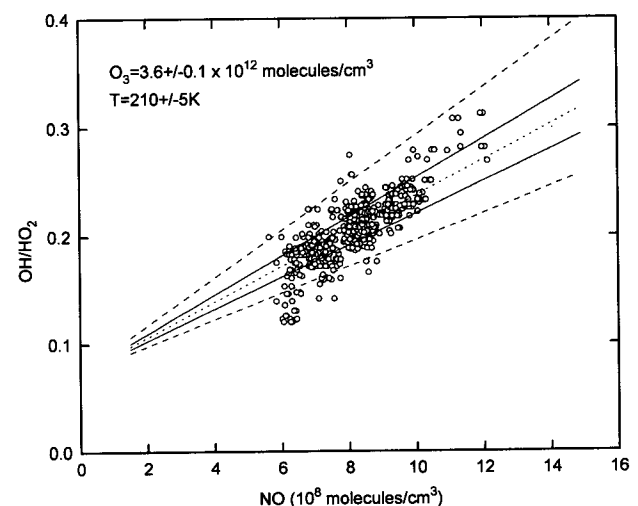


FIG. 7. Measured (o) and modeled ratio of OH to HO<sub>2</sub> versus simultaneously measured [NO] at constant [O<sub>3</sub>] (taken from Cohen et al. 1994). The dotted line is as in Fig. 6. Dashed lines are calculations at JPL 92 1-σ error limits for the rate of HO<sub>2</sub> with NO (Reaction 4). Solid lines correspond to the 1-σ error in the measured NO.

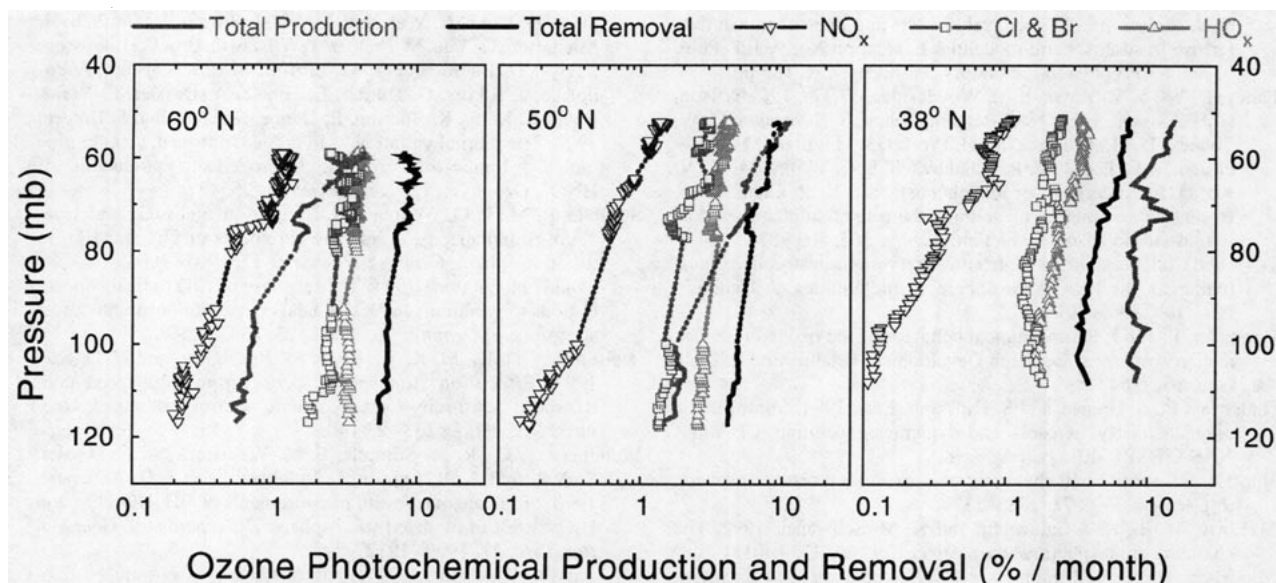


FIG. 8. Photochemical removal and production rates for  $O_3$  (taken from Wennberg et al. 1994b). Measurements of the concentrations of OH,  $HO_2$ , ClO, NO, and  $O_3$  obtained during three altitude profiles on 1 May 1993 are used to calculate the  $O_3$  removal rates from free radical catalysis. The in situ measurements are scaled according to the observed diurnal profiles to obtain the integrated loss rates. The odd-hydrogen radicals were responsible for >40% of the photochemical loss in the lower stratosphere. Copyright 1994 by the AAAS.

ER-2 ceiling (21 km). As a result of the demonstrated coupling between NO and  $HO_x$  (reaction 4), and between  $NO_2$  and ClO (Stimpfle et al. 1994), ozone loss rates were inversely correlated with total  $NO_x$  loading in the airmasses interrogated. Because of the long lifetime of ozone, however, measurements at higher altitude, other seasons, and under different aerosol loading conditions (the SPADE campaign took place 18 months after the eruption of Mount Pinatubo) are required to fully determine how  $[NO_x]$  changes affect ozone.

### 3. Conclusions

We have demonstrated that OH can be measured by laser-induced fluorescence accurately and with high precision throughout the upper troposphere and lower stratosphere. The unique capability of the ER-2 payload has allowed us to test our understanding of the photochemistry of  $HO_x$  and atmospheric ozone between 10 and 20 km altitude. These tests have demonstrated (i) that our theory of the partitioning between  $HO_2$  and OH is well described by photochemical theory; (ii) that a significant, but unknown,  $HO_x$  source exists that is not described by present models; and (iii) that the photochemical removal of ozone in the lower stratosphere can be dominated by processes involving  $HO_2$ .

The relative wealth of information on  $HO_x$  in the lower stratosphere is in stark contrast with the paucity of data at altitudes both above and below the ER-2 operating range (15–21 km). Limitations of the ER-2

platform make these regions difficult or impossible to study. We look forward to the near future when remotely piloted aircraft will carry ER-2-class payloads to these undersampled regions.

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