

# Simultaneous measurements of stratospheric HO<sub>x</sub>, NO<sub>x</sub>, and Cl<sub>x</sub>: Comparison with a photochemical model

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**Abstract.** We report simultaneous measurements of the stratospheric concentration profiles of OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, HNO<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O, HCl, HOCl, and ClO during a midlatitude balloon flight in 1989. Measurements were made over almost an entire diurnal cycle by the Smithsonian Astrophysical Observatory Far-Infrared Spectrometer (FIRS-2) and the Jet Propulsion Laboratory Balloon Microwave Limb Sounder (BMLS). We analyze these measurements using a photochemical model constrained by observations of long-lived gases. Measured HO<sub>x</sub> species (OH and HO<sub>2</sub>) and H<sub>2</sub>O<sub>2</sub> show fair agreement with theory throughout the diurnal cycle. Measurements of HNO<sub>3</sub> are higher than theory near the concentration peak, while the levels of NO<sub>2</sub> are consistent with the model at most altitudes. Measurements of ClO and HOCl are less than predicted concentrations, suggesting a source of HCl in addition to the reaction of Cl with CH<sub>4</sub>. Possibilities for such a source include a minor HCl + O<sub>2</sub> product channel for the reaction of ClO with OH and a minor HCl + O<sub>3</sub> channel for the reaction of ClO with HO<sub>2</sub>.

## Introduction

Catalytic destruction of ozone from the HO<sub>x</sub>, Cl<sub>x</sub>, and NO<sub>x</sub> reaction cycles is a central feature of the chemistry of the Earth's ozone layer. However, it has been difficult to obtain simultaneous measurements of these radical species and their reservoirs over a range of altitudes. We report the first simultaneous measurement of HO<sub>x</sub>, Cl<sub>x</sub>, and NO<sub>x</sub> species throughout the middle atmosphere. These observations represent the most comprehensive description yet obtained of the distribution of free radicals and photochemically related gases involved in catalytic destruction of ozone.

Stratospheric balloon platforms carrying several instruments are effective at making simultaneous measurements of multiple species. The molecules currently measured by the FIRS-2 instrument include OH, HO<sub>2</sub>,

H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, O<sub>2</sub>, O<sup>3</sup>P (in the mesosphere and thermosphere), HCl, HF, HOCl, HBr, CO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O, CO, HCN, and CO<sub>2</sub> (temperature and pressure profiles are derived from the 16-μm bands of CO<sub>2</sub>). The Balloon Microwave Limb Sounder (BMLS) instrument measures ClO and O<sub>3</sub>. In this paper we concentrate on measurements of HO<sub>x</sub> (OH and HO<sub>2</sub>), the closely related H<sub>2</sub>O<sub>2</sub>, and the Cl<sub>y</sub> and NO<sub>y</sub> species ClO, HOCl, HCl, NO<sub>2</sub>, and HNO<sub>3</sub>. Measurements of radical precursors H<sub>2</sub>O, O<sub>3</sub>, and N<sub>2</sub>O and temperature are used to constrain the photochemical model calculations as described below.

Measurements of the species considered in this analysis have been described in the literature. OH has been measured in the stratosphere using balloon-borne far-infrared thermal emission spectroscopy [Kendall and Clark, 1980; Traub *et al.*, 1991; Carli *et al.*, 1989; Park and Carli, 1991; Pickett and Peterson, 1993], in situ resonance fluorescence [Stimpfle *et al.*, 1990; Wennberg *et al.*, 1990, 1994], and balloon-borne lidar [Heaps *et al.*, 1985]. Ground-based measurements that include the stratospheric content as a part of the total column have also been made [Burnett *et al.*, 1988; Iwagami *et al.*, 1995]. The measurements presented here are the first to include the altitude profile in the stratosphere and its time variation through most of a diurnal cycle.

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HO<sub>2</sub> has been measured in remote sensing by balloon-borne far-infrared thermal emission spectroscopy [Traub *et al.*, 1990; Park and Carli, 1991] and submillimeter heterodyne spectroscopy [Stachnik *et al.*, 1992] and by ground-based millimeter-wave spectroscopy [de Zafra *et al.*, 1984]. HO<sub>2</sub> has also been measured in situ with two techniques: chemical conversion followed by resonance fluorescence [Anderson *et al.*, 1981; Stimpfle *et al.*, 1990; Wennberg *et al.*, 1994] and matrix isolation followed by ESR spectroscopic analysis [Helten *et al.*, 1984]. H<sub>2</sub>O<sub>2</sub>, which is photochemically closely related to OH and HO<sub>2</sub>, has only been measurable in the stratosphere using far-infrared thermal emission spectroscopy [Chance and Traub, 1987; Chance *et al.*, 1991; Park and Carli 1991]. Stratospheric NO<sub>2</sub> has been well determined by using infrared and visible measurement techniques [Roscoe *et al.*, 1990; Russell *et al.*, 1988; Webster *et al.*, 1990]; to our knowledge the present study is the first quantitative determination of its concentration profile using far-infrared emission spectroscopy. Concentrations of H<sub>2</sub>O, O<sub>3</sub>, HNO<sub>3</sub>, N<sub>2</sub>O, and HCl have been measured by a number of investigators; reviews of most techniques for the measurement of these gases can be found in the reports of the *World Meteorological Organization (WMO)* [1986, 1989]. HOCl has been measured in far-infrared thermal emission [Chance *et al.*, 1989] and in infrared solar absorption [Toon *et al.*, 1992]. ClO has been measured by remote sensing from balloon platforms [Stachnik *et al.*, 1992] and the Upper Atmosphere Research Satellite [Waters *et al.*, 1993], by in situ experiments from balloons [Dessler *et al.*, 1993] and aircraft [Avalone *et al.*, 1993] and by ground-based millimeter-wave spectroscopy [de Zafra *et al.*, 1987; Emmons *et al.*, 1995].

The strength of this set of measurements is the simultaneous observation of a large number of individual species, covering a large range of altitudes in the stratosphere and nearly one full diurnal cycle. The completeness of the data set provides a basis for examining our understanding of processes that regulate the partitioning of radicals using a photochemical model constrained by observations of the longer-lived radical precursors.

## Balloon Observations

The observations discussed in this paper were made during a balloon flight from Fort Sumner, New Mexico (34°N, 104°W) on September 26, 1989. The balloon reached the float altitude of 36 km at 1105 mountain daylight time (MDT) and began a gradual descent at 1235 MDT on September 27. The flight was terminated at 1426 MDT. No data were recorded from 0430 to 0801 because of a telemetry problem. The spectra included in this study were taken mostly with the telescope pointing to 15°±3° in geographic azimuth, corresponding to an average sampling latitude of 37.0°N, with the later afternoon scans on September 26 pointing to 188°±3°, corresponding to an average sampling latitude of 31.8°N. Solar zenith angles corresponding to the measurement locations that are calculated below

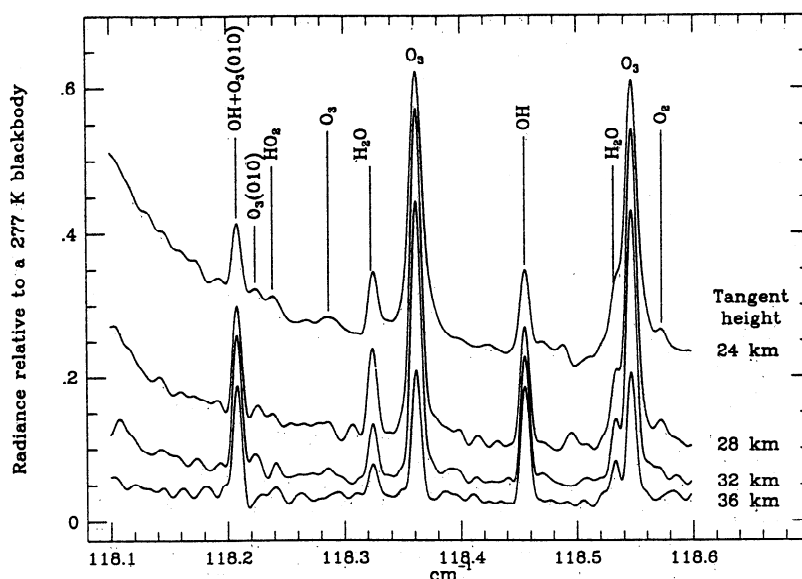
include these offsets in the sampling latitude from the actual location of the gondola.

The Smithsonian Astrophysical Observatory (SAO) FIRS-2 instrument was designed specifically to make thermal emission measurements of the stratosphere from a balloon platform. Its capabilities have been described previously [Traub *et al.*, 1991; Johnson *et al.*, 1995a]. Briefly, it is a two-beam, high-resolution (0.004 cm<sup>-1</sup> unapodized) Fourier transform spectrometer, which measures thermal emission in the far-infrared (80-210 cm<sup>-1</sup>) and mid-infrared (350-700 cm<sup>-1</sup>). Measurements are made at various angles above the Earth's limb, with absolute pointing referenced to an accelerometer- and gyroscope-stabilized single-axis platform. Most observations with the FIRS-2 were made using a standard limb-scan sequence, which included blackbody calibration spectra, high-elevation spectra, and measurements at 0° elevation followed by measurements at elevation angles corresponding to five successive 4 km altitudes below the gondola float height. These measurements took place in a time sequence that included 6 min of integration time (two complete spectra) at each angle. Thus each complete limb-scan sequence took approximately 48 min. The results presented here are from both the daytime and the nighttime portions of the flight.

The BMLS is a remote sensing heterodyne radiometer measuring thermal emission spectra near 205 GHz [Waters *et al.*, 1984]. The data presented here are an average of the data taken from 1100 to 1600 MDT on September 26, 1989. The BMLS was oriented on the gondola to view in the same azimuth direction as the FIRS-2 instrument.

## Data Analysis and Results

FIRS-2 spectra are analyzed to obtain concentration profiles using the nonlinear least squares fitting procedure developed at the SAO [Johnson *et al.*, 1995a] and the SAO92 spectral line database [Chance *et al.*, 1994]. Retrievals are based on multilayered, curved shell atmospheric models using distributions of pressure and temperature derived from radiosonde data obtained in the vicinity of the balloon flight. The temperature and pressure profiles are refined by fitting selected temperature- and pressure-sensitive portions of the 16-μm bands of CO<sub>2</sub>. A comprehensive search for suitable spectral lines of each species has been carried out based upon line intensities, accuracy of spectral line parameters, and freedom from spectral interference. The selection includes eight lines of OH which are above the FIRS-2 noise equivalent width detection limit of ~10<sup>-5</sup> cm<sup>-1</sup> (hyperfine components are not counted as separate lines here, although they are fully included in the radiative transfer calculations), twenty-seven lines of HO<sub>2</sub>, the <sup>R</sup>Q<sub>5</sub> branch of the lowest H<sub>2</sub>O<sub>2</sub> rotational-torsional band, six lines of H<sub>2</sub>O, thirty-six lines of O<sub>3</sub>, thirty-three lines of NO<sub>2</sub>, seven lines of HCl, twenty-two fitting windows, including the Q<sub>2</sub> and Q<sub>4</sub> branches, of HOCl, and numerous lines contained in seventeen fitting windows in



**Figure 1.** Portions of a single limb-scan sequence (6 min of integration time per spectrum) for the best features of OH in the far-infrared spectrum, the  $F_{1,7/2} \leftarrow F_{1,5/2}$  lines at  $118 \text{ cm}^{-1}$ . Spectral transitions with significant intensity are identified. The limb-scan sequence shown is from September 26, 1989, centered in time at 1128 MDT.

the  $\nu_9$  vibrational band of  $\text{HNO}_3$  and twenty-two fitting windows in the  $\nu_2$  vibrational band of  $\text{N}_2\text{O}$ . As an example of the quality of spectra obtained in this balloon flight, Figure 1 shows portions of a single limb scan (6 min of integration time per spectrum) containing the best features of OH in the far-infrared spectrum, the  $F_{1,7/2} \leftarrow F_{1,5/2}$  lines at  $118 \text{ cm}^{-1}$ . Spectral transitions with significant intensity are identified in the figure.

Most of the molecules measured here have altitude distributions that permit the onion-peeling retrieval process to proceed in a well-behaved fashion. Their mixing ratios are either nearly constant or decrease with increasing height above the balloon gondola. More importantly, the total amount of gas overhead is sufficiently small that the actual shape of the overhead distribution has a negligible effect on the retrieved concentrations from measurements taken at elevation angles corresponding to measurement heights below the gondola altitude.

The molecules whose concentrations increase with altitude above the gondola height, OH and  $\text{HO}_2$  for the FIRS-2 measurements, present a greater challenge in the retrieval process because of the potential for the shape of the overhead distribution to affect concentrations retrieved at lower altitudes. This is particularly true because FIRS-2 does not fully resolve molecular lines, which have widths that are  $\sim 3 \times 10^{-4} \text{ cm}^{-1}$  at 40 km and decrease with increasing altitude. The effect of the shape of the overhead distribution on retrieved concentrations is investigated by assuming overhead distributions highly skewed with respect to standard model profiles (M. Allen, private communication, 1990). Overhead profile shapes affect the derived OH and  $\text{HO}_2$  by 6% or less for the  $0^\circ$  elevation angle measurements when

the mesospheric concentrations of OH and  $\text{HO}_2$  relative to the concentrations at gondola altitude are changed by as much as 25% from the values in the standard distributions. The effects on measurements made at lower-elevation angles are negligible. Line of sight column densities for OH and  $\text{HO}_2$  are calculated using an initial-guess model profile for the molecule to be fitted and an altitude step size of 0.1 km. The fitting procedure then scales the initial profile using a retrieval grid matched to the viewing angles.

The FIRS-2 data in this study include a total of 24 limb-scan sequences: 9 from the first day of the flight (1105-1818 MDT), 3 from the second day (1011-1235 MDT), and 12 during the night (2028-0337 MDT). OH and  $\text{HO}_2$  retrievals are performed for sums of three successive limb-scan sequences during the daytime for use in comparison with photochemical modeling predictions. The limitation to sums of three limb-scan sequences is caused by the low signal to noise ratios of the measured  $\text{HO}_2$  lines; OH can be determined well from individual limb-scan sequences. All other molecules are analyzed by making separate averages of (1) all 9 limb-scan sequences obtained on September 26, (2) all 12 limb-scan sequences obtained during the nighttime, and (3) the first 3 limb-scan sequences obtained on September 27 (the same sum of limb scans coadded for OH and  $\text{HO}_2$  retrieval on the morning of September 27). We do not see evidence for diurnal variation of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{HCl}$ , which have long photochemical lifetimes. Our measurement sensitivity is sufficient to distinguish between the average daytime and the average nighttime concentrations for  $\text{NO}_2$  and  $\text{HOCl}$  but not to determine their diurnal variation on a finer timescale.

$\text{ClO}$  was measured by the BMLS instrument, which

Table 1. Retrieved FIRS-2 Mixing Ratio Profiles

z, km	Mixing ratio <sup>a</sup>							
	H <sub>2</sub> O (10 <sup>-6</sup> )	H <sub>2</sub> O <sub>2</sub> (10 <sup>-12</sup> )	O <sub>3</sub> (10 <sup>-6</sup> )	HNO <sub>3</sub> (10 <sup>-9</sup> )	N <sub>2</sub> O (10 <sup>-8</sup> )	NO <sub>2</sub> (10 <sup>-9</sup> )	HCl (10 <sup>-9</sup> )	HOCl (10 <sup>-11</sup> )
<i>September 26, 1989 (9 Limb Scans, 1105-1818 MDT, SZA=51.4°)</i>								
37.51	5.25(0.42)	98.1( 53.0)	7.16(0.42)	0.58(0.35)	3.72(0.42)	9.82( 3.40)	2.04(0.18)	10.1(2.47)
32.49	5.48(0.38)	118. ( 16.2)	8.71(0.46)	2.17(0.24)	8.68(0.79)	7.26( 1.12)	1.87(0.16)	10.6( 1.0)
28.71	4.66(0.33)	68.7( 18.1)	7.47(0.41)	4.18(0.43)	14.5(1.30)	2.84( 1.22)	1.43(0.13)	7.36(0.90)
24.91	4.17(0.37)	11.2( 12.5)	4.24(0.25)	6.56(0.66)	19.1(1.65)	1.49( 0.97)	1.15(0.10)	3.31(0.68)
20.66	4.18(0.38)	20.9( 11.6)	3.06(0.25)	5.37(0.54)	21.1(1.78)	0.88( 1.24)	1.07(0.10)	0.88(0.60)
16.84	1.85(0.50)	19.9(151. )	0.79(1.51)	1.20(0.13)	29.5(2.52)	5.0( 11.9)	0.18(0.06)	...
<i>September 26-27, 1989 (13 Limb Scans, 2028-0337 MDT, Night Measurement)</i>								
36.63	5.06(0.35)	101. ( 39.7)	7.28(0.42)	0.53(0.35)	4.12(0.45)	14.2( 2.6)	1.90(0.17)	12.9( 2.1)
31.72	5.13(0.36)	81.9( 14.1)	8.45(0.44)	2.64(0.28)	9.22(0.84)	8.22( 1.03)	1.76(0.15)	5.80(0.95)
27.91	4.75(0.32)	58.6( 13.2)	6.73(0.37)	4.89(0.50)	15.1(1.35)	4.87( 1.08)	1.28(0.11)	3.86(0.76)
24.40	4.91(0.34)	18.7( 11.2)	5.21(0.30)	6.75(0.68)	18.7(1.36)	2.13( 1.05)	1.28(0.11)	1.02(0.68)
20.36	3.47(0.36)	18.6( 11.9)	1.78(0.21)	4.71(0.47)	22.4(1.88)	2.54( 1.83)	0.81(0.09)	0.25(0.56)
15.96	2.30(0.60)	61.1(333. )	0.22(1.44)	0.64(0.07)	28.3(2.39)	...	0.07(0.05)	2.46(1.80)
<i>September 27, 1989 (3 Limb Scans, 1011-1235 MDT, SZA=43.5°)</i>								
38.57	5.23(0.77)	...	7.14(0.52)	2.27(0.87)	1.97(0.53)	10.9( 4.6)	2.04(0.20)	6.54(4.11)
33.34	5.53(0.46)	75.0( 27.4)	8.04(0.49)	1.69(0.25)	6.98(0.72)	5.79( 1.65)	1.79(0.16)	11.6( 1.3)
29.87	5.21(0.41)	9.3( 23.6)	7.94(0.48)	4.31(0.49)	10.6(1.10)	2.00( 1.33)	1.67(0.15)	5.44(1.33)
25.63	4.71(0.35)	19.3( 13.3)	5.42(0.33)	6.20(0.65)	12.2(1.17)	0.65( 0.93)	1.27(0.12)	4.37(0.69)
21.96	4.50(0.39)	18.4( 16.6)	2.47(0.25)	8.23(0.86)	16.6(1.56)	0.76( 1.40)	1.44(0.13)	...
18.14	4.06(0.55)	...	2.70(0.87)	2.60(0.29)	22.7(2.89)	5.54( 6.25)	0.49(0.07)	...

<sup>a</sup> 1σ errors include uncertainties from molecular parameters: H<sub>2</sub>O (5%), H<sub>2</sub>O<sub>2</sub> (2%), O<sub>3</sub> (5%), HNO<sub>3</sub> (10%), N<sub>2</sub>O (8%), NO<sub>2</sub> (5%), HCl (8%), HOCl (3%).

**Table 2.** Time variation of OH and HO<sub>2</sub>

Altitude, km	Mixing ratio <sup>a</sup>	
	OH (10 <sup>-12</sup> )	HO <sub>2</sub> (10 <sup>-11</sup> )
<i>September 26, 1989, 1105-1324 MDT, SZA=40.2°</i>		
37.89	192. (22. )	19.1 (4.5)
32.78	34.8 ( 3.9)	7.75(1.36)
29.17	16.6 ( 3.1)	2.46(1.52)
25.22	-0.9 ( 1.8)	0.91(0.82)
20.49	1.1 ( 1.1)	0.47(0.62)
<i>September 26, 1989, 1325-1559 MDT, SZA=47.1°</i>		
37.43	160. (16. )	14.8 (3.7)
32.23	42.1 ( 4.0)	6.48(1.13)
28.19	12.7 ( 2.2)	5.59(1.02)
24.16	2.24( 1.59)	1.60(0.79)
21.15	3.62( 2.46)	0.72(1.28)
<i>September 26, 1989, 1600-1811 MDT, SZA=67.0°</i>		
37.08	98.1 ( 9.9)	10.0 (3.6)
33.16	20.9 ( 2.3)	4.80(1.08)
28.14	4.59( 1.29)	3.61(0.87)
24.59	0.74( 1.23)	...
20.55	0.88( 1.19)	...
<i>September 27, 1989, 1011-1235 MDT, SZA=43.5°</i>		
38.57	183. (19. )	16.5 (4.2)
33.34	50.3 ( 4.7)	6.62(1.30)
29.87	15.6 ( 2.5)	7.42(1.12)
25.63	3.88( 1.29)	1.87(0.63)
21.96	1.46( 1.99)	1.25(0.72)

<sup>a</sup>1 $\sigma$  errors include uncertainties from molecular parameters: OH (8%), HO<sub>2</sub> (2%).

uses the manifold of lines centered at 204.325 GHz for atmospheric retrievals. The data are reduced using both constrained least squares and sequential estimation fitting procedures [Waters *et al.*, 1984, 1988]. The radiative transfer calculation is also based on multilayered curved shell models of the atmosphere, with stratospheric temperature profiles derived from local radiosonde data. The 206.132-GHz O<sub>3</sub> line is used to calibrate instrument pointing. The estimated uncertainty for ClO includes random spectral noise, radiometric calibration errors, and spectral line parameter errors. The data presented here are an average of the ClO concentrations retrieved from 1100 MDT to 1600 MDT on September 26, 1989. During this time, little diurnal variation was seen or expected since ClO varies rapidly at sunrise and sunset but is relatively constant during midday [de Zafra *et al.*, 1987].

Results are presented for each species for the range of tangent heights that provide meaningful retrievals for

the particular period of averaging. The results of the fitting and error analysis are presented in Tables 1, 2, and 3. Table 1 contains results from the first day average, the nighttime average, and the second day average. The sums for the second day include only observations made before the balloon began descending. Table 2 contains the OH and HO<sub>2</sub> retrievals for the four sets of short sums (three limb scans in each sum), three for the first day of the flight and one for the second day, which constitute the primary time-dependent measurements of HO<sub>x</sub> from the present flight. The total FIRS-2 uncertainty estimate includes effects due to the following: nonlinear least squares fitting of the spectra, intensity calibration of the spectra, pointing errors, overhead abundance (discussed above), determination of ambient pressure, propagation of abundance uncertainties to lower layers in the onion-peeling process, and uncertainties in the molecular parameters (including their temperature uncertainties). Further laboratory measurements may improve the spectral line parameters enough to significantly decrease the systematic uncertainties for some molecules. The effect of diurnal variation of OH and HO<sub>2</sub> on the onion-peeling retrieval process (that is, concentrations in upper layers change during the limb-scanning process before observations at lower layers are completed) is found to be negligible for the present observations. Table 3 contains the BMLS measurements of ClO with 1 $\sigma$  errors that include all known systematic errors. Tables 1, 2, and 3 also include the measurement altitudes and average solar zenith angles for the locations of limb-sampling regions.

### Photochemical Model

The observations are compared with the calculations made with a photochemical model constrained by measured concentrations of radical precursors [Logan *et al.*, 1978; McElroy and Salawitch, 1989; Salawitch *et al.*, 1994a]. Input to the model includes vertical profiles for O<sub>3</sub>, NO<sub>y</sub> (defined as the sum of [NO] + [NO<sub>2</sub>] + [HNO<sub>3</sub>] + [ClNO<sub>3</sub>] + 2[N<sub>2</sub>O<sub>5</sub>] + [HNO<sub>2</sub>] + [HNO<sub>4</sub>]), Cl<sub>y</sub> (defined as [Cl] + [ClO] + [HCl] + [ClNO<sub>3</sub>] + [HOCl] + 2[Cl<sub>2</sub>]), H<sub>2</sub>O, CH<sub>4</sub>, temperature, and aerosol surface area. We have obtained input profiles for O<sub>3</sub>, H<sub>2</sub>O, and temperature from an average of measure-

**Table 3.** BMLS ClO Mixing Ratio Profile

Altitude, km	ClO Mixing Ratio <sup>a</sup> (10 <sup>-12</sup> )
<i>September 26, 1989, 1100-1600 MDT, SZA=44°</i>	
40.0	450.(80.)
35.0	410.(70.)
30.0	250.(50.)
25.0	73.(30.)
20.0	5.(30.)

<sup>a</sup>1 $\sigma$  errors include uncertainties from molecular parameters.

ments for the first day, second day, and night, interpolated to a common altitude grid. The input profile for CH<sub>4</sub> is derived from FIRS-2 measurements of N<sub>2</sub>O, using a relation developed from 1985 Atmospheric Trace MOlecule Spectroscopy (ATMOS) measurements [Gunsong *et al.*, 1990], adjusted for the change in concentration of CH<sub>4</sub> between 1985 and 1989. NO<sub>y</sub> is derived from the FIRS-2 measurements of N<sub>2</sub>O using correlations measured by the ER-2 aircraft and by ATMOS [Loewenstein *et al.*, 1993; Russell *et al.*, 1988]. Total Cl<sub>y</sub> is estimated from its relationship with N<sub>2</sub>O based on measurements of chlorinated organic source gases [Woodbridge *et al.*, 1995] and is adjusted to match the chlorine levels in 1989. This relationship is consistent with ATMOS measurements of HCl and ClNO<sub>3</sub> [Zander *et al.*, 1990] as well as ATMOS measurements of chlorine source gases [Zander *et al.*, 1992] at the higher altitudes of the present measurements. The input profile of aerosol surface area peaks at  $2 \times 10^{-8}$  cm<sup>-1</sup> at 16 km and is representative of nonvolcanic, background conditions based on measurements by the Stratospheric Aerosol and Gas Experiment II (SAGE II) (G.K. Yue, private communication, 1994). Thus to the extent feasible, the model reflects the state of the atmosphere at the time of the balloon flight, as determined from measurements of the long-lived species that are precursors to radicals and reservoir species. Using this set of input parameters, the model is used to calculate diurnally varying concentration profiles by balancing production and loss of each species over a 24-hour period [Logan *et al.*, 1978] using reaction rates and photolysis cross sections from the current Jet Propulsion Laboratory recommendation [DeMore *et al.*, 1994] (JPL94). A reaction probability of 0.1 is used for the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> (JPL94); the formulation of Hanson *et al.* [1994] is adopted for the rate of the heterogeneous hydrolysis of ClNO<sub>3</sub>. A radiative transfer model that includes Rayleigh and aerosol scattering is used to calculate photolysis rates [Prather, 1981]. The calculated rate for photolytic production of O<sup>1</sup>D from O<sub>3</sub> is based on a study that allows for production of O<sup>1</sup>D via excited rovibrational states of O<sub>3</sub> [Michelsen *et al.*, 1994]. This rate leads to ~40% enhancements in O<sup>1</sup>D production and ~15% enhancements in concentrations of OH in the lower stratosphere relative to models using the rate given by JPL94 but has a negligible effect on OH in the upper stratosphere. Additionally, the absorption cross sections for H<sub>2</sub>O<sub>2</sub>, HNO<sub>4</sub>, and HNO<sub>2</sub> have been extrapolated to longer wavelengths than given in JPL94 in order to accurately represent photolysis of these molecules at high solar zenith angle (SZA).

## Discussion

### HO<sub>x</sub> Species

Our midday measurements of OH fall within the range of the previous measurements shown in Figure 4 of Pickett and Peterson [1993]. The variations between our measurement and previous measurements are

reasonable considering the accumulated errors and atmospheric variability with latitude and season. Present measurements of HO<sub>2</sub> in the stratosphere are in good agreement with previous measurements summarized by Park and Carli [1991]. The strengths of the present set of observations are the simultaneous measurement of the full HO<sub>x</sub> chemical family during a full diurnal cycle, and the ability to compare these observations with a model constrained by simultaneous measurements of H<sub>2</sub>O and O<sub>3</sub>, which regulate concentrations of HO<sub>x</sub>. Similar measurements have been made in the lower stratosphere from the NASA ER-2 during the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) mission [Wennberg *et al.*, 1994; Salawitch *et al.*, 1994a, 1994b]. The present work extends this type of comparison to an altitude range that includes most of the stratosphere.

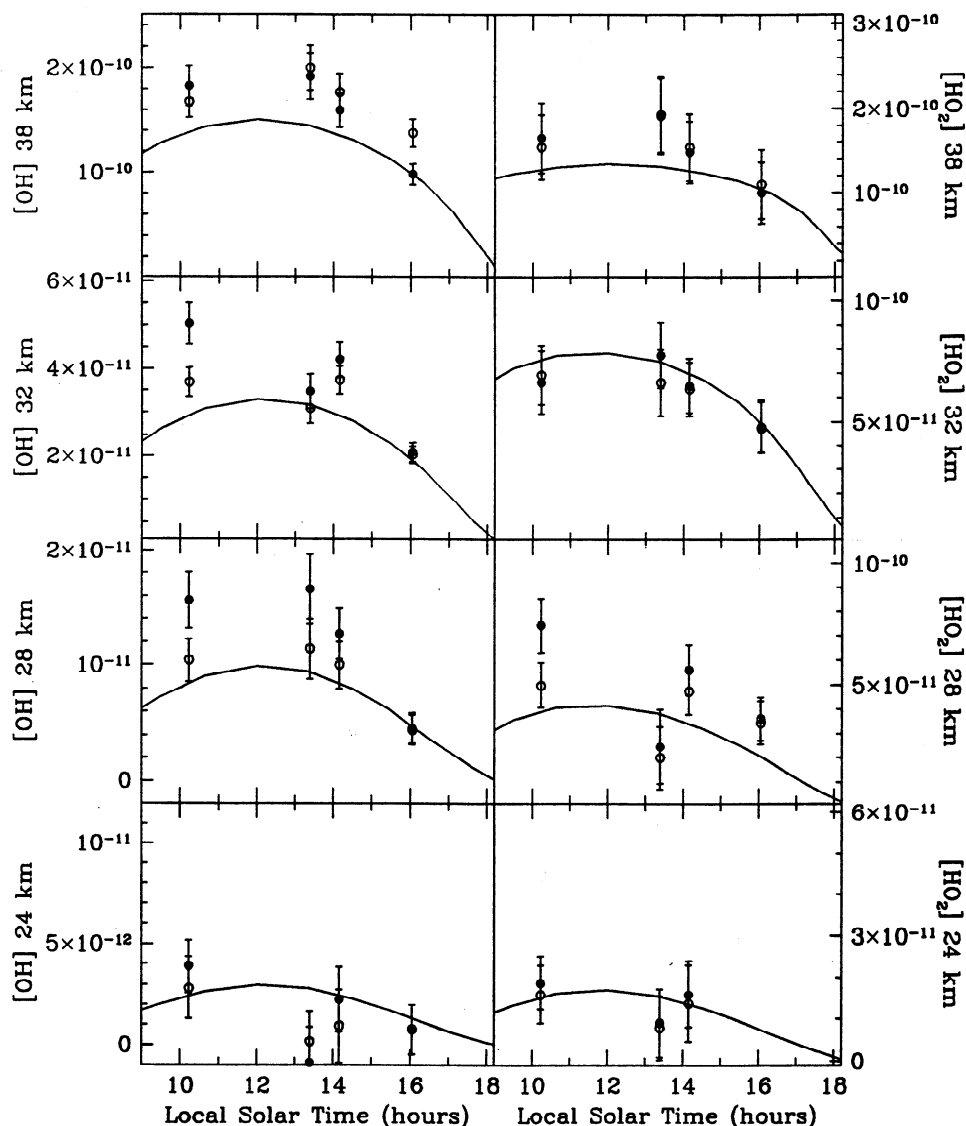
Comparisons of concentrations of OH and HO<sub>2</sub> measured at four solar zenith angles and model calculations are shown in Figure 2. Measurements from Table 2 are plotted at the nearest corresponding altitudes used for modeling (solid circles) and are linearly interpolated vertically to provide values on the same altitude grid as the model calculations (38, 32, 28, and 24 km), to emphasize comparison of the solar zenith dependence between the data and the model and to remove the effects of different tangent altitudes in the various sums of limb-scan sequences. The interpolated values are plotted as open circles. The average SZAs for the measurements, which determine the average local solar time used in Figure 2, are calculated from the latitude, longitude, and viewing direction of the instrument.

Chi-square statistics are used to test the quality of the agreement between the interpolated measurements and photochemical model results by determining whether differences can be explained simply by random errors of the measurements. We assume for this purpose that the measurements are normally distributed around the actual values with the uncertainties representing the 1 $\sigma$  random errors of the measurements. Chi-square values are calculated as

$$\chi^2 = \sum_{i=1}^n ((x_{\text{meas}}(i) - x_{\text{model}}(i)) / \delta x(i))^2,$$

where  $n$  is the number of degrees of freedom,  $x_{\text{meas}}(i)$  and  $x_{\text{model}}(i)$  are measurements and modeled values, respectively, and  $\delta x(i)$  is the 1 $\sigma$  measurement uncertainty. Chi-square comparisons are used only in cases where potential systematic uncertainties due to molecular line parameters are negligible.

With the exception of OH at 38 and 32 km and HO<sub>2</sub> at 28 km the  $\chi^2$  values for the HO<sub>x</sub> measurements are all less than 4, with 4 degrees of freedom, suggesting a better than 50% probability of agreement between the measurements and the model. For the three with larger  $\chi^2$  values (23.05 for OH at 38 km, 12.56 for OH at 32 km, and 7.84 for HO<sub>2</sub> at 28 km) the diurnal trends for the theory and observation are consistent but the probabilities of agreement are small (less than 1%, 1.4%, and



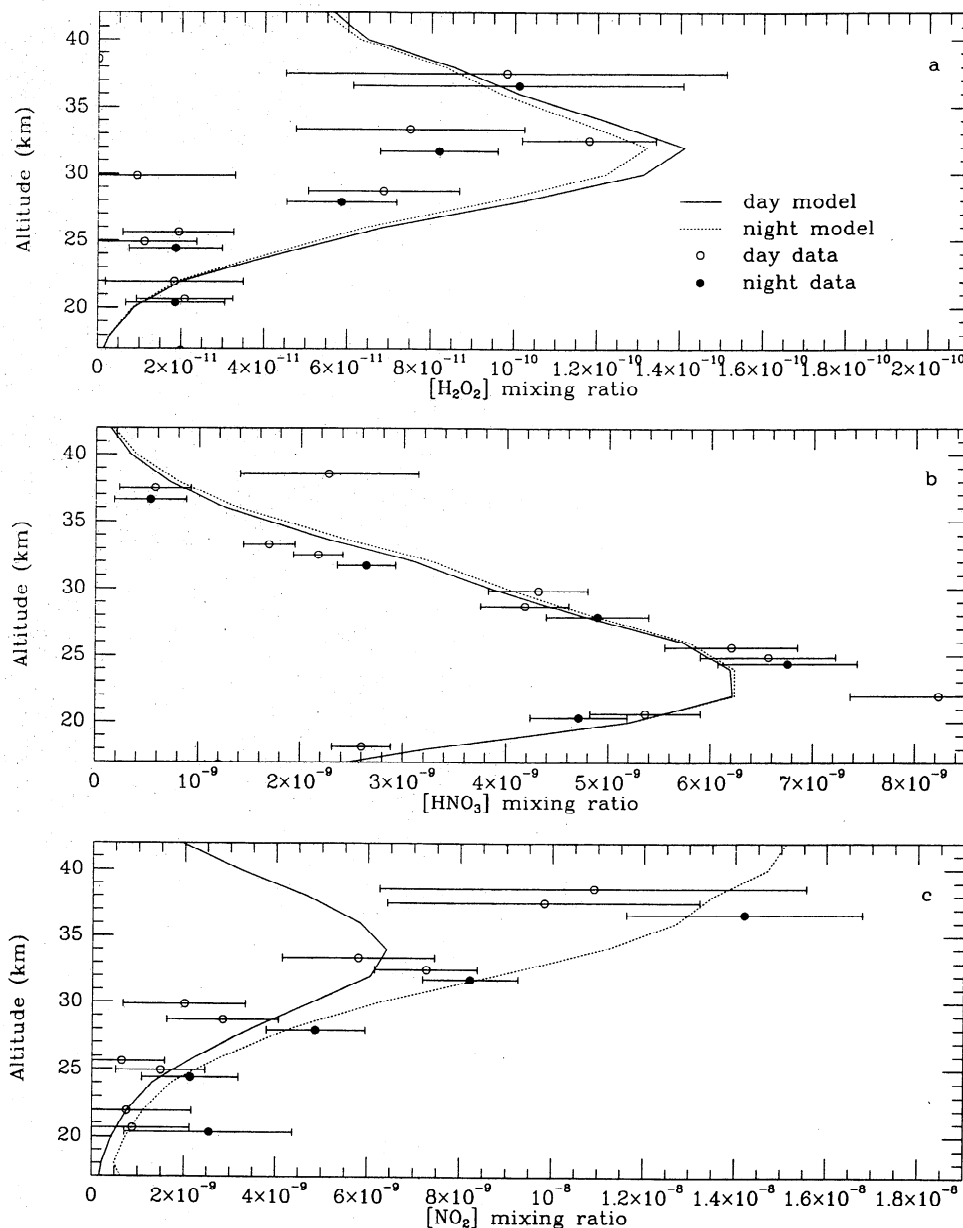
**Figure 2.** Measured and modeled OH and HO<sub>2</sub> concentrations versus solar zenith angle. Solid circles are the measured mixing ratios from Table 2, plotted at nearest corresponding altitudes of the modeling grid. Open circles are these concentrations linearly interpolated to the modeling grid altitudes of 38, 32, 28, and 24 km.

9.8% for the three cases, respectively). In particular, measurements of OH are significantly higher (~33%) than model values at 38 km. This difference is unlikely to be due to uncertainty in the UV flux and O<sub>3</sub> concentration involved in estimating the production of OH from the reaction of O<sup>1</sup>D with H<sub>2</sub>O since the model is constrained by the observed concentrations of O<sub>3</sub> (1 $\sigma$  uncertainties of 6-7% at this altitude) and the overhead column abundance of O<sub>3</sub> used in the model agrees with the column inferred from the measurements to within 10%.

Figure 3a compares the retrieved and calculated profiles of H<sub>2</sub>O<sub>2</sub>. Both the magnitude and the shape of the calculated profiles disagree with the data at about the 2 $\sigma$  level, implying that our current understanding of the relative creation (HO<sub>2</sub> + HO<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>) and photolysis rates for H<sub>2</sub>O<sub>2</sub> may be incomplete.

### NO<sub>y</sub> Species

Measurements of HNO<sub>3</sub> by FIRS-2 for this flight show very good agreement with previous balloon-borne remote and in situ measurements. Our measurements are consistent with observations of HNO<sub>3</sub> by the Balloon-borne Laser In Situ Sensor (BLISS) at 31 km in 1988 to within the error bars [May and Webster, 1989] and are also consistent with many previous measurements at similar latitudes summarized in Figure 3 of May and Webster [1989]. However, our observation of HNO<sub>3</sub> are consistently 30-40% higher than retrievals by ATMOS for the northern hemisphere [Russell et al., 1988], especially for altitudes below 28 km. The most likely explanation for these differences is that the measurements were taken 4 years apart, in different seasons, and at slightly different latitudes. The ATMOS measure-



**Figure 3.** Far-Infrared Spectrometer (FIRS-2) balloon measurements from September 26-27, 1989, and corresponding model calculations. (a) H<sub>2</sub>O<sub>2</sub>, (b) HNO<sub>3</sub>, (c) NO<sub>2</sub>.

ments were obtained at slightly lower latitudes ( $\sim 28^\circ$ ) than our measurements ( $32^\circ$ - $37^\circ$ N), which could explain some of the discrepancy. The fact that different vibrational bands are used by FIRS-2 and ATMOS retrievals is unlikely to cause the discrepancy, since all previous balloon measurements, including BLISS, use the same vibrational bands for retrieval as ATMOS, and the uncertainties in band strengths are about 10% [Goldman *et al.*, 1975; Giver *et al.* 1984; May *et al.*, 1987].

Figure 3b compares measured and modeled profiles for HNO<sub>3</sub>. The measurements are about 10-30% higher than the model at the peak of the mixing ratio profile, where HNO<sub>3</sub> comprises 50-70% of the total NO<sub>y</sub>, and slightly lower than the model at the upper altitudes. Some of this discrepancy could be due to uncertainty in

the spectroscopic transition intensity ( $\sim 10\%$ ), which is included in the error analysis. Also, measurement uncertainties for O<sub>3</sub> and N<sub>2</sub>O, used as inputs to the model, affect calculated HNO<sub>3</sub> at the 10% level. (N<sub>2</sub>O is used to infer NO<sub>y</sub>, which will have a direct effect on HNO<sub>3</sub>.) Additionally, error in the NO<sub>y</sub>/N<sub>2</sub>O relationship could affect modeled HNO<sub>3</sub> in a similar manner. If the NO<sub>y</sub> levels were higher, as suggested by the measurements of HNO<sub>3</sub>, then the modeled levels of NO<sub>2</sub>, ClO, and HO<sub>x</sub> species near the peak of the HNO<sub>3</sub> mixing ratio profile would be significantly different.

The FIRS-2 daytime observations of NO<sub>2</sub>, shown in Figure 3c, differ slightly from previous observations [Webster *et al.*, 1990; Russell *et al.*, 1988] and from model profiles. Our measurements in the 37 to 40 km re-



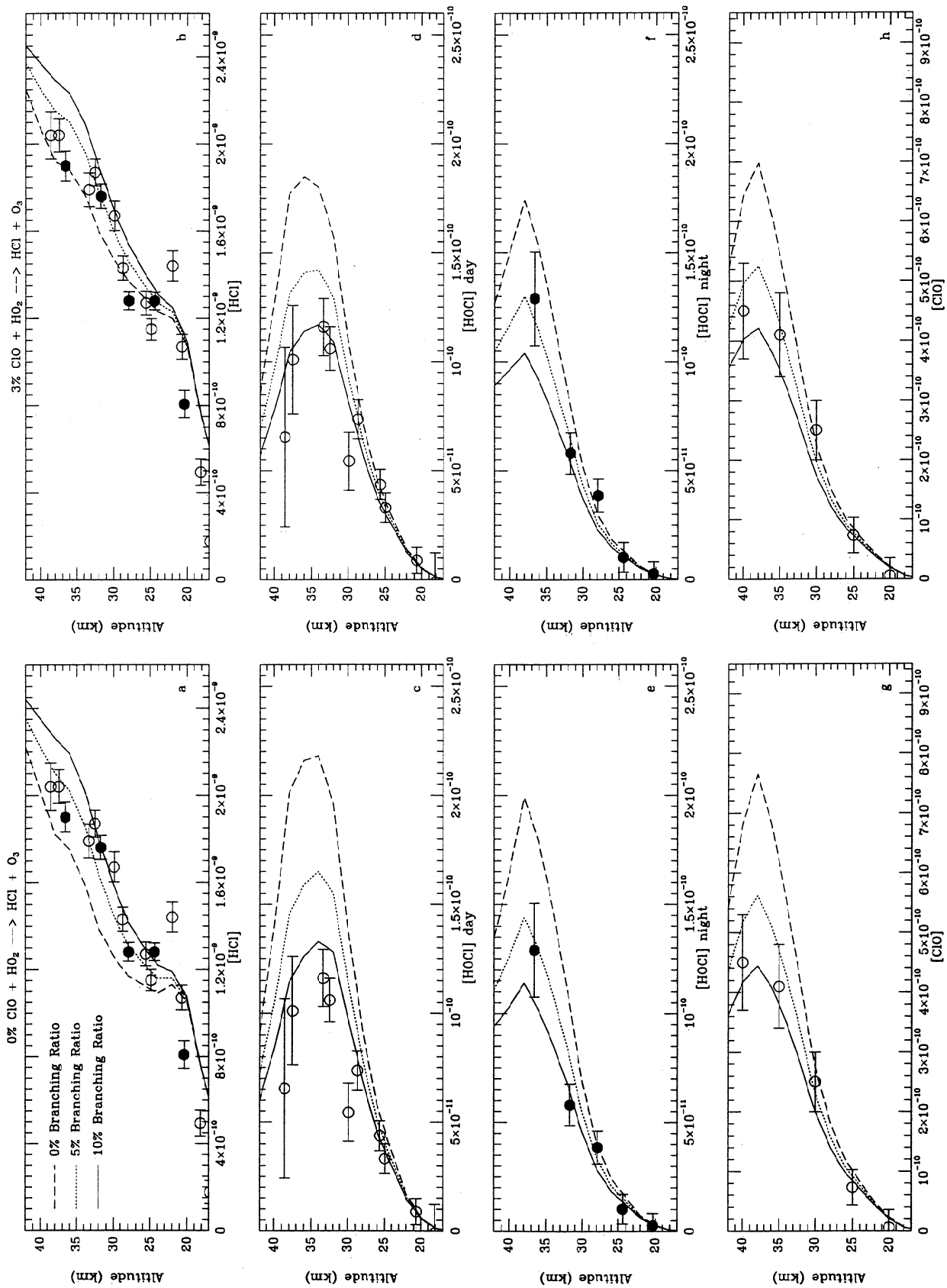


Figure 4. FIRS-2 and Balloon Microwave Limb Sounder (BMLS) balloon measurements from September 26-27, 1989, for Cl<sub>y</sub> species and corresponding model calculations using varying branching ratios for the reactions of ClO with OH and HO<sub>2</sub> to produce HCl.

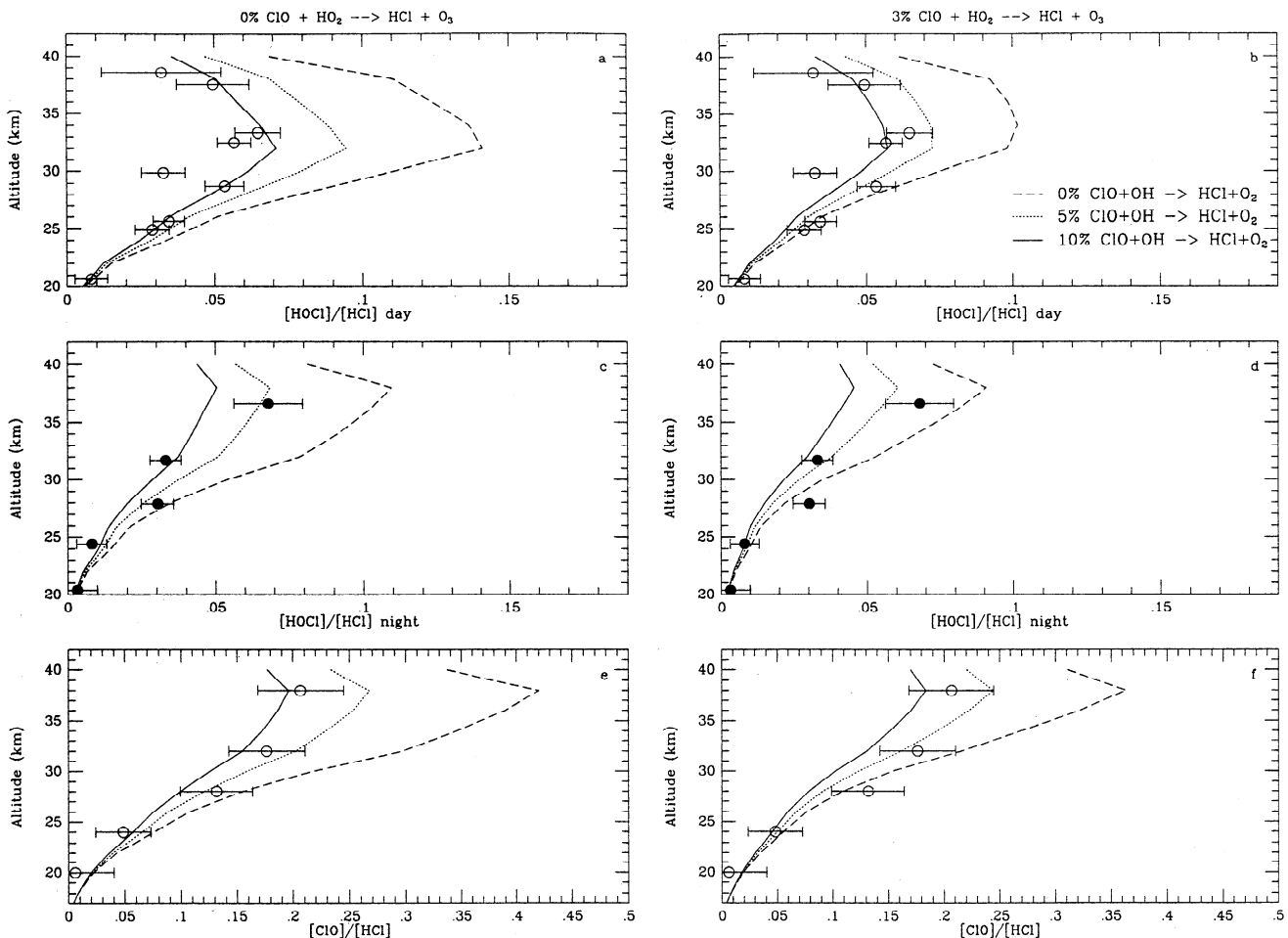
gion are consistently  $\sim 1\sigma$  higher than the previously reported measurements and model values. The nighttime measurements agree well with the model. The ability of FIRS-2 to measure NO<sub>2</sub> was limited at the time of this balloon flight, making it difficult to draw more definite conclusions from the comparison. Improved measurements of NO<sub>2</sub>, enabled by improved noise performance in the far-infrared channel, will become available from more recent FIRS-2 flights. This will permit more detailed evaluation of NO<sub>y</sub> partitioning.

### Cl<sub>y</sub> Species

Recently reported measurements of HCl and ClO from the Submillimeter Limb Sounder (SLS) [Stachnik *et al.*, 1992] show that the ClO/HCl ratio is much lower than suggested by photochemical models. Investigations of ATMOS measurements of HCl and ClNO<sub>3</sub> similarly indicate that the ClNO<sub>3</sub>/HCl ratio is lower than expected [Natarajan and Callis, 1991; Minschwaner *et al.*, 1993; H.A. Michelsen, unpublished results, 1994]. One proposal that would explain this is that ClO and OH react to produce HCl, as suggested by McElroy and Salawitch [1989]. JPL94 suggests a lower limit of 0%

for the HCl branching ratio, with an upper limit of 14%, since production of HCl is a four-center reaction involving the breaking and making of multiple chemical bonds. Similarly, the possibility of production of HCl from the reaction of ClO + HO<sub>2</sub> may also be important for resolving the discrepancy (the JPL94 recommended branching ratio is 0% with an upper limit of 3%). Uncertainties in the photolysis of HOCl are not responsible for this discrepancy since HOCl has been shown to be a good proxy for ClO when measured simultaneously with HO<sub>2</sub>, OH, and O<sub>3</sub> [Johnson *et al.*, 1995b]. Also, in the comparison shown below, HOCl and ClO are both lower than model calculations; uncertainties in the photolysis cross sections would affect them in opposite senses.

The set of measurements from this balloon flight is ideally suited for addressing partitioning within the Cl<sub>y</sub> family. Besides the direct measurement of ClO, HCl, and HOCl, we also measure concentrations of most of the reactants (OH, HO<sub>2</sub>, and NO<sub>2</sub>) involved in the creation and destruction of the main reservoir species in the Cl<sub>y</sub> family. The only important species not measured is CH<sub>4</sub>, whose reaction with Cl is the main source of HCl. CH<sub>4</sub> can be estimated quite accurately from its



**Figure 5.** Comparisons of measured and modeled  $[\text{HOCl}]/[\text{HCl}]$  and  $[\text{ClO}]/[\text{HCl}]$  ratios, assuming various branching ratios of the reactions of ClO with OH and HO<sub>2</sub> to produce HCl. The measured ClO and HCl concentrations are interpolated onto the altitude grid of the model.

observed correlations with N<sub>2</sub>O [Gunson *et al.*, 1990; M.R. Gunson, private communication, 1990]. The main sink for HCl is its reaction with OH to produce Cl + H<sub>2</sub>O. As stated earlier, the modeled OH agrees well with the measured OH except at the highest measurement altitudes, suggesting that the loss rate of HCl should be well described by the model assuming the validity of the current rate constant for OH + HCl. Especially given the high measured [OH] at 38 km, a very substantial decrease in the OH + HCl reaction rate would be required to explain the observed HCl. Uncertainties in OH do not provide an explanation for discrepancies in Cl<sub>y</sub> in the present data set.

Figure 4 shows our measurements of three Cl<sub>y</sub> species along with model calculations, corresponding to the average SZA of the measurements, assuming different branching ratios for the production of HCl from the reaction of ClO with both OH and HO<sub>2</sub>. The left-hand side of the figure shows results from models incorporating a 0% branching ratio for the ClO + HO<sub>2</sub> reaction, and the right-hand side shows results for a 3% branching ratio. Each panel shows three model calculations, assuming branching ratios for the ClO + OH reaction of 0%, 5%, and 10%. Assuming the total Cl<sub>y</sub> used in the model is correct, these plots suggest that there must be some production of HCl at the expense of ClO and HOCl, possibly through one or both of these mechanisms. We have found that inclusion of these alternate branching ratios has a negligible effect on HO<sub>x</sub> and NO<sub>x</sub>, as determined from direct comparison of model results.

To quantify the amount of any additional HCl production (and loss of ClO and HOCl) and to remove the uncertainty associated with model estimates of total Cl<sub>y</sub>, we have plotted the ratios of [ClO]/[HCl] and [HOCl]/[HCl] (day and night) in Figure 5 using the same set of model branching ratios as in Figure 4. A statistical comparison of the measured ratios above 20 km and the model calculations shows improvement in the agreement with enhanced HCl production from both mechanisms, up to limits for the production of HCl given by the JPL94 recommendation. The best agreement is  $\chi^2 = 29$  for 16 degrees of freedom, corresponding to a 2.5% confidence limit, obtained for 10% production of HCl from ClO + OH and 0% production of HCl from ClO + HO<sub>2</sub>; similar results are obtained for 5% HCl production from ClO + OH and 3% HCl production from ClO + HO<sub>2</sub> and for 10% HCl production from ClO + OH and 3% HCl production from ClO + HO<sub>2</sub>. (The 16 degrees of freedom correspond to the number of measurement points above 20 km; the [ClO]/[HCl] in Figure 5 are actually shown on the model grid since they were measured at different altitudes and interpolated to this common grid for comparison.) These results are consistent with the conclusions from the recent SLS results [Stachnik *et al.*, 1992; Toumi and Bekki, 1993] as well as the ongoing analysis of ATMOS data [H.A. Michelsen, unpublished results, 1994]. The sensitivity of the measurements is not sufficient to make firm conclusions about the extent of HCl production from the

reaction with HO<sub>2</sub> relative to the reaction with OH. However, our observations indicate that production of HCl occurs by some process other than the reaction of Cl with CH<sub>4</sub>.

## Conclusions

We now have the most extensive set of measurements obtained to date of stratospheric radical species from the HO<sub>x</sub>, Cl<sub>x</sub>, and NO<sub>x</sub> families and a number photochemically related gases. An atmospheric model constrained by measurements of long-lived radical precursors enables us to critically examine processes that regulate the abundance of radicals.

We have found HO<sub>x</sub> concentrations that are largely in agreement with the model values, except for OH at the highest measurement altitudes, near 38 km. Concentrations of H<sub>2</sub>O<sub>2</sub> are consistent with calculated values for 30 km and above.

Daytime concentrations of NO<sub>2</sub> are somewhat higher than model values at the highest measurement altitudes, and nighttime concentrations are in good agreement. Concentrations of HNO<sub>3</sub> are higher than model values near 25 km and slightly lower at altitudes above 32 km. The partitioning of NO<sub>y</sub> agrees with the model to within the limited measurement capability for NO<sub>2</sub> at the time of this flight.

The major discrepancy between the measurements and standard model calculations is for the chlorine species HCl, ClO, and HOCl. We find concentrations of HCl to be higher and concentrations of ClO and HOCl to be lower than those calculated with the model. The discrepancy could be explained by small branching ratios to form HCl in the reactions of ClO with OH and/or HO<sub>2</sub>. Uncertainty in the main HCl loss term, reaction with OH, implied by uncertainty in the OH concentration, can be ruled out as the cause of this discrepancy.

The measurement set includes most of the radical species involved in the rate-determining steps for catalytic ozone loss [Wennberg *et al.*, 1994]. Detailed comparisons are currently in progress of the contributions of the different radical families over the wide range of altitudes sampled by the FIRS-2 and BMLS instruments to photochemical loss of ozone and concurrent ozone production.

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