

Balloon-borne observations of mid-latitude hydrofluoric acid

B. Sen¹, G.C. Toon¹, J.-F. Blavier¹, J.T. Szeto¹, E.L. Fleming², and C.H. Jackman³

Abstract. Measurements of stratospheric HF have been made by the JPL MkIV interferometer during high-altitude balloon flights. Infrared solar absorption spectra were acquired near 35° N at altitudes between local tropopause and 38 km. Volume mixing ratio profiles of HF derived from 4 flights (1990-93), in conjunction with simultaneously observed N₂O profiles, indicate an average rate of HF increase of (5.5±0.3)% per year, in agreement with time-dependent, two-dimensional model simulations (6% per year) and ATMOS measurements.

Introduction

For almost a decade the importance of measurements of molecular concentration of stratospheric hydrofluoric acid (HF) has been emphasized for its distinctive role in the chemistry of halogenated gases and their effect in the depletion of stratospheric ozone (e.g. McElroy and Salawitch, 1989). Gaseous HF in the Earth's stratosphere is believed to be entirely due to photodissociation of chlorofluorocarbons (CFCs). Therefore, the abundance of HF can be viewed as an indicator of the past rate of CFC photolysis in the stratosphere. Its stability in the atmosphere and its dominance in the stratospheric fluorine abundance are believed to prevent any catalytic reactions involving fluorine-species leading to ozone destruction (Stolarski and Rundel, 1975). HF's primary path of destruction is its slow diffusion into the troposphere and eventual rainout.

Instrument and Balloon Measurements

The MkIV Interferometer (Toon, 1991) is the latest in a series of solar absorption FTIR spectrometers designed at JPL for the purpose of remotely measuring the atmospheric composition. The high spectral resolution (0.01 cm⁻¹) and broad spectral coverage (650-5500 cm⁻¹) of the MkIV instrument allows it to measure the large number of different gases simultaneously in the same airmass. This simultaneity allows the relationships between different gases, e.g. HF and N₂O, to be determined to high precision.

Four sunset occultations were analyzed for this work. The three earlier flights were conducted from Ft. Sumner, New Mexico, and the last flight was launched from Daggett, California. Relevant flight parameters for these four balloon flights are summarized in Table 1. The minimum tangent height were generally determined by cloud tops except in 1992 when Pinatubo aerosols made limb paths opaque below 22 km. Typically, 0.01 cm⁻¹ spectral resolution was employed at solar zenith angles up to 93° (~28 km altitude), at which point we switched to 0.02 cm⁻¹ to allow more rapid sampling, and thereby prevent the tangent point separation of successive pairs of spectra from exceeding 3 km. Each analyzed spectral pair (forward & reverse runs) therefore represents 100 or 200 seconds of observations.

Data Analysis

The JPL MkIV interferometer data analysis consists of two distinct procedures. Nonlinear least square fitting is first used to calculate the slant column abundance for each target gas in each spectrum. This is performed by adjusting an initial guess of the volume mixing ratio (vmr) profile until the calculation best matches the observed spectrum. These slant columns, together with the matrix of computed geometrical slant path distances, are then inverted using a linear equation solver subject to a derivative constraint to yield vmr profiles. The entire process is then repeated using the new retrieved vmr profile as the initial guess.

In addition to HF, spectral analyses and retrievals were performed on many other gases including CO₂, N₂O, and N₂. Solar zenith angles of individual spectra were determined by constraining retrieved mixing ratios of CO₂ to be consistent with *in-situ* measurements (Schmidt and Khedim, 1991). This procedure was of particular importance for analysis of spectral data from the 1992 balloon flight where elevated concentrations of Pinatubo aerosols caused significant sun tracker pointing anomalies in spectra recorded below 26 km altitude. The pressure-temperature relation used in the spectral fitting was initially derived from radiosonde measurements compiled from the stations around the launch site and then refined using vmr profiles of CO₂ derived from temperature-sensitive lines near 2390 cm⁻¹. As a final

¹B.Sen, G.C.Toon, J.-F.Blavier, and J.T.Szeto, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA.

²E.L.Fleming, Applied Research Corporation, Landover, MD,

³C.H.Jackman, Laboratory for Atmospheres, NASA Goddard Space Flight Center, Greenbelt, MD

Copyright 1995 by the American Geophysical Union.

Paper number 95GL00006

0094-8534/95/95GL-00006\$03.00

Table 1. MkIV Flight Parameters.

| | 1990 | 1991 | 1992 | 1993 |
|----------------|---------|-------|---------|--------|
| Date | 27 Sep. | 5 May | 14 Sep. | 4 Apr. |
| Latitude (°N) | 34.2 | 37.5 | 35.2 | 34.8 |
| Longitude (°E) | 254.0 | 248.2 | 249.8 | 244.5 |
| Altitude (km) | 17-38 | 16-38 | 23-39 | 17-37 |

independent check of the end-to-end analysis procedure, N_2O vmr profiles were retrieved using the lines near 2400 cm^{-1} . The retrieved values ranged between 0.77 and 0.82 having a rms deviation of only 1% over the 20-35 km altitude range from the known value of 0.78. The molecular spectral parameters used in the spectral fitting calculation were taken from the ATMOS compilation (Brown et al., 1987) but incorporating recent improvements from the HITRAN 92 linelist. Parameters for HF transitions used in the present work are reproduced in Table 2.

Table 2. Spectroscopic Parameters of HF Transitions.

| Position (cm^{-1}) | Strength ($\text{cm} \cdot \text{molec}^{-1}$) | Half-Width ($\text{cm}^{-1} \cdot \text{atm}^{-1}$) | E'' (cm^{-1}) |
|----------------------------------|---|--|-------------------------------|
| 3877.7071 | 1.888×10^{-18} | 0.0897 | 123.3 |
| 4038.9621 | 2.369×10^{-18} | 0.0895 | 41.1 |
| 4109.9359 | 1.585×10^{-18} | 0.0505 | 246.4 |

Results and Discussion

Since its presence was first confirmed in 1977, stratospheric HF has been extensively studied (Mankin et al., 1990) because of its dominance in the stratospheric fluorine budget. Aircraft observations by the MkIV instrument of stratospheric HF have previously been reported by Toon et al. (1989) from their analysis of HF absorptions at 4038.96 cm^{-1} and 4109.94 cm^{-1} . In addition, the HF line at 3877.71 cm^{-1} was included in this study and the derived HF slant columns were a weighted mean of all three. Errors associated with calculation of HF slant columns from MkIV spectra have been extensively discussed in Toon et al., (1989).

Figure 1 reproduces the measured vmr profiles of HF and N_2O for the years 1990 through 1993. The vertical separation of the retrieved vmr profiles was chosen to be 1 km, despite the tangent point spacing being 2-4 km typically. There are two reasons for this choice (i) compatibility with the forward

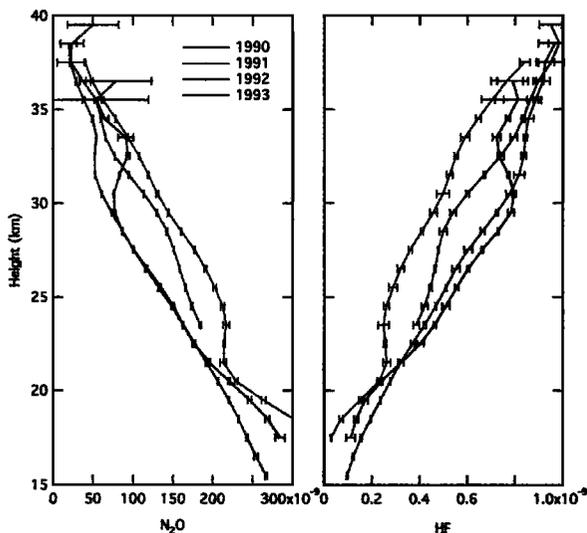


Figure 1. Mixing ratio profiles of N_2O and HF retrieved from MkIV measurements for 1990 through 1993. Error bars represent 1σ precision in retrieval.

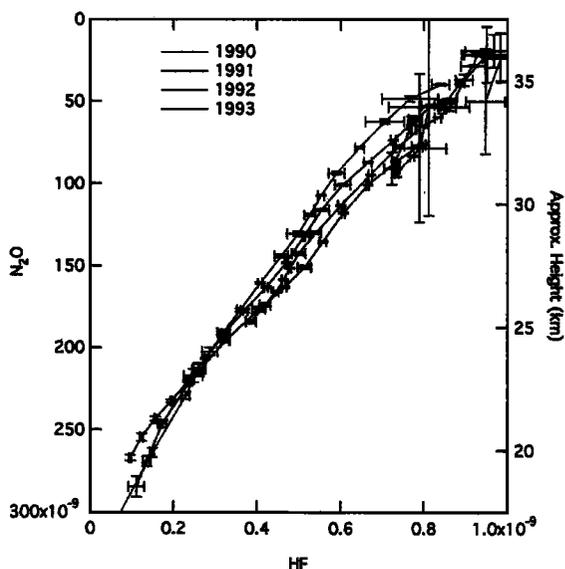


Figure 2. Mixing ratio scatter plots of measured N_2O and HF, with 1σ precision. The slight displacements arise from the secular increases of HF and N_2O .

model inputs, and (ii) not to degrade the high vertical resolution immediately below the balloon where the tangent point separation is small. The error in retrieval represents the relative precision of the retrieved vmr at the various levels. These are the changes to the vmr that would change the slant columns by the one sigma uncertainty in the measured slant columns. The figure clearly illustrates the considerable transport-induced variations between flights. That these variations are the result of transport, and not chemical changes in HF, is evident from careful scrutiny of the N_2O profiles, which are almost perfectly anti-correlated with those of HF. Consequently, plotting HF versus N_2O (Figure 2)

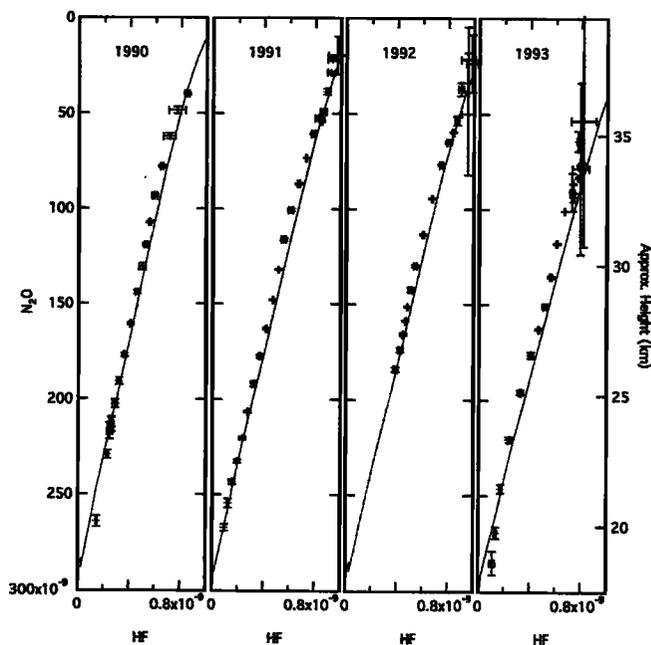


Figure 3. Mixing ratio scatter plots of measured N_2O and HF (symbols) and prediction from 2-D zonal model (solid lines) for 1990 through 1993.

yields a very smooth and compact set of lines, the slight displacements arising from the secular increases of HF and N₂O.

The HF volume mixing ratio for the four flights at specific N₂O levels is summarized in Table 3a. Also tabulated is an estimate of the annual linear increase in HF. The estimated 0.3%/year increase in stratospheric N₂O (Woodbridge et al., 1994) has been subtracted from the computed linear trend in HF. The weighted average of the trend in HF across the altitude range represented by the N₂O isopleths is (5.5±0.3)% per year. While other reports of long-term increases in HF (Gunson et al., 1994) are 20–40% higher than those calculated here, most have been determined from measurements starting a decade or more earlier. When comparing HF increases deduced from measurements made at different times it must be noted that the annual growth in HF column is a declining percentage of the total burden.

Model Comparison

The two-dimensional model of stratospheric photochemistry and transport used in this study has been used previously in a number of stratospheric studies (Jackman et al., 1990). The model domain extends from the ground to approximately 90 km with a vertical grid equally spaced in log-pressure at ~2 km intervals. The latitudinal extent is from 85° S to 85° N with a 10 degree spacing. Reaction rates and photodissociation cross sections from JPL-92 were used (Demore et al., 1992). The climatological temperature field is based on National Meteorological Center (NMC) data for the ground to 0.4 mb, and CIRA (1972) for levels above 0.4 mb. Heating rates and the residual circulation were calculated following Rosenfield et al., (1987), and the horizontal eddy diffusion field (K_y) was determined self-consistently from the residual circulation described elsewhere (Fleming et al., 1994).

There are 27 transported species or families, including HF, CFC₁, CF₂Cl₂, CHClF₂, C₂Cl₃F₃, C₂Cl₂F₄, C₂ClF₅, CBrClF₂, CBrF₃, CClFO, and CF₂O. Formation of inorganic fluorine is assumed to be due solely to the breakdown of CFC's. Details of the fluorine photochemistry contained in the model are described in a previous study of the stratospheric fluorine reservoir distributions (Kaye et al., 1991). Time dependent model calculations were carried out for the period 1970 - 2010, with source gas boundary conditions at the ground updated each year based on the scenarios described in detail in a recent international report (WMO, 1991).

The 2-D model simulates the shape of the observed HF mixing ratio profile reasonably well (Figure 3), but always predicts more at altitudes above the 220 ppbv N₂O isopleth. However, the model rate of increase is in agreement with observations at most stratospheric heights except at lowest altitudes. The qualitative agreement between the zonal mean model and MkIV measurement at a specific location illustrates the effectiveness with which the N₂O mixing ratio profile can be used to eliminate local transport effects. The compactness of the N₂O-HF relation indicates that the transport is quick compared to the local chemical lifetimes of both gases. The good agreement between observations and model calculation suggests that the overall chemistry of HF is generally understood and reproduced by the model.

Table 3a. Measured HF Volume Mixing Ratio (ppbv).

| N ₂ O Isopleth | Sep. 1990 | May 1991 | Sep. 1992 | Apr. 1993 | incr. (%/yr.) |
|------------------------------|--------------|-------------|--------------|--------------|------------------|
| 50 ppbv | 0.76 | 0.84 | 0.86 | 0.90 | 5.2±1.3 |
| 100 ppbv | 0.57 | 0.60 | 0.65 | 0.67 | 5.8±0.4 |
| 150 ppbv | 0.44 | 0.46 | 0.48 | 0.51 | 4.8±0.6 |
| 200 ppbv | 0.29 | 0.29 | 0.34 | 0.31 | 4.3±2.9 |

Table 3b. Measured HF Column (10¹⁴ molec.cm⁻²)

| | | | | | |
|---------|-------|-------|-------|-------|---------|
| >17.5km | 5.1±2 | 7.6±2 | 7.0±1 | 7.3±3 | 8.6±7.6 |
| >ground | 5.8±4 | 7.9±6 | 7.6±4 | 7.6±9 | |

Comparison With Column Measurements

For the purpose of comparing these balloon results with ground-based measurements of HF, column abundance above 17.5 km were determined (Table 3b) by integrating vmr with respect to pressure. For the September 1992 flight, HF vmr profiles were extrapolated down to 17.5 km by assuming a similar shape as in other years. Ground-based solar spectra were acquired by MkIV one day prior to the balloon launch on all four years. The total HF columns derived from these spectra are summarized at the bottom of Table 3b. They are in close agreement with the values determined from balloon measurements; a clear reflection of lack of significant HF below 17.5 km. The ground based column abundances exceed those above 17.5 km by (0.5±0.3)×10¹⁴ molec.cm⁻². If uniformly mixed below 17.5 km, it indicates a tropospheric HF vmr of 27±14 pptv.

While the linear trend computed from our column measurements is in agreement with rates inferred from other column measurements (Rinsland et al., 1991) and the 2-D model (~6%/year), its uncertainty is large because there is no simple way of removing variations caused by differing airmass origins, tropopause heights, and seasonal changes in stratospheric conditions between observations. This is demonstrated in Figure 1 where the smaller HF vmr in fall 1990 produced the pronounced minimum column value.

Conclusions

This study has primarily dealt with the determination of HF mixing ratio profiles in northern mid-latitudes. The main results confirm the continuing increase in stratospheric HF. The observed trend is in agreement with other measurements and with 2-D model predictions, demonstrating that the HF chemistry is reasonably represented, as is the rate of increase of stratospheric HF due to the anthropogenic increase of CFC's. The use of N₂O, in place of altitude or pressure, allows a more exacting comparison of HF mixing ratio profiles by removing the transport-induced variations. This allows a trend to be accurately determined from a relative

short (2½ years) baseline of sparse measurements, a feat not possible from ground-based measurements. It also enables meaningful comparison of disturbed measurements with 2-D (i.e. zonal) model predictions.

Acknowledgements. The authors wish to thank D.C. Pettersen, P.W. Schaper, J.H. Riccio, R.D. Howe, and W.B. Wilson of JPL for their considerable assistance in operation of JPL MkIV during the four balloon flights, and the NSBF which conducted the balloon launches, flight operations and recovery of the payload. This research was performed at Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References

- Brown, L.R., C.B. Farmer, C.P. Rinsland, and R.A. Toth, Molecular line parameters for the ATMOS experiment, *Appl.Opt.*, 26, 5154-5182, 1987.
- CIRA, COSPAR International Reference Atmos., Akademie, Berlin, 1972.
- Demore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ.* 92-20, 1992.
- Fleming, E.L., S. Chandra, C.H. Jackman, D.B. Considine, and A.R. Douglass, The middle atmospheric response to short and long term solar UV variations: analysis of observations and 2-D model results, *J.Atmos.Terr.Phys.*, in press, 1994.
- Gunson, M.R., M.C. Abrams, L.L. Lowes, E. Mahieu, R. Zander, C.P. Rinsland, M.K.W. Ko, N.D. Sze, and D.K. Weisenstein, Increase in levels of stratospheric chlorine and fluorine loading between 1985 and 1992, *Geophys.Res.Lett.*, 21, 2223-2226, 1994.
- Jackman, C.H., A.R. Douglass, R.B. Rood, R.D. McPeters, and P.E. Meade, Effect of solar proton events on the middle atmosphere during the past two solar cycles as computed using a two-dimensional model, *J.Geophys.Res.*, 95, 7417-7428, 1990.
- Kaye, J.A., A.R. Douglass, C.H. Jackman, R.S. Stolarski, R. Zander, and G. Roland, Two-dimensional model calculation of fluorine-containing reservoir species, *J.Geophys.Res.*, 96, 12865-12881, 1991.
- Mankin, W.G., M.T. Coffey, K.V. Chance, W.A. Traub, B. Carli, F. Mencaraglia, S. Piccioli, I.G. Nolt, J.V. Radostitz, R. Zander, G. Roland, D.W. Johnson, G.M. Stokes, C.B. Farmer, and R.K. Seals, Intercomparison of measurements of stratospheric hydrogen fluoride, *J.Atmos.Chem.*, 10, 219-236, 1990.
- McElroy, M.B. and R.J. Salawitch, Changing composition of the global stratosphere, *Science*, 243, 763-770, 1989.
- Rinsland, C.P., J.S. Levine, A. Goldman, N.D. Sze, M.K.W. Ko, and D.W. Johnson, Infrared measurements of HF and HCl total column abundances above Kitt Peak, 1977-1990: seasonal cycles, long-term increases, and comparisons with model calculations, *J.Geophys.Res.*, 96, 15523-15540, 1991.
- Rosenfield, J.E., M.R. Schoeberl, and M.A. Geller, A computation of the stratospheric diabatic residual circulation using an accurate radiative transfer model, *J.Atmos.Sci.*, 44, 859-876, 1987.
- Schmidt, U.R. and A. Khedim, *In-situ* measurements of carbon dioxide in the winter Arctic vortex and at midlatitudes: an indicator of the 'age' of stratospheric air, *Geophys.Res.Lett.*, 18, 763-766, 1991.
- Stolarski, R.S. and R.D. Rundel, Fluorine photochemistry in the stratosphere, *Geophys.Res.Lett.*, 2, 433-434, 1975.
- Toon, G.C., The JPL MkIV interferometer, *Optics & Photonics News*, 2, 19-21, 1991.
- Toon, G.C., C.B. Farmer, L.L. Lowes, P.W. Schaper, J.-F. Blavier, and R.H. Norton, Infrared aircraft measurements of stratospheric composition over Antarctica during September 1987, *Geophys.Res.Lett.*, 94, 16571-16596, 1989.
- Woodbridge, E.L., J.W. Elkins, D.W. Fahey, L.E. Heidt, S. Solomon, T.J. Baring, T.M. Gilpin, W.H. Pollock, S.M. Schaffler, E.L. Atlas, M. Lowenstein, J.R. Podolske, C.R. Webster, R.D. May, J.M. Gilligan, S.A. Montzka, and R.J. Salawitch, Estimates of total organic and inorganic chlorine in the lower stratosphere from *in-situ* measurements during AASE II, *J.Geophys.Res.*, in press, 1994.
- World Meteorological Organization (WMO), *Sci. assessment of ozone depletion: 1991*, WMO Rep. 25, 1991.

¹B.Sen, G.C.Toon, J.-F.Blavier, and J.T.Szeto, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA, 91109. (sen@mark4sun.jpl.nasa.gov)

²E.L.Fleming, Applied Research Corporation, Landover, MD, 20785.

³C.H.Jackman, Laboratory for Atmospheres, NASA Goddard Space Flight Center, Greenbelt, MD, 20771.

(Received September 1, 1994; Accepted November 3, 1994)