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BALLOON MEASUREMENTS OF STRATOSPHERIC HCl AND HF BY FAR INFRARED EMISSION SPECTROSCOPY

KAZUO SHIBASAKI

Kokugakuin University, Shibuya-ku, Tokyo 150, Japan

KELLY V. CHANCE, DAVID G. JOHNSON, KENNETH W. JUCKS, WESLEY A. TRAUB
Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138

ABSTRACT We have analyzed atmospheric thermal emission spectra obtained with the balloon-borne FIRS-2 far infrared Fourier transform spectrometer during balloon flights from Palestine, Texas on May 12-13, 1988 and from Fort Sumner, New Mexico on September 26-27, 1989 and on July 4-5, 1990. Seven and two pure rotational transition lines in 100-205 cm^{-1} range are analyzed for deriving vertical profiles of stratospheric HCl and HF, respectively. We obtain both the daytime and nighttime average vertical profiles from 15 to 50 km. We compare these profiles with the ones obtained in June, 1983 with the first version of FIRS spectrometer during the Balloon Intercomparison Campaign (BIC-2). BIC-2 results were revised to be consistent with the present analysis which uses the latest spectral parameters. According to our comparison results no increase is recognized for HCl but about 3% yr^{-1} increase for HF from 1983 to 1990, assuming a linear trend. These annual increase rates are smaller than those reported by other groups. Recently *Rinsland et al. (1991)* and *Wallace and Livingston (1991)* reported long term behavior of total HCl and HF observed on Kit Peak between 1977 and 1990. As Kit Peak is located near the both balloon launching sites, Palestine and Fort Sumner, we think our results are favorably comparable with theirs. Comparison results with ours and ground-based measurements will be presented and discussed.

1. INTRODUCTION

The importance of chlorine contained species in the stratosphere has been recognized since the establishment of catalytic destruction of ozone by ClOx [*Stolarski and Cicerone, 1974; Molina and Rowland, 1974*]. The principal source for stratospheric chlorine radicals is photodissociation of the anthropogenic chlorofluorocarbons (CFCs), mainly CFCl₃ and CF₂Cl₂, while methyl chloride (CH₃Cl) is an important natural source produced by microbial activities. Hydrogen chloride (HCl) is one of the major reservoir and sink species for chlorine radicals in the stratosphere. Recent steady increase of anthropogenic CFCs in the troposphere [*WMO, 1990*] is believed to cause the increase in HCl burden in the stratosphere which affect the ozone chemistry.

Hydrogen fluoride (HF) is the reservoir species for stratospheric fluorine. The only significant source of gaseous fluorine in the stratosphere is believed to be anthropogenic species such as CFCs. Photolysis of these species in the stratosphere produces short lived species which react rapidly to form HF. The HF burden in the stratosphere thus reflects an emission level of anthropogenic CFCs by man's activities. We can infer the deposition rate of fluorine into the stratosphere from measurements of stratospheric HF. Further, simultaneous measurements of HF and HCl in the stratosphere provide us an important indication for potential strength of anthropogenic sources (CFCs) compared to natural ones.

Simultaneous measurements of HCl and HF have been made

by several groups using spectroscopic remote sensing methods [*WMO, 1986; 1990*]. These groups also reported HF/HCl ratios which is considered to give some aspects regarding anthropogenic versus natural chlorinated sources.

In this paper we present stratospheric HCl and HF profiles derived from three balloon measurements of atmospheric far infrared emission spectra with FIRS-2 far infrared Fourier transform spectrometer. We compare these results with our previous ones obtained during BIC-2 campaign in the early summer of 1983 [*Mankin et al., 1990; Farmer et al., 1990*]. We also compare our results with those reported by *Rinsland et al. [1991]* and *Wallace and Livingston [1991]*.

2. BALLOON EXPERIMENT

The balloon observations were made with the FIRS-2 far infrared Fourier transform spectrometer from National Balloon Science Facility at Palestine, Texas, on May 12, 1988 and at Fort Sumner, New Mexico, on September 26, 1989 and on June 4, 1990. Detailed descriptions of our FIRS-2 instrument and its performance have been reported elsewhere [*Chance et al., 1989; Coyle et al., 1986; Traub et al., 1986*]. In *Chance et al. [1989]* and *Traub et al. [1990]* are also reported the balloon flight of May 12, 1988. Therefore brief description is given of the flight from Fort Sumner on September 26, 1989 and on June 4, 1990.

Our FIRS-2 spectrometer on board the gondola provided and supported by Jet Propulsion Laboratory (JPL) was flown from Fort Sumner (34.5°N, 104.3°W), New Mexico, on September 26 at around 0815 MDT and reached its floating altitude of about 36 km at about 1035 MDT. On board the same gondola were the Far Infrared Limb Observing Spectrometer (FILOS) using a far infra-red triple Fabry-Perot spectrometer and the Balloon Microwave Limb Sounder (BMLS), both from JPL. Measurements of atmospheric emission spectra were stopped at 1430 MDT, September 27, after 30 hours' observation including both the daytime and the nighttime measurements. For the time of 0120 - 0800 MDT of September 27 we lost our data because of a telemetry trouble.

On the morning of June 4, 1990 JPL gondola was launched from Fort Sumner and reached its floating altitude of about 37 km after 2 hours ascent. We stopped data acquisition on June 5 at 1411 MDT. Besides the same instruments with the 1989 balloon experiment a UV ozonometer and a multichannel UV-Visible photometer were on board this JPL gondola.

3. DATA ANALYSIS AND RESULTS

Spectral lines used for this analysis are listed in Table 1. We used 7 pure rotational transition lines, R4, R5, R6, R7, and R8, including both chlorine isotopes, for deriving HCl profile. For HF two pure rotational transition lines, R3 and R4, are selected. Basically we used HITRAN86 [*Rothman et al., 1987*]

and JPL84 [Poynter and Pickett, 1984] data bases. Center frequency of each transition line was accurately measured by Noll *et al.*, [1987]. The air-pressure broadening parameters of both molecules are calculated based on the result by Pine and Looney [1987].

Figure 1 shows portions of daytime-summed spectra obtained during the 1988 balloon experiment which contained HCl rotational transition lines used for our analysis. As described in Chance *et al.* [1989] and Traub *et al.* [1990], we added all the spectra in two groups at each observation angle to create daytime-summed and nighttime-summed spectra in order to maximize the signal to noise ratio of the data. For example the daytime-summed spectra are centered in time at 1641 CDT, and nighttime-summed ones are centered in time at 0112 CDT for the 1988 balloon experiment [see details in Chance *et al.* (1989)]. All the spectra are normalized to the spectral radiance of a 277-K blackbody reference.

As the gondola was relatively stable only for the morning period of June 5, 1990, only morning-summed spectra for the morning of June 5, 1990 are analyzed for the 1990 balloon experiment in this work. These spectra are centered in time at 1130 MDT and consist of 6 spectra at each observing angle.

The method of nonlinear least squares fitting of the atmospheric spectra is essentially the same as that described previously for the first version of FIRS system used during the BIC-2 campaign [Chance and Traub, 1987]. A layered atmospheric model was first constructed based on radiosonde data of temperature and pressure obtained from weather stations around the balloon bases [Chance *et al.*, 1989]. The original 1989 and 1990 atmospheric models were modified to reproduce a CO₂ profile properly, since the original atmo-

spheric models were proved to introduce inappropriate CO₂ and O₂ concentration profiles. We did not measure the thermal emission of mid infrared region, where CO₂ lines could be analyzed, during the 1988 balloon experiment. We used the original 1988 model atmosphere.

The HCl and HF mixing ratios are determined with an application of standard onion-peeling procedure [Chance *et al.*, 1989; Traub *et al.*, 1990]. We constructed 7 layered atmosphere corresponding to observing elevation angles from -4.62° to +30°, respectively. Above the gondola altitude is divided into two layers. Starting with the uppermost layer corresponding to 30° elevation angle and working down, we compared each emission line to a synthetic spectrum, and the HCl and HF amounts in the lowest layer for each elevation angle were adjusted until the measured and synthetic spectra agreed in least squares sense. However, for the two layers above the gondola altitude, mixing ratios are not derived straightforwardly, because the atmospheric emission for both the 30° and 0° rays reached the detector passing through both of the two layers above the gondola. The signal to noise ratios of the emission spectra obtained at 30° viewing angle were sometimes not so good as to deduce accurate abundances of HCl and HF. We set an *a priori* ratio of the mixing ratio between upper two layers in consideration of the results by Zander *et al.* [1990] and a theoretical model (M. Allen, personal communication); a mixing ratio in the uppermost layer is 1.1 times of that in the second layer.

The mixing ratio profiles derived for each line were combined in a weighted average profile, where the weights were the inverse squares of the fitting uncertainties. Error sources considered are uncertainties from spectrum intensity calibration, reference blackbody temperature, atmospheric temperature, and telescope pointing as well as the uncertainty due to fluctuation of gondola altitude during the observation. Estimate of error due to each error source is calculated every each line and then combined in a weighted average value, respectively. Another error sources included are uncertainties from line strength, pressure broadening coefficients, and error propagated from upper to lower layers. The final uncertainty in the mixing ratio profile was taken to be a quadrature sum of the above errors and the larger of the inverse square root of the sum of the fitting errors or the weighted rms scatter of data points about the mean. Usually 1-sigma error is less than 10 % for each layer. For HF analysis we used only one line, R3 line, to deduce the profile; the 1 sigma uncertainty is the quadrature sum of each error source for one line.

In Figure 2 are shown the retrieved HCl and HF profiles for both the daytime and the nighttime of 1988, 1989, and 1990 balloon experiments as well as the BIC-2 results. Also shown is the ATMOS measurement by Zander *et al.* [1990]. Error bars in Figure 2 are 1 sigma errors including the fitting and the systematic uncertainties. The difference between the daytime and nighttime profiles of the same flight is noticeable. This difference also reflects on column densities in Figure 3 calculated for the daytime and nighttime profiles, although these differences are within experimental uncertainties. The diurnal variation is not predicted theoretically for both HCl and HF. So far we cannot find any cause for this.

The profiles obtained during the BIC-2 campaign [Farmer *et al.*, 1990] were grouped into three, one of which, we call it west, was obtained just after the sunset (0320 GMT = 2220 CDT) and adopted for the intercomparison study with other measurements. The other two, so called early and late, profiles have their mean time of about 2020 GMT and 0530 GMT, respectively. We reevaluated these data to make precise comparison with current works, using new line parameters for transitions revised since the BIC-2 analysis. A change of

Table 1. HCl and HF lines used for this work

Molecule	Transition	Line position (cm ⁻¹)
H ³⁵ Cl	R4	104.138
H ³⁵ Cl	R5	124.827
H ³⁷ Cl	R6	145.222
H ³⁵ Cl	R6	145.440
H ³⁷ Cl	R7	165.717
H ³⁵ Cl	R7	165.965
H ³⁵ Cl	R8	186.390
HF	R3	163.936
HF	R4	204.540

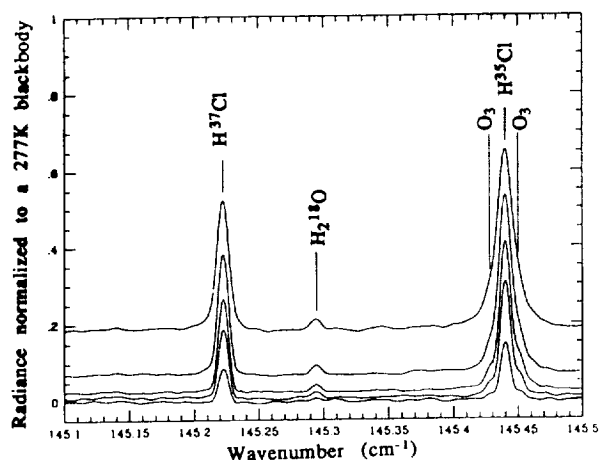


Figure 1. Variation of emission intensity of two HCl lines with viewing angle. Spectra are daytime-summed ones from 1988 balloon experiment. Viewing angles are, from bottom to top, 0.0°, -2.31°, -3.03°, -3.65°, and -4.17°.

pressure broadening coefficient directly affects a calculated column density, because HCl and HF emission lines analyzed are all saturated. The current data bases adopt smaller pressure broadening parameters than old ones (BIC-2) for all HCl and HF lines analyzed here. These differences range from about 0.4% (R4) to about 17% (R8) for HCl, which produce almost the same amount of difference in column density: larger mixing ratio is derived with the use of current parameter. In the case of HF, current pressure broadening parameters are about 5% lower for R3 line and about 57% lower for R4 line. This large difference in pressure broadening parameter for R4 line is one main reason why we analyzed the R3 line only as mentioned above. Thus the revised BIC-2 HF profiles in Figure 2 are deduced from the analysis of R3 emission line only, while our HF profile in the inter-comparison study [Farmer *et al.*, 1990] is the mean of profiles derived from R3 and R4 emission spectra. The BIC-2 profiles in Figure 2 are all revised ones and are according to the present data analysis procedure for creating an average profile.

4. DISCUSSION

We calculated column densities of HCl and HF above 20 km to estimate a trend. In Figure 3a) and b) are shown our results. For HCl no clear trend is drawn; BIC-2 data is nearly the largest. However, a positive trend is apparent, if BIC-2 data is ignored. Mankin and Coffey (1984) reported an increased HCl column amount in September and October 1982, about six months after the eruption of El Chichón. Relatively large HCl amounts are also reported in the 1980's by other groups (see WMO, 1990). We suspect that the stratospheric HCl was still affected by the eruption of El Chichón even in

1983. In the case of HF, a positive trend can be seen, with an increasing rate of about 3 % yr⁻¹ which is smaller than those reported so far [WMO, 1990]. This rate is derived assuming a linear trend, while large seasonal and latitudinal variation for HCl and HF column density was reported [WMO, 1990]. We must take into account the seasonal variation of these species in case of comparison or trend estimation. Recently long term trend was reported by two groups [Rinsland *et al.*, 1990; Wallace and Livingston, 1990] using the ground-based measurement from Kitt Peak where is located at the same latitudinal zone with balloon launching sites of Palestine and Fort Sumner. After the corrections due to the season of our balloon observations according to the work of Rinsland *et al.* [1991], we compare our results with them. Within 25 % difference rather good agreement is obtained for both HCl and HF considering a fairly large variability seen in their data. But a hypothesis adopted by Wallace and Livingston [1991] for a profile of HCl is inappropriate according to our study; no HCl is assumed in the troposphere by them.

FIRS-2 observation results seem to be consistent with the ground-based measurement, although the BIC-2 data should be made extensive reevaluation. Zander [1989] indicated a small increase rate, about 2.3 % yr⁻¹, for stratospheric HCl based on their balloon experiments from 1978 through 1988 carried out at Palestine. He used the data integrated above 24.5 km and did not consider a seasonal variation. He mentioned in his paper that, below 30 km, a significant variability was recognized in profiles. This variability is due to a dynamic process in the stratosphere that is the main reason for the seasonal behavior of total HCl and HF measured from the ground. According to our profiles fairly large variability is also seen even above 24.5 km, above peak altitude in con

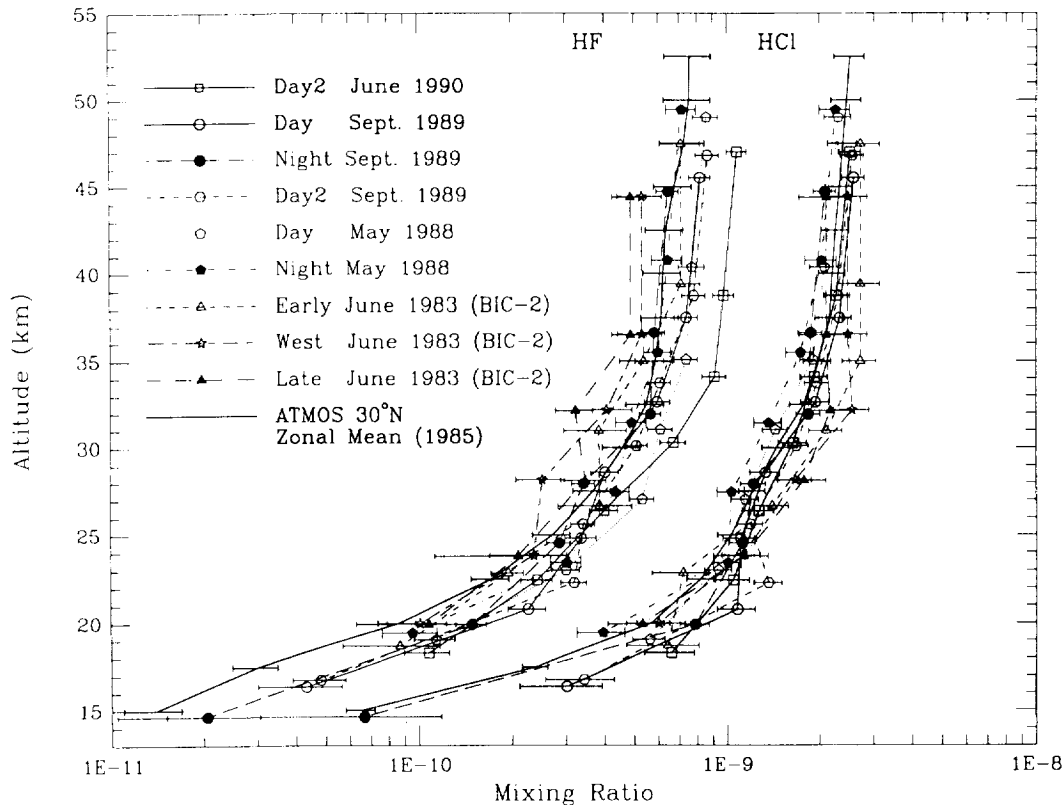


Figure 2. Retrieved profiles of stratospheric HCl and HF from three 1988, 1989, 1990 balloon experiments with BIC-2 and ATMOS results. Error bars show estimated 1-sigma precision as described in the text.

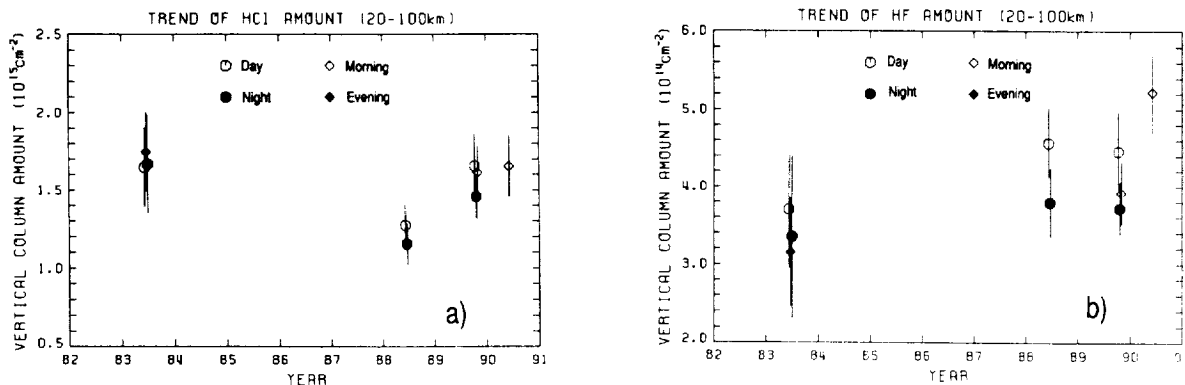


Figure 3. Vertical column amount integrated between 20 and 100 km versus time; a) HCl and b) HF. Error bars indicate estimated 1-sigma precision.

centration. We should take care of the season of observation in case of trend analysis using even only stratospheric observation results.

We could not deduce the long term trend of stratospheric HCl and HF burden straightforwardly from our balloon observation results, but reveal the consistency of the results obtained from balloon-borne measurements and from ground-based measurements. Our work also indicates a large variability of stratospheric HCl and HF as is the case for ground-based observations. This is reasonable, because dynamically controlled region covers till well above the peak altitudes in concentration for HCl and HF. Balloon observation has the limitation in trend study because of its limited season and small number of observation, usually 2 times per year at maximum. However, a study on a long term behavior in stratospheric profiles of HCl and HF may provide a useful information for our understanding of stratospheric chemistry. From this aspect further research will be continued.

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REFERENCES

Chance, K.V. and W.A. Traub, Evidence for stratospheric hydrogen peroxide, *J. Geophys. Res.*, 92, 3061-3066, 1987.
 Chance, K.V., D.G. Johnson, and W.A. Traub, Measurements of stratospheric HOCl: Concentration profiles, including diurnal variation, *J. Geophys. Res.*, 94, 11,059-11,069, 1989.
 Coyle, L.M. et al., Design of a single-axis platform for balloon-borne remote sensing, *Rev. Sci. Instrum.*, 2512-2518, 1986.
 Eyle, J.R., and H.K. Roscoe, Radiometric measurement of stratospheric HCl, *Nature*, 266, 243-244, 1977.
 Farmer, C.B. et al., Balloon intercomparison campaigns: Results of remote sensing measurements of HCl, *J. Atmos. Chem.*, 10, 237-272, 1990.
 Mankin, W.G. and M.T. Coffey, Latitudinal distribution and temporal changes of stratospheric HCl and HF, *J. Geophys. Res.*, 88, 10,776-10,784, 1983.
 Mankin, W.G. and M.T. Coffey, Increased stratospheric Hydrogen Chloride in the El Chichón cloud, *Science*, 226, 170-172, 1984.
 Mankin, W.G. et al., Intercomparison of measurements of stratospheric hydrogen fluoride, *J. Atmos. Chem.*, 10, 219-236, 1990.

Molina, M.J. and F.S. Rowland, Stratospheric sink for chlorofluoromethanes: Chlorine atom-catalyzed destruction of ozone, *Nature*, 249, 810-812, 1974.
 Nolt, I.G., et al., Accurate rotational constants of CO, HCl and HF: Spectral standards for the 0.3 to 6 THz (10 to 200cm⁻¹) region, *J. Mole. Spectr.*, 125, 274-287, 1987.
 Pine, A.S. and J.P. Looney, N₂ and air broadening in the fundamental bands of HF and HCl, *J. Mole. Spectr.*, 122, 41-55, 1987.
 Poynter, R.L., and H.M. Pickett, Submillimeter, millimeter, and microwave spectral line catalogue, Publ. 80-23, revision 2, Jet Propul. Lab., Pasadena, Calif., 1984.
 Rinsland, C.P. et al., Infrared measurements of HF and HCl total column abundances above Kitt Peak, 1977-1990: Seasonal cycles, long term increases, and comparison with model calculations, *J. Geophys. Res.*, 96, 15,523-15,540, 1991.
 Rothman, L. S. et al., The HITRAN database: 1986 edition, *Appl. Opt.*, 26, 4058-4097, 1987.
 Stolarski, R.S. and R.J. Cicerone, Stratospheric chlorine: A possible sink for ozone, *Can. J. Chem.*, 52, 1610-1615, 1974.
 Traub W.A., K.V. Chance, and L.M. Coyle, Performance of a single-axis platform for balloon-borne remote sensing, *Rev. Sci. Instrum.*, 57, 2519-2522, 1986.
 Traub W.A., D.G. Johnson, and K.V. Chance, Stratospheric Hydroperoxyl measurements, *Science*, 247, 446-449, 1990.
 Wallace, L. and W. Livingston, Spectroscopic observations of atmospheric trace gases over Kitt Peak 3. Long term trends of hydrogen chloride and hydrogen fluoride from 1978 to 1990, *J. Geophys. Res.*, 96, 15,513-15,521, 1991.
 WMO, Atmospheric ozone 1985: Assessment of our understanding of the process controlling its present distribution and change, Report No.16, 1986.
 WMO, Report of the international ozone trend panel 1988, Report No.18, 1990.
 Zander, R., Secular variation of stratospheric HCl based on 1978-1988 solar infrared balloon observations, in Proc. of 28th Liège Intern. Astrophys. Colloq. Our Changing Atmosphere, edited by P.J. Crutzen, J.C. Gerard, and R. Zander, pp71-84, University of Liège, Belgium, 1989.
 Zander, R. et al., Monitoring of the integrated column of hydrogen fluoride above the Jungfraujoch station since 1977 - the HF/HCl column ratio, *J. Atmos. Chem.*, 5, 385-394, 1987a.
 Zander, R. et al., Column abundances and the long-term trend of hydrogen chloride (HCl) above the Jungfraujoch station, *J. Atmos. Chem.*, 5, 395-404, 1987b.
 Zander, R. et al., Stratospheric ClONO₂, HCl, and HF concentration profiles derived from Atmospheric Trace Molecule Spectroscopy Experiment Spacelab 3 observations: An update, *J. Geophys. Res.*, 95, 20,519-20,525, 1990.