

# Seasonal Variations in the Total Content of Hydrogen Fluoride in the Atmosphere

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**Abstract**—The results of ground-based measurements of the total content (TC) of hydrogen fluoride in the atmosphere in Peterhof near St. Petersburg for one year (from April 2009 through April 2010) using a Bruker IFS125 Fourier spectrometer with a high spectral resolution ( $0.005\text{ cm}^{-1}$ ) are presented. The well-known computer code SFIT2 (Zephyr-2) was used for the radiation data inversion. Random measurement errors were 1–5% and the systematic error was 5–10%. The seasonal trend of the HF TC in Peterhof is characterized by a minimum in summer and a maximum in winter through early spring and is very close to the seasonal HF TC trend obtained at the Harestua Network for the Detection of Atmospheric Composition Change (NDACC) station located at about the same latitude. A comparison of the St. Petersburg State University (SPbSU) ground-based measurements with the data of satellite HF TC measurements (with an ACE-FTS instrument) showed a good quantitative agreement of the results for the entire period of observations. According to our ground-based measurements and the satellite measurements with the ACE-FTS instrument, the mean values of the HF TC and its rms variations during the period under investigation are  $1.77 \times 10^{15}$  and  $1.80 \times 10^{15}\text{ cm}^{-2}$  (difference 1.5%) and 21 and 18%, respectively.

**Keywords:** atmosphere, gas composition, hydrogen fluoride, total content, seasonal variations, Fourier spectrometry.

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## INTRODUCTION

The problem of present-day changes in the climate of the Earth and the problem of the conservation and restoration of the ozone layer of the Earth have stimulated intense investigations in recent decades of the content of various minor gaseous constituents of the atmosphere, including chlorine and fluorine compounds [1]. Hydrogen fluoride does not play an active role in ozone photochemistry; however, it is a good indicator of the dynamic processes in the atmosphere. The ratio of the HCL and HF contents (HCL/HF) also characterizes the intensity of heterogeneous processes on particles of polar stratospheric clouds [2].

The presence of HF in the atmosphere was fixed for the first time during ground-based spectroscopic measurements in 1975 [3]. Subsequently, the total content of the HF (HF TC) has been regularly measured by different scientific groups and, in recent years, at stations of the Network for the Detection of Atmospheric Composition Change (NDACC) international network of observations. Balloon and airborne measurements of vertical and latitudinal distributions of the HF content were also performed (see, for example, [3, 4]). Satellite measurements of HF profiles were conducted with the ATMOS instrument [5], and, in the period from September 1991 through November 2005, with the HALOE instrument, which made it possible

to form the global climatology of this gas content in the Earth's stratosphere [7]. Currently, satellite measurements of HF profiles are carried out with the use of the occultation method and ACE-FTS instrumentation [8].

These measurements detected the growth of the atmospheric HF content caused by the growth of the content of chlorofluorocarbons, whose photolysis in the stratosphere is the main source of HF. Thus, the results of HF TC measurements in the period from May 1977 through June 2001 from an analysis of the solar radiation spectra at the Kitt Peak station are presented in work [9]. It is shown in the cited work that, during the 24-year period under analysis, a permanent HF TC growth was observed. Over this period, the TC increased by a factor of 4.7, from  $2.03 \times 10^{14}\text{ cm}^{-2}$  in May 1977 to  $9.49 \times 10^{14}$  in June 2005. The TC trends were estimated at  $4.30 \pm 0.15\% \text{ yr}^{-1}$ , which is half as much as the trend over the period 1977–1990, and this estimate points to a substantial slowing down of the HF content growth [10]. The trend estimates in later years show a further decrease in the growth rate of the HF content in the atmosphere. Thus, virtually zero trends are obtained in work [11], which is associated with decreasing contents of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in the stratosphere.

The results of the first ground-based HF TC measurements in Russia, which were obtained through

interpreting the direct solar IR radiation spectra of a high spectral resolution near St. Petersburg, are presented in work [12]. At present, the volume of accumulated data has made it possible to study seasonal variations in the HF content in the atmosphere, and this work is devoted precisely to such studies.

#### GROUND-BASED MEASUREMENTS OF SOLAR IR RADIATION SPECTRA AND METHODS FOR THEIR INTERPRETATION

The high-resolution IR spectra of direct solar radiation were measured with the aid of a spectral complex developed at the Faculty of Physics at St. Petersburg State University (SPbSU) on the basis of the Bruker IFS125 Fourier spectrometer (FS) [13]. Measurements of the solar spectra with a high resolution started in January 2009. This paper considers the spectra over the period April 2009–April 2010 obtained after the completion of works on the adjustment of the spectral complex and the investigation of its characteristics. The total number of spectra measured over this period was 476. These spectra encompassed a spectral region rich in information about the HF TC measurements. We selected from the measured spectra 406 high-quality spectra based on the criteria of the limitation of the autocorrelation function of measurement noise at distances exceeding  $0.05 \text{ cm}^{-1}$  and the absence of harmonic distortions of the spectrum caused by disturbances in the optical adjustment of the setup, which sometimes take place. In this paper we analyze the results of determining the daily mean HF TC values. Different limiting factors allowed us to obtain the daily mean values for 78 days. The daily number of measurements was from 1 to 15 spectra (typically 5–6 spectra).

The measured spectra had spectral resolution of about  $0.005 \text{ cm}^{-1}$ ; the signal-to-noise ratio determined along the noise track of the zero signal varied within 400–1600 (typically it was about 1200).

The measurements were interpreted with the aid of the SFIT2 program used at stations of the NDACC network. Note that the results previously presented in work [12] are obtained with the use of the original method developed at SPbSU. A selective comparison of the results obtained in [12] with the SFIT2 results showed the presence of distinctions attaining 10%. Such distinctions are caused by an approximate inclusion of the spectral instrument function in work [12] (the Gaussian form of the instrument function was used) and the difference between the spectral intervals used ( $4038.0\text{--}4039.7 \text{ cm}^{-1}$ ) used in this work against an interval thinner than  $0.2 \text{ cm}^{-1}$ , including the HF absorption line  $4038.9625 \text{ cm}^{-1}$  used in work [12]).

The use of a wider spectral interval is reasonable because, in the automatic regime, the SFIT2 program refines the spectral connection, the calibration of measurements, and the content of interfering gases in the atmosphere (in this case, primarily, water vapor),

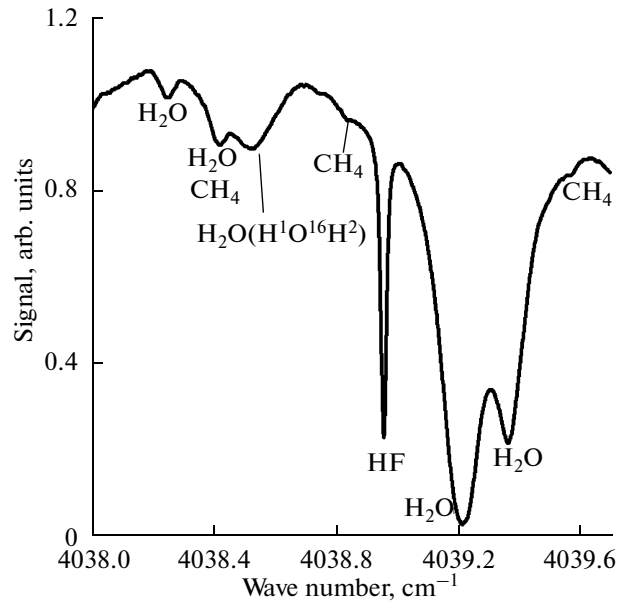


Fig. 1. Typical spectrum of the Sun measured in the region  $4038.0\text{--}4039.7 \text{ cm}^{-1}$  with absorption lines of different gases.

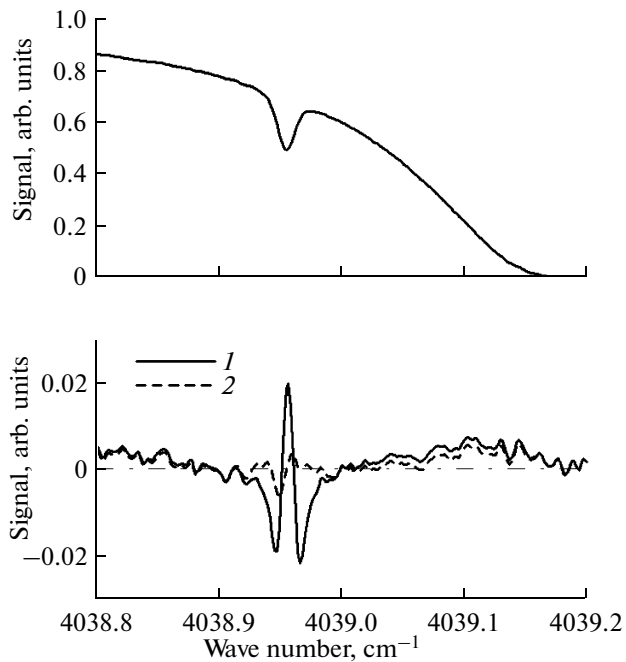
and the use of a wider interval makes it possible to obtain a greater volume of information about these parameters.

We introduced small changes into the Zephyr2.393.3.21.07 software package (based on SFIT2) in order to include the parameters of spectral lines (the position, intensity, half-width, etc.) from the HITRAN-2008 data bank, because the HITRAN-2004 version [14] does not contain four absorption lines of the  $\text{H}^1\text{O}^{16}\text{H}^2$  isotope (isotope 4 in the HITRAN nomenclature) of water vapor, whose contribution is noticeable in the vicinity of the HF absorption line ( $4.038.0\text{--}4.039.7 \text{ cm}^{-1}$ ).

The typical form of the measured solar spectrum, which was used for calculating the HF TC values, is presented in Fig. 1 with the indication of positions of different spectral absorption lines. As can be seen from the figure, water vapor plays the main role of the absorber in the region  $4039 \text{ cm}^{-1}$  and the HF line is observed against the background of the wings of a group of water-vapor lines.

Note that the SFIT2 program makes it possible to determine the total contents of different gases by two methods: (1) with the use of an a priori HF profile and by finding a correction multiplier to it (the “scalar” option) and (2) by reconstructing the vertical profile of the HF content and obtaining the HF TC through the integration over height (the “profile” option).

The site of the solar spectrum measured on June 11, 2009, which demonstrates on a large scale the HF absorption line, is shown in Fig. 2 (the upper panel). The lower panel of Fig. 2 shows the discrepancy between the measured and calculated spectra of solar



**Fig. 2.** Example of (top) the measured solar radiation spectrum weakened by the atmosphere and (bottom) spectral discrepancies for two options of the SFIT2 program: (1) “scalar” and (2) “profile.”

radiation after solving the inverse problem by two methods. This discrepancy is, at maximum, about 2% for the “scalar” variant and less than 0.5% for the “profile” variant, and it indirectly characterizes the quality of the inverse problem solution at two types of specification of a priori information in the SFIT2 program. It follows from Fig. 2 that the minimal deviation of the calculated and measured spectra after the inverse problem solution are observed if the “profile” algorithm is used. The distinctions between the HF TC values reconstructed by the two methods are, on average, 5–10%. This scatter can characterize the maximal systematic errors in the HF TC determination caused by the method of inverse problem solution.

Note also that the data on the temperature profile in the atmosphere and (as the initial approximation) on the profile of the water-vapor mixing ratio based on the data from three measurements of the Aqua satellite (AIRS and AMSU-A instruments) were used in the interpretation of ground-based measurements [15]. The mean climatic profile of methane was used as its a priori profile.

Our estimates of the random component of the error in the TC determination based on the TC variability in periods of stable states of the atmosphere and the instrument functioning make it possible to estimate it at 1–2%. Further, we will analyze the HF TC determinations obtained from the “profile” software packet of the SFIT2.

Note that different error sources in the HF TC determination were investigated in work [16]. According to the estimates presented in the cited work, the random component of the errors in the TC measurements (at close signal-to-noise values) is 2.7%, and the main contribution to the systematic error (4.3%) is introduced by the error of specification of the HF line intensity. Analogous estimations in work [17] yielded a random component of the error of 6% and a systematic error of ~5% (mainly due to errors in the specification of the HF absorption line intensity). Note that small variations in the error estimates in different works are caused by the use of different spectral intervals, distinctions in instrumentation characteristics, conditions of measurements (zenith angles of the Sun, etc.), and the state of the atmosphere at measurement moments.

## RESULTS OF HF TC MEASUREMENTS AND THEIR ANALYSIS

The photodissociation of chlorofluorocarbons (CFCs) in the tropics and the stratospheric transport control the latitudinal HF distribution, which is generally characterized by minimum values in the tropical region and maximal values in polar regions. Thus, the HF TC values in the tropics are  $0.3\text{--}0.4 \times 10^{15} \text{ cm}^{-2}$ . At polar latitudes in the summer time, these values increase 2–3 times, reaching  $\sim 1.0 \times 10^{15} \text{ cm}^{-2}$  [4, 18]. Seasonal HF TC variations widely differ for different latitudes. These variations are very small in the tropics ( $0.3\text{--}0.5 \times 10^{15} \text{ cm}^{-2}$ ) and are significant in polar regions. At middle and high latitudes, the TC maxima are observed in winter–early spring and the TC minima are observed in summer. The intensity of the downward motions of air masses controls the TC values in different seasons in polar regions. In these regions the TC values in summer are  $\sim 1.0 \times 10^{15} \text{ cm}^{-2}$  and, in the winter–spring period, they reach  $1.5\text{--}2.0 \times 10^{15} \text{ cm}^{-2}$  and greater; i.e., they increase by 50–100% and more. Significant TC variations are observed at midlatitudes; in particular, these variations noticeably increase in the winter–spring period due to the penetration of polar air into midlatitudes during the destruction of winter polar eddies. Figure 3 clearly illustrates latitudinal variations in the HF TC and the HF variability, showing the TC values obtained through the integration of the HF profiles measured with the ACE-FTS satellite instrumentation in 2004–2010 over the Northern Hemisphere [19].

The ground-based HF TC measurements during 2009–2010 in Peterhof can be characterized by the following statistical parameters: the average diurnal mean TC value  $1.77 \times 10^{15} \text{ cm}^{-2}$ , rms of the diurnal mean values of  $3.59 \times 10^{14} \text{ cm}^{-2}$  (21%), and rms variability for 24 h of  $0.82 \times 10^{14} \text{ cm}^{-2}$  (4.5%). The variability range of the diurnal mean TC values is from  $1.2$  to  $2.9 \times 10^{15} \text{ cm}^{-2}$ ; i.e., it is close to 100%.

The annual trends of the monthly mean HF TC values for SPbSU in 2009–2010, Peterhof (59.9°N),

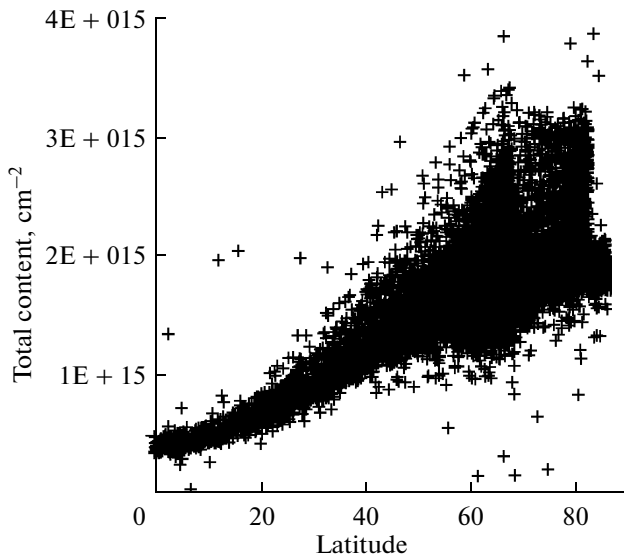


Fig. 3. HF TC values for the Northern Hemisphere obtained from measurement data of the ACE FTS instrument [19].

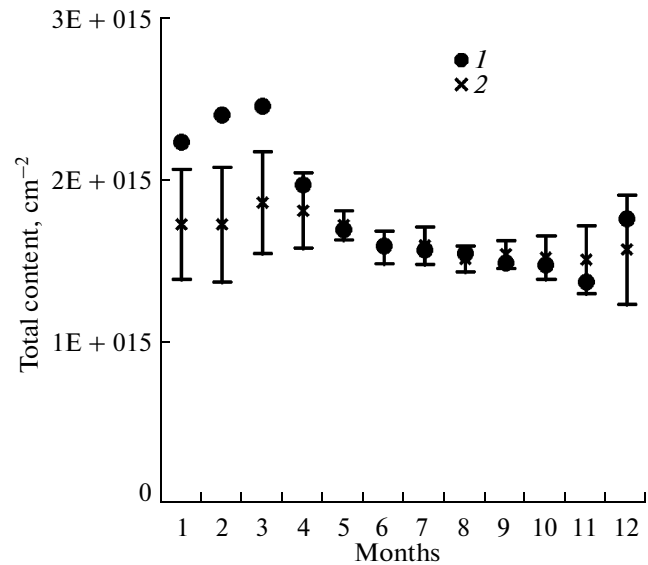


Fig. 4. Monthly mean HF TC values and their variabilities: (1) from the SPbSU data and (2) for the NDACC Harestua station. Ranges of the interannual variability are indicated for the data of the Harestua station.

and for the Harestua station ( $60.2^{\circ}\text{N}$ ) are presented in Fig. 4. The interannual variability for the Harestua station is shown over the period 2002–2007 (for which the data were available). It can be seen that the seasonal trends at these points with a minimum in summer and a maximum in winter or at the beginning of spring are similar (both observational stations are located at approximately  $60^{\circ}\text{N}$ ). In the largest part of the period under consideration, the seasonal trends at the SPbSU and Harestua stations agree within variations in the annual variability of TC measurements for the Harestua station in different months with the exception of the SPbSU data obtained in the winter months of 2010, when the TC values noticeably exceeded those obtained at the Harestua station, which was probably caused by specific features of the atmospheric dynamic, namely, the penetration of air masses of the polar eddy into the Peterhof region.

The HF TC measurements in Peterhof were compared with the satellite HF TC measurements by using the ACE-FTS instrument. Specific features of the occultation method and the orbital parameters of the Atmospheric Chemistry Experiment (ACE) satellite allowed only two comparisons over the period under investigation, when satellite and ground-based measurements coincided within 500 km and were made on

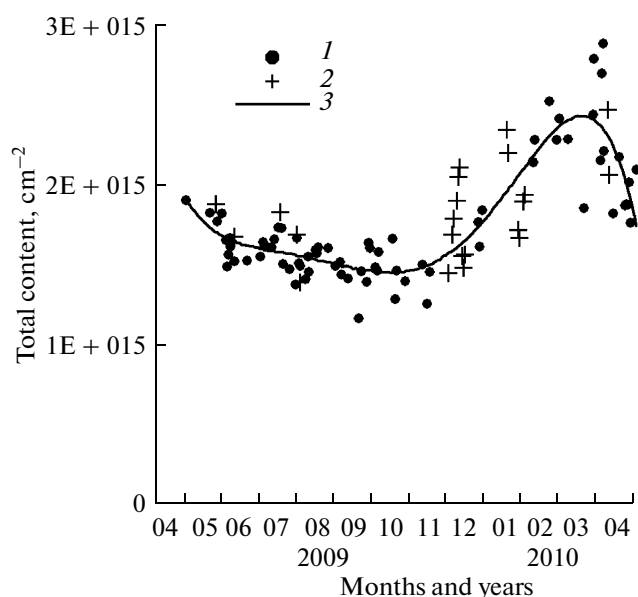
the same day. The table gives the conditions of comparisons, the TC values measured at SPbSU, and their daily variability (caused by natural variations and measurement errors), as well as the relative differences between the results of the two types of measurements (satellite minus ground-based related to ground-based). The distinctions vary from 1.3 to 7%, which is within the summarized errors of ground-based and satellite measurements.

A more general comparison is given in Fig. 5 showing the data of ground-based and satellite measurements during the entire period under consideration. The data presented in most cases do not coincide in days; however, they clearly show the agreement between ground-based and satellite data in the description of the TC seasonal trend in the St. Petersburg area (Peterhof). Using the approximation of the seasonal trend presented in Fig. 5 with the aid of the polynomial of the 5th degree, we estimated the amplitude of the seasonal trend at 25%. The experimental and model estimates of this quantity vary from ~10–15% to 30–40% at different latitudes [9, 10, 18, 21].

According to our ground-based satellite measurements and the ACE-FTS satellite measurements during the period under investigation, the HF TC mean values

#### Examples of comparisons of ground-based and satellite HF TC measurements

Date	Distance between observational points, km	HF TC, $\text{cm}^{-2}$ (SPbSU)	HF TC variability, %	Number of measurements	Distinction from ACE data, %
July 21, 2009	455.4	$1.68 \times 10^{15}$	8	4	1.3
July 24, 2009	151.7	$1.51 \times 10^{15}$	2.4	5	-7.0



**Fig. 5.** Comparison of the satellite and ground-based HF TC measurements in the period April 2009–April 2010: (1) from the SPbSU data, (2) data calculated from the HF mixing ratio profiles measured with the ACE-FTS instrument, and (3) approximation of the SPbSU HF TC by the polynomial of the 5th degree.

and rms variations were 1.77 and  $1.80 \times 10^{15} \text{ cm}^{-2}$  (difference 1.5%) and 21 and 18%, respectively.

## CONCLUSIONS

(1) The first investigations in Russia of the seasonal HF TC trends based on ground-based measurements of solar radiation spectra with a high spectral resolution were carried out in Peterhof near St. Petersburg from April 2009 through April 2010. The spectra were interpreted with the aid of the well-known SFIT2 computer code, which is used for analogous purposes at the NDACC stations. Variations with the use of different SFIT2 options (different a priori covariance matrices, an a priori HF profile, interval boundaries, and so on) were, on average, 5–10%. Different estimates of HF TC measurement errors in Peterhof showed that the random errors amount to 1–5% and the systematic error is 5–6%.

(2) The seasonal trend of the HF TC in Peterhof is characterized by the minimum of the HF TC in summer and its maximum in winter–early spring. A comparison of the seasonal HF TC trends in Peterhof and at the Harestua station of the NDACC network [20] located at about  $60^\circ\text{N}$  showed their similarity, which is in compliance with the results of ground-based and satellite measurements obtained by other authors.

(3) The SPbSU ground-based measurements are compared with satellite measurements of the HF TC (the ACE-FTS instrument). Two cases of the comparison give distinctions of 1.4 and 7% (the distance

between the observational points is less than 500 m; the measurements are on the same day). A good quantitative agreement between the seasonal HF TC trends obtained with the use of two types of measurements for the entire period of comparisons is also observed. According to our ground-based measurements and the satellite ACE-FTS measurements during the period under investigation, the mean values of the HF TC and their rms deviations were 1.77 and  $1.80 \times 10^{15} \text{ cm}^{-2}$  (the difference is 1.5%) and 21 and 18%, respectively.

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## REFERENCES

1. *Scientific Assessment of Ozone Depletion: 2006*, WMO. Rep. No. 50 (2007).
2. M. P. Chipperfield, M. Burton, W. Bell, et al., “On the Use of HF as a Reference for the Comparison of Stratospheric Observations and Models,” *J. Geophys. Res.* **102** (D11), 12901–12919 (1997).
3. R. Zander, “Recent Observations of HF and HCl in Upper Stratosphere,” *Geophys. Res. Lett.* **8** (4), 413–416 (1981).
4. V. G. Mankin and M. T. Coffey, “Latitudinal Distributions and Temporal Changes of Stratospheric HCl and HF,” *J. Geophys. Res.* **88** (C15), 10776–10784 (1983).
5. R. Zander, M. R. Gunson, J. Foster, et al., “Stratospheric ClONO<sub>2</sub>, HCl, and HF Concentration Profiles Derived From Atmospheric Trace Molecule Spectroscopy Experiment Spacelab 3 Observations: An Update,” *J. Geophys. Res.* **95** (D12), 20519–20525 (1990).
6. J. M. III. Russell, L. L. Gordley, J. H. Park, et al., “The Halogen Occultation Experiment,” *J. Geophys. Res.* **98** (D6), 10777–10797 (1993).
7. G. M. Beaver and J. M. Russell Iii, “The Climatology of Stratospheric HCl and HF Observed by HALOE,” *Adv. Space Res.* **21** (10), 1373–1382 (1998).
8. P. F. Bernath, C. T. McElroy, M. C. Abrams, et al., “Atmospheric Chemistry Experiment (ACE): Mission Overview,” *J. Geophys. Res.* **32** (2005). doi: 10.1029/2005GL022386
9. C. P. Rinsland, R. Zander, E. Mahieu, et al., “Stratospheric HF Column Abundances above Kitt Peak

- (31.9° N Latitude): Trends from 1977 to 2001 and Correlations with Stratospheric HCl Columns,” *J. Quant. Spect. Radiat. Trans.* **74** (2), 205–216 (2002).
10. J. S. Levine and A. Goldman, et al., “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** (D8), 15523–15540 (1991).
  11. C. P. Rinsland, C. Boone, R. Nassar, et al., “Trends of HF, HCl, CCl<sub>2</sub>F<sub>2</sub>, CCl<sub>3</sub>F, CHClF<sub>2</sub> (HCFC-22), and SF<sub>6</sub> in the Lower Stratosphere from Atmospheric Chemistry Experiment (ACE) and Atmospheric Trace Molecule Spectroscopy (ATMOS) Measurements Near 30° N Latitude,” *Geophys. Res. Lett.* **32** (2005). doi: 10.1029/2005GL022415
  12. A. V. Poberovskii, A. V. Polyakov, and Yu. M. Timofeev, “Measurements of the Hydrogen Fluoride Total Column Amount in the Atmosphere over the Vicinity of St. Petersburg,” *Izv. Atmos. Ocean. Phys.* **46** (2), 261–264 (2010).
  13. A. V. Poberovskii, “Ground-Based Measurements of the IR Spectra of Solar Radiation with a High Spectral Resolution,” *Opt. Atmos. Okeana* **23** (1), (2010).
  14. Access to the HITRAN Spectroscopic Data Bank 2004, 2008. <http://www.cfa.harvard.edu/hitran/>
  15. Access to AQUA Satellite Remote Sensing Data. [http://airs.jpl.nasa.gov/data\\_products/data\\_products\\_toc/](http://airs.jpl.nasa.gov/data_products/data_products_toc/)
  16. M. Schneider and T. Blumenstock, “Subtropical Trace Gas Profiles Determined by Ground-Based FTIR Spectroscopy at Izana (28° N, 16° W): Five-Year Record, Error Analysis, and Comparison with 3-D CTMs,” *Atmos. Chem. Phys. Discuss.* **4**, 5261–5301 (2004).
  17. C. Senten, M. De Maziere, B. Dils, et al., “Technical Note: New Ground-Based Ftir Measurements at Ile De La Reunion: Observations, Error Analysis, and Comparisons with Independent Data,” *Atmos. Chem. Phys.* **8**, 3483–3508 (2008).
  18. M. Luo, R. J. Cicerone, J. M. Russell, et al., “Observations of Stratospheric Hydrogen Fluoride by Halogen Occultation Experiment (HALOE),” *J. Geophys. Res.* **99** (D8), 16691–16705 (1994).
  19. ACE FTS Site. [http://www.ace.uwaterloo.ca/instruments\\_acefts.html](http://www.ace.uwaterloo.ca/instruments_acefts.html)
  20. Access to the NDACC Network Data. <ftp://ftp.cpc.ncep.noaa.gov/ndacc/station/>
  21. P. Duchatelet, P. Demoulin, F. Hase, et al., “Hydrogen Fluoride Total and Partial Column Time Series above the Jungfraujoch from Long-Term FTIR Measurements: Impact of the Line-Shape Model, Characterization of the Error Budget and Seasonal Cycle, and Comparison with Satellite and Model Data,” *J. Geophys. Res.* **115** (D22306) (2010). doi: 10.1029/2010JD014677