

# Spectroscopic Measurements of Total CFC-11 Freon in the Atmosphere near St. Petersburg

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Received March 31, 2010; in final form, May 26, 2010

**Abstract**—On the basis of ground based measurements of the infrared spectra of solar radiation with a high spectral resolution, estimates of total CFC-11 freon content in the atmosphere near St. Petersburg in January and May 2009 have been yielded in Russia for the first time. These data are conformed to various independent measurements within the limits of spectroscopic measurement errors.

**Keywords:** freon, total atmospheric freon, ground based interferometer measurements, atmosphere composition, technogenic pollution of atmosphere, greenhouse gases.

**DOI:** 10.1134/S0001433811020125

## INTRODUCTION

It is well known that freons, i.e., fluorine-containing derivatives of saturated hydrocarbons (mostly methane and ethane), can have a substantial influence on the ozone content in the stratosphere and magnify the greenhouse effect in the earth's atmosphere [1]. The production of the first artificial freons ( $\text{CCl}_3\text{F}$  or CFC-11 and  $\text{CCl}_2\text{F}_2$  or CFC-12) started in the early 1930s. From then on, their quantity increased up to the 1980s. Measurements of the freon content were carried out in ground based, airplane, balloon, and satellite experiments with the help of local and various remote methods; in particular, the measurement of solar radiation spectra with a high spectral resolution was used (see, for instance, [2–7]).

After the Montreal Protocol was enacted in 1987, which is the reason many freons were replaced by other compounds with shorter lifetimes in the atmosphere and which are less harmful for the ozone layer, the rates of freon content growth decreased and then freon contents themselves decreased as well [8]. For example, the CFC-11 content began to decrease as early as in 1993 and, currently, the mean values of its tropospheric mixing ratio are from 240 to 260 ppt [9] (hereinafter, ppt designates the concentrations as the ratio between the gas quantity and the quantity of host air multiplied to  $10^{12}$ , i.e., parts per trillion).

The variations of the total content (TC) of some freons were performed at the stations of the NDACC network via recording solar radiation by instruments with high spectral resolutions. In Russia, ground based measurements of the spectra of solar infrared radiation with the use of a Bruker IFS-125 high-resolution Fourier spectrometer were started in January 2009 at St. Petersburg State University (SPSU). The spectral

complex and the first results of measurements of TCs for some gases were given in [10–12].

Measurements of solar radiation with the help of the spectral complex are being performed in a wide infrared range and additionally make it possible to determine the total CFC-11 Freon content by the spectra of solar radiation. The first results of such observations in Russia are presented in this paper.

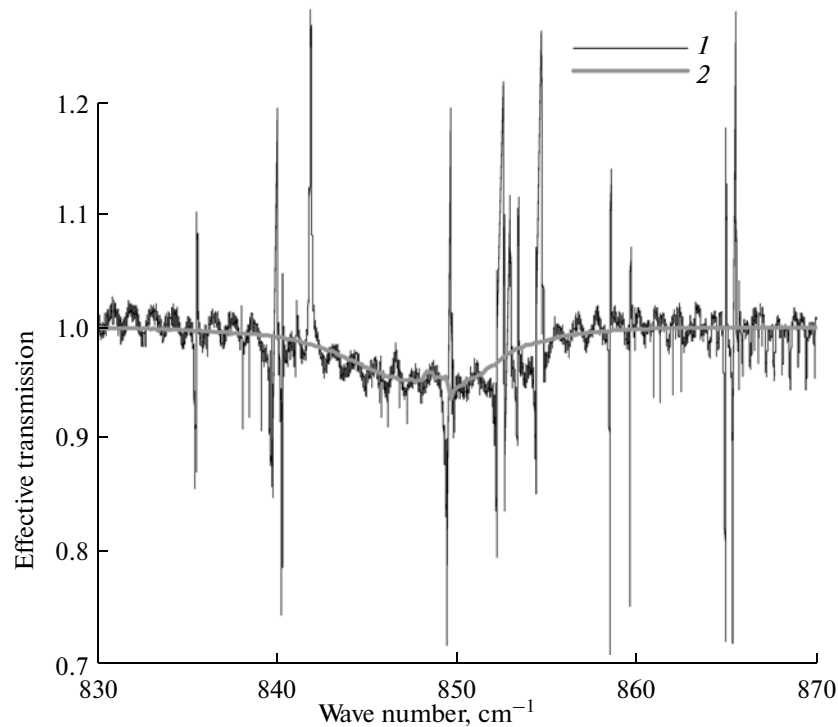
## INTERPRETATION TECHNIQUE FOR GROUND BASED SPECTROSCOPIC OBSERVATIONS

CFC-11 freon has absorption bands in the infrared spectrum in the ranges 810–880 and 1050–1120  $\text{cm}^{-1}$ . In order to determine the total freon content, we used measurements in the range 810–880  $\text{cm}^{-1}$ .

The expression for solar radiation  $I_{\Delta\nu}^{\downarrow}$  passing through the atmosphere and measured on the earth's surface at pressure  $p_0$  in finite spectral interval  $\Delta\nu$ , taking into account the instrument function, can be written as follows:

$$I_{\Delta\nu}^{\downarrow} = \int_{\Delta\nu} \varphi(\nu) S_{\nu} \times \exp \left\{ -\frac{\sec \theta}{g} \int_0^{p_0} \sum_j k_{\nu,p,j}(p) q_{p,j}(p) dp \right\} d\nu. \quad (1)$$

Here  $\varphi(\nu)$  is the instrument function;  $S_{\nu}$  is spectrum of solar radiation at the upper boundary of atmosphere; and  $k_{\nu,p,j}$  and  $q_{p,j}$  are absorptances of all the lines and continuums and mixing ratios for various



Transmission function for freon (CFC-11) (1) derived from the instrumental measurements (May 27, 2009) and (2) calculated.

gases, respectively, ( $j$  is the index of gas) at level with pressure  $p$ .

Freon absorption has a small-selective character and is described with the help of absorption coefficients given in the HITRAN database [13].

The interpretation technique for the measured solar spectra, which is elaborated at SPSU, implies that, at the first stage, the absorption of freons is distinguished on the basis of calculations of transmission functions caused by the absorption of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_3$ . With the help of a program for directly calculating the atmospheric transmission functions [14], the monochromatic functions of transmission for the gases mentioned above are calculated. Satellite data on the altitude derived from three measurements of AIRS and AMSU instruments were used as vertical profiles of temperature and  $\text{H}_2\text{O}$  [15]. These data corresponded to the data from ground based measurements of solar spectra. In addition, we used the average climatic profiles of altitudinal variations for carbon dioxide and ozone mixing ratios following from [16]. The data on the vertical profiles of the freon content were taken from the paper by L. Hoffmann et al. [7] and used in determining the values of the total freon content.

In order to derive the transmission function caused only by freon absorption, we divided the recorded signal of solar radiation by the transmission function of the spectral filter used in measurements and by the transmission function of the interfering gases; the latter was preliminarily convoluted with the instrument

function in order to reduce it to the spectral resolution of measurements:

$$F_{\text{CFC}}(\nu_i) = I_{\Delta\nu_i}^{\downarrow} / (F(\nu_i)F_{\text{ig}}(\nu_i)), \quad (2)$$

where  $F_{\text{CFC}}(\nu_i)$  is the transmission function for freons,  $F(\nu_i)$  is the spectral variation of the transmission of the F3 instrument filter [10],  $F_{\text{ig}}(\nu_i)$  is the transmission function of interfering gases, and  $\nu_i$  is the central wave number of the  $i$ th spectral channel of the instrument.

Next we determined the coefficient of the climatological profile for CFC-11 freon via the simple numerical method (a combination of trial-and-error methods and bisection). This coefficient provides the best mutual fit of the experimentally derived and calculated freon transmission functions. To characterize this fit, let us present the figure, where the measured and calculated (after solving the inverse problem) freon transmission functions are compared. Note that spikes in the experimental curve, which is derived after excluding the absorption contributions of interfering gases, are caused by the imprecision of the information on the state of atmosphere in the measurement time and by the division of the experimental spectrum by small (approximate to zero) transmission values upon imprecisely determining the zero line in measurements.

In order to improve the precision of the total freon measurement, we averaged the measured spectra by the frequency (reducing them to the spectral resolu-

Total CFC-11 content (TC) and volume mixing ratio (VMR) for CFC-11

Date	TC, $\text{cm}^2 \times 10^{-6}$	TC, $\text{cm}^{-2} \times 10^{15}$	VMR, ppt
02.01.2009	1.21	5.3	270
03.01.2009	1.12	4.9	250
04.01.2009	1.12	4.9	250
08.01.2009	1.21	5.3	270
18.05.2009	1.21	5.3	270
25.05.2009	1.21	5.3	270
27.05.2009	1.12	4.9	250
28.05.2009	1.07	4.7	240
January	1.17	5.1	260
May	1.15	5.0	260

tion of the absorption coefficients from the database [13]) as well as by time.

Our numerical estimates of various factors determining the errors of the total freon values (errors in determining the zero level of the signal; random errors of measurements and atmosphere state setting, namely, the temperature and humidity profiles; influences of a priori profiles; etc.), have shown that the random component of errors is  $\sim 13\%$ , while the systematic one is  $\sim 10\%$  (which is caused, in particular, by errors in setting the freon absorption coefficients and by using an a priori profile of their content).

### ANALYSIS OF THE RESULTS

In the table, for the purpose of a convenient comparison with various independent measurements, we present the results of the total CFC-11 content that we obtained in January and May 2009 near St. Petersburg in different units, as well as the values of the mean tropospheric ratio of the mixture. The mean values for 4 days in May and 4 days in January are also given here.

The obtained values of the total CFC-11 content are within the limits of  $(4.69\text{--}5.30) \times 10^{15} \text{ cm}^{-2}$  or  $(1.07\text{--}1.21) \times 10^{-6} \text{ g/cm}^2$ . Measurements at the Jungfrau mountain station (2000 m altitude) in 2006 yielded the value of the total CFC-11 content at  $3 \times 10^{15} \text{ cm}^{-2}$  [17]. However, taking into consideration that the 2000-m layer of lower troposphere is absent in these measurements explains the small value of total freon. The introduction of the tropospheric layer correction substantially approximates the CFC-11 values from Jungfrau to those measured near St. Petersburg. Additionally, the time difference should be taken into consideration: according to the data from ground based observations of the Advanced Global Atmospheric Gases Experiment (AGAGE) network, the CFC-11 concentration in the troposphere has been decreasing since 1993.

There are also abundant data on the near-surface values of the volume ratio of freon mixtures. The measurements carried out in 2008–2009 at the stations of the AGAGE network located between the latitudes  $60\text{--}70^\circ \text{ N}$  yield values of a near-surface mixing ratio at 242–245 ppt for CFC-11 (this information is available at the web site of the AGAGE network [18]). As can be seen from the table, the values of the mixing ratio for CFC-11 measured near St. Petersburg agree well with the direct measurements of the AGAGE network, taking into account the errors of spectroscopic measurements.

Finally, the measurements of the tropospheric mixing ratio of CFC-11 during the MIPAS satellite experiments [7] in 2002–2004 yielded the values  $\sim (240\text{--}250)$  ppt.

### CONCLUSIONS

Measurements of the total CFC-11 content in the atmosphere with the help of the ground based spectroscopic technique while interpreting the infrared spectra of solar radiation with high spectral resolution derived via a Bruker Fourier spectrometer have been carried out for the first time in Russia. Random and systematic errors in determining the total freon content caused by the influence of various factors are 13 and 10%, respectively.

The total CFC-11 content, as measured in January and May 2009 near St. Petersburg, is  $(4.69\text{--}5.30) \times 10^{15} \text{ cm}^{-2}$  and conformed well to the independent measurements. The tropospheric ratios of the mixture near St. Petersburg are within the range of 241–275 ppt, which conformed to independent ground based and satellite measurements within the limits of measurement error.

### ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research (project no. 08-05-00857) and by the goal-oriented program “The Development of the Scientific Potential of Higher Education” (grant no. 2.1.1/1138 and 2.2.1.1/3846).

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