Secular Evolution of the Vertical Column Abundances of CHClF₂ (HCFC-22) in the Earth’s Atmosphere Inferred from Ground-Based IR Solar Observations at the Jungfraujoch and at Kitt Peak, and Comparison with Model Calculations

R. ZANDER, E. MAHIEU and PH. DEMOULIN
Institute of Astrophysics, University of Liège, 4000 Liège, Belgium

C. P. RINSLAND
Atmospheric Sciences Division, NASA Langley Research Center, Hampton, VA 23681, U.S.A.

D. K. WEISENSTEIN, M. K. W. KO and N. D. SZE
Atmospheric and Environmental Research, Inc., Cambridge, MA 02139, U.S.A.

and

M. R. GUNSON
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, U.S.A.

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Abstract. Series of high-resolution infrared solar spectra recorded at the International Scientific Station of the Jungfraujoch, Switzerland, between 06/1986 and 11/1992, and at Kitt Peak National Observatory, Tucson, Arizona (U.S.A.), from 12/1980 to 04/1992, have been analyzed to provide a comprehensive ensemble of vertical column abundances of CHClF₂ (HCFC-22; Freon-22) above the European and the North American continents. The columns were derived from nonlinear least-squares curve fittings between synthetic spectra and the observations containing the unresolved 2ν₆ Q-branch absorption of CHClF₂ at 829.05 cm⁻¹. The changes versus time observed in these columns were modeled assuming both an exponential and a linear increase with time. The exponential rates of increase at one-sigma uncertainties were found equal to (7.0 ± 0.35)%/yr for the Jungfraujoch data and (7.0 ± 0.23)%/yr for the Kitt Peak data. The exponential trend of 7.0%/yr found at both stations widely separated in location can be considered as representative of the global increase of the CHClF₂ burden in the Earth’s atmosphere during the period 1980 to 1992. When assuming two realistic vertical volume mixing ratio profiles for CHClF₂ in the troposphere, one quasi constant and the other decreasing by about 13% from the ground to the tropopause, the concentrations for mid-1990 were found to lie between 97 and 111 pptv (parts per trillion by volume) at the 3.58 km altitude of the Jungfraujoch and between 97 and 103 pptv at Kitt Peak, 2.09 km above sea level. Corresponding values derived from calculations using a high vertical resolution-2D model and recently compiled HCFC-22 releases to the atmosphere, were equal to 107 and 105 pptv, respectively, in excellent agreement with the measurements. The model calculated lifetime of CHClF₂ was found equal to 15.6 years. The present results are compared critically with similar data found in the literature. On average, the concentrations found here are lower by 15–20% than those derived from in situ investigations; this difference cannot be explained by the absolute uncertainty of ±11% assigned presently to the
infrared remote measurements.

Key words: CHClF₂, atmospheric composition, infrared solar observations.

1. Introduction

In 1990, CFC₃ (CFC-11), CF₂Cl₂ (CFC-12) and CHClF₂ (HCFC-22) remained by far the three ‘Freons’ most produced in the world, with reported 1990 productions, expressed in metric tons (mt), equal to 232,916 mt, 230,950 mt, and 213,714 mt, respectively [see AFEAS, 1991a, b, for all numerical quantities and uncertainties (including nonreporting countries) dealing with production and releases to the atmosphere of CFC-11, CFC12, and HCFC-22 referred to in this work]. However, CFC-11 and CFC-12, still intensively used in the refrigeration industry, as aerosol propellants and as foam blowing agents, have undergone a stagnating production during 1975–1987, followed by a marked decrease of almost 50% from 1987 to 1990 as a consequence of the regulations by the ‘Montreal Protocol on substances that deplete the ozone layer’ and by the London Amendment [e.g., Johnston, 1987; WMO-Report No. 25, 1992]. That regulated decrease is supposed to further apply throughout the 90s, until full elimination by the year 2000. Best estimates of total cumulative production and releases to the atmosphere up to 1990 amounted to \(7.98 \times 10^6\) mt and \(6.98 \times 10^6\) mt for CFC-11, and \(10.4 \times 10^6\) mt and \(9.84 \times 10^6\) mt for CFC-12. HCFC-22, on the other hand, has seen its production steadily on the rise since its first reported production of 56,071 mt in 1970, doubling between 1978 and 1990; its reported total cumulative production and release to the atmosphere until 1990 were equal to \(2.96 \times 10^6\) mt and \(2.46 \times 10^6\) mt, respectively [AFEAS-1991b].

The main uses of CHClF₂ are also aerosol propulsion, refrigeration and as a foam blowing agent. Nonregulation of HCFC-22 by the Montreal Protocol resulted from the fact that the existence of one (or more) hydrogen atom in the HCFCs’ (hydro-chloro-fluoro-carbons, mainly CHClF₂) structures implies that these compounds are partly removed in the lower atmosphere by reactions with the hydroxyl radical OH, and consequently have shorter lifetimes than fully halogenated gases such as CFC-11 and CFC-12. HCFCs are, therefore, expected to have less effect on ozone depletion in the stratosphere and on global warming in the troposphere [see Ch. 6 and 7 in WMO-Report No. 25, 1992]. The lifetimes of CFC-11 and CFC-12 are not yet known with great accuracy [see Ch. 8 in WMO-Report No. 25, 1992]. For HCFC-22, reported lifetimes have ranged from \(~20\) years (Prinn, 1988) to 15.5 years (Golombek and Prinn, 1989), with the most likely value now appearing to be 15.8 years, based on 2- and 3-D model calculations incorporating production- and release data [see Ch. 8 in WMO-Report No. 25, 1992]. It is because of the unregulated production increase of HCFC-22 and the tendency for industry to substitute it for the regulated CFC-11 and CFC-12 applications that careful monitoring of the atmospheric burden of the former one has become critical.