

SPECTROSCOPIC DETECTION OF CH₃CL IN THE UPPER TROPOSPHERE AND LOWER STRATOSPHEREJ. H. Park¹, R. Zander², C. B. Farmer³, C. P. Rinsland¹, J. M. Russell III¹,
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Abstract. Absorptions due to the ν_1 band of CH₃Cl have been identified for the first time in infrared solar absorption spectra of the upper troposphere and lower stratosphere. The spectral data were obtained with the ATMOS Fourier transform spectrometer onboard Spacelab 3 in May 1985 during four solar occultation events near latitudes of 30°N, 26°N, 25°N, and 49°S. Volume mixing ratio profiles of CH₃Cl retrieved for the altitude range 12 to 23 km at these four latitudes do not show appreciable differences. Vertical mixing ratio distributions vary from 6×10^{-10} at 12 km to 3×10^{-10} at 23 km with an average uncertainty of about 25%. The retrieved mixing ratio does not decrease with altitude as rapidly as the data obtained by in situ techniques.

Introduction

The sources of odd chlorine which catalytically destroy ozone in the stratosphere are known to be photochemical decompositions of both the man-made halocarbons such as CF₂Cl₂, CFC₁₃, CCl₄, and CH₃CCl₃ (Molina and Rowland, 1974a, 1974b; Crutzen, 1974; Cicerone et al., 1974; Wofsy et al., 1975; and Crutzen et al., 1978) and the naturally produced halocarbons such as methyl chloride (CH₃Cl) (Lovelock, 1975; and Cicerone et al., 1975).

Tropospheric detections of CH₃Cl were first reported by Lovelock (1975) using gas chromatography analysis and, independently, by Grimsrud and Rasmussen (1975) using mass spectrometer analysis. It was proposed by these authors that CH₃Cl is most likely produced by natural processes. Subsequent measurements of CH₃Cl by in situ cryogenic sampling and laboratory analysis using gas chromatograph/mass spectrometer techniques have provided further distributions of CH₃Cl in the troposphere and lower stratosphere (Cronn et al., 1977; Robinson et al., 1977; Penkett et al., 1980; Schmidt et al., 1980; Fabian et al., 1981; and Leifer et al., 1981). Profiles measured by these methods, however, differ from each other by as much as a factor of 2 in the altitude range 10 to 25 km.

In parallel with these in situ measurements of CH₃Cl (see also WMO/NASA 1982), photochemical modeling activities were initiated to study the degree of stratospheric ozone destruction due to odd chlorine liberated by photolysis and chemical reactions (see e.g. Logan et al., 1981; Cicerone et al., 1983; Gidel et al., 1983; Cariolle, 1983; Ko et al., 1984; and Solomon and Garcia, 1984).

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Since, however, theoretical predictions rely on measured values in the troposphere for lower boundary conditions, model results become uncertain owing to the large scatter of results among in situ techniques. Independent methods of measurements of CH₃Cl (as well as other halocarbons) may provide not only the clues as to whether the reported variations of CH₃Cl are real, but also confidence in the theoretical assessment of odd-chlorine production processes in the stratosphere.

Recently, Kendall and Buijs (1983) attempted spectroscopic measurement of CH₃Cl in the stratosphere using solar absorption spectra recorded with a balloon-borne Michelson interferometer (unapodized resolution 0.02 cm⁻¹). They could not detect absorption due to Q-branch manifolds of the ν_1 band of CH₃Cl, and they estimated an upper limit of 1.25×10^{-9} for the volume mixing ratio at the bottom of the stratosphere; this value is approximately twice the average value determined by in situ methods.

In the spring of 1985, the ATMOS (Atmospheric Trace Molecule Spectroscopy) experiment (Farmer and Raper, 1986) was carried out onboard the Shuttle-borne Spacelab 3. The ATMOS instrument, a high resolution Michelson interferometer, provided high quality solar absorption spectra (unapodized resolution 0.01 cm⁻¹) in the spectral region from 600 to 4700 cm⁻¹ using six spectral isolating filters. Three sunset occultations around 30°N and one sunrise occultation near 49°S covered the region from 1580 to 3400 cm⁻¹; from these spectra, absorptions due to Q-branch manifolds of the ν_1 band of CH₃Cl have been clearly identified for the first time, and vertical distributions have been determined for the altitude range 12 to 23 km.

Analysis Method and Input Data

The analysis method that we have used is based on the nonlinear least-squares fit technique (see Chang and Shaw, 1977; and Park, 1984). Independent parameters in the analysis of a spectrum are gas mixing ratio, instrument line shape, background level, and frequency calibration. The instrument line shape is simulated using an effective apodization function and a simple phase error formula (see Park et al., 1984).

The instrument measured two-sided interferograms of solar radiation with a scan velocity of 50 cm/sec and with its field of view (1 mrad) tracking a point near the center of the solar disk during sunset and sunrise; the zero-path difference (ZPD) point was common to both interferograms. These phenomena created an interferogram smearing effect for the two-sided interferogram. As shown by Park (1982), when the

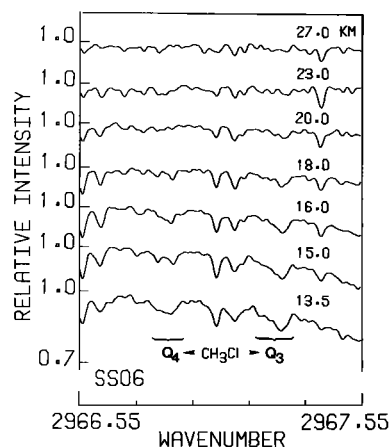


Fig. 1 Absorption spectra for the sunset SS06 obtained by the ATMOS instrument. Each spectrum is shifted in the vertical. These spectra are not calibrated in frequency.

interferogram smearing phenomenon occurs during a solar occultation, the ray path corresponding to the time the ZPD of the interferogram is recorded defines the effective ray path for the spectrum, and the other components define the instrument line shape of the Fourier transformed spectrum. Each two-sided interferogram measured by the ATMOS instrument, therefore, provided two spectra which would be the same in total absorption, but different in line shape; the retrieved gas mixing ratios from the two spectra, therefore, should be the same for the tangent layer. These phenomena have been verified by computing areas of CO₂ absorption lines in the ATMOS data and also by analyzing the spectrum with the spectral fitting technique. Consequently, the gas mixing ratio can be retrieved uniquely only at a vertical spacing corresponding to the time required to collect a two-sided interferogram; i.e., a 2.2-sec period that corresponds to a vertical height interval of approximately 4 km. Below about 25 km, this vertical height interval becomes less than 4 km due to atmospheric refraction.

The solar absorption spectra analyzed for the retrieval of CH₃Cl have been obtained, as mentioned earlier, with the ATMOS Fourier spectrometer by using a broadband filter that covered a spectral range of 1580 to 3400 cm⁻¹ during three sunset events, SS06, SS09, and SS13, and one sunrise event, SR02. The SS06 event occurred at lat. 30°N and long. 70°W, the SS09 at lat. 26°N and long. 14°E, the SS13 at lat. 25°N and long. 78°W, and the SR02 at lat. 49°S and long. 66°W. An average set of spectra, SSAV, has been obtained from the three sunset data sets (when their scan altitudes are within 1 km from each other) to increase signal-to-noise ratios and accuracy in the retrieval. The effective tangent heights for SSAV data are assumed to be the average heights of the sunset data.

Because of uncertainties in the spacecraft ephemeris, instrument pointing knowledge, and adopted pressure profile, the tangent heights were calculated by fitting absorption features of CO₂ and N₂ in the region from 1950 cm⁻¹ to 2600 cm⁻¹ including atmospheric refraction effects. Uncertainties in the determinations of tangent heights from this procedure are estimated to be less than 0.5 km.

A series of absorption spectra obtained during the sunset SS06 occultation are shown in Figure 1 for the spectral interval between 2966.55 to 2967.55 cm⁻¹. Each spectrum is the average of two spectra, each from one side of the two-sided interferogram. The resulting average spectrum is then divided by an exoatmospheric spectrum to eliminate features due to absorptions by residual gases in and around the instrument (e.g., H₂O and CO₂), effects due to the interference filter, and absorptions by solar lines. The spectra have been apodized by the "strong" apodization function of Norton and Beer (1976). The spectra in this figure have not been calibrated in frequency to correct for Doppler shift due to relative motion between the spacecraft and the atmosphere. Approximate locations of CH₃Cl absorption features are indicated in the figure. These absorptions are due to Q₃- and Q₄-branch manifolds of the ν₁ band of CH₃Cl (see Margolis and Toth, 1977; Dang-Nhu et al., 1981; and Elkins et al., 1984). Other Q-branch manifolds are strongly interfered by CH₄, H₂O, and O₃, and they are not used for analysis.

The spectroscopic line parameters used in the analysis are adopted from the latest version of the Air Force Geophysical Laboratory (AFGL) line compilation (Rothman, private communication, 1984; see also Rothman et al., 1983a, 1983b) for H₂O, O₃, CH₄, and CH₃Cl. The temperature correction for the line intensity including the vibrational partition term has been applied. Absorption coefficients have been computed using a Voigt profile.

The atmospheric pressure and temperature profiles adopted for the four events are from the National Meteorological Center (NMC) global satellite and radiosonde measurements (Nagatani, private communication, 1985) given at approximately 2-km intervals from the ground to about 50 km for the times and locations close to those of each event. Uncertainties in the data are about 8% for pressure and 5 K for temperature. The NMC profiles have been selected because the ATMOS pressure and temperature profiles determined from analyses of CO₂ absorptions only cover the altitude range down to 20 km. The NMC values are different from the ATMOS values by not more than

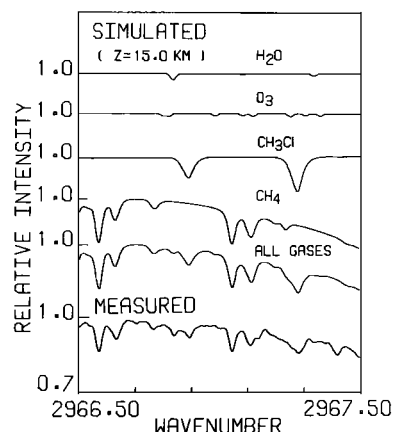


Fig. 2 Simulated absorption spectra (from top) due to H₂O, O₃, CH₃Cl, CH₄, and all gases, respectively, for tangent height 15.0 km, compared with a measured spectrum from sunset SS06 (bottom). The measured spectrum is calibrated in frequency.

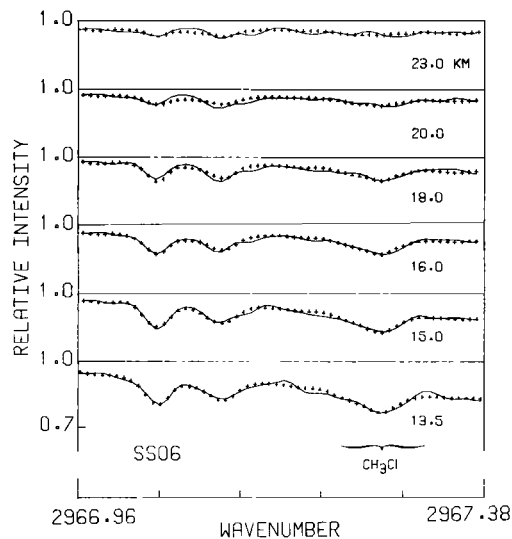


Fig. 3 Comparison of the simulated spectra for retrieved parameter values (crosses) and the measured spectra (solid lines) for sunset SS06.

6% for pressure and 5 K for temperature for altitudes from 20 to 45 km.

The mixing ratio profiles of all gases which are used either as background profiles for computing absorptions above the first retrieval layer or as the interference gases are from the ATMOS reference profiles. These reference profiles have been constructed from both available measurements and theoretical predictions.

Results and Discussions

The mixing ratios of CH₃Cl and CH₄ are retrieved for each tangent layer (1 km thick), but during numerical iterations, mixing ratios of these gases between two measurement points are scaled exponentially to obtain smooth retrieved profiles. An onion-peeling method is employed for the profile retrievals.

The measured spectrum between 2966.5 and 2967.5 cm⁻¹ for a tangent altitude of 15.0 km (the sixth spectrum of Figure 1) is shown again in Figure 2 (bottom curve). Simulated spectra for the same tangent altitude are also shown in Figure 2 for various gases (i.e., H₂O, O₃, CH₃Cl, CH₄, and all gases) included in the computations. The simulations are performed by using the ATMOS reference profiles in order to estimate the relative magnitudes of absorptions by various gases. The measured spectrum is not normalized by the background. The effective apodization function and a phase error formula, which were mentioned earlier, are not included in the simulation of instrument line shape. In spite of these approximations, absorption features (mostly due to CH₃Cl and CH₄) have been simulated well. The observed small feature at around 2967.41 cm⁻¹, which is not shown in the simulation, is due to O₃ (Damon et al., 1981). The spectral fittings have been done for the interval including Q₃-branch manifolds of CH₃Cl but excluding this O₃ feature. Error in retrieved CH₃Cl mixing ratio caused by not including wing absorption of this O₃ line is estimated to be less than 1%.

Shown in Figure 3 are simulated spectra (crosses) using the retrieved parameter values and

measured spectra (solid lines) for SS06. The tangent height used for each simulation is shown for each spectrum. For SS06, most of the absorption features are simulated very well.

The CH₃Cl mixing ratio profiles retrieved using the four sets of occultation data (i.e., SS06, SS09, SS13, and SR02) and one set of average data (i.e., SSAV) are shown in Figure 4. The standard deviations of retrieved values of CH₃Cl from the five sets of data are less than 11% of the mean value at each altitude (the value from SR02 at 20 km is excluded because of large noise in the data). Shown also in Figure 4 is the range of reported values of CH₃Cl obtained by in situ methods (Robinson et al., 1977; Penkett et al., 1980; Schmidt et al., 1980; Fabian et al., 1981; and Leifer et al., 1981). The profile of Penkett et al. (1980) is in the upper limit of the range. Our retrieved values are within the range of results obtained by the in situ techniques between 12 and 17 km, but they are near or exceed the upper limits of the in situ measurements above 17 km; there is an indication that the CH₃Cl profile may decrease less rapidly above 17 km than indicated by previous studies. Our values above 21 km are not as reliable as those of the lower altitudes because of weak absorption. Predicted profiles for mid-latitudes shown in the figure (Gidel et al., 1983; and Ko et al., 1984) also resemble the upper limit of results by the in situ techniques.

Random errors in the retrieved profiles are estimated to be about 20% for the altitude range 12 to 15 km, about 25% for the altitude range 15 to 21 km, and 35% at altitudes above 21 km. These errors are caused by uncertainties in the analysis algorithm, in pressure and temperature profiles, in inferred values of tangent heights, and in the interference effects (e.g., primarily of CH₄). The CH₄ profiles retrieved simultaneously do not deviate by more than 15% from mean values of other reported data for latitudes 25° to 35°N (e.g., WMO/NASA, 1982). Bias errors due to line parameter uncertainties are estimated to be about 10%, although they are not included in the error budget.

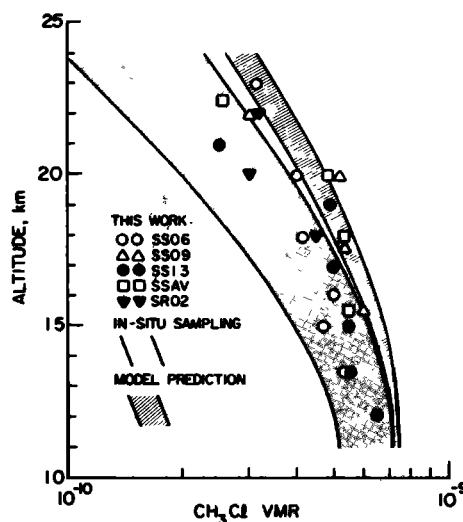


Fig. 4 Retrieved volume mixing ratio profiles of CH₃Cl from various occultation data. The range of other reported values for CH₃Cl by in situ methods and the range of theoretical predicted profiles for mid-latitudes are also shown.

Differences that may exist in the CH₃Cl mixing ratios in the northern and southern hemispheres are masked at present by the uncertainties in our retrieved values (~ 30%) and by the limited number of spectra available for the southern hemisphere.

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