

DETECTION OF CARBONYL FLUORIDE IN THE STRATOSPHERE

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Abstract. Infrared solar absorption spectra of the stratosphere recorded at a resolution of 0.01 cm^{-1} by the ATMOS (Atmospheric Trace Molecule Spectroscopy) instrument from onboard Spacelab 3 (04/30 to 05/6/85) have revealed the existence of many previously unobserved absorption features in the 1925 to 1960 cm^{-1} and 1249 to 1255 cm^{-1} regions and one at 774 cm^{-1} . On the basis of comparisons with laboratory spectra, these features have been identified as belonging to the ν_1 , ν_4 , and ν_6 bands of carbonyl fluoride, respectively. Volume mixing ratios of COF_2 between 17 and 40 km have been deduced from analysis of the ν_1 and ν_6 bands.

Introduction

During its first mission onboard Spacelab 3 (SL3), April 30 to May 6, 1985, the ATMOS (Atmospheric Trace Molecule Spectroscopy) instrument recorded more than 3000 infrared solar spectra with a spectral resolution of 0.01 cm^{-1} . About 2000 of these are "high sun" scans containing only solar features (absorption and emission). The remaining ones, recorded over long atmospheric limb paths during 12 sunsets and 5 sunrises with tangent heights ranging from 10 to 150 km, contain a wealth of absorption features arising from several dozen gaseous constituents of the earth's atmosphere. In the present letter, we report the first stratospheric measurement of COF_2 from analysis of its absorption features near 1937 cm^{-1} and 774 cm^{-1} with the additional identification of features near 1250 cm^{-1} . The importance of this molecule lies in the fact that it has been postulated to be an intermediate product of the decomposition of chlorofluorocarbons (CFC's) in the upper atmosphere [Rowland and Molina, 1975; Sze, 1978].

Data and Analysis

The ATMOS instrument consists basically of a double-pass Michelson interferometer, a telescope, a suntracker, and a cooled (77 K) HgCdTe detector; details of the instrument and its operation during the SL3 mission have been described elsewhere [Farmer and Raper, 1986]. Successive million-point, double-sided interferograms were recorded from about 360 km altitude in 2.2 seconds, corresponding to a tangent height separation of ~ 4.1 km. During each occultation, the data were

collected using one of six overlapping broadband filters, covering altogether the 600 to 4700 cm^{-1} spectral region. The spacecraft ephemeris and measurements of suitable atmospheric absorption features (e.g. CO_2 vibration-rotation and N_2 quadrupole lines) have been used to determine the tangent heights of the spectra to better than 1 km.

As the atmospheric absorption of COF_2 is relatively weak, its detection and subsequent analysis by spectroscopic techniques require good knowledge of molecular line parameters of both the target and interfering gases. For example, Figure 1 reproduces excerpts from two observed ATMOS spectra along with two spectra computed to correspond with the bottom observed one; the four traces are displayed with the same scale, but offset from one another for clarity. The top spectrum is an average of 46 high sun scans recorded from an orbital altitude of 360 km near 26°N lat., 54°W long.; it contains only features of solar CO . The next lower trace is a synthetic spectrum computed from COF_2 parameters (described later) using an adjusted concentration profile obtained from model predictions (L. Froidevaux, private communication, 1985). The trace labeled "Calc." is a computed atmospheric spectrum based on line parameters similar to those of the AFGL compilations [Rothman et al., 1983a,b] with no COF_2 included. The bottom spectrum, an observed ATMOS scan corresponding to a tangent height of 20.8 km, is seen to be the composite of the upper three spectra; the presence of COF_2 features, indicated by tick marks, is clearly evident.

Improvements to existing parameters in the AFGL compilations were necessary prior to the present analysis. Near 1937 cm^{-1} , new values for CO_2 [Rinsland et al., 1983, 1985], and H_2O (R. Toth, private communication, 1986) were adopted, while changes in CO_2 and O_3 line parameters in the vicinity of 774 cm^{-1} , which were made as a prerequisite for quantitative investigations of C_2ONO_2 at 780.2 cm^{-1} [Zander et al., 1986] and of HO_2NO_2 near 802.7 cm^{-1} [Rinsland et al., 1986], were also included here.

At the outset of this work, parameters of COF_2 similar in quality to those of other molecular species had not been published for the bands observed by ATMOS. There existed published spectral plots [Murcray and Goldman, 1981; Murcray et al., 1984], vibrational band assignments for the fundamentals [Mallinson et al., 1975], measurements for integrated band strengths [Hopper et al., 1968; Adams et al., 1971; Modica and Brochu, 1969], and ground state parameters based on microwave data [Carpenter, 1974]. However, no high resolution line-by-line analyses of the ν_1 , ν_4 , and ν_6 fundamentals were available.

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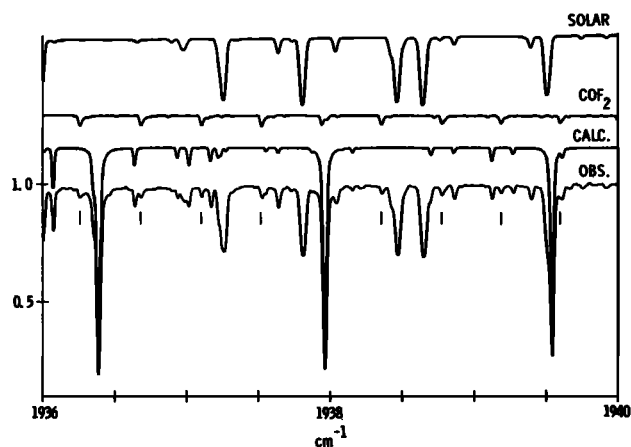


Fig. 1. The first detection of stratospheric CO_2 . The four spectra are an ATMOS high sun (SOLAR), a synthetic CO_2 , a synthetic stratospheric spectrum without CO_2 (CALC.), and an ATMOS spectrum at 20.8 km (see text for details). The absorptions of CO_2 are indicated by tick marks.

As a result, this study has had to rely on interim parameters of limited absolute accuracy, particularly for line strengths. In turn, this lack of data has required that retrievals of stratospheric mixing ratios versus altitude be done in two different ways, one method using equivalent widths, and the other fitting the shapes of spectral features, depending on the wavelength region considered.

For the 1925 - 1965 cm^{-1} region containing transitions of the ν_1 fundamental, we have utilized line positions from a laboratory spectrum recorded at 0.01 cm^{-1} resolution with the McMath Fourier transform spectrometer (FTS) at the National Solar Observatory on Kitt Peak. Line positions have been calibrated using H_2O standards [Brown and Toth, 1985]. With these, numerous weak features of CO_2 were identified in the ATMOS data (Figure 1). As seen in Table 1, positions determined by taking first and second derivatives of both laboratory and atmospheric features of CO_2 agree in all cases to within 0.002 cm^{-1} ; this agreement is within the combined uncertainties of the ATMOS and laboratory positions, considering that each feature may represent several unresolved transitions. Line

Table 1. Positions of selected CO_2 features in cm^{-1} **

ATMOS	Laboratory	ATMOS - Lab
1936.2570	1936.2587	-0.0017
1936.6821	1936.6820	0.0001
1937.1038	1937.1037	0.0001
1937.5232	1937.5218	0.0014
1938.3580	1938.3567	0.0013
1938.7750	1938.7736	0.0014
1939.1857	1939.1872	-0.0015

** determined from first and second derivatives of the apodized spectra

Table 2. Experimental line parameters of CO_2 used in this analysis*

POSITION	S	POSITION	S	POSITION	S
1936.1970	0.32	1936.4863	0.55	1936.8465	0.49
1936.2130	1.42	1936.5056	1.98	1936.8679	2.88
1936.2298	1.26	1936.5201	0.82	1936.8806	1.34
1936.2533	9.16	1936.5518	0.19	1936.9369	0.71
1936.2643	8.84	1936.5791	0.82	1936.9507	0.94
1936.2814	3.25	1936.5940	0.59	1936.9751	1.18
1936.2936	1.31	1936.6132	1.56	1936.9900	0.73
1936.3055	2.14	1936.6277	1.00	1937.0344	1.49
1936.3164	1.64	1936.6781	10.70	1937.0482	0.91
1936.3306	1.87	1936.6895	7.06	1937.0661	0.50
1936.3366	0.88	1936.7046	3.53	1937.0991	9.18
1936.3574	2.07	1936.7222	2.05	1937.1091	7.78
1936.3816	1.37	1936.7384	2.24	1937.1209	1.21
1936.4076	0.67	1936.7523	1.59	1937.1279	2.07
1936.4195	1.16	1936.7757	0.65	1937.1441	2.50
1936.4499	1.02	1936.7848	2.48	1937.1558	2.24
1936.4705	0.94	1936.8136	0.30	1937.1791	2.32

* line positions are given in units of cm^{-1} and strengths in S units of $\text{cm}/\text{molecule} \times 10^{-20}$ at room temperature

strengths at room temperature were also obtained from the Kitt Peak laboratory data using a non-linear least squares procedure [Brown et al., 1983]. However, since assignments were unavailable, manifold heads were artificially represented as a smaller number of lines than is actually present. In addition, because of the rapid chemical decomposition of the sample, the absolute strengths were unreliable. Therefore, observed relative strengths were normalized to conform to a mean of three integrated band strengths [Hopper et al., 1968; Adams et al., 1971; Modica and Brochu, 1969], with the additional assumptions that 80% of this mean value belongs to ν_1 (the remainder to a nearby overtone band, $2\nu_2$) and that the interval between 1936.5 and 1939.4 cm^{-1} contains about 5% of the total strength of the band (K.B. Thakur, private communication, 1986). A later check of the normalization was made using more recent Kitt Peak laboratory data. The absolute accuracies of the resulting strengths is thought to be 25%. The individual line parameters finally adopted are given in Table 2.

These parameters were used in a curve-fitting procedure to retrieve the values of the stratospheric volume mixing ratio of CO_2 . Air-broadened half widths and lower state energies were set to 0.1 $\text{cm}^{-1}/\text{atm}$ at 296 K and 120 cm^{-1} , respectively. For the analysis, we used a set of zonal average spectra covering the 1100 to 2000 cm^{-1} region, obtained by coadding the runs from three sunset occultations occurring near 32°N, 69°E; 31°N, 92°W; and 26°N, 54°W with approximately equal tangent heights of 38.5, 34.5, 30.5, 26.8, 23.5, 20.4, and 17.7 km; these spectra had initially been ratioed to a coadded "high sun" solar spectrum. Special emphasis was given to the optimum fitting of the ATMOS zonal spectra between 1936.1 and 1937.2 cm^{-1} , where three CO_2 features appear relatively free of

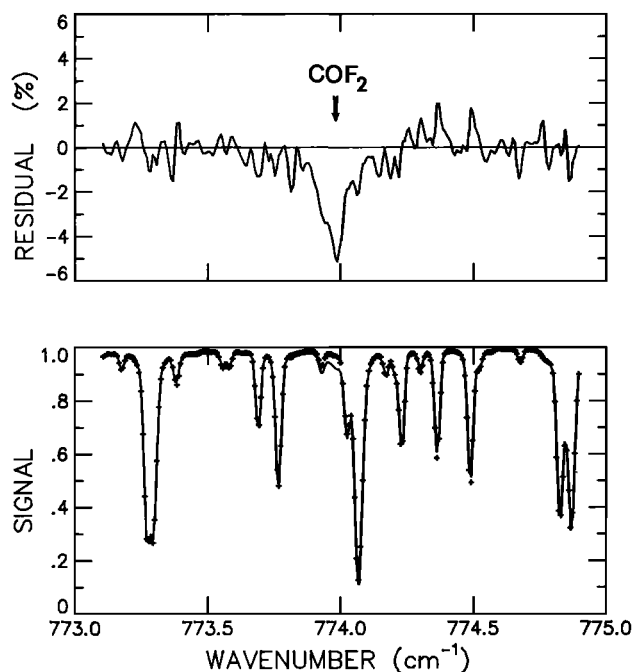


Fig. 2. Fitting results for an ATMOS spectrum in the region of the ν_6 band Q branch. The measured spectrum (solid line), produced by averaging spectra recorded at a tangent height of 25.5 km during 3 sunset occultations (lat. 30–33 N), and the best-fit calculated spectrum (crosses) are plotted beneath the residuals (observed-calculated). An arrow marks the location of the strongest absorption by the COF_2 Q branch.

any interferences by other telluric absorptions. The resulting volume mixing ratio (VMR) profile deduced from these fittings is represented by the solid curve in Figure 3.

Analysis of COF_2 using the ν_6 band at 774 cm^{-1} required a different approach because no line parameters were available there, and the band occurs in a region of relatively strong absorption by stratospheric O_3 and CO_2 . Therefore, to detect its absorption, only the lines of the interfering molecules were included in calculations of the expected spectrum in this region, in the absence of COF_2 . Figure 2 illustrates this procedure. In the top panel, the weak residual absorption peak at $774.00 \pm 0.02 \text{ cm}^{-1}$ is in good agreement with the Q branch of ν_6 observed at $773.987 \pm 0.005 \text{ cm}^{-1}$ (S. P. Sander and R. R. Friedl, private communication, 1986) in recent laboratory spectra of COF_2 recorded at 0.005 cm^{-1} resolution. An analysis of these laboratory data is in progress to obtain accurate positions and assignments for the ν_6 band (K. B. Thakur, private communication, 1986). Following identification, VMR profiles of COF_2 were obtained by measuring the equivalent widths of the residual curve (e.g. Figure 2). To obtain the integrated intensity of this Q branch, laboratory spectra were recorded at 0.06 cm^{-1} resolution and at room temperature with a Nicolet FTS and a sample of 99% pure COF_2 , purchased from SCM Specialty Chemicals, Gainesville, Fla. The spectra were recorded within 1 month of receipt of the cylinder to minimize the slow decomposition in the container

noted by Adams et al. [1971]. The derived integrated Q-branch intensity of $1.47 \pm 0.22 \times 10^{-18} \text{ cm/molecule}$ was extrapolated on the basis of the observed decay rate of the absorption (approximately 2% per hour) to the time the absorption cell (made of Pyrex with KCl wedged windows and Teflon valves) was filled. Decomposition of COF_2 is believed to result from reaction with H_2O outgassing from the cell walls. Carbon dioxide was identified as a decomposition product by its absorption between 2200 and 2400 cm^{-1} . Assuming the integrated ν_6 Q-branch intensity noted above, linear absorption by COF_2 in the atmospheric spectra, and correlative pressure-temperature profiles derived from a set of CO_2 lines measured by ATMOS, we have deduced the profile represented by the dotted line in Figure 3.

Numerous weak features of the ν_4 band have also been identified in the 1249 – 1254 cm^{-1} region. Because of strong interference by CH_4 , N_2O , CO_2 , and H_2O lines in this interval, and the lack of complete COF_2 line parameters, these features are less suitable for quantitative analysis than those in the other regions.

Results and Discussion

The COF_2 volume mixing ratios are given versus altitude in Figure 3. They constitute the first measurement of COF_2 in the stratosphere; since many of the strongest absorption features of that molecule have been simultaneously observed in the ATMOS spectra, its detection is unambiguous. The values obtained from both the least squares fitting of lines belonging to the ν_1 fundamental of COF_2 (dark solid line) and from equivalent width measurements of its ν_6 Q branch (dark dotted line) are shown. The difference between these two curves (as high as a factor of 1.5 below 30 km) is not likely to be attributable to the fact that they were retrieved from two different sets of zonal average spectra; the latitudes and

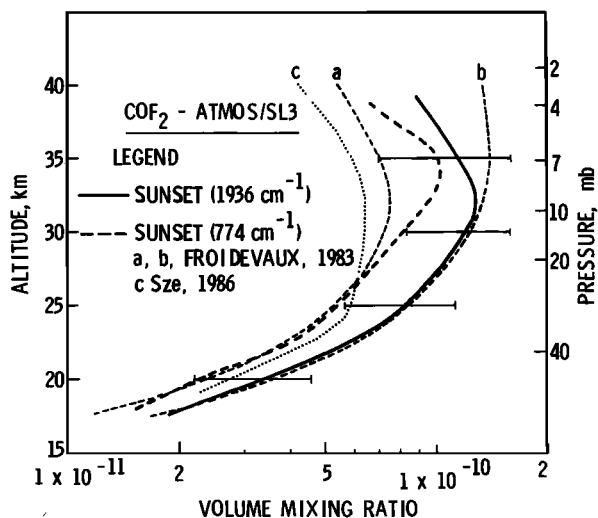


Fig. 3. Volume mixing ratios of carbonyl fluoride derived from ATMOS sunset spectra, using lines belonging to the ν_1 band (heavy full line) and the ν_6 Q branch (heavy dotted line). Model predictions by Froidevaux [1983] and by Sze (private communication, 1986) are reproduced for comparison (for details, see text).

longitudes of the individual occultations were not markedly different. Rather, we suspect the absolute values of the strengths involved in both spectral regions used for the retrievals to be in question; future work on laboratory spectra is likely to provide a clue to that discrepancy.

The potential sources of both random and systematic errors and the resulting uncertainties in the COF₂ volume mixing ratios (values between parentheses) are (i) in curve fitting of the 1936 cm⁻¹ features (10 to 40%) or equivalent width measurements of the ν₆ Q branch (10 to 50%), (ii) in the tangent height altitudes (15%), (iii) in the pressure-temperature profiles adopted (10%), (iv) in the simulation of interfering lines in the ν₆ Q branch region (20%), and (v) in the ν₁ strengths (25%) or the ν₆ Q branch strength (15%). The resulting total uncertainties (1 sigma) range from 50% above 37 km to 32% at 20 km for the 1936 cm⁻¹ region and from 58% above 37 km to 33% at 20 km for the 774 cm⁻¹ Q branch. For clarity in Figure 3, we have only reproduced the error bars for the full curve.

Model calculations by Froidevaux [1983] (curves a and b) and by Sze (private communication, 1986) (curve c), all computed for April, 30°N, show the range of volume mixing ratios predicted by adopting a quantum yield for the photolysis of COF₂ equal to 1 (curve a) or 0.25 (curve b), as well as differences in the predicted profiles for a COF₂ photolysis yield of 1 (e.g., curve a versus curve c). Nonetheless, considering the uncertainties in both observational and theoretical results, it can be concluded that the agreement is reasonably good. Retrievals made for a sunrise occultation at 47°S have produced results similar to those found at northern latitudes; slightly larger concentrations were found below 30 km, but it is premature to speculate about their significance, owing to the large uncertainties involved. The present observational data, supplemented by additional laboratory work on COF₂ and by further observations from future ATMOS missions, should help in establishing both the quantum yield for COF₂ photolysis in the stratosphere and latitudinal variations in its profile.

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