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SF₆ ground-based infrared solar absorption measurements: long-term trend, pollution events, and a search for SF₅CF₃ absorption

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Abstract

Infrared solar spectra recorded with the Fourier transform spectrometer in the McMath solar telescope complex on Kitt Peak (31.9°N latitude, 111.6°W, 2.09 km altitude), southwest of Tucson, Arizona, have been analyzed to retrieve average SF₆ tropospheric mixing ratios over a two-decade time span. The analysis is based primarily on spectral fits to absorption by the intense, unresolved ν_3 band Q branch at 947.9 cm⁻¹. A best fit to measurements recorded with SF₆ near typical background concentrations yields a SF₆ increase in the average tropospheric mixing ratio from 1.13 pptv (10⁻¹² per unit volume) in March 1982 to 3.77 pptv in March 2002. The long-term increase by a factor of 3.34 over the time span is consistent with the rapid growth of surface mixing ratios measured in situ at Northern Hemisphere remote stations, though the infrared measurements show a large scatter. Average tropospheric mixing ratio enhancements above background by 2–3 orders of magnitude have been identified in spectra recorded on 5 days between November 1988 and April 1997. These spectra were individually analyzed in an attempt to detect the strongest 8–12 μm band of SF₅CF₃, a molecule recently identified with an atmospheric growth that has closely paralleled the rise in SF₆ during the past three decades. Absorption by the strongest SF₅CF₃ band was predicted to be above the noise level in the Kitt Peak spectrum with the highest average mean tropospheric SF₆ mixing ratio, assuming the reported atmospheric SF₅CF₃/SF₆ ratio and a room temperature absorption cross sections reported for the SF₅CF₃ 903-cm⁻¹ band. An upper limit of 8 × 10¹⁵ molecules cm⁻² for the SF₅CF₃ total column was estimated for this case. We hypothesize that the highly elevated SF₆ levels above Kitt Peak resulted from a local release experiment rather than production via electrochemical fluoridation of intermediate products, the

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proposed source of atmospheric SF₅CF₃. The absence of the SF₅CF₃ feature in the spectra with elevated SF₆ is consistent with the absence of SF₅CF₃ reported in a pure SF₆ sample.

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1. Introduction

Sulfur hexafluoride (SF₆) is an extremely stable molecule and a strong absorber in the thermal infrared window region. Its lifetime is estimated as 3200 years [1] with a global warming potential of 22,000 relative to CO₂ over a 100-year time horizon [2]. The SF₆ molecule is recognized as one of the most potent greenhouse gases known [3] and is one of the species the Kyoto Protocol of the United Nations Framework Convention on Climate Change seeks to control. The presence of SF₆ in the atmosphere results almost entirely from anthropogenic releases except for a small natural source from radiochemical production in natural fluorite (CaF₂) minerals [4,5]. The identified pathways for removal are through reactions with O(¹D), photolysis, and electron capture and ion reaction above the stratosphere [1,6]. Production of SF₆ began in 1953 with subsequent in situ measurements showing an increase in its global mean concentration at the ground from 0.4 pptv (1 pptv = 10⁻¹² per unit volume) in early 1970s to 3.81 pptv at the end of 1996 [7]. As emissions originate primarily from industrialized regions of the Northern Hemisphere, higher mixing ratios are observed there than in the Southern Hemisphere. The main source is related to its use as an insulator of electrical equipment, such as gas-insulated switchgear (GIS), gas-insulated high-voltage circuit breakers, substations, and other high-voltage equipment [7,8]. The rapid increases that occurred during the 1980s are attributable to venting into the atmosphere prior to servicing, while recycling procedures have been used since the early 1990s [9]. A recent analysis suggests the trend of rising annual releases ended in 1995 [10]. A 40–60% mixture of electrical to non-electrical applications has been estimated with lesser though significant sources of SF₆ emissions that include blanketing and degassing of molten reactive metals such as aluminum and magnesium [7]. The molecule has also been widely used to study the atmospheric transport and dispersion [11] because it is inert and readily detected because of its very large electron capture cross section.

The infrared spectroscopic detection of SF₆ in the upper troposphere and lower stratosphere was reported from solar occultation measurements recorded by the atmospheric trace molecule spectroscopy (ATMOS) Fourier transform spectrometer during its first flight in April–May, 1985 [12]. The identification was based on the absorption by the intense, unresolved ν₃ band Q branch at 947.9 cm⁻¹. Measurements of SF₆ in ground-based solar spectra were first reported based on the detection of the same spectral feature in solar spectra recorded at the International Scientific Station of the Jungfrauoch (ISSJ) in Switzerland (46.5°N, 8.0°E, 3.58 km altitude) and the US National Solar Observatory on Kitt Peak (31.9°N, 111.6°W, 2.09 km altitude) [13].

Recently, the detection of atmospheric trifluoromethyl sulfur pentafluoride (SF₅CF₃) was reported based initially on an unidentified peak in a stratospheric air sample analyzed by gas chromatography–mass spectrometry and a subsequent confirmation by the detection of 3 ions in their correct relative atmospheric abundances in a sample of the pure compound diluted with nitrogen [14]. An analysis of air samples extracted from deep consolidated snow at Dome Concordia in eastern Antarctica

(75°S, 123°E, 3.23 km altitude) in 1999 showed SF₅CF₃ and SF₆ mixing ratio vs. depth profiles that tracked each other closely over a 30-year period, leading to the hypothesis that their growth in the atmosphere is related to the manufacturing of SF₆, though a sample of pure SF₆ diluted with nitrogen showed no SF₅CF₃. As SF₆ is used primarily in high-voltage electrical equipment, Sturges et al. [14] speculate that SF₅CF₃ originates from the breakdown of SF₆ in the presence of fluoropolymers in such equipment that provides a source of CF₃ groups that might attack SF₆ radicals formed by high-voltage discharges. A room-temperature 0.5 cm⁻¹ resolution infrared spectrum of a laboratory sample purified to remove SF₆ as a contaminant showed strong SF₅CF₃ bands in the thermal infrared. They were analyzed to estimate an adjusted cloudy sky radiative forcing of 0.57 W m⁻² ppb⁻¹ in the global atmosphere, slightly higher than 0.52 W m⁻² ppb⁻¹ for SF₆ [14].

The purpose of this paper is to report a two-decade time series of average SF₆ tropospheric mixing ratios from high spectral resolution infrared solar absorption measurements recorded at the US National Solar Observatory on Kitt Peak, a remote mountaintop station in southern Arizona. This study extends by more than a decade the previously reported time series [13]. Measurements of SF₆ elevated by up to 3 orders of magnitude above background first noted in the previous study [13] have been further analyzed to derive average SF₆ tropospheric mixing ratios based on spectral fittings of the ³⁴SF₆ ν₃ band Q branch at 930.5 cm⁻¹. Additional measurements of highly elevated SF₆ have been identified and also quantified from this isotopic SF₆ feature. A total of 5 days between November 30, 1988 and April 9, 1997 show highly elevated SF₆ with variations from spectrum to spectrum suggesting dilution of emissions from a regional or local source. A search for the strongest SF₅CF₃ band in the climatically important 8–12 μm window in the same spectra is also reported. The SF₆ average tropospheric mixing ratio trend from background measurements which comprise most of the database is also reported and compared with values from in situ Northern Hemisphere surface flask sampling measurements.

2. Measurement database and analysis

The infrared solar absorption spectra were recorded with a 1-m Fourier transform spectrometer (FTS) [15]. Dual liquid-helium-cooled As-doped Si detectors with filters covering 825–1000 or 750–1300 cm⁻¹ were used to record the solar spectra. Typically, 5 coadded interferograms requiring 25 min to record were averaged and transformed to produce a solar spectrum with a signal-to-noise ratio of 500 at 947.9 cm⁻¹. The resolution of the spectra ranged from 0.005 to 0.019 cm⁻¹, with resolution defined as 1/2Δ_{max} where Δ_{max} is the maximum optical path difference. Most spectra were recorded at a resolution of 0.005 cm⁻¹.

Retrievals were performed with version 3.8 of the SFIT2 algorithm [16,17], which is based on the optimal estimation formalism of Rodgers [18] with the selection of covariance matrix parameters based on a semi-empirical implementation [19,20]. Vertical profiles of one or more species may be retrieved from simultaneous fits to one or more microwindows.

The a priori profile of SF₆ is based on a reference set of balloon-borne Fourier transform solar absorption measurements, multiplicatively scaled to account for recent increases (G.C. Toon, Jet Propulsion Laboratory, private communication, 2000). The scaled profile has a mixing ratio of 3.9 pptv at the surface and was adjusted to be constant to 14 km, the mean altitude of the

tropopause above Kitt Peak. The stratospheric portion of the profile was assumed to decrease to a value of 0.18 pptv at 50 km, with lower values above. This profile was adopted for all retrievals. As the lifetime of SF₆ is long in both the troposphere and stratosphere, we retrieved its vertical distribution by multiplicatively scaling the a priori profile by a single factor. The typical measurement signal-to-noise ratio of 500 was assumed in the analysis. As the absorption by SF₆ is weak, spectra recorded under background conditions were fit between solar astronomical zenith angles of 60–87° to achieve sufficient SF₆ absorption for quantitative analysis. Vertical profiles were retrieved for H₂O and CO₂, the primary interferences in the SF₆ window.

The atmosphere was modeled with 29 layers with a vertical thickness of 2 km below 50 km and extended from the altitude of the station at 2.09–100 km. Refractive ray-tracing calculations were performed with the FSCATM program [21], modified and updated to achieve improved accuracy for ground-based remote sensing [22]. Airmass distributions, density-weighted temperatures, and density-weighted pressures were calculated for each atmospheric path based on the mean time of the measurement and same-day temperatures from the National Centers for Environmental Prediction (NCEP).

Precise spectroscopic parameters for SF₆ and interferences are required for the atmospheric analysis. The depth of the strongest absorption, the ³²SF₆ Q branch is only 5% at a zenith angle of 84° under recent background loadings, with shallower depths in the earliest measurements, superimposed on absorption by nearby H₂O and CO₂ lines that often saturates at line center (see Fig. 2 of [13]). Absorption depths of both molecules frequently reach 100% at the zenith angles required for SF₆ retrievals at background abundances (see Fig. 2 of [13]).

Spectral parameters adopted for the analysis were taken from several sources with the ones for the most important absorbers described next. Positions, intensities, and air-broadening coefficients for H₂O were adopted from the HITRAN 2001 compilation (available from <http://www.hitran.com>) with positions and intensities from the work of Toth [23]. Line parameters for CO₂ were also adopted from HITRAN 2001 except ¹²CO₂ positions, pressure shifts, and air-broadening coefficients at 296 K were taken from reported laboratory measurements [24]. As shown in that work, the inclusion of the measured air-broadened shift improves fits to high spectral resolution ground-based solar spectra covering the SF₆ absorption region. The air-broadened pressure shift coefficient for the H₂O line at 948.262940 cm⁻¹, a strong absorber in ground-based solar spectra was changed from 0.007690 to 0.009690 cm⁻¹ atm⁻¹ to improve fits to this line. Spectral parameters for SF₆ and CCl₂F₂ (chlorofluorocarbon 12, a minor absorber) were based on absorption cross sections from HITRAN 1996 [25] measured at 0.03 cm⁻¹ resolution between 200 and 296 K by Varanasi et al. [26,27]. The laboratory cross sections were analyzed with the Jet Propulsion Laboratory GFIT algorithm to generate sets of “pseudolines” by fitting transmission spectra simulated from the laboratory absorption coefficients (G.C. Toon, private communication, 2001). The linelist was generated for each molecule by fitting for the intensity at 296 K and the lower state energy of each “pseudoline” based on all of the laboratory measurements. The pressure-broadening coefficient of each “pseudoline” was determined empirically by trying different values and selecting the one that gave the best overall fit. All lines were assumed to have the same pressure-broadening coefficient and temperature dependence. The molecular weight of SF₆ was set to 1.0 to increase the line widths to simulate a continuous spectrum consistent with the laboratory cross sections [26,27].

3. Results and discussion

Fig. 1 illustrates SF₆ volume mixing ratio averaging kernels calculated for the 947.2–948.9-cm⁻¹ region with the spectral parameters and settings mentioned above. This region is the primary interval analyzed in the study. The kernels are displayed for vertically merged atmospheric layers of 2.09–14, 14–50, and 2.09–100 km, the total column. Values for 2.09–14 km and the total column are nearly coincidence with maxima at 5.1 km. The kernel for 2.09–14 km is nearly constant at 0.17 below 5 km, declining to 0.07 at 15 km, 0.01 at 25 km with lower values above. The altitude of 14 km corresponds approximately to the annual mean tropopause height above the station, and we refer to 2.09–14 km mixing ratios averaged from the six layers below 14 km as mean tropospheric mixing ratios in the remainder of the paper. There is low sensitivity in the 14–50 km layer (short dashed curve).

Fig. 2 presents a sample fit to the primary window under background conditions. As displayed in the expanded scale of the residual plot in the upper panel, the measurements are fitted close to the noise level with the selected spectroscopic parameters and retrieval method. The most prominent absorption features are marked and identified above and beneath the measured spectrum in the lower panel.

Table 1 reports random and systematic error sources and their estimated uncertainties for the tropospheric average mixing ratio retrievals from the primary microwindow. The estimates refer to typical daily averages. The primary source of random error is the finite signal-to-noise of the

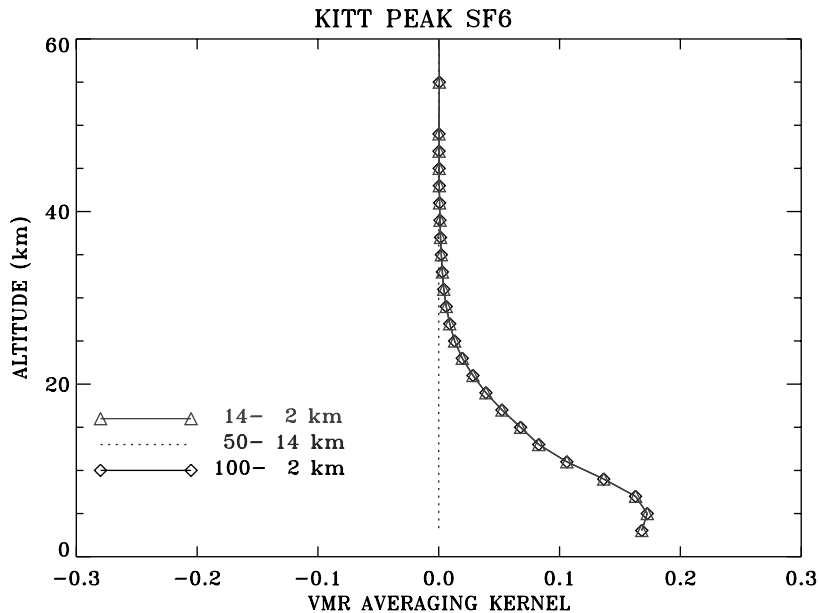


Fig. 1. Volume mixing ratio (VMR) averaging kernels for merged layers calculated for Kitt Peak based on the assumptions described in the text. The solid curve with open triangles marking values at individual layers illustrates the kernel for the troposphere. The overlapping curve with open diamonds for individual layers shows the total column VMR kernel, and dotted line presents the VMR kernel for the stratosphere.

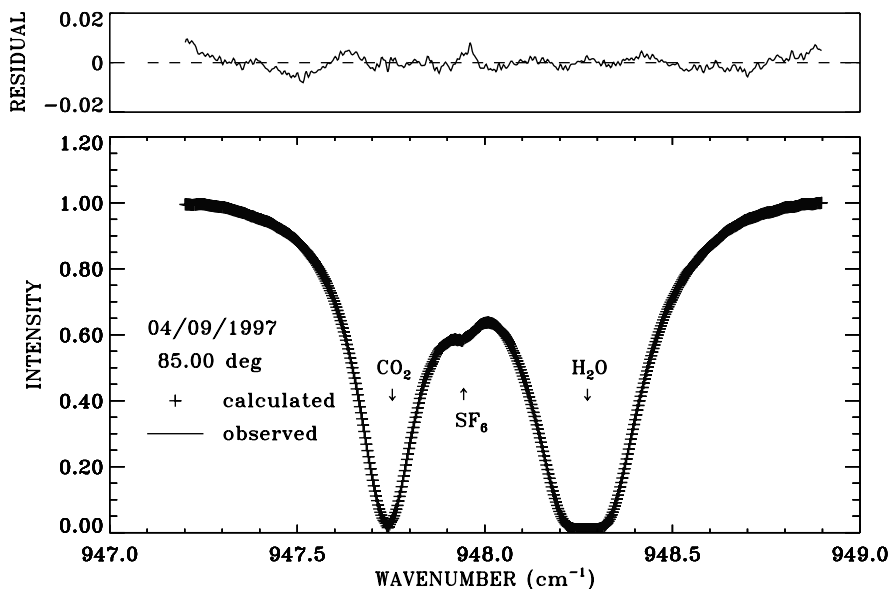


Fig. 2. Sample fit for the interval (947.20–948.90 cm^{-1}) used to retrieve SF_6 tropospheric columns from solar spectra recorded at Kitt Peak under background conditions. The measured spectrum has been normalized to the highest value in the interval. Primary absorption features are marked by arrows and identified above or beneath the spectrum trace; the astronomical zenith angle and measurement date are also reported. The upper panel shows residuals (measured minus calculated values) on an expanded vertical scale.

Table 1

Random and systematic error sources and their estimated relative uncertainties for retrievals of SF_6 tropospheric columns from daily average measurements recorded under background conditions

Source of error	Type	Relative error (%)
Finite signal–noise ^a	R	10–40
Zenith angle uncertainty	R	< 1
Channeling in spectrum	S	3
Interferences ^b	S	2–5
Forward model	S	1
A priori relative contribution	S	< 5
SF_6 spectroscopic parameters	S	5
Zero-level offsets	S	1
Retrieval algorithm	S	2
Total random error		10–40
Total systematic error		7–8

R=random, S=systematic.

^aLarger errors for the spectra recorded early in the time series due the weak absorption.

^bDue to errors in fitting nearby H_2O and CO_2 lines. Varies with the H_2O column.

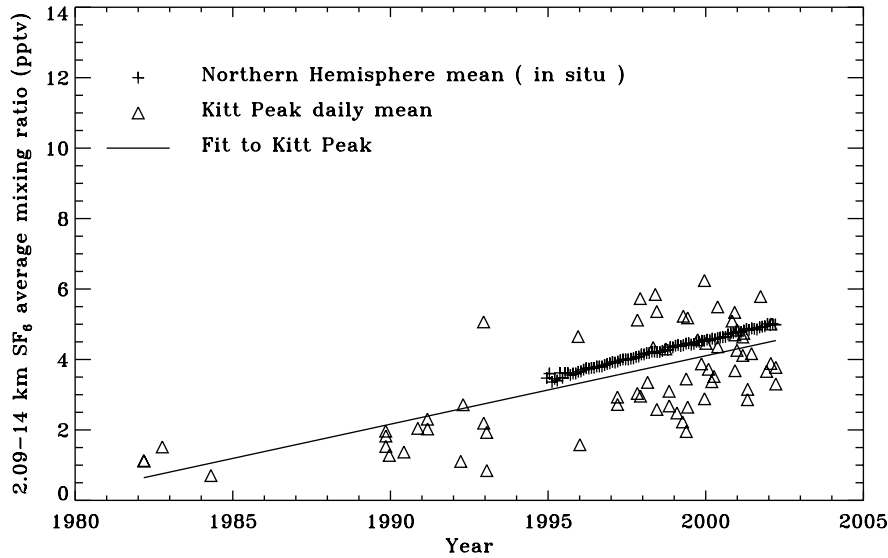


Fig. 3. Daily average (open triangles) SF_6 mean tropospheric mixing ratios above Kitt Peak retrieved from fits to the $947.20\text{--}948.90\text{ cm}^{-1}$ interval after adopting objective criteria to exclude observations with weak SF_6 absorption, low signal to noise, or elevated SF_6 total columns. The solid line shows the fit to the Kitt Peak time series assuming the average tropospheric mixing ratio increased linearly with time. Plus symbols show the time series of mean Northern Hemisphere SF_6 in situ surface mixing ratios derived from flask samples (see text).

measurements, with larger errors for the early measurements when the absorption by SF_6 was weak. Although Kitt Peak is located on a mountain peak, it is 1.5 km lower than the Jungfraujoch station, which has less attenuation by H_2O and its continuum, particularly on humid days. Important sources of systematic error are uncertainties in modeling the absorption by H_2O and CO_2 near the 947.9-cm^{-1} SF_6 Q branch, errors in modeling the local spectral background, and uncertainties due to the use of the pseudolines and their calculated temperature dependence in the retrievals. Total random and systematic errors of the daily mean Kitt Peak average tropospheric mixing ratios are estimated as 10–40% and 7–8%, respectively. The reduced relative uncertainty assigned to spectroscopic SF_6 line parameters relative to those adopted previously [13] reflects the improved accuracy of the absorption cross sections from which they were derived [25–27].

Fig. 3 illustrates retrieved daily mean SF_6 average tropospheric mixing ratios (open triangles). Low signal-to-noise measurements and spectra with weak SF_6 absorption have been excluded from the time series based on objective criteria [17]. Measurements with total columns above 1×10^{14} molecules cm^{-2} have also been removed, and are discussed later. A total of 69 daily averages are retained between March 1982 and March 2002. The number of SF_6 measurements per day recorded under background conditions ranged from 1 to 11. There are fewer days during the early years because few spectra were recorded and the absorption by SF_6 was weak due to its low abundance. Furthermore, channel spectra were often present in the early observations, and excluded by the selection criteria, further reducing the frequency of the coverage. Few summer measurements are included throughout the time series because of the increased attenuation by water vapor and its continuum during typically humid conditions. A best fit to the time series assuming a linear increase

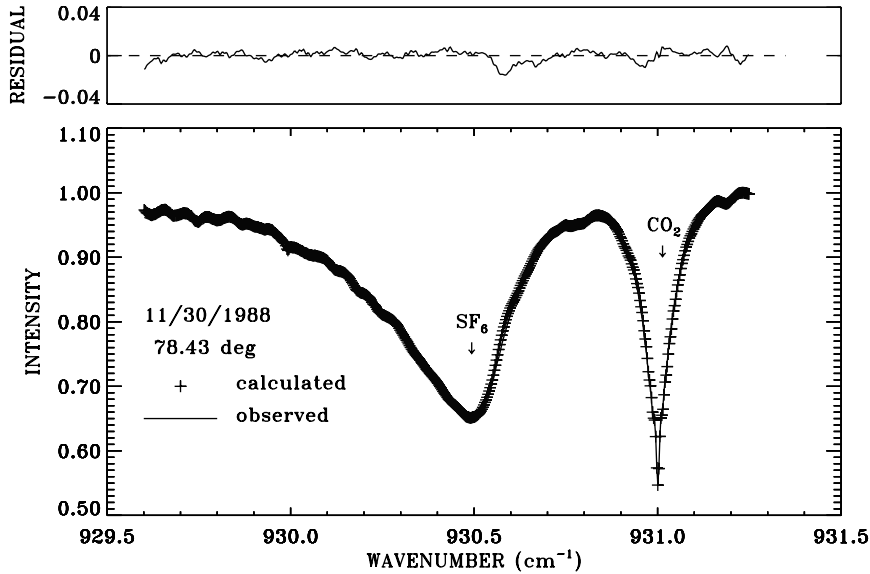


Fig. 4. Fit to the 929.60–931.30 cm^{-1} interval containing the $^{34}\text{SF}_6$ Q branch in the Kitt Peak solar spectrum recorded during the afternoon of November 30, 1988. The astronomical zenith angle is reported, and the measured spectrum and fit are displayed in the same format as Fig. 2. The isotopic SF_6 Q branch and a strong CO_2 line are marked with arrows.

(solid line) with time is shown. It indicates an increase by a factor of 3.34 from 1.13 pptv in March 1982 to 3.77 pptv in March 2002. Plus symbols show weekly to monthly flask measurements at remote Northern Hemisphere surface stations of the Climate Monitoring and Diagnostic Laboratory (CMDL, available from <http://cmdl.noaa.gov>). The CMDL time series extends from 1994–96 to 2002–21. The trends from both time series are consistent, but the Kitt Peak mean tropospheric mixing ratios are on average lower by 9.4% relative to the CMDL values.

Measurements on a total of 5 days between November 30, 1988 and April 9, 1997 show average SF_6 tropospheric mixing ratios elevated above background by 2–3 orders of magnitude. Individual solar spectra with elevated SF_6 have been further analyzed and searched for absorption by the strongest SF_5CF_3 band in the 8–12 μm window.

Fig. 4 presents a fit to the 929.60–931.25- cm^{-1} interval containing the unresolved ν_3 band Q branch of $^{34}\text{SF}_6$ in the last spectrum recorded during the afternoon of November 30, 1988 at an astronomical zenith angle of 78.43°. Absorption features of the main species are identified above the measured spectrum with residuals plotted on an expanded vertical scale in the top frame. The SF_6 a priori profile assumed in the analysis was increased by a factor of 10 to account for the highly elevated SF_6 observed in the spectrum and achieve convergence. As illustrated in Fig. 4 of Zander et al. [13], the SF_6 column above the station was highly elevated. Spectra recorded on the next day show a return to near background SF_6 abundances [13].

A SF_6 tropospheric vertical column of $(2.99 \pm 0.40) \times 10^{16}$ molecules cm^{-2} was retrieved from the spectrum displayed in Fig. 4, fitting for the profiles of SF_6 , CO_2 , and H_2O simultaneously. The set of spectroscopic parameters as described previously was assumed. Weak absorption by CCl_2F_2 in the region was also fitted by scaling its a priori volume mixing ratio in each layer by a single

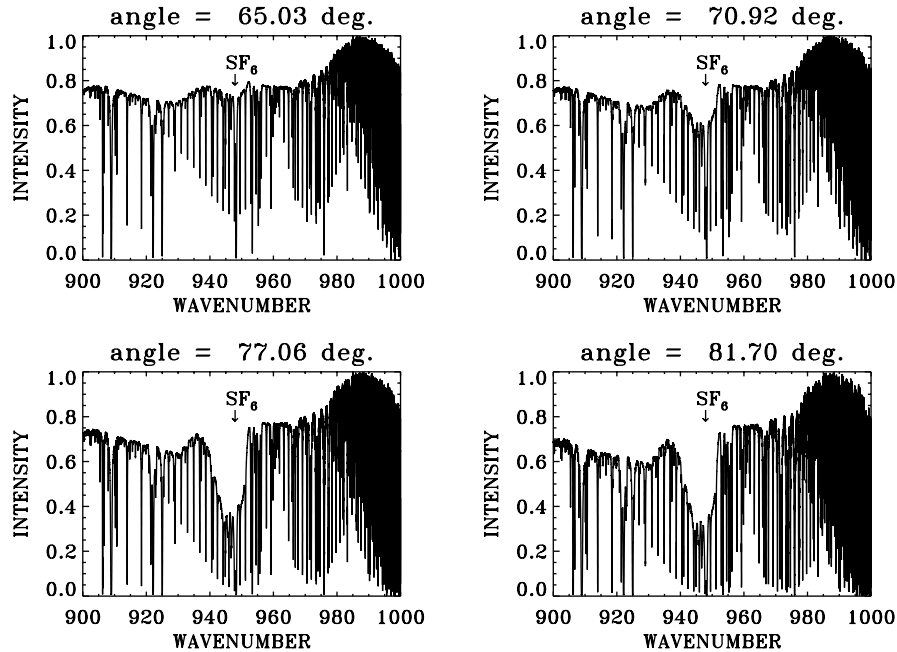


Fig. 5. Sequence of 4 solar spectra recorded on the afternoon of September 20, 1996. The 900–1000 cm^{-1} interval is displayed with each spectrum normalized. The astronomical zenith angle is indicated above the spectrum, and the location of the ν_3 $^{32}\text{SF}_6$ band Q branch is marked with an arrow. The last spectrum recorded at 84.81° solar zenith angle on that day (not displayed) also shows elevated SF_6 absorption.

multiplicative factor. The error estimate is based on differences in the retrieved total column obtained with different assumptions for the SF_6 vertical distribution in the troposphere (where the enhancement is assumed to have originated) plus 5% relative uncertainty to account for spectroscopic and minor uncertainties, such as the error in the assumed temperature profile. The retrieved column is consistent with a preliminary estimate [13] and represents an enhancement by 3 orders of magnitude above background (average retrieved tropospheric mixing ratio of 2186 pptv). The 947.9-cm^{-1} $^{32}\text{SF}_6$ Q branch normally used for quantification was completely saturated in the measured spectrum (see Fig. 4 of Ref. [13]).

The highly elevated SF_6 measured on the afternoon of November 30, 1988 suggests a local or regional source. Kitt Peak is a remote location with no industrial activity and previous efforts to identify a SF_6 source on the site were unsuccessful [13]. Spectra from another day with elevated SF_6 are illustrated in Fig. 5. The sequence was recorded on the afternoon of September 20, 1996. The location of the $^{32}\text{SF}_6$ ν_3 band Q branch is marked with an arrow and the astronomical zenith angle of each spectrum is displayed. Retrieved average tropospheric SF_6 volume mixing ratios from the three spectra with solar astronomical zenith angles of 65.03° , 70.92° , and 77.06° are 64, 146, and 358 pptv, respectively (accurate to about $\pm 25\%$ based on fits with different a priori tropospheric mixing ratios). The 81.70° , 84.81° , and 87.37° spectra recorded later that day (not displayed in Fig. 5) also show elevated SF_6 , but the retrievals did not converge.

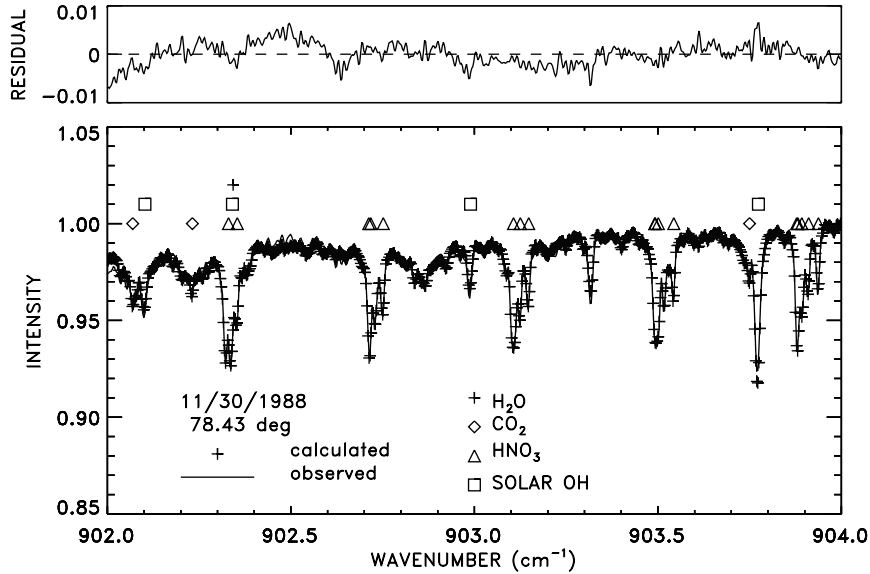


Fig. 6. Fit to the 902–904 cm^{-1} region of the Kitt Peak solar spectrum recorded at a solar astronomical zenith angle of 78.43° on November 30, 1988. The interval contains the strongest infrared band of SF_5CF_3 [14]. Symbols report identifications of prominent atmospheric and solar lines. The fit is displayed in the same format as Fig. 2. The measurement corresponds to the highest tropospheric SF_6 column in the entire time series (see Fig. 4 of this paper and Fig. 4 of [13]).

Fig. 6 presents a fit to the 902–904- cm^{-1} region of the 78.43° spectrum from the afternoon of November 30, 1988, the same spectrum displayed in Fig. 4. The region coincides with the location of the strongest SF_5CF_3 band in the 8–12 μm window [14]. Prominent spectral features of H_2O , CO_2 , HNO_3 , and solar OH are marked and identified. The analysis includes modeling and fitting of solar OH lines based on the line parameters and partition function of Goldman et al. [28]. Solar lines computed for a temperature of 4600 K were assumed and modeled with an approach similar to that adopted for solar CO lines in the SFIT program [17]. Modeling of a weak channel spectrum was also included. Residuals displayed in the upper panel on an expanded vertical scale are close to the noise level in the spectrum.

The limit for detection of a molecular species in a solar spectrum depends on the quality of modeling atmospheric absorption, the depth of the absorption feature, the magnitude and vertical distribution of its volume mixing ratio, and the signal to noise of the measured spectrum. The 903- cm^{-1} spectral region has a relatively low density of lines, which are modeled to near the noise level, and the SF_5CF_3 903- cm^{-1} band is a sharp feature in the 0.5 cm^{-1} resolution laboratory spectrum displayed in Fig. 3 of [14]. We estimate the SF_5CF_3 absorption feature could have been detected in the Kitt Peak spectrum if its absorption depth exceeded $\sim 5\%$. Based on this conservative upper limit, its reported room temperature absorption cross section, and an assumed constant vertical volume mixing ratio profile, we deduce an upper limit of 8×10^{15} molecules cm^{-2} for the SF_5CF_3 vertical column above Kitt Peak. These calculations assume the room temperature base absorption cross section of 7.6×10^{-18} cm^2 molecule $^{-1}$ at 903 cm^{-1} [14], the only published measurement.

To evaluate the feasibility of detecting SF₅CF₃ from solar ground-based spectra recorded in the present-day atmosphere, we assumed the SF₆ slant total column retrieved from the same spectrum (Fig. 3) of 2.11×10^{17} molecules cm⁻² and the atmospheric SF₅CF₃/SF₆ abundance ratio of 0.05 [14]. Assuming this ratio, the SF₅CF₃ slant column is calculated as 1.06×10^{16} molecules cm⁻². A corresponding 8% deep SF₅CF₃ absorption feature is predicted at the 903-cm⁻¹ SF₅CF₃ peak, well above the detection limit. However, similar to the SF₆ Q branch feature used for quantitative analyses [26], the SF₅CF₃ absorption cross section is likely to vary significantly with temperature in some spectral regions, complicating the attempt to derive a quantitative upper limit for its atmospheric detection.

Although the 903-cm⁻¹ SF₅CF₃ band is located in a favorable window region, detection in atmospheric spectra is unlikely due to its low current atmospheric abundance. The room temperature absorption coefficient of this band is also significantly weaker than that of the SF₆ 947.9-cm⁻¹ ν_3 band with an integrated intensity of 18.89×10^{-17} cm molecule⁻¹ [26]. As displayed in Fig. 3 of [14], the SF₅CF₃ molecule has its intensity distributed among six bands in the 8–12 μ m atmospheric window, whereas the SF₆ molecule has nearly all of its window intensity in a single strong band [29], the ν_3 fundamental. A highly elevated SF₅CF₃ column is required for its detection by infrared spectroscopy.

The additional individual Kitt Peak spectra with retrieved SF₆ total columns above 1.0×10^{14} molecules cm⁻² were examined for absorption that might be attributable to the SF₅CF₃ 903-cm⁻¹ band. No evidence for the SF₅CF₃ feature was found.

4. Summary and conclusions

Solar absorption spectra recorded with the high spectral resolution Fourier transform spectrometer on Kitt Peak (31.9°N latitude, 111.6°W, 2.09 km altitude) over a two-decade time period have been analyzed to derive the growth in the tropospheric column and mean tropospheric mixing ratio of SF₆. After excluding SF₆ measurements with low signal to noise, spectra with weak SF₆ absorption, and highly elevated SF₆ columns measured on 5 days between November 1988 and April 1997, an increase in the SF₆ background average tropospheric mixing ratio from 1.13 pptv in March 1982 to 3.77 pptv in March 2002 has been derived from a fit to 69 daily averages. The long-term increase by a factor of 3.34 over two decades of the mean tropospheric mixing ratio is consistent with the rapid growth of surface mixing ratios measured in situ at Northern Hemisphere remote stations [7], though the ground-based measurements are 9.4% lower, and show a much larger scatter than the in situ time series.

Tropospheric SF₆ columns elevated by 2–3 orders of magnitude above background levels were quantified from fits to the 930.5-cm⁻¹ ³⁴SF₆ ν_3 band Q branch. These spectra were also examined at 903 cm⁻¹, where the most intense SF₅CF₃ band in the 8–12 μ m window is located. Assuming a SF₅CF₃/SF₆ ratio equals 0.05, the value measured at the surface in the background atmosphere [14], a 8% deep SF₅CF₃ absorption feature is predicted in the Kitt Peak spectrum with the highest SF₆ slant column. This feature should have been detected assuming the reported room temperature intensity of the SF₅CF₃ 903-cm⁻¹ band [14]. Neither this nor any of the several other solar spectra with highly enhanced SF₆ show the 903-cm⁻¹ SF₅CF₃ band. Absence of information on the emission source or its location precludes further analysis and a quantitative interpretation. If the emissions

originate from an atmospheric release from a local or regional tracer experiment, as we suspect was the source, our spectroscopic findings of no detectable SF₅CF₃ in these plumes support the results of a mass spectrum analysis that show no detectable SF₅CF₃ in a sample of pure SF₆ [14].

An understanding of the origin and chemistry of atmospheric SF₅CF₃ is important given its rise at a current rate of 270 metric ton year⁻¹, its long lifetime, and its importance as a strong greenhouse gas [14]. Our analysis and the current growth rate of SF₅CF₃ indicate that its absorption will remain well below the detection limit at background levels in infrared ground-based solar spectra for many years. Laboratory measurements of the IR bands of SF₅CF₃ in the 8–12 μm window are needed as a function of temperature and pressure to provide spectral parameters for simulating its absorption and emission and a more accurate evaluation of its radiative forcing on a per molecule basis for climate studies. Preliminary temperature-dependent absorption cross sections for these bands have been reported recently [30].

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