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Measurements of long-term changes in atmospheric OCS (carbonyl sulfide) from infrared solar observations

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ABSTRACT

Multi-decade atmospheric OCS (carbonyl sulfide) infrared measurements have been analyzed with the goal of quantifying long-term changes and evaluating the consistency of the infrared atmospheric OCS remote-sensing measurement record. Solar-viewing grating spectrometer measurements recorded in April 1951 at the Jungfraujoch station (46.5°N latitude, 8.0°E longitude, 3.58 km altitude) show evidence for absorption by lines of the strong ν_3 band of OCS at 2062 cm^{-1} . The observation predates the earliest previously reported OCS atmosphere remote-sensing measurement by two decades. More recent infrared ground-based measurements of OCS have been obtained primarily with high-resolution solar-viewing Fourier transform spectrometers (FTSs). Long-term trends derived from this record span more than two decades and show OCS columns that have remained constant or have decreased slightly with time since the Mt. Pinatubo eruption, though retrievals assuming different versions of public spectroscopic databases have been impacted by OCS ν_3 band line intensity differences of ~10%. The lower stratospheric OCS trend has been inferred assuming spectroscopic parameters from the high-resolution transmission (HITRAN) 2004 database. Volume mixing ratio (VMR) profiles measured near 30°N latitude with high-resolution solar-viewing FTSs operating in the solar occultation mode over a 22 years time span were combined. Atmospheric Trace MOlecucle Spectroscopy (ATMOS) version 3 FTS measurements in 1985 and 1994 were used with Atmospheric Chemistry Experiment (ACE) measurements during 2004–2007. Trends were calculated by referencing the measured OCS VMRs to those of the long-lived constituent N_2O to account for variations in the dynamic history of the sampled airmasses. Means and 1-sigma standard deviations of VMRs (in ppbv, or 10^{-9} per unit air volume) averaged over 30–100 hPa from measurements at 25–35°N latitude are 0.334 ± 0.089 ppbv from 1985 (ATMOS Spacelab 3 measurements), 0.297 ± 0.094 ppbv from 1994 ATLAS 3 measurements, 0.326 ± 0.074 ppbv from ACE 2004 measurements, 0.305 ± 0.096 ppbv from ACE 2005 measurements, 0.328 ± 0.074 ppbv from ACE 2006 measurements, and 0.305 ± 0.090 ppbv from ACE measurements through August 2007. Assuming these parameters, we conclude that there has been no statistically significant trend in lower stratospheric OCS over the measurement time span. We discuss past measurement sets, quantify the impact of changes in infrared

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spectroscopic parameters on atmospheric retrievals and trend measurements, and discuss OCS spectroscopic uncertainties of the current ν_3 band parameters in public atmospheric databases.

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1. Introduction

High-precision and well-calibrated measurements of long-term changes in atmospheric composition are key atmospheric science need. Recently, *in situ* measurements of OCS (carbonyl sulfide) from 2000 to 2005 flask samples of ambient air at a network of surface sites in both hemispheres and aircraft-based ambient air measurements from eight continental sites over the western US during 2004 and 2005 were reported [1]. Despite the high precision of both sets of results and the important insights they provided on the distribution of OCS sources and the seasonal variation of OCS mixing ratio as a function of location in both hemispheres, no information on the long-term trend of OCS in the troposphere or information on the trend of OCS in the stratosphere was inferred. Although major advances have been made, there remains incomplete understanding of the dominant sources and sinks of atmospheric OCS in both hemispheres [2,3].

Atmospheric OCS is important as it is the predominant sulfur-bearing molecule in the remote troposphere with a complex biogeochemical cycle, a globally averaged lifetime of about 4 years and an average concentration in that region of ~ 500 parts per trillion (10^{-12} per unit volume) [1]. It is readily measured in the infrared due to the occurrence of the strong ν_3 fundamental band at 2062 cm^{-1} [4,5]. Measurements of absolute intensities of strong lines of that band have a precision (3σ) of 0.5–1% and 1.0–9.0% for the weaker lines and accuracies of 3% [4], though the dependence of the intensities with rotational quantum number does not agree with those reported in the other study [5]. As global warming increases in the next century, climate feedback likely will change the baseline atmospheric chemistry and lead to altered biosphere–atmosphere exchanges [6]. Atmospheric chemical composition and trends are also changing as a consequence of restrictions imposed by the Montreal Protocol and its strengthening amendments and adjustments limiting emissions by substances that deplete the stratospheric ozone layer [7].

The objective of this work is to report measurements of atmospheric OCS based on infrared remote-sensing measurements from ground- and space-based infrared remote sensors. Our findings include evidence for the identification of atmospheric OCS absorption features in solar spectra recorded in 1951 at the International Scientific Station of the Jungfraujoch (ISSJ), Switzerland (46.5°N latitude, 8.0°E longitude, 3.58 km altitude), with a Pfund-type grating spectrometer [8]. Those spectra were recorded at spectral resolutions of $0.12\text{--}0.40\text{ cm}^{-1}$ and have signal-to-noise ratios of 40–80 [8]. The earliest previously reported measurements of atmospheric OCS were obtained from the analysis of ambient surface air collected from several locations in 1975 with a condensed cryogenic procedure followed by infrared Fourier transform spectrometer (FTS) measurements of the sample in the region of the ν_3 band to determine sample mixing ratios [9].

More recent infrared OCS spectral measurements have been obtained with high-spectral resolution (FTSs) viewing the Sun from the ground [10–12], during ship cruises [13], and from space in solar occultation mode [14–16]. We describe these results and show that the spectroscopic parameters adopted for the strong ν_3 band in public atmospheric remote-sensing databases have varied substantially (by up to 15%) with changes in those parameters that have been a significant source of systematic error in atmospheric remote-sensing retrievals and atmospheric long-term OCS trend evaluations. We report OCS solar absorption measurements recorded in the infrared from the ground and in the lower stratosphere. We estimate the long-term OCS trend, discuss its uncertainty, compare our results with previous measurements obtained by solar occultation and other techniques, and quantify sources of error.

Transport of OCS from the lower and free troposphere to the stratosphere occurs mainly through the tropical tropopause. There, its photooxidation forms SO_2 , which is then photochemically destroyed to produce the background aerosol (Junge) layer during quiet volcanic periods [17], as first suggested by Crutzen [18]. Direct injection of sulfur into the stratosphere occurs during massive volcanic eruptions, as was observed during the eruptions of El Chichón in 1982 [19] and Mt. Pinatubo in 1991 [20]; such events likely will increase the background stratospheric sulfur and aerosol loading shortly after major volcanic eruptions and lead to lower atmosphere cooling. As ranked by flux transported from the troposphere through the tropical tropopause layer, OCS is highest among the background aerosol source gases due to its long atmospheric lifetime [21].

2. Jungfraujoch 1951 observations

Fig. 1 presents simulations for the most significant absorption features and a measurement covering the strong ν_3 band of OCS recorded from the Jungfraujoch station (46.5°N , 8.0°E longitude, 3.58 km altitude). It was obtained with a Pfund-type grating spectrometer (labeled atlas measured) on April 21, 1951 [8] at an elevation angle of $46.18\text{--}51.00^\circ$. Simulations for the atmospheric species with the strongest absorption and solar CO have been normalized and offset vertically for clarity. Also, the spectral resolution for the simulations has been adjusted to approximate that of the measured spectrum.

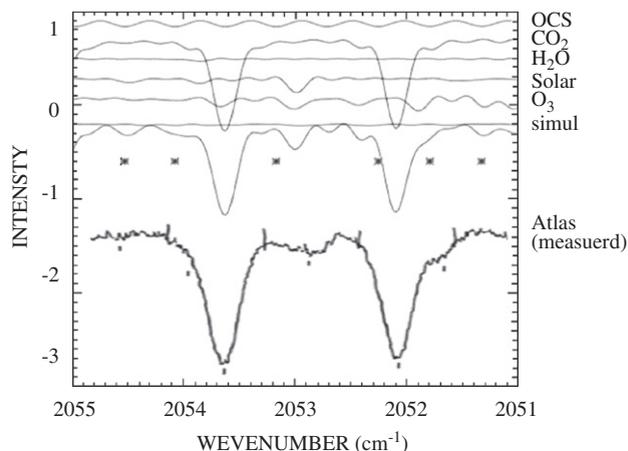


Fig. 1. Molecule-by-molecule normalized transmittances displaced vertically for clarity covering the 2051–2055 cm^{-1} region containing strong absorption lines of the ν_3 band of OCS. The most significant molecular absorbers are individually simulated and identified: OCS, CO, CO₂, H₂O, O₃, and solar CO (labeled solar). The sum of the transmission by all molecular absorption species and solar CO (labeled simul) is displayed with asterisks marking locations of strong OCS lines. The measured spectrum (bottom) is labeled Atlas (measured). It was obtained with a Pfund-type grating spectrometer on April 21, 1951, at an elevation of 46.18–51.00°. The simulated transmittances were generated for the solar elevation angle of the ISSJ spectrum with the spectral resolution adjusted to yield agreement. The Atlas (measured) curve shows vertical spikes made by the recorder pen at regular intervals.

Identifications of atmospheric and solar features from those solar spectra spanning 2.8–23.7 μm included key atmospheric molecules such as CO, CH₄, CO₂, N₂O, and O₃ [22]. A series of features of the intense ν_7 C₂H₆ band were later detected in an April 1951 ISSJ spectrum [23]. However, the assignments of telluric molecular and isotopic lines from that past work did not include OCS. The simulations in the figure assume the solar elevation angle of the measured spectrum, the 1976 US Standard Atmosphere temperature profile [24], and the reference set of molecular mixing ratio profiles for background atmospheric conditions assumed by the SFIT2 algorithm (see Ref. [25] for references to algorithms commonly used for ground-based atmospheric retrievals). As can be seen from the measured spectrum and simulations with asterisks showing the location of stronger lines, despite the high signal-to-noise, OCS absorption is weak and only marginally visible in the observation despite the high signal-to-noise ratio.

3. ATMOS/ACE measurements

The potential for recording high-spectral resolution infrared solar occultation measurements from space was pioneered by the Atmospheric Trace MOleculE Spectroscopy (ATMOS) FTS which flew successfully in low Earth orbit during four US shuttle flights, namely Spacelab 3 (April 29–May 6, 1985), ATLAS-1 (March 24–April 3, 1992), ATLAS 2 (April 8–16, 1993), and ATLAS 3 (November 8–14, 1994). Two-sided interferograms with a maximum optical path difference of 50 cm were recorded in 2.2 s intervals and Fourier transformed to yield sets of measurements at 0.01 cm^{-1} resolution with a vertical spacing of 3–4 km. Volume mixing ratio (VMR) profiles were retrieved from occultations recorded with one of a set of nine broadband interference filters. In total, profiles of 30 molecules were retrieved from measurements covering altogether 600–4800 cm^{-1} with a HgCdTe detector [14,15,26–28].

A similar set of infrared FTS measurements are now being recorded by the Atmospheric Chemistry Experiment (ACE FTS). The Canadian ACE instrument has a fully tilt and shear compensated design. The ACE satellite was successfully launched on August 12, 2003 into a 74° inclined orbit by a US-supplied Pegasus XL at 650 km altitude. The ACE FTS operates at 0.02 cm^{-1} resolution (maximum optical path difference of 25 cm) and yields a set of VMR profiles from occultations recorded with a near-linear photovoltaic HgCdTe detector and an InSb detector providing simultaneous 740–4500 cm^{-1} coverage in addition to measurements with a UV–visible spectrometer and imagers with filters at 0.525 and 1.02 μm [16].

An important geographic measurement overlap occurred near 30°N latitude between ATMOS measurements recorded during its 1985 and 1994 missions [26]. Trends in lower stratospheric mixing ratios of OCS and other molecular species were derived from ATMOS version 2 measurements near that latitude by referencing the measured VMRs to those from the long-lived constituent N₂O to account for variations in the dynamic history of the sampled airmasses [26].

4. ATMOS/ACE trend analysis

ACE and ATMOS retrievals provide VMRs with statistical uncertainties from algorithms that retrieve profiles of individual molecules from fits to multiple species in microwindows over pre-specified altitude ranges. We assume a linear N₂O VMR growth rate of 0.75 ppbv (10^{-9} per unit volume) yr^{-1} since 1977 based on surface sampling measurements from

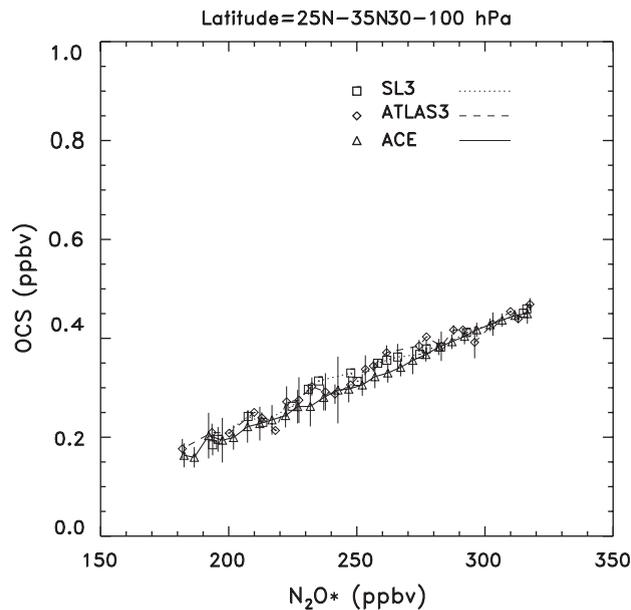


Fig. 2. Volume mixing ratio of OCS vs. N_2O^* at 25–35°N latitude and 30–100 hPa altitude obtained from ATMOS Spacelab 3 (SL3) measurements during April 29–May 6, 1985, ATMOS ATLAS 3 measurements on November 8–14, 1994, and ACE measurements from February 2004 to August 2007 from overlapping 5 ppbv N_2O^* intervals. Vertical bars indicate one standard deviation errors. See text for details.

the Climate Monitoring and Diagnostics Laboratory (CMDL) surface stations in the northern and southern hemispheres (J. W. Elkins, private communication, 2004).

Version 2 ATMOS results assumed in an earlier trend analysis [26] were replaced by ATMOS version 3 retrievals [27] because of their improved precision with the ν_3 band intensities increased by 9% [28]. The accuracy estimate of 9% for OCS (see Table 12 of Ref. [28]) is consistent with the uncertainty estimate of 8% for ATMOS version 3 intensities for OCS reported in Table 2 of Ref. [27]. Additionally, ACE version 1 retrievals [29] assumed previously for trend analysis [32] have been replaced with those from ACE version 2.2, though both versions assume spectroscopic parameters and cross sections in the HITRAN (high-resolution transmission) 2004 compilation [30].

Fig. 2 illustrates the ATMOS/ACE OCS vs. N_2O^* relation for 1985, 1994, and 2004–2007 measurements obtained at latitudes 25–35°N at 30–100 hPa, where N_2O^* is the N_2O VMR after correcting the measured N_2O VMR of each time period for the temporal increase in N_2O . As reported previously [32], we assume a linear N_2O VMR growth rate of $0.75 \text{ ppbv yr}^{-1}$ ($1 \text{ ppbv} = 10^{-9}$) per year since 1977 based on measurements from the CMDL surface stations. We include ACE FTS solar occultation measurements recorded near the same latitude from February 2004 to August 2007 in the present analysis. We refer to the N_2O measurements corrected for the assumed N_2O increase rate as N_2O^* . Objective criteria were applied to eliminate ATMOS and ACE OCS and N_2O^* measurements with large statistical uncertainties (measurements with a certainty/mixing ratio > 1 were excluded). Vertical lines show the reported 1-sigma uncertainty of each measurement. Lines connect average OCS mixing ratios versus average N_2O^* with a mean and standard deviation calculated for average OCS measurements in overlapping 5 ppbv N_2O^* increments. The number of ATMOS occultations from Spacelab 3 is 4 with 32 measurements and a mixing ratio of 0.334 ± 0.089 ppbv, and 9 occultations with 64 measurements yielded a mixing ratio of 0.297 ± 0.094 ppbv from ATLAS 3. Measurements from ACE during 2004 included 69 occultations with 489 measurements with a mixing ratio of 0.326 ± 0.074 ppbv; 97 occultations with 679 measurements returning a mixing ratio of 0.305 ± 0.096 ppbv from ACE 2005 spectra; 2006 ACE measurements included 47 occultations with 325 measurements resulting in mixing ratio of 0.328 ± 0.074 ppbv, and 36 occultations with 256 measurements from the January to August 2007 time period resulted in a OCS mixing ratio of 0.305 ± 0.090 ppbv, 1 sigma.

The exponential model for the long-term trend mixing ratios used in the ATMOS–ACE trend study [32] has been used in the analysis for the OCS lower stratospheric long-term trend. The trend was derived from average mixing ratios from each year, which were fitted with the polynomial expression [32]:

$$V = a_0 + a_1(t - t_0) + a_2(t - t_0) \times 2 \quad (1)$$

where V is the VMR, t is time, and t_0 is the time of the measurements from the first ATMOS mission. The coefficients a_0 , a_1 , a_2 , and their statistical uncertainties were determined from a nonlinear least-squares fit to the measurement time series.

Fig. 3 displays the OCS measurements from ATMOS and ACE and the best-fit trend derived with Eq. (1). Solid circles indicate the mean value for the time period of the ATMOS measurements and each year spanned by the ACE measurements from 2004 to August 2007. As can be seen from the plot, no evidence has been found for a statistically significant trend in

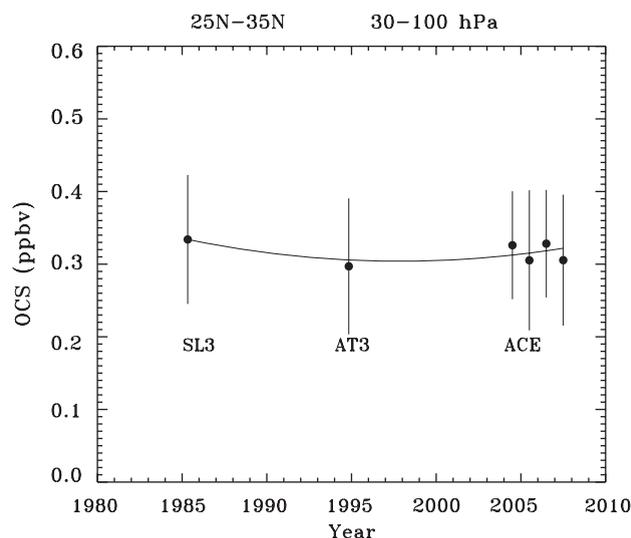


Fig. 3. Time series of OCS volume mixing ratios from ATMOS and ACE measurements at 25–35°N latitude and 30–100 hPa. Solid circles indicate mean mixing ratios and vertical lines indicate standard deviations. The curve line indicates the best-fit to the time series obtained by fitting the average mixing ratios with Eq. (1). Results for ACE are fitted based on measurements for each of the years in the time series.

lower stratospheric OCS from the combined set of measurements. The ACE instrument is continuing to record new observations.

5. Other measurements

The long-term OCS increase rate of $(0.1 \pm 0.4)\% \text{ yr}^{-1}$, 1 sigma, reported based on the version 2 comparison of the 1985 ATMOS measurements from Spacelab 3 and ATLAS 3 spectra [26] included measurements recorded shortly after Mt. Pinatubo erupted [20]. Although enhanced upper stratospheric SO_2 mixing ratios were measured by ATMOS during the ATLAS 1 shuttle mission in March–April 2002 [33] shortly after that eruption [20] and from Mauna Loa, Hawaii (19.5°N, 155.58°W, 3400 m altitude) on July 9 and 12, 2002 with a high-resolution FTS [34], no statistically significant trend in lower stratospheric OCS was inferred from the combined Spacelab 3 (SL3) and ATLAS 3 version 2 analysis [26].

Measurements of the long-term trend of OCS have been reported previously from high-resolution solar FTS absorption measurements at several ground stations. To our knowledge, the longest analyzed trend is the 24-year time series of solar absorption spectra recorded typically at 0.01 cm^{-1} spectral resolution with the FTS located at the US National Solar Observatory on Kitt Peak (altitude 2.09 km, latitude 31.9°N, long. 111.6°W) spanning May 1978 to February 2002 [10]. An average free tropospheric mixing ratio of 566 pptv was measured between 2.09 and 10 km altitude. It further revealed a seasonal variation with a summer maximum and winter minimum with a peak amplitude of $(1.3 \pm 0.4)\% \text{ yr}^{-1}$ in addition to a small but statistically significant long-term decrease equal to $(-0.25 \pm 0.04)\% \text{ yr}^{-1}$, 1 sigma. Updated results covering May 1978 through June 2005 from measurements on 208 days (after excluding noisy measurements) yield a best-fit long-term 2.09–10 km trend of $(-0.1005 \pm 0.028)\% \text{ yr}^{-1}$, 1 sigma, from a fit to the full time series, indicating a continued statistically significant downward trend. However, the mean 2.09–10 km mixing ratio from the updated fit is lower, 499.9 pptv, which we attribute primarily to an increase in the OCS line intensities [30] of the ν_3 band main isotopologue ($^{16}\text{O}^{12}\text{C}^{32}\text{S}$) by 12.4% in HITRAN 2004 [30] as compared to HITRAN 2000 [31]. The updated mean mixing ratio derived from the Kitt Peak measurements is roughly consistent with annual mean surface, aircraft, and long-path absorbance measurements near the same latitude (see Fig. 2 of Ref. [1]). The higher Kitt Peak mean tropospheric measurements reported previously [10] are in poorer agreement with measurements [1] near the same latitude. Fig. 4 illustrates the fit to the updated time series.

Measurements of monthly mean total columns and the long-term trend of tropospheric and stratospheric OCS at the Jungfraujoch station (46.5°N, 8.0°E, 3580 m altitude) were reported for the 1988–2004 time period from 5000 high-spectral resolution solar absorption spectra [12]. The stratospheric total column time series and the best-fit showed a seasonal cycle and no evidence for a systematic long-term trend. A small decrease in the tropospheric column (below 12 km) over the time span was also reported. Variations and trends in atmospheric OCS columns were reported from 1992 to 2004 high-resolution solar absorption total and tropospheric columns measured at four ground-based sites: Arrival Heights, Antarctica (77.8°S, 166.6°E), Wollongong, Australia (34.45°S, 150.88°E), Lauder, New Zealand (45.0°S, 169.7°S), and Mauna Loa [11], assuming spectral parameters from the HITRAN 2000 database [31]. Seasonal variations, an interhemispheric difference, and a small but statistically significant downward trend were inferred from measurements at three of the four sites, a result attributed to a decline in anthropogenic OCS emissions (no trend was found from the Arrival Heights time series). The very small downward trend is also consistent with the small decline obtained from the Jungfraujoch

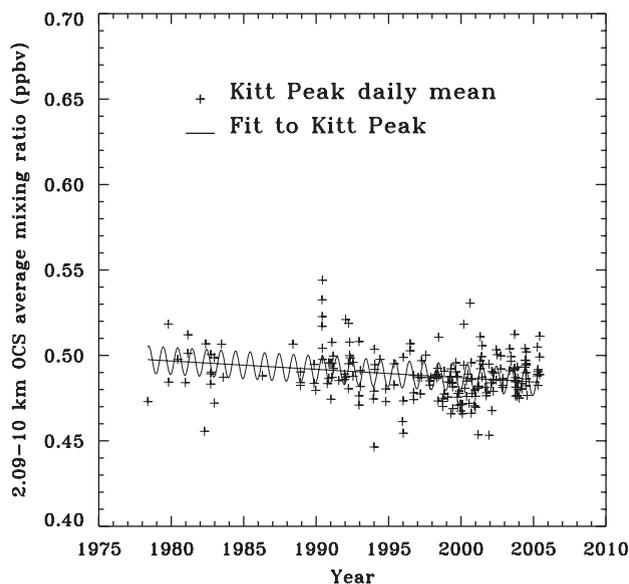


Fig. 4. Daily average 2.09–10 km mean mixing ratio of OCS above Kitt Peak. The solid line and curve show fits to the time series for the long-term trend and seasonal cycle, respectively, assuming Eq. (1) from Ref. [10].

tropospheric time series from 1998 to 2004 [12], the results from Kitt Peak [10], and our update to that time series. Analysis by gas chromatography of deep polar firn air samples at one Arctic station (Devon Island, Canada at 75°N, 82°W) and two Antarctic stations (Dronning Maud Land, Antarctica at (−77°S, 10°W) and Dome Concordia, Antarctica at (75°S, 123°E) representing atmospheric air composition from the early mid-19th century to the present were reported [35]. Little evidence for a change in OCS during the 20th century was found apart from a slight rise during the earliest part of the record and a northern hemisphere decline of 8 ± 5 during the last decade [35]. More recently, an analysis of Antarctic air samples measured at Siple Dome, West Antarctica (81.65°S, 148.81°S), with air ages of 1616–1694 A.D yielded a mean mixing ratio of 372.8 ± 37.2 ppbv [36].

6. Summary and conclusions

Evidence has been found for spectral absorption features of the strong ν_3 band of OCS in solar absorption spectra recorded from the Jungfraujoch station in April 21, 1951. The measurement occurred two decades prior to the earliest previously reported observation of atmospheric OCS [1,9]. Average lower stratospheric mixing ratios and the long-term trend of OCS have been inferred from solar occultation measurements near 30°N latitude recorded by the ATMOS FTS in 1985 and 1994 and the ACE FTS during 2004–2007. The combined result spans 22 years and is, to our knowledge, the longest set of remote-sensing measurements that have been analyzed for the lower stratospheric trend of OCS. No long-term trend in OCS was found, though evidence exists for a small recent statistically significant decline in post-Mt. Pinatubo tropospheric OCS from solar absorption measurements at both Jungfraujoch [12] and Kitt Peak [10], including an updated analysis for the trend from that station spanning August 1978–June 2005 assuming HITRAN 2004 parameters [30] for OCS. The conclusion is also consistent with an analysis of columns from solar absorption measurements from three of the four ground-based stations during 1992–2004 [11]. The tropospheric decrease may be too small to have yet propagated to a measurable impact on the lower stratospheric trend. Mixing ratio retrievals and trend evaluation have been impacted by changes in the OCS line parameters in Earth [27–31,37] and planetary atmosphere databases [38].

As noted in Section 1, the strong lines of the ν_3 band widely used for atmospheric remote-sensing retrievals from ground-based solar and solar occultation spectra can be measured with high precision (e.g., Fig. 2), and intensities of individual lines in that band have high precision [4,5]. Although the same spectroscopic parameters [30] for OCS were adopted in our ACE and Kitt Peak retrievals, and hence those results should be consistent, there remains a need for spectroscopic parameters with both high precision and accuracy. Despite the recent high-precision intensity measurements [4,5], discrepancies remain in the predicted rotational dependence of intensities for the ν_3 band of $\sim 5\%$ [4,5,30]. Until the predicted differences are resolved, line parameters for the ν_3 band have limited absolute accuracies for retrievals and trend assessments. Accuracies of 8–9% were estimated from version 3 ATMOS results [27,28] with similar systematic errors for total OCS columns from high-spectral resolution ground-based spectra recorded at Kitt Peak [10]. Analysis of the ACE time series of OCS measurements in the upper troposphere and stratosphere assuming HITRAN 2004 parameters [30] for OCS has resulted in a measurement of its distribution in both regions in addition to an estimated global stratospheric lifetime of 62 ± 18 years [39].

Acknowledgments

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