

Tropospheric methane retrieved from ground-based near-IR solar absorption spectra

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[1] High-resolution near-infrared solar absorption spectra recorded between 1977 and 1995 at the Kitt Peak National Solar Observatory are analyzed to retrieve column abundances of methane (CH_4), hydrogen fluoride (HF), and oxygen (O_2). Employing a stratospheric “slope equilibrium” relationship between CH_4 and HF, the varying contribution of stratospheric CH_4 to the total column is inferred. Variations in the CH_4 column due to changes in surface pressure are determined from the O_2 column abundances. By this technique, CH_4 tropospheric volume mixing ratios are determined with a precision of $\sim 0.5\%$. These display behavior similar to Mauna Loa in situ surface measurements, with a seasonal peak-to-peak amplitude of approximately 30 ppbv and a nearly linear increase between 1977 and 1983 of 18.0 ± 0.8 ppbv yr^{-1} , slowing significantly after 1990. **INDEX TERMS:** 0330 Atmospheric Composition and Structure: Geochemical cycles; 0394 Atmospheric Composition and Structure: Instruments and techniques; 1610 Global Change: Atmosphere (0315, 0325); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0325 Atmospheric Composition and Structure: Evolution of the atmosphere. **Citation:** Washenfelder, R. A., P. O. Wennberg, and G. C. Toon, Tropospheric methane retrieved from ground-based near-IR solar absorption spectra, *Geophys. Res. Lett.*, 30(23), 2226, doi:10.1029/2003GL017969, 2003.

1. Introduction

[2] Methane (CH_4) is the most abundant hydrocarbon in the atmosphere and plays an important role in both radiative and chemical processes. Between 1984 and 1996, the globally averaged CH_4 mole fraction increased from ~ 1625 to 1730 parts per billion by volume (ppbv) [Dlugokencky *et al.*, 1998]. Although the rate of increase is slowing, the cause of the variability has not been fully explained. Additional constraints on CH_4 sources and sinks are necessary to understand current behavior and to predict future trends.

[3] Active in situ monitoring programs are in place, including those undertaken by the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA CMDL) [Dlugokencky *et al.*, 1998] and the Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment

(GAGE/AGAGE) [Cunnold *et al.*, 2002]. Although these measurements are highly accurate, they have limited spatial coverage.

[4] Space-based column measurements of CH_4 using scattered sunlight in the near-infrared (near-IR) have been proposed (e.g., SCIAMACHY and MOPITT) as a means of providing better spatial coverage. The near-IR region is a good candidate for space-based remote sensing because (i) it is near the peak of the solar Planck function; (ii) the column averaging kernels peak at the surface, facilitating identification of CH_4 sources and sinks; (iii) thermal emission from the atmosphere and instrument are negligible compared with reflected sunlight, simplifying calibration and radiative transfer calculations. Unfortunately, CH_4 spectroscopy is poorly characterized in this region and suffers from both missing weak lines and incomplete quantum assignments [Brown, 1992]. In this letter, we examine solar absorption spectra from the Kitt Peak National Solar Observatory to determine the suitability of the $2\nu_3$ band centered at 6001 cm^{-1} for remote sensing of tropospheric CH_4 .

[5] This analysis provides a long-term CH_4 column time series beginning in 1977. Sampling of CH_4 by the NOAA CMDL network did not begin until 1983 and GAGE/AGAGE network measurements were not initiated until 1985. Flask samples [e.g., Blake and Rowland, 1986; Khalil and Rasmussen, 1983] extend the record back to the mid-1970s. The scarcity of frequent, high precision measurements between 1977 and 1983 makes the Kitt Peak dataset especially valuable.

2. Determination of Tropospheric CH_4

[6] Column CH_4 exhibits variability driven by (i) changes in surface pressure, (ii) changes in the tropospheric CH_4 volume mixing ratio (VMR), and (iii) changes in the amount of stratospheric CH_4 due to changes in tropopause altitude. The CH_4 mole fraction decreases significantly in the stratosphere due to oxidation by $\text{O}(\text{D})$, OH, and Cl. A 30 ppbv change in tropospheric CH_4 or a 30 hPa change in tropopause altitude will each produce $\sim 1.5\%$ variation in the sea level CH_4 column. Thus, to accurately determine the tropospheric CH_4 VMR, it is necessary to correct for variations in both surface pressure and stratospheric contribution.

[7] Analysis of the pressure-broadened lineshape is commonly used to gain altitude information for gases retrieved in the mid-IR. However, this method is not optimal for the near-IR Kitt Peak spectra. For a typical CH_4 line at

6000 cm⁻¹, the Doppler width exceeds the air-broadened width at ~14 km, preventing retrieval of stratospheric profile information. In addition, profile retrievals are limited by the spectral resolution of the available Kitt Peak measurements (typically $\delta\nu = 0.02$ cm⁻¹), knowledge of the instrument lineshape, and lack of accurate air-broadening parameters for the CH₄ 2ν₃ band.

[8] In this analysis, we instead use simultaneous column measurements of HF to more accurately quantify stratospheric CH₄ variations. Previous studies have demonstrated that HF and CH₄ are inversely correlated in the stratosphere [Luo *et al.*, 1995]. As stratospheric air ages and CH₄ is oxidized, the photolysis of chlorofluorocarbons (CFC) initiates a chain of reactions, eventually yielding F atoms which react with H₂O and CH₄ to form HF in the stratosphere.

[9] Provided the relationship between the CH₄ and HF VMRs is sufficiently linear, the CH₄-HF slope in the stratosphere can be applied directly to correct the CH₄ total column for stratospheric variations. Mathematically, this argument is shown by:

$$CH_4_{VMR} = a + b \times HF_{VMR}, \quad b = \frac{\partial(CH_4_{VMR})}{\partial(HF_{VMR})}. \quad (1)$$

The integrated column is:

$$X_{column} = \int_0^{P_s} X_{VMR} dp \quad (2)$$

with pressure (p) in units of molecules cm⁻² and P_s equal to surface pressure. Therefore, by substitution:

$$CH_4_{column} = \int_0^{P_s} (a + b \times HF_{VMR}) dp = a \times P_s + b \times HF_{column}. \quad (3)$$

Since HF_{VMR} = 0 in the troposphere, parameter *a* in (1) is equal to the tropospheric CH₄ VMR, assuming that CH₄ is well-mixed in the troposphere. Because the atmospheric O₂ VMR (0.2095) is highly constant, the relationship O₂_{column} = 0.2095 × P_s can be used to eliminate P_s from (3) yielding:

$$CH_4_{top\ VMR} = a = \frac{0.2095 \times (CH_4_{column} - b \times HF_{column})}{O_2_{column}}. \quad (4)$$

Equation (4) includes both the surface pressure correction using O₂_{column} and the stratospheric correction using HF_{column}. Dividing by O₂_{column} also removes possible systematic errors in the spectra, temperature profile, or calculated airmass that are common to CH₄, HF, and O₂. This equation implicitly assumes that CH₄ and HF have similar averaging kernels in the stratosphere (see S3)¹. In this letter, we determine tropospheric CH₄ VMRs by simultaneously retrieving CH₄, HF, and O₂ columns from the Kitt Peak solar spectra and by employing two additional

datasets to determine the stratospheric CH₄-HF relationship, *b*, and its time dependence.

3. The Kitt Peak Spectra

[10] The spectra analyzed in this work have been described previously [Yang *et al.*, 2002]. The dataset includes more than 400 high-resolution near-IR solar absorption spectra ($\delta\nu = \sim 0.02$ cm⁻¹) obtained with the 1-m Fourier transform spectrometer (FTS) at the McMath telescope complex of the Kitt Peak National Solar Observatory (31.9 N, 111.6 W, 2.09 km above sea level) between 1977 and 1995. Each of these spectra include the 4000–8000 cm⁻¹ region necessary for the simultaneous retrieval of CH₄, O₂, and HF. Many of these observations were used by Wallace and Livingston [1990] to determine the column-averaged dry air VMR of CH₄ and CO₂. Their work used equivalent widths to analyze 12 manifolds of the 2ν₃ CH₄ (ν₀ = 6001 cm⁻¹) band and 14 lines of the O₂ 0-0 ¹Δ_g - ³Σ_g⁻ (ν₀ = 7882 cm⁻¹) band.

[11] Here, we reanalyze the Kitt Peak solar spectra using an improved spectral retrieval algorithm with updated spectroscopic linelists for CH₄, O₂, H₂O, and solar absorption lines. We simultaneously fit the entire O₂ band (containing more than 200 significant lines), the CH₄ 2ν₃ P-branch (containing ten significant manifolds), and the strong HF R(1) (1-0) line at 4038.96 cm⁻¹.

4. Spectral Analysis and Retrievals

[12] The line-by-line fitting algorithm used in this work (GFIT) was developed at the Jet Propulsion Laboratory (JPL) for the analysis of solar absorption spectra. The use of the GFIT algorithm, temperature profiles for Kitt Peak, O₂ spectral parameters, and solar linelist have been described previously [Yang *et al.*, 2002]. The atmospheric CH₄ and HF a priori VMR profiles are based on JPL MkIV measurements recorded during balloon flights from Ft. Sumner, New Mexico, and Daggett, California (both at ~34°N).

[13] Spectral parameters for the HF R(1) (1-0) line are taken from the HITRAN database [Rothman *et al.*, 1998]. Line position, intensity, and ground-state energy parameters for the CH₄ 2ν₃ manifolds [Margolis, 1988; Margolis, 1990] are taken from HITRAN, but different air-broadened widths are employed. Since measurements of 2ν₃ linewidths have never been reported, in HITRAN these lines are assigned air-broadened widths based on measurements of the ν₂ and ν₄ CH₄ bands [Brown, 1992]. When these parameters were used to fit laboratory and atmospheric spectra, however, the residuals showed that the assigned widths are systematically large. Additionally, CH₄ columns initially retrieved from the Kitt Peak spectra had unreasonably large, symmetric daily variations of about 6% that peaked at noon. In our retrieval of CH₄, we have substituted broadening parameters from the ν₃ band as these are expected to be more closely related to the 2ν₃ band than the values assigned in HITRAN. (See S1 for a detailed discussion and linelist¹.) To further minimize the airmass dependence of the analysis, we fit only the P-branch (5880–5996 cm⁻¹). These manifolds are weaker than the R- and Q-branch manifolds, making this region less susceptible to errors in linewidth. The retrieved tropospheric CH₄ VMR is observed to vary by about 1% between 1 and 10 airmasses.

¹ Auxiliary material is available at <ftp://ftp.agu.org/apend/gl/2003GL017969>.

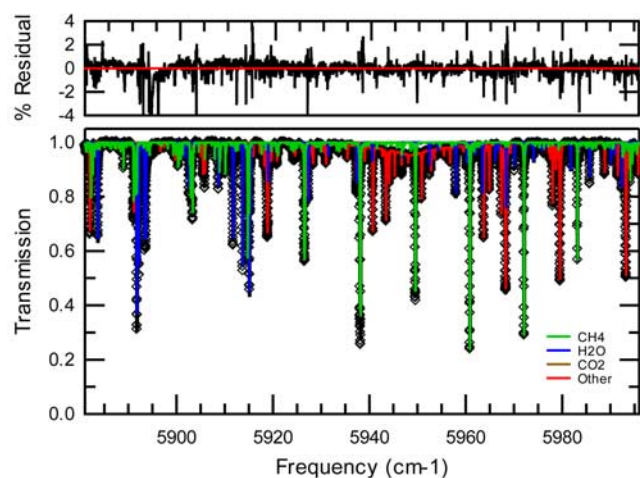


Figure 1. Example of a spectral fit to the 5880–5996 cm^{-1} region, containing the CH₄ $2\nu_3$ P-branch, of a Kitt Peak spectrum measured at 70.94° SZA on 9 May 1981. Diamonds are the measurements and black lines are the fitted transmittance. Contributions from individual gases are shown in color.

[14] Fits to the $2\nu_3$ P-branch include a full range of ground-state energies, so retrieved column CH₄ is only weakly dependent on the assumed temperature profile ($0.01\% \text{ K}^{-1}$). Considering O₂ and HF temperature sensitivities as well ($0.02\% \text{ K}^{-1}$ and $0.26\% \text{ K}^{-1}$ respectively), a systematic error of 5 K at all levels within a temperature profile would change the retrieved tropospheric CH₄ VMR in (4) by ~ 2 ppbv ($\sim 0.1\%$).

[15] A spectral fitting example for the CH₄ $2\nu_3$ P-branch is shown in Figure 1. A fit to the O₂ $0-0 \ ^1\Delta_g - ^3\Sigma_g^-$ band ($\nu_0 = 7882 \text{ cm}^{-1}$) has been shown previously in Yang *et al.* [2002] and a fit to the HF R(1) (1-0) line is included in S2¹. The residuals (model-observed) are also illustrated in Figure 1. We have excluded from further analysis 32 observations (7.7%) that produce column errors greater than 3.0% for O₂ or CH₄, as estimated from the spectral residuals. An additional 94 observations (22.7%) that produce column errors greater than 9.0% for HF have also been eliminated. The remaining 288 spectra typically have column errors of 1.4–2.8% for O₂, 1.7–2.7% for CH₄, and 3.5–6.7% for HF. The required HF precision is modest, as it is used as a linear correction with relatively small sensitivity. A 30 hPa change in tropopause pressure results in a $\sim 1.5\%$ change in the CH₄ column, while the HF column changes by $\sim 15\%$.

[16] The retrieved slant column amounts were divided by the calculated airmasses to determine vertical column amounts. The airmass calculation includes the 226 m optical path inside the telescope [L. R. Brown, private communication, 2002] and the effects of refraction. The column-averaged CH₄ VMRs ($0.2095 \times \text{CH}_{4\text{column}}/\text{O}_{2\text{column}}$) without the HF correction described in (4) are shown in Figure 2a.

[17] Monthly average CH₄ flask data from NOAA CMDL's Mauna Loa site are also shown in Figure 2a. The dotted trend line through the May 1983 to 1995 data is the twelve-month running average. The average seasonal cycle is determined by subtracting the running average from the data and binning the results by month. No evidence has

been found for changes in the amplitude of the CH₄ seasonal cycle [Dlugokencky *et al.*, 1997], so this approximation is reasonable. The trend prior to May 1983, for which no Mauna Loa flask data are available, is a linear extrapolation with a slope that is consistent with the reported global tropospheric CH₄ increase of $18 \pm 2 \text{ ppbv yr}^{-1}$ during 1978 to 1983 [Blake and Rowland, 1986]. The average Mauna Loa seasonal cycle was then applied to the linear growth rate for 1977 to May 1983. The extrapolation of the seasonal cycle is used here only as a visual guide.

[18] The retrieved Kitt Peak column-average CH₄ VMRs are systematically lower (4%) than the Mauna Loa flask samples. Some of this difference is expected as the CH₄ VMR is lower in the stratosphere, but geographical differences and uncertainty in the absolute CH₄ line strengths and widths preclude meaningful comparison of the column-average CH₄ VMRs.

5. Tropospheric CH₄ Volume Mixing Ratios

[19] The column-average CH₄ VMRs in Figure 2a include significant variability driven by changes in tropopause altitude. This is illustrated by the anti-correlation of CH₄ in Figure 2a with retrieved HF columns in Figure 2b (see S3). In many years the HF column varies by as much as a factor of two between summer and winter. The seasonal variation in HF is superimposed on its increasing burden due to increasing CFC VMRs. Figure 2b shows the fluorine-

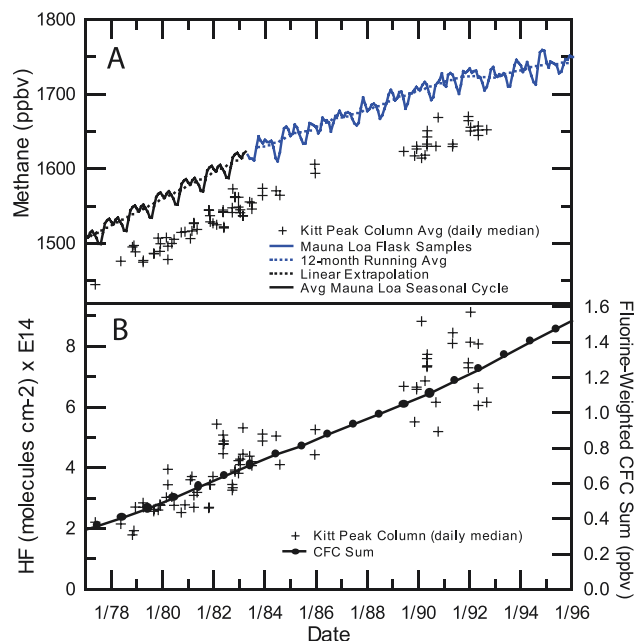


Figure 2. (a) Time series of Kitt Peak column-averaged CH₄, determined from $0.2095 \times \text{CH}_{4\text{column}}/\text{O}_{2\text{column}}$. Mauna Loa flask samples (monthly average) are shown with their twelve-month running average. No Mauna Loa flask data exists prior to May 1983. A linear extrapolation with slope $18.0 \text{ ppbv yr}^{-1}$ is shown for this period, with the average Mauna Loa seasonal cycle applied. (b) Time series of Kitt Peak column HF. The fluorine-weighted CFC sum (CFC-11 + $2 \times$ CFC-12 + $3 \times$ CFC-113 + $2 \times$ HCFC-22) has been lagged by six years to account for atmospheric transport into the stratosphere.

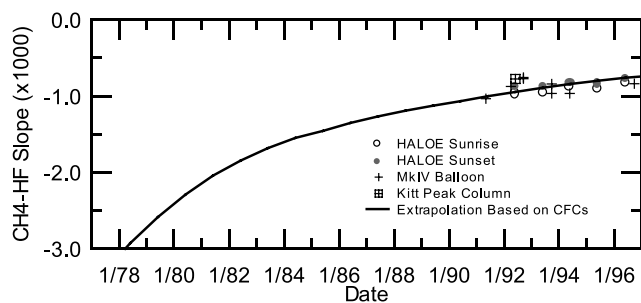


Figure 3. CH₄-HF slope values, *b*, obtained from the HALOE, MkIV, and Kitt Peak data. Slope values have been extrapolated back to 1977 using the CFC sum shown in Figure 2b.

weighted CFC trend (CFC-11 + 2 × CFC-12 + 3 × CFC-113 + 2 × HCFC-22) reconstructed from measurements by the ALE/GAGE/AGAGE network at Cape Grim, Tasmania. The fluorine-weighted CFC sum is lagged by six years to account for atmospheric transport within the stratosphere. Further details are given in S3¹.

[20] To retrieve the tropospheric CH₄ VMR using (4), the correlation of CH₄ with HF, *b*, is needed. This slope is determined here from two datasets. The Halogen Occultation Experiment (HALOE) instrument on the Upper Atmosphere Research Satellite (UARS) has been measuring CH₄ and HF simultaneously in solar occultations since 1991 using the gas filter correlation technique [Russell *et al.*, 1993]. The CH₄-HF plots for that data are characterized by tightly fitted curves for different latitude bands [Luo *et al.*, 1995]. Using sunrise and sunset data measured at tangent latitudes of 20–40°N, we have fitted a linear CH₄-HF relationship. The second CH₄-HF dataset was recorded by the JPL MkIV Interferometer during 8 balloon flights at tangent latitudes between 32–38°N during 1990 to 1996. The MkIV is an FTS that uses the solar occultation technique to record mid-IR spectra [Toon, 1991].

[21] Figure 3 shows the slope of the CH₄-HF correlation, *b*, obtained from the HALOE and MkIV data for pressure levels between 10 and 100 hPa. The value calculated from the retrieved Kitt Peak CH₄ and HF columns is also shown. The CH₄-HF slope has increased significantly between 1977 and 1995, due to increasing HF VMRs. The slope has been extrapolated back to 1977 using the time-lagged VMR of fluorine-weighted CFCs, shown in Figure 2b. Although this extrapolation is not ideal, it is necessary due to the lack of simultaneous CH₄ and HF profile measurements available from the 1970s and 1980s. Further explanation of the HALOE, MkIV, and Kitt Peak *b* values, as well as extrapolation of *b* using CFC data is given in S3¹.

[22] Tropospheric CH₄ VMRs calculated from (4) are shown in Figure 4a and provided in tabular form in S3. The Mauna Loa data in Figure 4a are identical to those in Figure 2a. The Kitt Peak tropospheric CH₄ VMRs are scaled by 1.015 to bring their values into agreement with the Mauna Loa data. This scaling was empirically determined to minimize bias between the Kitt Peak and Mauna Loa data. The linear slope of the 1977 to 1983 Kitt Peak tropospheric VMRs is 18.0 ± 0.8 ppbv yr⁻¹, consistent with the value of 18 ± 2 reported by Blake and Rowland [1986] for this period.

[23] The average seasonal cycle (and 2σ variability) for the 1983 to 1995 Mauna Loa data is shown in Figure 4b. The Kitt Peak data were detrended by subtracting the linear trend and twelve-month running average shown in Figure 4a. Figure 4b shows that approximately ±2% seasonal variation is evident in the Kitt Peak data, consistent with the Mauna Loa data.

6. Conclusions

[24] Reanalysis of the high-resolution near-IR spectra obtained at the Kitt Peak National Solar Observatory demonstrates that tropospheric CH₄ VMRs can be retrieved with 0.5% precision. However, our results are limited by current CH₄ spectroscopy (linewidths, intensities, and missing weak lines) and by our ability to accurately separate tropospheric and stratospheric variability using (4). The largest errors in this analysis include noise in our HF retrievals, the assumption of a linear CH₄-HF relationship in the stratosphere, and the difficulty of extrapolating this relationship into the past. Despite these challenges, reanalysis of the Kitt Peak spectra allows the tropospheric CH₄ record to be extended back to 1977. These results show that high precision measurements of column CH₄ are possible using ground-based FTS, and that this technique can be used to validate future space-based observations. However, to determine CH₄ sources and sinks from column measure-

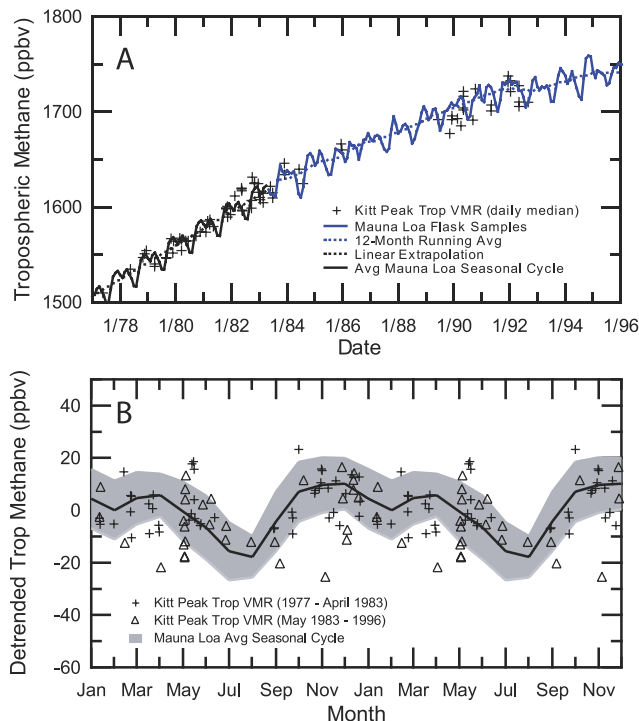


Figure 4. (a) Time series of Kitt Peak tropospheric CH₄ VMR, determined from (4). The data have been multiplied by 1.015 (see text) to bring them into agreement with the Mauna Loa data. (b) Detrended Kitt Peak tropospheric CH₄ VMR shown together with the average Mauna Loa seasonal cycle (2σ variability). Kitt Peak data prior to May 1983 are represented by crosses and later data are represented by triangles.

ments, it will be necessary to separate the tropospheric and stratospheric column contributions. This letter uses HF as a stratospheric tracer to achieve this separation. In the future, higher resolution spectra and precise laboratory measurements of air-broadened widths may allow direct retrieval of tropospheric CH₄ VMRs.

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