Multi-decade measurements of the long-term trends of atmospheric species by high-spectral-resolution infrared solar absorption spectroscopy

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A R T I C L E   I N F O

Article history:
Received 23 July 2009
Received in revised form 16 September 2009
Accepted 29 September 2009

Keywords:
Atmospheric remote sensing
Infrared
Long-term trends

A B S T R A C T

Solar absorption spectra were recorded for the first time in 5 years with the McMath Fourier transform spectrometer at the US National Solar Observatory on Kitt Peak in southern Arizona, USA (31.91°N latitude, 111.61°W longitude, 2.09 km altitude). The solar absorption spectra cover 750–1300 and 1850–5000 cm⁻¹ and were recorded on 20 days during March–June 2009. The measurements mark the continuation of a long-term record of atmospheric chemical composition measurements that have been used to quantify seasonal cycles and long-term trends of both tropospheric and stratospheric species from observations that began in 1977. Fits to the measured spectra have been performed, and they indicate the spectra obtained since return to operational status are nearly free of channeling and the instrument line shape function is well reproduced taking into account the measurement parameters. We report updated time series measurements of total columns for six atmospheric species and their analysis for seasonal cycles and long-term trends. As an example, the time series fit shows a decrease in the annual increase rate in Montreal-Protocol-regulated chlorofluorocarbon CCl₂F₂ from 1.51 ± 0.38% yr⁻¹ at the beginning of the time span to 1.54 ± 1.28% yr⁻¹ at the end of the time span, 1 sigma, and hence provides evidence for the impact of those regulations on the trend.

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1. Introduction

Long-term atmospheric constituent measurements provide an important record of how the atmosphere has evolved. The Fourier transform spectrometer (FTS) at the McMath–Pierce Solar Telescope of the National Solar Observatory on Kitt Peak [1] has provided an important long-term record of those changes, and an archive of those measurements in the infrared since 1977 has been maintained at the NASA Langley Research Center in Hampton, VA, USA. The spectra obtained with the refurbished FTS are the first recorded in 5 years and were obtained with the east auxiliary telescope of the Kitt Peak FTS on 20 days between March and June 2009. Individual spectra cover 750–1300 or 1850–5000 cm⁻¹ and were recorded with a maximum optical path difference of 62.489 cm. Measurements recorded over a range of solar zenith angles have been used to retrieve total columns of tropospheric and stratospheric constituents.

Fig. 1 provides sample spectra and fits in example windows used to retrieve the key species HF, HCl, CH₂Cl, CCl₂F₂, CH₄, SF₆, and ClONO₂. The selected species are a
subset of those that can be measured routinely with the instrument and were chosen primarily because of their relatively long lifetimes, availability of spectral windows, and minimal interferences as demonstrated by the quality of example spectral fits and previous studies. The procedure for refractive ray tracing and deriving air-mass-weighted pressures and temperatures in 37 atmospheric layers extending from the surface to 100km assuming temperature profiles determined for the day of observation has been described previously [2]. As can be seen
from these examples, the Kitt Peak spectra show that a high signal-to-noise ratio has been achieved, and the spectra are fitted close to the measurement noise level.

Profiles are derived for each molecular species from simultaneous fits to one or more microwindows based on a semi-empirical implementation [3,4] of the optimal estimation method [5]. The algorithm (SFIT2) is widely used and the retrieved results shown here cover the full time span of the measurements based on version 3.93 and spectroscopic parameters derived from the HITRAN 2004 spectroscopic database [6] combined with “pseudolines” derived from temperature-dependent absorption cross-sections. The pseudolines list was generated from laboratory cross-sections (G.C. Toon, Jet Propulsion Laboratory, private communication, 2006). The procedure is widely used for atmospheric retrievals from ground-based solar spectra and has also been implemented for retrievals from balloon-borne and solar occultation spectra recorded with the Atmospheric Trace MOleculE Spectroscopy (ATMOS) FTS spectra. All the relevant laboratory transmittance spectra were fitted simultaneously while solving for the 296 K intensity and the ground state energy ($E^0$) of each pseudoline. The procedure for deriving pseudolines assumes all lines in a given absorption band have the same pressure-broadened half-width and the same half-width dependence on temperature. Pseudolines have been adopted in simulating the absorption spectra of CHF$_3$ (CFC-11), CHFClF (CFC-113), CCl$_2$F$_2$ (CFC-12), CCl$_3$FCCIF$_2$ (CFC-113), CCl$_4$F (CFC-11), SF$_6$, CF$_4$, CCl$_4$ CIONO$_2$, HCFC-142b (CH$_3$CCl$_2$F), PAN (CH$_3$ClO)OONO$_2$, CH$_3$CHO, C$_2$H$_6$, CH$_3$CN, and N$_2$O$_5$. Examples of studies that included the use of pseudolines in atmospheric trend studies are reported in Refs. [7–10].

2. Measurements, data reduction, and comparisons with previous results

Time series of daily mean total-column measurements have been used in our analysis. Objective criteria based on the depth of absorption feature in the spectrum and the signal-to-noise ratio in the window were used to discard low-quality measurements for each molecule. Vertical lines show standard deviations of each daily mean. Previous papers have provided evaluations of both random and systematic sources of error (e.g. Refs. [2,7,9]) and depend on the species and the quality of the parameters in the combined HITRAN 2004 [6] and pseudoline database.

The total-column time series for each species was fitted with the expression

$$C_A = a_0 + a_1(t-t_0) + a_2(t-t_0)^2 + a_3(t-t_0)^3 + a_4 \cos(2\pi(t-t_0-\phi))$$

(1)

where $C_A$ is the daily average total column at time $t$, $a_0$ the mean total column at time $t=t_0$, and $t_0$ the reference time of the time series. We have used the mid point of the whole time period for each species as the reference time. The derivative of the combination of second to fourth terms on the right hand side represents the trend at time $t$, $a_4$ is the amplitude of the seasonal cycle, and $\phi$ the phase relative to the reference day for the seasonal cycle. Previous studies have reported time series of total columns or altitude-resolved mean volume mixing ratios (VMRs) over pre-selected altitude ranges to determine the seasonal variation and corresponding time of seasonal maximum when the results are statistically significant.

Table 1 provides the results of regression fit using Eq. (1) for each molecule. The time span, number of measurement days, seasonal amplitude, and trends at the beginning of every 5 years, including 2009, are listed in the columns. Standard deviations are also shown in the entries for seasonal amplitudes and trends. We next discuss the results for each molecule, provide the measured time series, the corresponding time series best fit with Eq. (1), and briefly compare the results with previous key observations.

Fig. 2 presents the daily mean total-column time series for inorganic chlorine (Cl$_2$), calculated as the sum of HCl and CIONO$_2$. In Fig. 2 as well as in the following four figures (Figs. 3–6), regression fit using all terms in Eq. (1) is represented by solid lines while the fitting omitting the seasonal term is represented by dashed lines. Since the first detection of stratospheric ozone depletion, the abundance and trend of total inorganic chlorine consisting primarily of HCl and CIONO$_2$ have been identified as the key in triggering stratospheric ozone depletion in the stratosphere primarily from photodissociation by UV radiation of industrial emissions of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), carbon tetrachloride (CCl$_4$), and methyl chloroform (CH$_3$CCl$_3$) [11,12]. A previous study provided evidence, from ground-based solar absorption measurements, Halogen Occultation Experiment (HALOE) satellite solar occultation measurements, and model predictions, that the increase in total-column Cl$_2$ measured prior to 1991 had leveled off and was predicted to begin a slow decline reaching 12–14% of the peak by 2010 [13]. Measurements of HCl and CIONO$_2$ total columns from Jungfraujoch (46.5°N latitude, 8.0°E longitude, 3580 m altitude) solar spectra covering 1977–2007 show evidence of the stabilization and a recent onset of a slow Cl$_2$ total-column decline [14]. The Cl$_2$ total-column trend from the fit to the Kitt Peak time series with Eq. (1) indicates a 2009 trend of $-1.94 \pm 1.57 \text{yr}^{-1}$.

Hydrogen fluoride (HF) is a key molecule for monitoring anthropogenically produced changes in the composition of the Earth's middle atmosphere [15]. Although several natural sources exist, the molecule is believed to originate in the middle atmosphere almost solely from the photodissociation of man-made chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). The primary components are CCl$_2$F$_2$ (CFC-12) and CCl$_4$F (CFC-11), with more recent contributions from C$_2$Cl$_3$F$_3$ (CFC-113) and CHClF$_2$ (HCFC-22). Once produced, stratospheric HF is very stable, so it accumulates and is ultimately removed either by downward diffusion and rainout in the troposphere or by upward transport to the mesosphere, where its mixing ratio remains constant up to high altitudes where it is destroyed by photolysis. Fig. 3 presents the HF total-column time series derived from Kitt Peak measurements. Similar to the results reported recently from Jungfraujoch measurements, a slow down in the rate of...
accumulation is measured [14]. From the entries in the fifth row of Table 1, it is obvious that the rate of change of HF column was in the range of 4.32% yr\(^{-1}\) and 4.54% yr\(^{-1}\) during 1985 and 1990, respectively. However, the corresponding rates of change were greatly reduced to become 0.25% yr\(^{-1}\) in 2005 and even showed a sign of turnover with a 2009 rate of change of −2.15% yr\(^{-1}\). Fig. 4 illustrates the Kitt Peak CH\(_4\) total-column time series and the best fit to those measurements. Atmospheric methane is the second most important anthropogenic greenhouse gas with a radiative forcing half that of carbon dioxide (CO\(_2\)) [16]. The time series fit shows the increase in the total column during 1970s and 1980s has slowed, a result that is consistent with lower stratospheric mid-latitude solar occultation and surface station measurements [17]. Total-column time series measured from the Jungfraujoch

### Table 1

Kitt Peak daily mean total-column measurements and a best fit to them with Eq. (1).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Measurement days and time span</th>
<th>Amplitude(^a)</th>
<th>Trend at 1985 (% yr(^{-1}))</th>
<th>Trend at 1990 (% yr(^{-1}))</th>
<th>Trend at 1995 (% yr(^{-1}))</th>
<th>Trend at 2000 (% yr(^{-1}))</th>
<th>Trend at 2005 (% yr(^{-1}))</th>
<th>Trend at 2009 (% yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>256 (1977/05/30–2009/06/12)</td>
<td>0.17 ± 0.02</td>
<td>2.99 ± 0.17</td>
<td>1.91 ± 0.10</td>
<td>0.87 ± 0.16</td>
<td>−0.14 ± 0.34</td>
<td>−1.12 ± 0.66</td>
<td>−1.88 ± 0.99</td>
</tr>
<tr>
<td>ClONO(_2)</td>
<td>154 (1980/12/21–2009/05/16)</td>
<td>0.13 ± 0.01</td>
<td>0.53 ± 0.90</td>
<td>1.39 ± 0.41</td>
<td>1.06 ± 0.42</td>
<td>−0.48 ± 0.94</td>
<td>−3.22 ± 1.97</td>
<td>−6.28 ± 3.16</td>
</tr>
<tr>
<td>Cl(_y)</td>
<td>(1982/March–2009/ May)</td>
<td>0.28 ± 0.03</td>
<td>3.0 ± 0.54</td>
<td>1.79 ± 0.24</td>
<td>0.68 ± 0.20</td>
<td>−0.34 ± 0.45</td>
<td>−1.26 ± 0.96</td>
<td>−1.94 ± 1.57</td>
</tr>
<tr>
<td>HF</td>
<td>299 (1977/05/30–2009/06/12)</td>
<td>0.09 ± 0.01</td>
<td>4.32 ± 0.24</td>
<td>4.54 ± 0.14</td>
<td>3.93 ± 0.20</td>
<td>2.50 ± 0.44</td>
<td>0.25 ± 0.84</td>
<td>−2.15 ± 1.28</td>
</tr>
<tr>
<td>CCl(_2)F(_2)</td>
<td>211 (1980/12/21–2009/06/10)</td>
<td>0.12 ± 0.05</td>
<td>1.51 ± 0.38</td>
<td>1.74 ± 0.17</td>
<td>1.08 ± 0.17</td>
<td>0.27 ± 0.38</td>
<td>−0.68 ± 0.80</td>
<td>−1.54 ± 1.28</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>260 (1977/05/30–2009/06/12)</td>
<td>0.14 ± 0.09</td>
<td>0.51 ± 0.07</td>
<td>0.35 ± 0.04</td>
<td>0.20 ± 0.06</td>
<td>0.17 ± 0.14</td>
<td>0.27 ± 0.26</td>
<td>0.43 ± 0.40</td>
</tr>
<tr>
<td>CHF(_2)Cl</td>
<td>209 (1981/04/26–2009/05/16)</td>
<td>0.07 ± 0.02</td>
<td>4.74 ± 0.41</td>
<td>4.30 ± 0.18</td>
<td>4.14 ± 0.16</td>
<td>4.25 ± 0.38</td>
<td>4.64 ± 0.81</td>
<td>5.16 ± 1.31</td>
</tr>
<tr>
<td>SF(_6)</td>
<td>131 (1981/04/26–2009/03/22)</td>
<td>0.70 ± 0.27</td>
<td>1.77 ± 3.54</td>
<td>7.97 ± 1.47</td>
<td>10.83 ± 1.42</td>
<td>9.69 ± 3.38</td>
<td>4.55 ± 7.36</td>
<td>−2.45 ± 11.99</td>
</tr>
</tbody>
</table>

\(^a\) Amplitude units are 10\(^{13}\) molecules cm\(^{-2}\) for SF\(_6\), 10\(^{18}\) molecules cm\(^{-2}\) for CH\(_4\), and 10\(^{15}\) molecules cm\(^{-2}\) for all other compounds.
Fig. 3. Lower panel: hydrogen fluoride (HF) daily average total-column time series (open triangles) and the best fit to those measurements from a fit with Eq. (1). Vertical lines indicate measurement standard deviations. Upper panel: measured minus calculated residual on an expanded vertical scale.

Fig. 4. Lower panel: methane (CH$_4$) daily average total-column time series (plus symbols) and the best fit to those measurements obtained with Eq. (1). Vertical lines indicate measurement standard deviations. Upper panel: measured minus calculated residuals on an expanded vertical scale.
Fig. 5. Lower panel: daily mean total-column time series of CHF_{2}CI (HCFC-22, plus symbols) and the best fit to those measurements obtained with Eq. (1). Vertical lines indicate measurement standard deviations. Upper panel: measured minus calculated residuals derived from a best fit with Eq. (1) on an expanded vertical scale.

Fig. 6. Lower panel: daily mean total-column sulfur dioxide (SF_{6}) time series (plus symbols) and a best fit to those measurements obtained with Eq. (1). Vertical lines indicate measurement standard deviations. Upper panel: measured minus calculated residuals on an expanded vertical scale.
station derived no statistically significant increase for the 2003–2004 time span [14].

Fig. 5 presents the total-column time series for CHF$_2$Cl (HCFC-22). The molecule is a hydrochlorofluorocarbon, which means that unlike chlorofluorocarbons (CFCs), it reacts with OH radicals, shortening its tropospheric lifetime, though it does make a small contribution to stratospheric chlorine loading [18]. The molecule is readily measured from ground-based and space-based solar measurements based on its strong and narrow $2
u_6$ band Q branch at 829.05 cm$^{-1}$ [19]. Past studies include measurements of CHF$_2$Cl, and its trend and increase rate over southern California from 1985 to 1990 [20], Kitt Peak measurements of the trend from October 1987 to November 2002 [20], Jungfraujoch total-column time series [14], and southern hemisphere trend measurements between 1985 and 1994 [21].

Fig. 6 illustrates the long-term trend of total-column SF$_6$ measured from the Kitt Peak time series. Emissions of the molecule into the atmosphere are entirely anthropogenic. It is a widely used electrical insulating gas in high-voltage electrical and electronic equipment and has high stability and a long atmospheric lifetime. It was initially identified in ATMOS solar spectra of the upper troposphere and stratosphere on the basis of the intense, unresolved $v_3$ band Q branch at 947.9 cm$^{-1}$ [22]. Although the feature is a weak absorber in ground-based solar spectra, it has been detected [23], but absorption by a nearby H$_2$O line occurs at relatively low-altitude sites on days of high humidity [7]. Consistent with previous ground-based measurements [8], a continuous long-term rise has been observed above Kitt Peak in agreement with previous observations such as those from the Jungfraujoch station [14].

Fig. 7 presents the Kitt Peak CCl$_2$F$_2$ time series. As CCl$_2$F$_2$ is a chlorofluorocarbon, its emissions have been significantly reduced by the restrictions imposed by the fully amended and revised Montreal Protocol for substances that deplete the ozone layer [24]. The fit to the total-column time series shows a maximum was reached at the year 2001, though the trend for 2009 obtained with Eq. (1) is not statistically significant. The trend result can be compared with the tropospheric trend retrieved from Kitt Peak measurements between March 1982 and October 2003 [25]. The fit to those results showed a change in the annual increase rate from $1.51\pm0.38\%$ yr$^{-1}$ at the beginning of the time span to $-1.54\pm1.28\%$ yr$^{-1}$ at the end of the time span, 1 sigma.

3. Conclusions

The first solar absorption measurements in 5 years have been recorded in the infrared with the McMath solar telescope FTS on Kitt Peak in southern Arizona on 20 days between March and June 2009 from observations that cover 750–1300 and 1850–5000 cm$^{-1}$. The additional measurements have been analyzed and combined with earlier observations to derive updated total columns, seasonal cycles, and trends for HF, Cl$_y$ (HCl+ClONO$_2$),...
CH₄, CHF₂Cl (HCFC-22), SF₆, and CCl₂F₂. The updated database spans 1977–2009, and quantifies the significant changes in atmospheric composition that have occurred over the last three decades, for example, changes mandated by the Montreal Protocol and its strengthening amendments and adjustments [24]. The Clᵥ total-column trend from the fit to the Kitt Peak time series indicates the previously measured increase has leveled off with a 2009 trend of −1.94 ± 1.57% yr⁻¹. Our results and others [14] show the important impact of those restrictions, for example, a change in the chlorofluorocarbon 12 (CCl₂F₂) annual increase rate from 1.51 ± 0.38% yr⁻¹ at the beginning of the time span to −1.54 ± 1.28% yr⁻¹ at the end of the time span, 1 sigma. The three-decade time series presented here is only a subset of those for species that can be measured by infrared remote sensing, but the selected results highlight important changes in atmospheric chemistry that have occurred, e.g. growth of hydrofluorocarbon substitutes [10]. The Kitt Peak trend results have been compared and found to be in good agreement with previous ground-based and space-based measurements. Species with profiles having maximum VMRs in the troposphere such as CO, C₂H₆, HCN, OCS, and CH₃OH are also measured with the Kitt Peak FTS and will be retrieved and added to the time series record (e.g. Refs. [26,27]).

Acknowledgments

Analysis of the Kitt Peak spectra at the NASA Langley Research Center was supported by NASA’s Upper Atmospheric Chemistry and Modeling Program (ACMAP) and Upper Atmosphere Research Program (UARP). We acknowledge the US National Solar Observatory for providing the infrared solar spectra and observational parameters assumed in this study.

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