

## Infrared measurements of atmospheric CH<sub>3</sub>CN

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[1] For the first time CH<sub>3</sub>CN has been measured in the Earth's atmosphere by means of infrared remote sensing. Vertical profiles of volume mixing ratio were retrieved from 12 solar occultation measurements by the balloon-borne JPL MkIV interferometer between 1993 and 2004. Profile retrieval is possible in an altitude range between 12 and 30 km with a precision of ~20 ppt in the Arctic and ~30 ppt at mid-latitudes. The retrieved CH<sub>3</sub>CN profiles show mixing ratios of 100–150 ppt a few kilometers above the tropopause that decrease to values below 40 ppt at altitudes between 22 and 30 km. The CH<sub>3</sub>CN mixing ratios show a reasonably compact correlation with the stratospheric tracers CH<sub>3</sub>Cl and CH<sub>4</sub>. The CH<sub>3</sub>CN altitude profiles and tracer correlations are well reproduced by a 2-dimensional model, suggesting that CH<sub>3</sub>CN is long-lived in the lower stratosphere and that previously-proposed ion-molecule reactions do not play a major role as loss processes of CH<sub>3</sub>CN. **Citation:** Kleinböhl, A., G. C. Toon, B. Sen, J.-F. L. Blavier, D. K. Weisenstein, and P. O. Wennberg (2005), Infrared measurements of atmospheric CH<sub>3</sub>CN, *Geophys. Res. Lett.*, *32*, L23807, doi:10.1029/2005GL024283.

### 1. Introduction

[2] CH<sub>3</sub>CN (methyl cyanide or acetonitrile) is a long-lived trace gas in the Earth's atmosphere. It is mainly produced in the troposphere by biomass burning. Tropospheric values typically range from about 50 to 150 ppt [Hamm and Warneck, 1990; Singh *et al.*, 2003], although values can be considerably higher in localized areas, e.g. in the outflow of forest fires [Livesey *et al.*, 2004]. A major sink for CH<sub>3</sub>CN is wet removal in the troposphere and deposition in the ocean [Hamm *et al.*, 1984; Singh *et al.*, 2003]. Chemical loss of CH<sub>3</sub>CN is primarily caused by the reaction with OH, although there are still uncertainties about the products of this reaction [Tyndall *et al.*, 2001]. Reactions with O(<sup>1</sup>D) and O(<sup>3</sup>P) can also play a role at stratospheric and mesospheric altitudes [Arjis and Brasseur, 1986].

[3] First indications of the presence of CH<sub>3</sub>CN in the free atmosphere were derived from balloon-borne positive ion composition measurements using mass spectrometry [Arnold *et al.*, 1978]. This was the favored method used in several subsequent in-situ studies of CH<sub>3</sub>CN [e.g., Knop

and Arnold, 1987; Schneider *et al.*, 1997], although more recently in-situ measurements have been performed using gas chromatography [Singh *et al.*, 2003]. Atmospheric CH<sub>3</sub>CN has been measured remotely from space in the microwave region by the Microwave Limb Sounder (MLS) [Livesey *et al.*, 2001, 2004]. In the infrared wavelength region only an upper limit has been reported so far from the analysis of ground-based solar absorption spectra [Muller, 1985].

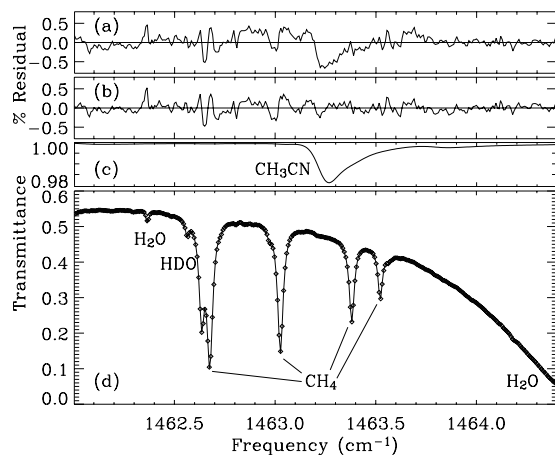
[4] Here we report the first infrared measurements of atmospheric CH<sub>3</sub>CN. Our analysis uses balloon-borne solar occultation measurements by the Jet Propulsion Laboratory (JPL) MkIV interferometer [Toon, 1991] between 1993 and 2004. We demonstrate the capability to retrieve vertical profiles of CH<sub>3</sub>CN in the lower and middle stratosphere, compare the results to previous measurements and 2D-model calculations, and interpret them in the context of atmospheric conditions.

### 2. Spectroscopic Database for CH<sub>3</sub>CN

[5] Until recently the availability of infrared cross-sections for CH<sub>3</sub>CN was limited to data with low spectral resolution obtained at room temperature. Spectroscopic line parameters for CH<sub>3</sub>CN are not part of the HITRAN database [Rothman *et al.*, 2005] and to the knowledge of the authors no linelists exist that would be suitable for the analysis of atmospheric observations with high spectral resolution.

[6] The recent laboratory measurements of CH<sub>3</sub>CN at the Pacific Northwest National Laboratory (PNNL) [Rinsland *et al.*, 2005] provide absorption cross sections of much higher quality (CH<sub>3</sub>CN absorption cross sections are available on the HITRAN Web site, <http://cfa-www.harvard.edu/HITRAN/>). These 29 spectra cover a region between 600 and 6500 cm<sup>-1</sup> with a resolution of 0.1125 cm<sup>-1</sup>, and were measured at three different temperatures (276 K, 299 K, and 324 K). They were recorded with different CH<sub>3</sub>CN volume mixing ratios (VMRs) at ~1 atm pressure using N<sub>2</sub> as pressure broadening gas.

[7] A pseudo-linelist with a pseudo-line spacing of 0.05 cm<sup>-1</sup> was created by fitting the PNNL spectra simultaneously and iteratively adjusting the strengths and ground-state energies of the pseudo-lines (see auxiliary material<sup>1</sup>).



**Figure 1.** Spectral fit to a MkIV limb transmittance spectrum at a tangent altitude of 11.96 km during a solar occultation measurement performed in May 1997. a) Residual without CH<sub>3</sub>CN linelist. b) Residual including CH<sub>3</sub>CN pseudo-linelist. c) Partial transmittance attributed to CH<sub>3</sub>CN. d) Measured transmission spectrum (symbols) and fit including CH<sub>3</sub>CN pseudo-linelist (solid line), and identification of major absorption features.

The pseudo-linelist covers a spectral region between 870 and 1650 cm<sup>-1</sup>, which includes the two bands with the strongest absorption features at 1463.3 cm<sup>-1</sup> and 1042.3 cm<sup>-1</sup>, respectively (a copy of the pseudo-linelist is available from the authors by request).

### 3. Analysis of Solar Occultation Spectra

#### 3.1. Spectral Fitting

[8] In the following paragraphs we show analyses of solar occultation measurements, taken with the JPL MkIV Fourier transform interferometer. The MkIV covers a spectral range between 650 and 5650 cm<sup>-1</sup> with a spectral resolution of  $\sim 0.01$  cm<sup>-1</sup>. During balloon-borne operation, the MkIV instrument views the sun through the atmospheric limb at sunset or sunrise, hence providing a high sensitivity to trace gases due to the long paths through the atmosphere.

[9] The present analysis comprises 12 balloon flights, which were performed between 1993 and 2004. Five flights were launched from Ft. Sumner, NM (34.5°N, 104.2°W), one from Daggett, CA (34.9°N, 116.8°W), two from Fairbanks, AK (64.8°N, 147.7°W), and four from Kiruna, Sweden (67.9°N, 21.1°E). During a sunset or sunrise measurement the duration of a single spectral scan leads to a tangent altitude separation of typically  $\sim 1$  km in the Arctic and 2–3 km at mid-latitudes. The measured sunset and sunrise spectra ratios were obtained using an ex-atmospheric spectrum derived from low-air mass measurements from float altitude. The spectral fitting was performed using a nonlinear least squares algorithm to determine the slant column abundances of each target gas in each spectrum. For a more detailed description of the retrieval process the reader is referred to *Sen et al.* [1996].

[10] Preliminary analyses showed that only the CH<sub>3</sub>CN absorption feature at 1463.3 cm<sup>-1</sup> is sufficiently strong to warrant quantitative analysis at typical atmospheric CH<sub>3</sub>CN

concentrations. A frequency window between 1462.0 and 1464.4 cm<sup>-1</sup> was chosen for analysis. This window contains significant absorptions of CH<sub>4</sub>, H<sub>2</sub>O, HDO, and HCN, so the amounts of these gases were adjusted simultaneously with the CH<sub>3</sub>CN amount. Additionally, a continuum level, a continuum tilt, a frequency shift, and a zero level offset were adjusted during the fitting of the atmospheric spectra.

[11] The H<sub>2</sub>O line parameters were taken from R. A. Toth et al. (Air-broadening of H<sub>2</sub>O as a function of temperature: 696 to 2163 cm<sup>-1</sup>, submitted to *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2005). The line parameters for the other gases were based on HITRAN 2004 [Rothman et al., 2005]. Initial spectral fits revealed some systematic residuals inside the fitting window. These were tracked down to errors in the CH<sub>4</sub> widths and positions. To remedy this deficiency, laboratory measurements of CH<sub>4</sub> from the Kitt Peak National Solar Observatory were analyzed, and line positions and/or broadening coefficients for some lines were adjusted accordingly (see auxiliary material). Additionally a pseudo-linelist for the ethane band centered around 1500 cm<sup>-1</sup>, which is missing in HITRAN, was included to further improve spectral fits.

[12] The diamond symbols in Figure 1d show the measured transmittance spectrum in the frequency window that was analyzed. The major absorption features of CH<sub>4</sub>, H<sub>2</sub>O, and HDO are identified. This particular spectrum was taken on a balloon flight from Fairbanks, AK, on 8 May 1997 at a tangent altitude of 11.96 km.

[13] Figure 1a shows the residual (measured spectrum - calculated spectrum) of a fit to this measurement without taking the CH<sub>3</sub>CN pseudo-linelist into account. The absorption feature of CH<sub>3</sub>CN around 1463.3 cm<sup>-1</sup> can be clearly identified. Other residuals present in Figure 1a correlate with lines of CH<sub>4</sub> (1462.68 and 1463.03 cm<sup>-1</sup>) or H<sub>2</sub>O (1462.37 cm<sup>-1</sup>).

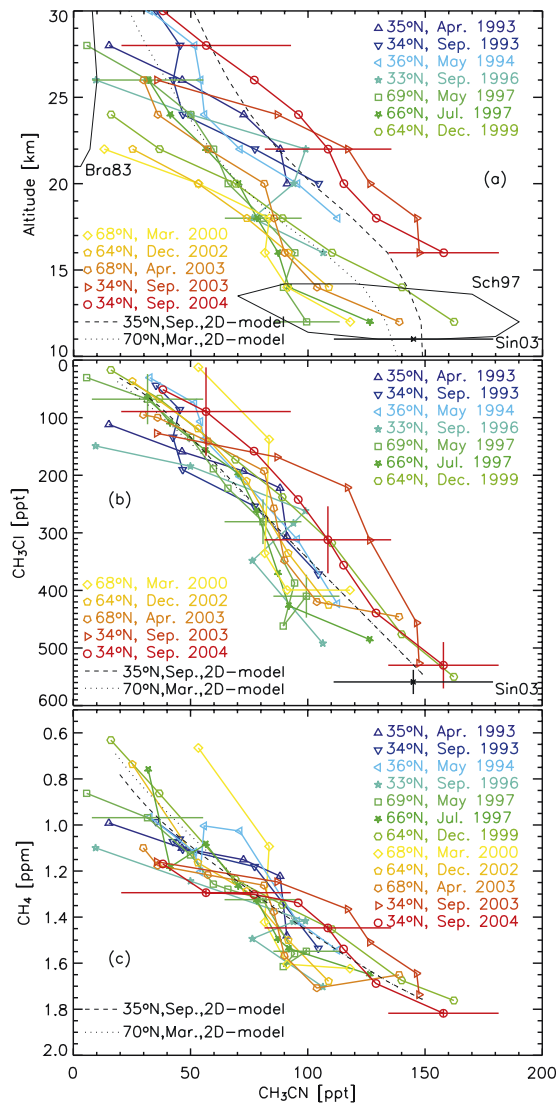
[14] Figure 1b shows the residual when including the new pseudo-linelist for CH<sub>3</sub>CN. The fit in the region around 1463.3 cm<sup>-1</sup> improves considerably, the overall root-mean-square error for the fit in the window decreases from 0.20% to 0.13%. The solid line in Figure 1d shows the actual fit to the measurement.

[15] Figure 1c shows the partial transmission attributed to CH<sub>3</sub>CN. The absorption feature is about 2% deep at this tangent altitude and its shape nicely matches the residual around 1463.3 cm<sup>-1</sup> in Figure 1a.

#### 3.2. Profile Retrieval

[16] To retrieve a vertical profile of CH<sub>3</sub>CN we solve the matrix equation that relates the measured slant columns to the calculated geometrical slant paths on a vertical grid of 2 km spacing. For this, a linear equation solver is used together with a smoothing constraint. Furthermore an a priori constraint is used for altitudes above the balloon.

[17] Figure 2a shows the retrieved CH<sub>3</sub>CN profiles from the 12 balloon flights. All profiles show VMRs around 100–150 ppt at low altitudes that decrease as altitude increases. The highest altitude level given in Figure 2a is the level where the error starts to exceed the retrieved value, for mid-latitude profiles this is the case at 26–30 km, for



**Figure 2.** Retrieved vertical profiles of CH<sub>3</sub>CN from 12 balloon flights between 1993 and 2004 vs. a) altitude, b) CH<sub>3</sub>Cl, and c) CH<sub>4</sub>, measured simultaneously in the same air mass by the MkIV instrument. The error bars give typical precisions for measurements at mid-latitudes (red) and in the Arctic (green). Black solid lines indicate measurements from literature sources (Sin03: mean and std. dev. of airborne gas chromatographic measurements in the upper troposphere [Singh *et al.*, 2003], Sch97: range of airborne mass spectrometric measurements in the lowermost stratosphere assuming a tropopause altitude of 10 km [Schneider *et al.*, 1997], Bra83: range of balloon-borne mass spectrometric measurements summarized by Basseur *et al.* [1983]). Black dashed and dotted lines show profiles calculated with a 2D model.

Arctic profiles this altitude is typically lower (22–24 km). The lowest usable altitude level is determined by the amount of water vapor absorption in the spectrum. Below a certain altitude some of the water vapor lines become very strong and difficult to fit, which disturbs the retrieved

CH<sub>3</sub>CN. This altitude region starts typically below 16 km at mid-latitudes and below 12 km in the Arctic.

[18] The two error bars given in Figure 2a show the precisions derived from the spectral residuals that are typical for retrievals in the Arctic and at mid-latitudes. In the Arctic the precision is in the order of 15–25 ppt, mainly due to longer occultation durations (1–2 hours). At mid-latitudes the shorter occultation duration (~35 minutes) leads to precisions around 25–35 ppt.

[19] Regarding the absolute accuracy of the retrievals, a fit to the 29 PNNL laboratory spectra shows that the pseudolines correctly represent the spectra to within 0.7% of the given CH<sub>3</sub>CN amount in this frequency region (see auxiliary material). We note that an additional uncertainty may arise from the extrapolation of the temperature dependence of the pseudolines from laboratory temperatures to atmospheric temperatures (~220 K). Cross comparisons between different laboratory measurements for several species suggest that the accuracy of the infrared cross-sections used to derive the pseudo-linelist should be in the order of 1.7% [Sharpe *et al.*, 2004]. Other contributions to the uncertainty are interferences with other gases. In the case of the CH<sub>3</sub>CN retrieval these are mainly CH<sub>4</sub> and H<sub>2</sub>O. Assuming that the improvements of the line parameters for the CH<sub>4</sub> are erroneous by 20% leads to a change in CH<sub>3</sub>CN VMR of ~2.5%. For H<sub>2</sub>O the strongest influence is expected to be due to the air broadening and its temperature dependence of the strong H<sub>2</sub>O line at 1464.905 cm<sup>-1</sup>. The uncertainty of these parameters leads to an additional uncertainty in the CH<sub>3</sub>CN VMR of ~1%.

#### 4. Discussion

[20] In the lower stratosphere the profiles retrieved from the MkIV spectra show VMRs around 100–150 ppt (Figure 2a). This compares well to the range given by airborne in-situ measurements in the lowermost stratosphere [Schneider *et al.*, 1997] and the upper troposphere [Singh *et al.*, 2003]. It has to be noted that these values are significantly higher than earlier in-situ measurements [e.g., Knop and Arnold, 1987] and the upper limit obtained from ground-based infrared measurements [Muller, 1985]. They are also higher than the MLS measurements from the 1990s [Livesey *et al.*, 2001] which did not exceed ~50 ppt in the extratropical lower stratosphere.

[21] In the middle stratosphere the mid-latitude MkIV profiles tend to exceed in-situ balloon measurements summarized by Basseur *et al.* [1983] while the error bars of the Arctic MkIV profiles overlap with the range given by these measurements. All profiles show a decreasing CH<sub>3</sub>CN VMR with increasing altitude. Due to the limited precision of the measurements no trend is derived from this data set.

[22] The mid-latitude VMRs generally exceed the Arctic VMRs at the same altitude, reflecting the large scale circulation of air in the stratosphere (i.e. ascending air motion in the tropics and descending air motion in the polar regions). The lower values are particularly visible in the measurements of Dec. 1999, Mar. 2000, and Dec. 2002, which took place inside the Arctic polar vortex

where significant diabatic descent of the air masses had occurred.

[23] We compare the measured CH<sub>3</sub>CN profiles with output of a 2D-model [Rinsland *et al.*, 2003] that uses gas-phase, non-ion CH<sub>3</sub>CN chemistry (see auxiliary material). Figure 2a shows modeled CH<sub>3</sub>CN profiles for 15 Sep. at 35°N and 15 Mar. at 70°N. The modeled profiles agree very well with the measurements in both mid-latitude and Arctic regions.

[24] Figures 2b and 2c show the MkIV CH<sub>3</sub>CN profiles vs. the tracers CH<sub>3</sub>Cl and CH<sub>4</sub> retrieved from the same MkIV balloon measurements. The sources of both tracers are in the troposphere, and the destruction in the stratosphere occurs mainly by the reaction with OH. Considering CH<sub>3</sub>CN VMRs on isopleths of CH<sub>3</sub>Cl or CH<sub>4</sub> should remove the variability induced by the large scale atmospheric circulation [Plumb and Ko, 1992]. The correlations of CH<sub>3</sub>CN with CH<sub>3</sub>Cl and CH<sub>4</sub> are more compact than the correlation with altitude, confirming the tracer characteristics of CH<sub>3</sub>CN in the stratosphere. We note that the CH<sub>3</sub>CN VMRs on isopleths >500 ppt CH<sub>3</sub>Cl compare well to the correlation derived from in-situ data in the upper troposphere [Singh *et al.*, 2003].

[25] Also included in Figures 2b and 2c are the modeled correlations of CH<sub>3</sub>CN with CH<sub>3</sub>Cl and CH<sub>4</sub>. The agreement with the observed CH<sub>3</sub>CN-tracer correlations is excellent. This shows that the model correctly calculates the loss of CH<sub>3</sub>CN in the stratosphere by using the established gas-phase reactions.

[26] Schneider *et al.* [1997] concluded from an observed decrease of CH<sub>3</sub>CN in the lowest 4 km above the tropopause that the lifetime of CH<sub>3</sub>CN should not be much longer than the timescale for vertical mixing (<~1 yr). The compact correlation between CH<sub>3</sub>CN and the tracers derived in this work indicates that CH<sub>3</sub>CN is rather long-lived, with a modeled lifetime of about 10–20 years in the lower stratosphere. This suggests that the ion-molecule reactions proposed by Schneider *et al.* [1997] do not play a major role as loss processes of CH<sub>3</sub>CN.

## 5. Summary and Outlook

[27] For the first time CH<sub>3</sub>CN has been measured in the Earth's atmosphere by means of infrared remote sensing. Vertical profiles were derived in an altitude range of about 12–30 km with a precision of ~20 ppt in the Arctic and ~30 ppt at mid-latitudes. The retrieved CH<sub>3</sub>CN profiles show VMRs of 100–150 ppt a few kilometers above the tropopause that decrease with altitude, reaching values below 40 ppt at altitudes between 22 and 30 km. The CH<sub>3</sub>CN VMRs reveal a reasonably compact correlation with the tracers CH<sub>3</sub>Cl and CH<sub>4</sub> in the considered altitude range, and are in excellent agreement with the 2D-model, which suggests that the known, gas-phase loss mechanisms are fully adequate to explain the abundance of CH<sub>3</sub>CN in the stratosphere.

[28] The demonstration of the retrieval of CH<sub>3</sub>CN vertical profiles in the infrared gives rise to several applications. We expect a retrieval of the kind presented here to be feasible for satellite remote measurements by the Atmospheric Chemistry Experiment (ACE) [Bernath

*et al.*, 2005], with the potential to give a global view on the distribution of CH<sub>3</sub>CN and to investigate the stratospheric source in the tropics suggested by Livesey *et al.* [2001]. The data presented in this paper will be a useful source for validation information for the satellite experiments ACE and the EOS MLS, which are currently in orbit. It is expected that detection of CH<sub>3</sub>CN in the infrared will be feasible also on spaceborne missions to other objects in the solar system, in particular Saturn's moon Titan, where CH<sub>3</sub>CN has already been detected by microwave techniques [Bezard *et al.*, 1993; Marten *et al.*, 2002].

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