

Infrared measurements of atmospheric CH₃CN

Armin Kleinböhl, Geoffrey C. Toon, Bhaswar Sen, and Jean-François L. Blavier
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA

Debra K. Weisenstein

Atmospheric and Environmental Research, Inc., Lexington, Massachusetts, USA

Paul O. Wennberg

California Institute of Technology, Pasadena, California, USA

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[1] For the first time CH₃CN 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 CH₃CN 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 CH₃CN mixing ratios show a reasonably compact correlation with the stratospheric tracers CH₃Cl and CH₄. The CH₃CN altitude profiles and tracer correlations are well reproduced by a 2-dimensional model, suggesting that CH₃CN is long-lived in the lower stratosphere and that previously-proposed ion-molecule reactions do not play a major role as loss processes of CH₃CN. **Citation:** Kleinböhl, A., G. C. Toon, B. Sen, J.-F. L. Blavier, D. K. Weisenstein, and P. O. Wennberg (2005), Infrared measurements of atmospheric CH₃CN, *Geophys. Res. Lett.*, **32**, L23807, doi:10.1029/2005GL024283.

1. Introduction

[2] CH₃CN (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 CH₃CN is wet removal in the troposphere and deposition in the ocean [Hamm *et al.*, 1984; Singh *et al.*, 2003]. Chemical loss of CH₃CN 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(¹D) and O(³P) can also play a role at stratospheric and mesospheric altitudes [Arjis and Brasseur, 1986].

[3] First indications of the presence of CH₃CN 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 CH₃CN [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 CH₃CN 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 CH₃CN. 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 CH₃CN 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 CH₃CN

[5] Until recently the availability of infrared cross-sections for CH₃CN was limited to data with low spectral resolution obtained at room temperature. Spectroscopic line parameters for CH₃CN 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 CH₃CN at the Pacific Northwest National Laboratory (PNNL) [Rinsland *et al.*, 2005] provide absorption cross sections of much higher quality (CH₃CN 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⁻¹ with a resolution of 0.1125 cm⁻¹, and were measured at three different temperatures (276 K, 299 K, and 324 K). They were recorded with different CH₃CN volume mixing ratios (VMRs) at ~ 1 atm pressure using N₂ as pressure broadening gas.

[7] A pseudo-linelist with a pseudo-line spacing of 0.05 cm⁻¹ was created by fitting the PNNL spectra simultaneously and iteratively adjusting the strengths and ground-state energies of the pseudo-lines (see auxiliary material¹).

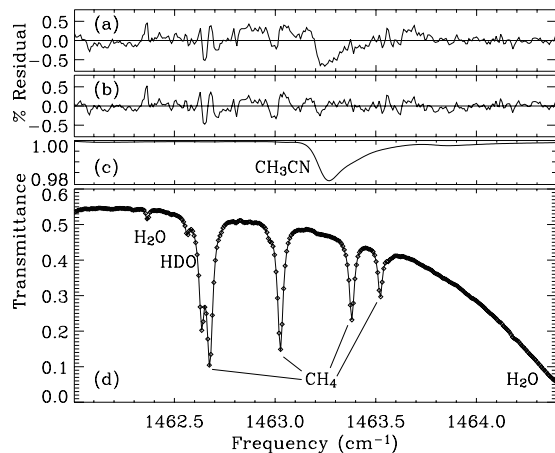


Figure 1. Spectral fit to a MkIV limb transmittance spectrum at a tangent altitude of 11.96 km during a solar occultation measurement performed in May 1997. a) Residual without CH₃CN linelist. b) Residual including CH₃CN pseudo-linelist. c) Partial transmittance attributed to CH₃CN. d) Measured transmission spectrum (symbols) and fit including CH₃CN pseudo-linelist (solid line), and identification of major absorption features.

The pseudo-linelist covers a spectral region between 870 and 1650 cm⁻¹, which includes the two bands with the strongest absorption features at 1463.3 cm⁻¹ and 1042.3 cm⁻¹, 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⁻¹ with a spectral resolution of ~ 0.01 cm⁻¹. 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 ~ 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 CH₃CN absorption feature at 1463.3 cm⁻¹ is sufficiently strong to warrant quantitative analysis at typical atmospheric CH₃CN

concentrations. A frequency window between 1462.0 and 1464.4 cm⁻¹ was chosen for analysis. This window contains significant absorptions of CH₄, H₂O, HDO, and HCN, so the amounts of these gases were adjusted simultaneously with the CH₃CN 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 H₂O line parameters were taken from R. A. Toth et al. (Air-broadening of H₂O as a function of temperature: 696 to 2163 cm⁻¹, 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 CH₄ widths and positions. To remedy this deficiency, laboratory measurements of CH₄ 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⁻¹, 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 CH₄, H₂O, 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 CH₃CN pseudo-linelist into account. The absorption feature of CH₃CN around 1463.3 cm⁻¹ can be clearly identified. Other residuals present in Figure 1a correlate with lines of CH₄ (1462.68 and 1463.03 cm⁻¹) or H₂O (1462.37 cm⁻¹).

[14] Figure 1b shows the residual when including the new pseudo-linelist for CH₃CN. The fit in the region around 1463.3 cm⁻¹ 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 CH₃CN. The absorption feature is about 2% deep at this tangent altitude and its shape nicely matches the residual around 1463.3 cm⁻¹ in Figure 1a.

3.2. Profile Retrieval

[16] To retrieve a vertical profile of CH₃CN 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 CH₃CN 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

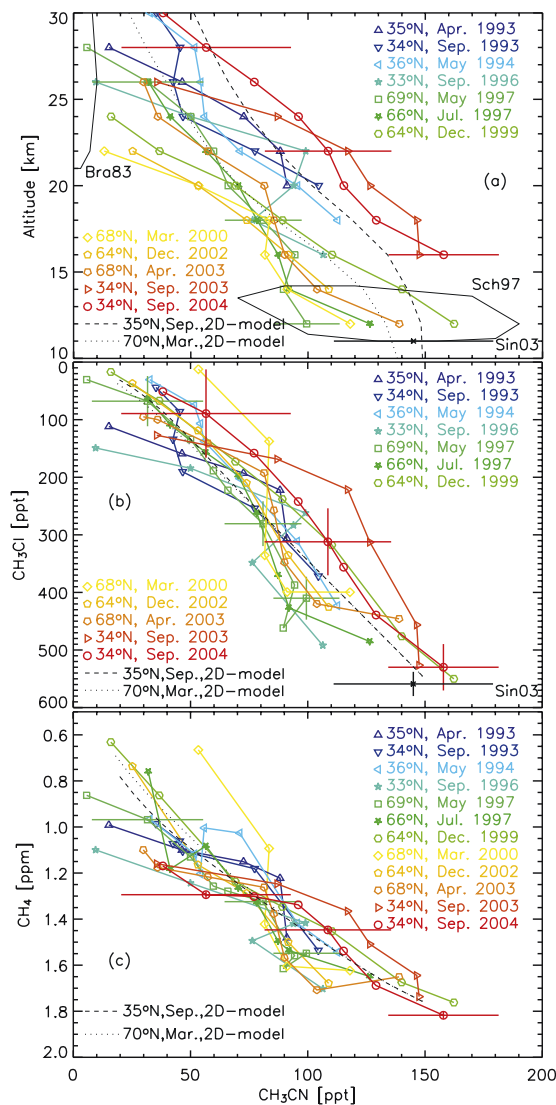


Figure 2. Retrieved vertical profiles of CH₃CN from 12 balloon flights between 1993 and 2004 vs. a) altitude, b) CH₃Cl, and c) CH₄, measured simultaneously in the same air mass by the MkIV instrument. The error bars give typical precisions for measurements at mid-latitudes (red) and in the Arctic (green). 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

CH₃CN. 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 CH₃CN 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 CH₃CN retrieval these are mainly CH₄ and H₂O. Assuming that the improvements of the line parameters for the CH₄ are erroneous by 20% leads to a change in CH₃CN VMR of ~2.5%. For H₂O the strongest influence is expected to be due to the air broadening and its temperature dependence of the strong H₂O line at 1464.905 cm⁻¹. The uncertainty of these parameters leads to an additional uncertainty in the CH₃CN 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 CH₃CN 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 CH₃CN profiles with output of a 2D-model [Rinsland *et al.*, 2003] that uses gas-phase, non-ion CH₃CN chemistry (see auxiliary material). Figure 2a shows modeled CH₃CN 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 CH₃CN profiles vs. the tracers CH₃Cl and CH₄ 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 CH₃CN VMRs on isopleths of CH₃Cl or CH₄ should remove the variability induced by the large scale atmospheric circulation [Plumb and Ko, 1992]. The correlations of CH₃CN with CH₃Cl and CH₄ are more compact than the correlation with altitude, confirming the tracer characteristics of CH₃CN in the stratosphere. We note that the CH₃CN VMRs on isopleths >500 ppt CH₃Cl 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 CH₃CN with CH₃Cl and CH₄. The agreement with the observed CH₃CN-tracer correlations is excellent. This shows that the model correctly calculates the loss of CH₃CN in the stratosphere by using the established gas-phase reactions.

[26] Schneider *et al.* [1997] concluded from an observed decrease of CH₃CN in the lowest 4 km above the tropopause that the lifetime of CH₃CN should not be much longer than the timescale for vertical mixing (<~1 yr). The compact correlation between CH₃CN and the tracers derived in this work indicates that CH₃CN 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 CH₃CN.

5. Summary and Outlook

[27] For the first time CH₃CN 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 CH₃CN 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 CH₃CN VMRs reveal a reasonably compact correlation with the tracers CH₃Cl and CH₄ 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 CH₃CN in the stratosphere.

[28] The demonstration of the retrieval of CH₃CN 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 CH₃CN 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 CH₃CN in the infrared will be feasible also on spaceborne missions to other objects in the solar system, in particular Saturn's moon Titan, where CH₃CN has already been detected by microwave techniques [Bezard *et al.*, 1993; Marten *et al.*, 2002].

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References

- Arjis, E., and G. Brasseur (1986), Acetonitrile in the stratosphere and implications for positive ion composition, *J. Geophys. Res.*, *91*, 4003–4016.
- Arnold, F., H. Böhringer, and G. Henschen (1978), Composition measurements of stratospheric positive ions, *Geophys. Res. Lett.*, *5*, 642–644.
- Bernath, P. F., et al. (2005), Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, *32*, L15S01, doi:10.1029/2005GL022386.
- Bezard, B., A. Marten, and G. Paubert (1993), Detection of acetonitrile on Titan, *Bull. Am. Astron. Soc.*, *25*, 1100.
- Brasseur, G., E. Arjis, A. De Rudder, D. Nevejans, and J. Ingels (1983), Acetonitrile in the atmosphere, *Geophys. Res. Lett.*, *10*, 725–728.
- Hamm, S., and P. Warneck (1990), The interhemispheric distribution and the budget of acetonitrile in the troposphere, *J. Geophys. Res.*, *95*, 20,593–20,606.
- Hamm, S., J. Hahn, G. Helas, and P. Warneck (1984), Acetonitrile in the troposphere, *Geophys. Res. Lett.*, *11*, 1207–1210.
- Knop, G., and F. Arnold (1987), Stratospheric trace gas detection using a new balloon-borne ACIMS method: Acetonitrile, acetone, and nitric acid, *Geophys. Res. Lett.*, *14*, 1262–1265.
- Livesey, N. J., J. W. Waters, R. Khosravi, G. P. Brasseur, G. S. Tyndall, and W. G. Read (2001), Stratospheric CH₃CN from UARS MLS, *Geophys. Res. Lett.*, *28*, 779–782.
- Livesey, N. J., M. D. Fromm, J. W. Waters, G. L. Manney, M. L. Santee, and W. G. Read (2004), Enhancements in lower stratospheric CH₃CN observed by the UARS MLS following boreal forest fires, *J. Geophys. Res.*, *109*, D06308, doi:10.1029/2003JD004055.
- Marten, A., T. Hidayat, Y. Biraud, and R. Morenco (2002), New millimeter heterodyne observations of Titan: Vertical distributions of nitriles HCN, HC₃N, CH₃CN, and the isotopic ratio ¹⁵N/¹⁴N in its atmosphere, *Icarus*, *158*, 532–544.
- Muller, C. (1985), Acetonitrile in the Earth's atmosphere: An upper limit deduced from infrared solar spectra, *Bull. Cl. Sci. Acad. R. Belg.*, *71*, 225–229.
- Plumb, R. A., and M. K. W. Ko (1992), Interrelationships of mixing ratios between long-lived stratospheric constituents, *J. Geophys. Res.*, *97*, 10,145–10,156.
- Rinsland, C. P., D. K. Weisenstein, M. K. W. Ko, C. J. Scott, L. S. Chiou, E. Mahieu, R. Zander, and P. Demoulin (2003), Post-Mount Pinatubo eruption ground-based infrared stratospheric column measurements of HNO₃, NO, and NO₂ and their comparison with model calculations, *J. Geophys. Res.*, *108*(D15), 4437, doi:10.1029/2002JD002965.
- Rinsland, C. P., S. W. Sharpe, and R. L. Sams (2005), Temperature-dependent infrared absorption cross-sections of methyl cyanide, *J. Quant. Spectrosc. Radiat. Transfer*, *96*, 271–280.
- Rothman, L. S., et al. (2005), The HITRAN 2004 molecular spectroscopic data base, *J. Quant. Spectrosc. Radiat. Transfer*, *96*, 139–204.

- Schneider, J., V. Bürger, and F. Arnold (1997), Methyl cyanide and hydrogen cyanide measurements in the lower stratosphere, *J. Geophys. Res.*, *102*, 25,501–25,506.
- Sen, B., G. C. Toon, J.-F. Blavier, E. L. Fleming, and C. H. Jackman (1996), Balloon-borne observations of midlatitude fluorine abundances, *J. Geophys. Res.*, *101*, 9045–9054.
- Sharpe, S. W., T. Johnson, R. Sams, P. Chu, G. Rhoderick, and P. Johnson (2004), Gas-phase databases for quantitative infrared spectroscopy, *Appl. Spectrosc.*, *58*, 1452–1461.
- Singh, H. B., et al. (2003), In situ measurements of HCN and CH₃CN over the Pacific Ocean: Sources, sinks, and budgets, *J. Geophys. Res.*, *108*(D20), 8795, doi:10.1029/2002JD003006.
- Toon, G. C. (1991), The JPL Mk IV interferometer, *Opt. Photonics News*, *2*, 19–21.
- Tyndall, G. S., J. J. Orlando, T. J. Wallington, and M. D. Hurley (2001), Products of the chlorine-atom- and hydroxyl-radical-initiated oxidation of CH₃CN, *J. Phys. Chem. A*, *105*, 5380–5384.

J.-F. L. Blavier, A. Kleinböhl, B. Sen, and G. C. Toon, Jet Propulsion Laboratory, MS 183-501, 4800 Oak Grove Drive, Pasadena, CA 91109, USA. (armin.kleinboehl@jpl.nasa.gov)

D. K. Weisenstein, Atmospheric and Environmental Research, Inc., 131 Hartwell Avenue, Lexington, MA 02421, USA.

P. O. Wennberg, Division of Engineering and Applied Sciences, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125, USA.