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## Measurement of HCN in the middle atmosphere by EOS MLS

H. C. Pumphrey,<sup>1</sup> Carlos J. Jimenez,<sup>1</sup> and J. W. Waters<sup>2</sup>

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[1] The EOS MLS instrument on NASA's Aura satellite has made the first continuous global measurements of HCN in the middle atmosphere. The measurements are in broad agreement with most earlier measurements, showing HCN to be a long-lived tracer with sources in the troposphere and sinks in the middle atmosphere. There is no evidence in the data for a proposed mesospheric source of HCN. **Citation:** Pumphrey, H. C., C. J. Jimenez, and J. W. Waters (2006), Measurement of HCN in the middle atmosphere by EOS MLS, *Geophys. Res. Lett.*, 33, L08804, doi:10.1029/2005GL025656.

### 1. Introduction

[2] It has been known for many years that hydrogen cyanide (HCN) is a minor constituent of the atmosphere. A compilation of early measurements and modelling work [Cicerone and Zellner, 1983] suggests that the gas has its sources at the Earth's surface, its sinks in the middle atmosphere and is well-mixed in the troposphere. A typical tropospheric mixing ratio is about 0.18 ppbv. More recent studies [Li *et al.*, 2000; Singh *et al.*, 2003] suggest a more complex picture in the troposphere, with stronger sources and the ocean as a stronger sink.

[3] In the middle atmosphere, HCN is believed to be lost slowly due to reactions with OH and O<sup>1</sup>D. As a result, the mixing ratio decreases with both altitude and latitude. This picture has, to date, been based on a small number of measurements using various techniques.

[4] The MLS instrument, one of four experiments on NASA's Aura satellite, has made global measurements of HCN continuously since August 2004. The signal from the HCN molecule is not large compared to the instrument noise, so that the measurements are best used to construct weekly zonal means. Despite their limitations, these data allow us, for the first time, to observe the seasonal cycle of middle-atmosphere HCN.

### 2. Measurements

[5] The Microwave Limb Sounder [Waters, 2006, 1999] is essentially a small radio telescope. The 1.6 m dish antenna is moved mechanically so that its field of view scans across the Earth's limb every 24.7 s. The radiation it receives is converted to a lower frequency in several heterodyne mixers (radiometers) and analyzed by 32 spectrometers (28 filter banks and 4 digital autocorrelators). Most of the filter banks are located so that they cover a frequency range centered on a single spectral line of a target

molecule. Microwave spectral lines show strong pressure broadening: a line which is 1 MHz wide at 0.3 hPa (56 km) will be 300 MHz wide at 100 hPa (16 km). For this reason the filter banks are designed with narrower filters at the band center. The heterodyne nature of the radiometers means that each filter bank is affected by two quite separate spectral regions or sidebands, one each side of the local oscillator (LO) frequency. The sideband not containing the target line is not filtered out. Instead, the LO frequency is chosen so that, for the most important measurements, the non-target sideband is in a spectral region with no strong lines.

[6] Hydrogen cyanide is a linear molecule with a large dipole moment. Linear molecules have a simple microwave spectrum, with lines at integer multiples of a fundamental frequency: 88.6 GHz in the case of HCN. (Each HCN line is split into several hyperfine components but these are too close together concern us here.) MLS has two filter banks (Band 6F and Band 27M) which are affected by the second of these lines, which lies at 177.26 GHz. Band 27M was included in the instrument specifically to measure HCN. However, as Figure 1 shows, although HCN is the largest signal in the lower sideband it is small compared to the signals from ozone and nitric acid in the upper sideband. Figure 2 shows some radiances as measured by the instrument. The HCN signal is not large compared to the random measurement noise for a single scan. By averaging the radiances for a week, over a 10° latitude band, the noise is reduced to a level which allows the HCN signal to be observed throughout the middle atmosphere.

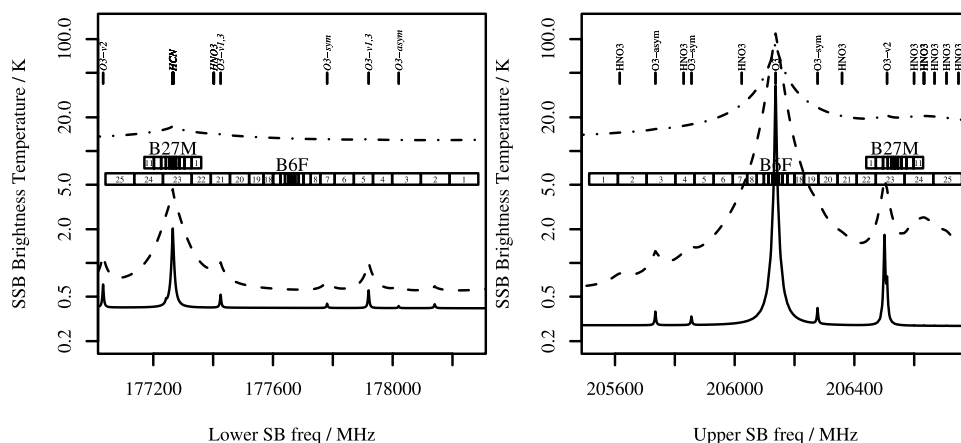
### 3. Retrieval of Mixing Ratios

[7] HCN is one of the products retrieved by the standard MLS retrieval software [Livesey and Wu, 1999; Livesey *et al.*, 2006]. However, the smallness of the signal means that the retrieved product is usable over only a very small vertical range. Above 48 km the signal is lost in the noise. Below 32 km the signal is superimposed on stronger emissions from HNO<sub>3</sub> and O<sub>3</sub>. The current operational retrieval software is unable to obtain usable HCN mixing ratios in these conditions, returning values which have obvious systematic errors, being frequently large and negative.

[8] In order to obtain HCN mixing ratios over a larger vertical range, we form a weekly zonal mean of the radiances and from these retrieve weekly zonal means of temperature and mixing ratio. The calibrated radiance (level 1B) data are provided with tangent altitude  $h_t$  as a vertical co-ordinate;  $h_t$  varies somewhat from one scan to the next. The weekly zonal mean is formed by interpolating the radiances onto a fixed set of tangent height values and taking the mean of these interpolated radiances for all scans within a given week and latitude bin. Operational issues mean that on some

<sup>1</sup>School of GeoSciences, University of Edinburgh, Edinburgh, UK.

<sup>2</sup>NASA Jet Propulsion Laboratory, Pasadena, California, USA.



**Figure 1.** Calculated limb radiances in the (right) upper and (left) lower sidebands of MLS. The solid, dashed and dot-dashed lines are for tangent heights of 45, 31 and 17 km respectively. The molecules responsible for some of the more prominent emission lines are marked at the top of the figure. Note that HCN causes the largest signal in the lower sideband, but that a line of vibrationally excited  $O_3$  appears in almost the same place in the upper sideband.

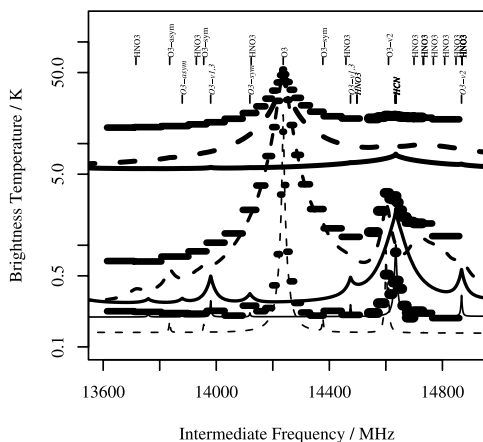
occasions, the 7 days may not be consecutive, but they are spread over no more than 17 days.

[9] The retrieval uses the maximum a posteriori probability (MAP) formula as described by Rodgers [2000]. The a priori mixing ratio for HCN is 0.18 ppbv in the troposphere and decreases monotonically with height throughout the middle atmosphere to a value of 1 pptv at 95 km. As the problem is somewhat nonlinear, the MAP formula is used iteratively, a Marquadt-Levenberg scheme ensures conver-

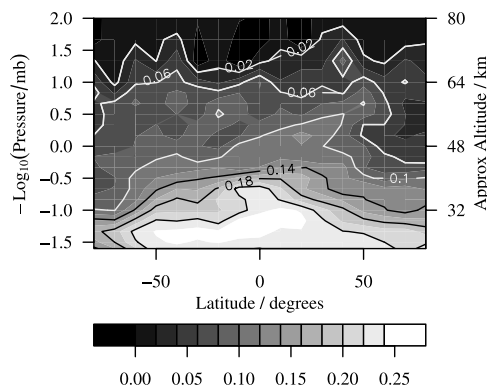
gence. The retrieval is performed in two phases. A first phase estimates the zonal mean temperature  $T$ ,  $O_3$  and the geopotential height  $h_r$  at a reference pressure, using radiances from Band 1F and a few channels from band 6F only. Band 1F is centered on the 118 GHz  $O_2$  line and is the main source of temperature information for MLS. Ozone is retrieved at the same time as there are interfering  $O_3$  lines in band 1F. A second phase adds bands 27M and most of band 6F to the measurement vector, while HCN and  $HNO_3$  are added to the list of quantities estimated. The results of the first phase are used as the starting point for the second phase. The two-phase strategy is used because the temperature retrieval is highly nonlinear and requires more iterations.

#### 4. Results

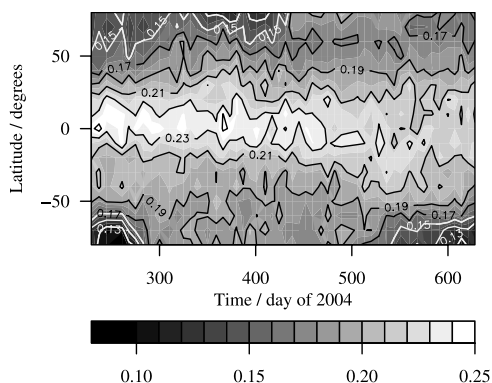
[10] Figure 3 shows a 7-day zonal mean of HCN mixing ratio. The mixing ratios of 0.25 ppmv which occur between 24 and 30 km are somewhat larger than the accepted value in the troposphere. This may be due to spectroscopic uncertainties and should not necessarily be interpreted as a source of HCN in the lower stratosphere. Qualitatively, the values above 24 km are much as one would expect for a



**Figure 2.** Measured radiances in bands 6 and 27 of MLS. The measurements are shown as horizontal bars, the width of the bar indicates the width of the spectrometer channel. Results are shown for three tangent heights: 17, 31 and 45 km. The data are averaged over a  $10^\circ$  latitude band centered on the equator; this reduces the measurement noise from the single-scan values of 0.2–1 K down to 0.007–0.04 K. The lower noise levels correspond to the broader channels. The curves are calculated radiances for tangent heights 17 km (thick), 31 km (medium) and 45 km (thin). Dashed lines are for the upper sideband, solid lines for the lower sideband. Note how the HCN line is clearly separated from the vibrationally excited Ozone line in the upper sideband at 45 and 31 km, but that the two lines merge into one broad feature at 17 km.



**Figure 3.** Weekly zonal mean HCN mixing ratio (in ppbv) for the days centered on 1 September 2004.



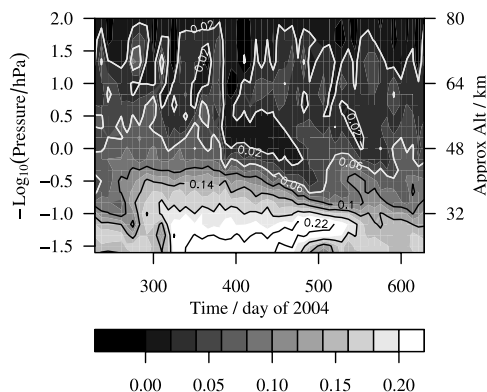
**Figure 4.** Time series of weekly zonal mean HCN mixing ratio (in ppbv) at 10 hPa (approx 32 km). Day 1 is 1 Jan 2004.

tropospheric source gas; they decrease with both altitude and latitude.

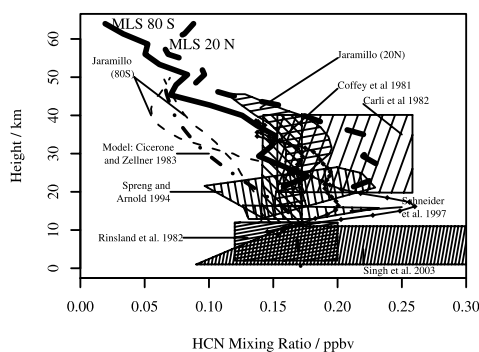
[11] Figure 4 shows a time series of mixing ratio at the 10 hPa pressure level. High values occur in low latitudes at all seasons, and extremely low values are seen in southern high latitudes during the winter; these are caused by the descent of air from the mesosphere in the polar vortex. The decrease in the equatorial values over the 12 months of data shown remains unexplained. However, we note that  $\text{CH}_3\text{CN}$  has been observed to show variability on timescales longer than a year [Livesey *et al.*, 2001]. Figure 5 shows a time series at 80°S. The pattern of decreasing values (and hence downward-sloping contours) for most of the year, with a sharp change as the polar vortex breaks up is also a feature that has been observed in  $\text{CH}_3\text{CN}$  [see Livesey *et al.*, 2001, Figure 5].

## 5. Comparisons With Other Measurements

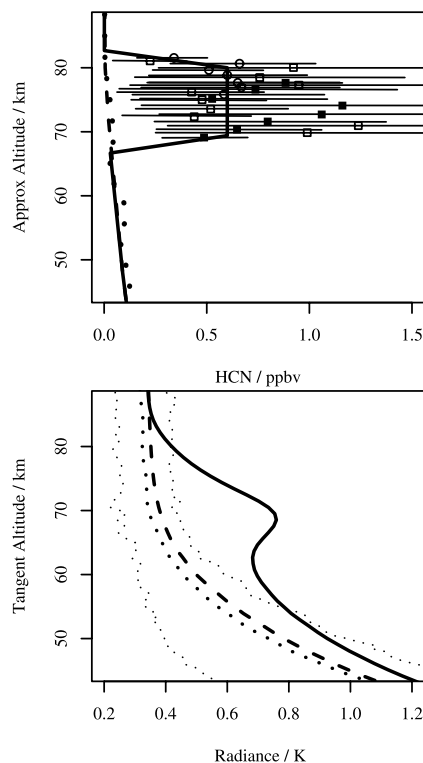
[12] Figure 6 shows the ranges of various HCN measurements, with the MLS data superimposed. The MLS data appear to show a positive bias, with the low-latitude values being greater than those returned by other measurement techniques. The high latitude values are also greater than the one other high-latitude measurement shown. Comparisons with ATMOS data (not shown) also suggest that the MLS data have a positive bias.



**Figure 5.** Time series of weekly zonal mean HCN mixing ratio (in ppbv) at 80°S. Day 1 is 1 Jan 2004.



**Figure 6.** MLS zonal means (thick lines) at 20°N (dashed) and 80°S (solid). Profiles from the MkIV balloon instrument (A. Kleinbohl *et al.*, On the stratospheric chemistry of hydrogen cyanide, submitted to *Geophysical Research Letters*, 2006) taken at 35°N in September 2004 and 2005 are shown black diamonds. The ranges of various historic in situ and ground-based measurements are also shown. Note that recent changes to the HITRAN database have increased the MkIV mixing ratios by 5–9% and would have a similar effect on some of the historical data. (Figure based on Schneider *et al.* [1997, and references therein].)



**Figure 7.** (top) Two HCN profiles (solid and dashed lines) used as input to the forward model. Points with error bars are Kopp's measurements. The dotted line is a retrieved HCN profile. (bottom) Radiance profiles (solid and dashed lines) corresponding to the profiles Figure 7 (top). The thick dotted line is a mean of the 7-day means, taken over all 7-day periods and all latitude bands. The thin dotted lines are the extrema of the 7-day means. For this channel, the noise is  $\approx 1$  K on a single scan and 0.04 K on a 7-day mean.

[13] Above 45 km the mixing ratio decreases with height. No correlative data are available in the lower mesosphere but the measurements of Kopp [1990] show values of 0.2–1.0 ppbv between 70 and 90 km. For these values to be reasonable, there would need to be a reaction producing HCN. Kopp [1990] proposes two possibilities:  $\text{CH}_3 + \text{N} \rightarrow \text{HCN} + \text{H}_2$  and  ${}^3\text{CH}_2 + \text{N} \rightarrow \text{HCN} + \text{H}$ . In both reactions the atomic nitrogen is assumed to be produced in auroral conditions. The MLS signal from these altitudes is small, so that the retrieved zonal mean is strongly affected by the a priori. We therefore ask: what would the radiances be like, if the mixing ratios were similar to those inferred by Kopp? Figure 7 shows two profiles: one being the a priori used for the retrieval, the other being identical except in the region of Kopp's data, where it matches those measurements. Corresponding calculated radiance profiles are also shown in Figure 7 along with the mean and limits of all the  $10^\circ$  7-day means of the MLS data. It is clear that a layer of upper mesosphere HCN of about 0.6 ppbv would cause a signal of about 0.4 K in the center channel of band 27M, and that this signal is not present in the measured data. We can tentatively suggest that the mixing ratio in the mesopause layer is not greater than 0.1 ppbv.

## 6. Conclusions

[14] Qualitatively, HCN as observed by MLS agrees well with that observed in the stratosphere by a variety of techniques and predicted theoretically. Quantitatively, the HCN estimates reported here appear to have a positive bias when compared to earlier measurements. These results make it clear that the MLS technique is a viable way to measure HCN mixing ratio in the middle atmosphere, but that to achieve good results, a system with a lower measurement noise would be required. Figures 1 and 2 suggest that an instrument designed specifically to measure HCN would have to be a single-sideband instrument or have a very different LO frequency from that used by EOS MLS.

[15] Recent work on HCN in the troposphere [Li *et al.*, 2000; Singh *et al.*, 2003] suggests that satellite observations of this molecule in the UTLS region would be valuable for tracking the fate of biomass-burning products. A microwave limb sounding instrument would be one way to achieve this result. The double-sideband nature of EOS MLS means that

routine observations of HCN in the UTLS are not practical. However, a case has been observed [Livesey *et al.*, 2004] in which an unusually large amount of  $\text{CH}_3\text{CN}$  (another biomass-burning product) was injected into the lower stratosphere. It is possible that events of this type would be observable with EOS MLS.

[16] **Acknowledgments.** We thank Armin Kleinboehl and Geoffrey Toon for providing preliminary HCN profiles from the JPL MkIV balloon interferometer. MLS work in the UK is funded by NERC.

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- C. J. Jimenez and H. C. Pumphrey, Institute for Atmospheric and Environmental Sciences, School of GeoSciences, University of Edinburgh, Edinburgh EH9 3JN, UK. (h.c.pumphrey@ed.ac.uk)
- J. W. Waters, NASA Jet Propulsion Laboratory, Mail Stop 183-701, 4800 Oak Grove Drive, Pasadena, CA 91109–8099, USA.