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Measurement of HCN in the middle atmosphere by EOS MLS

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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.


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’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 random measurement noise for a single scan. By averaging the radiances for a week, over a 1° 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 HNO3 and O3. 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 radiances (level 1B) data are provided with tangent altitude h, as a vertical co-ordinate; h 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
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 Marquardt-Levenberg scheme ensures convergence. 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
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 CH$_3$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 CH$_3$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 4. Time series of weekly zonal mean HCN mixing ratio (in ppbv) at 10 hPa (approx 32 km). Day 1 is 1 Jan 2004.

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 ≈1 K on a single scan and 0.04 K on a 7-day mean.
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: CH$_3$ + N $\rightarrow$ HCN + H$_2$ and CH$_2$ + N $\rightarrow$ HCN + 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 radiances 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

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.

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 CH$_3$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.

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References


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