RETRIEVALS of HCN from HIGH-RESOLUTION FTIR SOLAR SPECTRA RECORDED at the JUNGFRAUJOCH STATION

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1. INSTRUMENTATION AND OBSERVATIONAL DATABASE

- Two high-resolution Fourier Transform Infrared (FTIR) spectrometers operated under clear-sky conditions at the International Scientific Station of the Jungfraujoch (ISSJ, 46.5ºN, 8.0ºE, 3580m a.s.l.) which is part of the Network for Detection of Atmospheric Composition Change (NDACC, formerly NDSC, http://www.ndacc.org) primary Alpine station.
- More than 3000 high-resolution (0.004 to 0.009 cm^{-1}) absorption solar spectra relevant to the present study have been recorded regularly at the Jungfraujoch, essentially since the early 1990s.

Limits (cm^{-1})	Fitted species
3267.895 – 3268.300	HCN, H_2O, $H_2{}^{18}O$, $H_2{}^{17}O$
3277.775 – 3277.950	HCN, H_2O
3286.168 – 3288.482	H_2O
3286.950 – 3287.350	HCN, H_2O
3299.120 – 3299.620	HCN, H_2O, $H_2{}^{18}O$
3301.030 – 3301.300	$H_2{}^{17}O$
3304.825 – 3305.600	HCN, H_2O, $H_2{}^{18}O$, $H_2{}^{17}O$, C_2H_2

TABLE 1. List of microwindows used simultaneously to retrieve HCN. Two windows are included to allow precise adjustment of important interfering gases, i.e. H_2O (3286.16 to 3288.48 cm^{-1}) and $H_2{}^{18}O$ (3301.03 to 3301.30 cm^{-1}).

2. RETRIEVAL STRATEGY

- All retrievals have been performed with the SFIT-2 algorithm (v3.91) which is based on a semi-empirical implementation of the Optimal Estimation Method formalism of Rodgers [1]. This code allows to determine information on the vertical distribution of most of the species accessible to the ground-based FTIR technique.
- The latest HITRAN-2004 spectroscopic compilation has been used. The HCN a priori information (vertical distribution and covariance matrix assuming an inter-layer correlation of 4 km for extra diagonal elements) is essentially based on ACE-FTS occultation measurements performed in the 41-51ºN latitude range between March 2004 and September 2006.
- As shown by previous investigations (e.g. [2] and [3]), several lines from the ν_3 fundamental band of hydrogen cyanide (HCN) can be used for its retrieval from ground-based high-resolution IR absorption spectra. A systematic and careful look at ISSJ "dry and wet observations" has allowed to identify 6 candidate lines close to 3268, 3277, 3287, 3299, 3302 and 3305 cm^{-1}. The major interferences are water vapor (H_2O), two of its less abundant isotopologues ($H_2{}^{18}O$ and $H_2{}^{17}O$) and C_2H_2.
- Each of the identified lines has been characterized in terms of information content using a representative subset of spectra. Mean values for the degree of freedom for signal (DOFS) range from 1.1 to 1.6, except for the 3302 feature (DOFS = 0.75) which was subsequently discarded from the list of candidate lines.
- A strategy using simultaneously five HCN lines has therefore been developed and validated; the final adopted settings are summarized in TABLE 1.

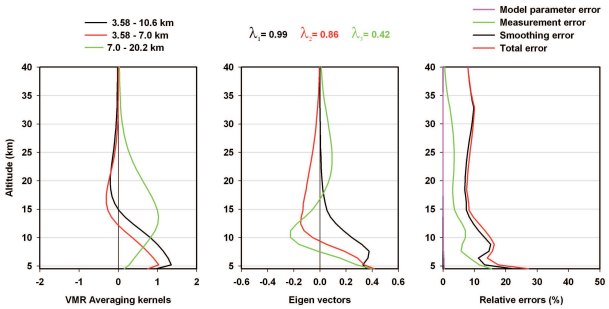

FIGURE 1. Information content expressed in terms of vmr for typical HCN retrievals at the Jungfraujoch station. Left frame shows vmr averaging kernels for selected merged layers. The three first eigenvectors are reproduced in the middle frame. Right frame gives the corresponding error budget, with identification of the main error components.

References

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Acknowledgments

Work at the University of Liège was primarily supported by the AGACC project funded by the Belgian Federal Science Policy Office (SSD Programme), Brussels. We thank the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG, Bern) and the University of Liège for supporting the facilities needed to respectively perform the observations and their analyses. We further acknowledge the vital contribution from all the Belgian colleagues in performing the observations used here.

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Poster presented at the EGU General Assembly 2007, Vienna, Austria, 15-20 April 2007.

3. CHARACTERIZATION OF THE RETRIEVED PRODUCTS

Information content and error budget have been carefully evaluated. FIGURE 1 displays typical results computed for vmr.

- vmr averaging kernels for merged layers are displayed on the left for the 3.58-10.6, 3.58-7.0 and 7.0-20.2 km altitude ranges. The first three eigenvectors and corresponding eigenvalues (see middle frame) show that information on the HCN tropospheric column is coming at 99% from the retrieval; discrimination between partial columns below and above 10 km is also mainly coming from the retrieval (86%). Further vertical resolution is available as indicated by the third eigenvector (in green), but with a more important contribution from the a priori (58%).
- The error budget affecting the retrieved vmrs below 40 km is given in the right panel of FIGURE 1. Total and individual error profiles are provided and identified (see color codes). These typical errors correspond to 5 and 9% of the total and tropospheric columns, respectively.

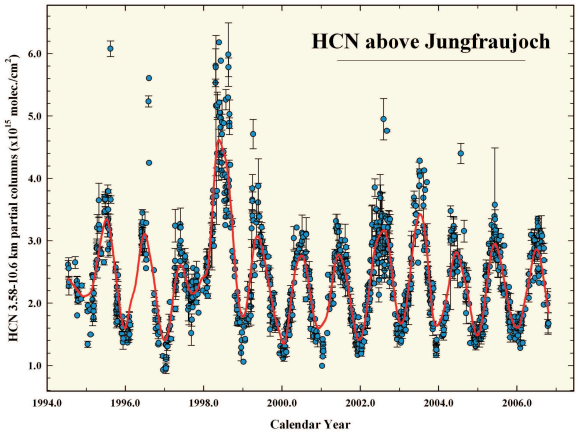

FIGURE 2. Time series of daily mean tropospheric columns of HCN above the Jungfraujoch station. Error bars correspond to the standard deviations around the daily means.

4. HCN TROPOSPHERIC COLUMN TIME SERIES

The retrieval approach described here has been applied to all available Jungfraujoch spectra from 1994 onwards. Resulting time series of daily mean partial tropospheric columns is displayed in FIGURE 2.

- Among striking features, we notice the very high tropospheric columns observed in 1998 (and to a lesser extent in 2003) correlated with documented high values of carbon monoxide resulting from important biomass burning [4]. Biomass burning is indeed believed to be the main HCN source. This characteristic, combined to a lifetime estimated to lie between 2 and 5 months, makes of HCN a useful tracer of emissions associated to intense fires.
- Our measurements also allow to characterize the strong seasonal variation of HCN, with maximum columns generally observed in July. The peak-to-peak amplitude determined for years corresponding to background conditions (here 2000 and 2001) amounts to about 80% of the mean column.