Empirical Pseudo-LineList for Isocyanic Acid: H–N=C=O

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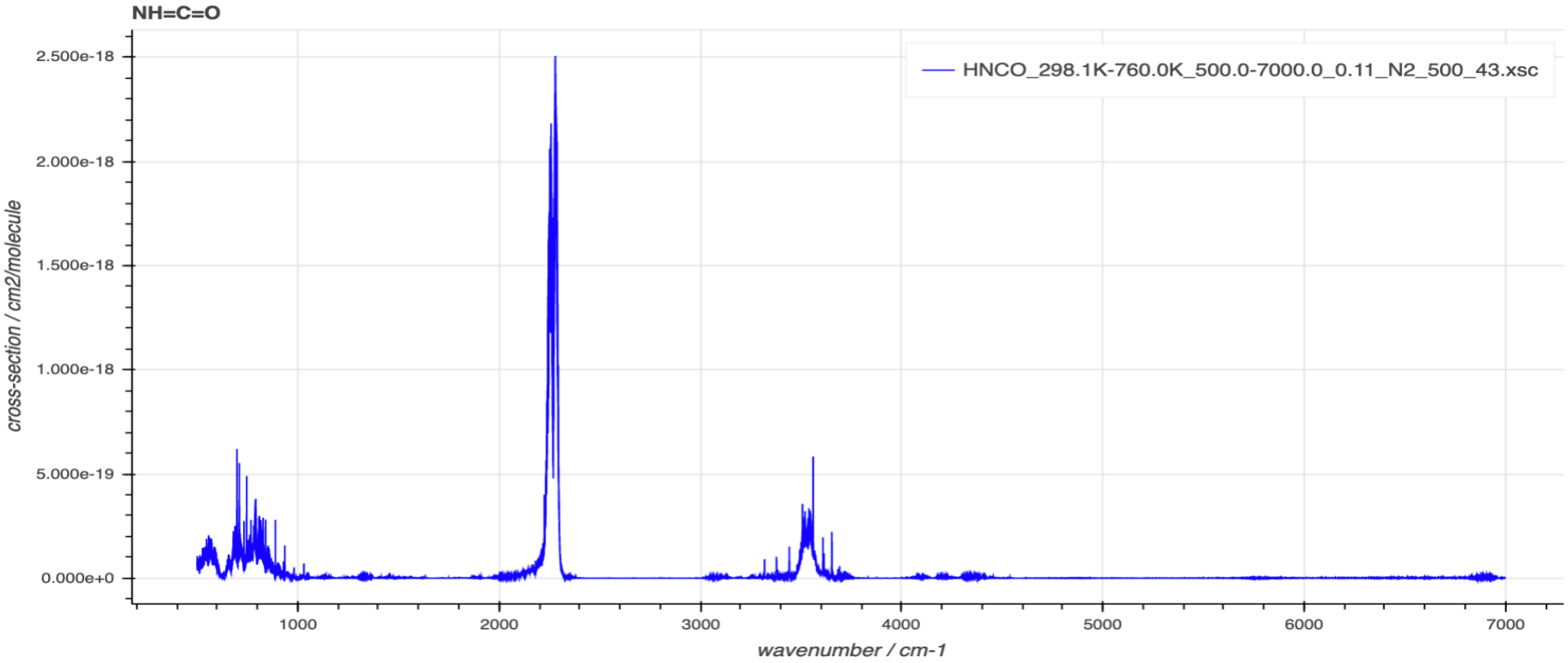
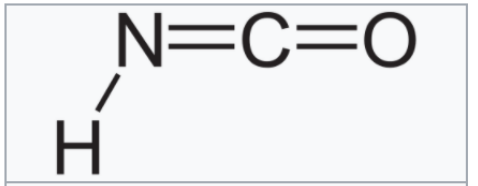
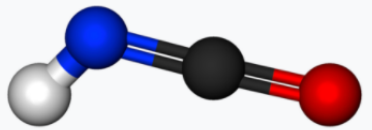
HITRAN does not yet provide a linelist for HNCO, but it does include an absorption spectrum (see figure below). It is evident that the band centered at 2260 cm^{-1} is by far the strongest, but there are lots of interfering absorbers there (CO_2, N_2O, etc.). The bands at 740-950 cm^{-1} are 4x weaker but in a better atmospheric window. The band at 3450-3600 cm^{-1} is completely blacked out from the ground. It could be accessed by solar occultation in the stratosphere, but HNCO amounts will normally be small there.



Isocyanic acid





Names	
IUPAC name	Isocyanic acid
Other names	Carbimide[1]
Identifiers	
CAS Number	75-13-8 ✓ 420-05-3 (cyanic acid) ✓
3D model (JSmol)	Isocyanic acid: Interactive image Cyanic acid: Interactive image
ChEBI	CHEBI:29202 ✓
ChemSpider	6107 ✓
ECHA InfoCard	100.109.068
PubChem CID	6347
UNII	QKG6U31925 ✓ 460E3FHT8O (cyanic acid) ✓
CompTox Dashboard (EPA)	DTXSID9073884
InChI	[show]
SMILES	[show]
Properties	
Chemical formula	CHNO
Molar mass	43.025 $g \cdot mol^{-1}$
Appearance	Colorless liquid or gas (b.p. near room temperature)
Density	1.14 g/cm^3 (20 °C)
Melting point	−86 °C (−123 °F; 187 K)[3]
Boiling point	23.5 °C (74.3 °F; 296.6 K)
Solubility in water	Dissolves
Solubility	Soluble in benzene, toluene, ether

Previous measurements of HNCO: Lab and Atmosphere

HNCO is produced in biomass burning in similar amounts to HCN but with a considerably shorter atmospheric lifetime (months) and so HNCO is much less abundant than HCN in the ambient troposphere (away from fires).

Having 4 atoms, the infrared HNCO spectrum is more complex than that of HCN.

It is currently measured in the atmosphere by in situ techniques (examples below).

Berichte der Bunsengesellschaft für physikalische Chemie

Article

Diode Laser Spectrum of the Fundamental v_2 Band of HNCO

B. Lemoine, Koichi Yamada, G. Winnewisser

First published: September 1982 | https://doi.org/10.1002/bbpc.19820860906 | Citations: 8

Abstract

Infrared spectrum of HNCO near 5 μm was measured by a diode laser spectrometer with source frequency modulation and Stark modulation methods. The subbands of the v_2 fundamental band were identified for K_a = 0 to 4. The subband origins and the effective rotational constants for these subbands were determined. The rotational fine structure of the v_2 band suggests that the levels are perturbed by accidental resonances.

https://doi.org/10.5194/acp-2019-1138
Preprint. Discussion started: 3 February 2020

Atmospheric Chemistry and Physics Discussions

Open Access

Chemical loss processes of isocyanic acid, HNCO, in the atmosphere

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HNCO Laboratory Spectra Analyzed

A single HNCO lab spectra downloaded from the HITRAN website (Supplemental folder). This spectrum was measured by PNNL at 1 atm and T=298K and was illustrated on slide #1.

25 Kitt Peak spectra measured on 870402. These are nominally H_2O spectra but were found to be contaminated with HNCO. The cell pressures varied between 1 and 7 Torr of pure H_2O, and up to 500 Torr of air.

2 more Kitt Peak spectra measured on 950131 and 950201 at 4.8 Torr and 294 K with a 433 m and 193 m paths.

All 27 Kitt Peak spectra were measured at 295-296K.

28 spectra in total.

Empirical Pseudo-Linelist

For the 540-1400 cm^{-1} region, the initial HNCO line positions and intensities were obtained by fitting the high-resolution (MOPD=90 cm, low-pressure Kitt Peak spectrum. 870402R0.006 H2O AT 1 TORR, 23.3 DEGREES, 192 METERS
In this spectrum individual HNCO transitions can be seen.

For the 2200 cm^{-1} region, the Kitt peak spectrum '950131R0.006','H2O 4.8torr 433m, 600-2750cm^{-1}
was used to determine initial line positions and relative intensities. The HNCO vmr is much lower in this spectrum than those measured on 870402 so the HNCO lines are much weaker, despite the longer path and the higher pressure.

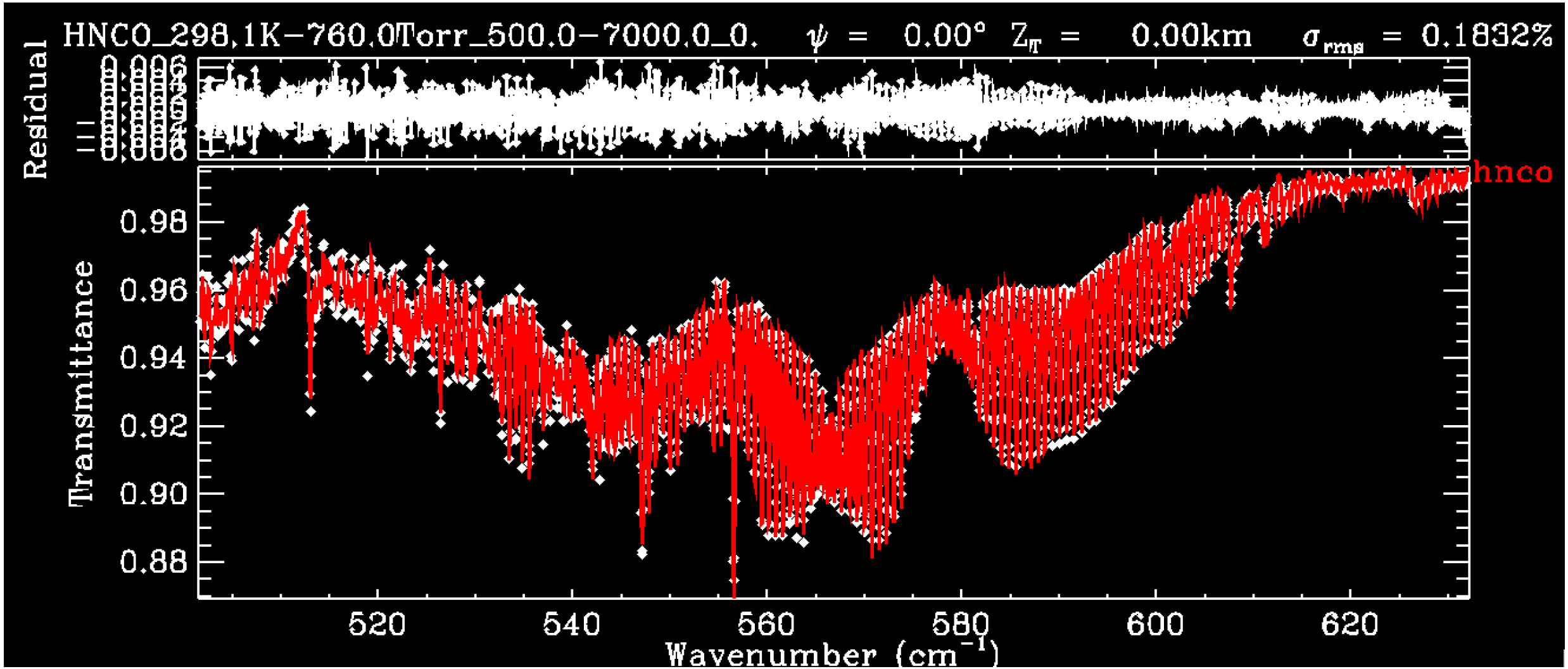
For the 3550 cm^{-1} region only one spectrum was available, that of PNNL.

From this initial linelist, all the spectra were fitted, including PNNL, and the pseudo-line positions and intensities were adjusted iteratively to improve the overall fits to all spectra.

HNCO is assigned the molecule #80 in this linelist.

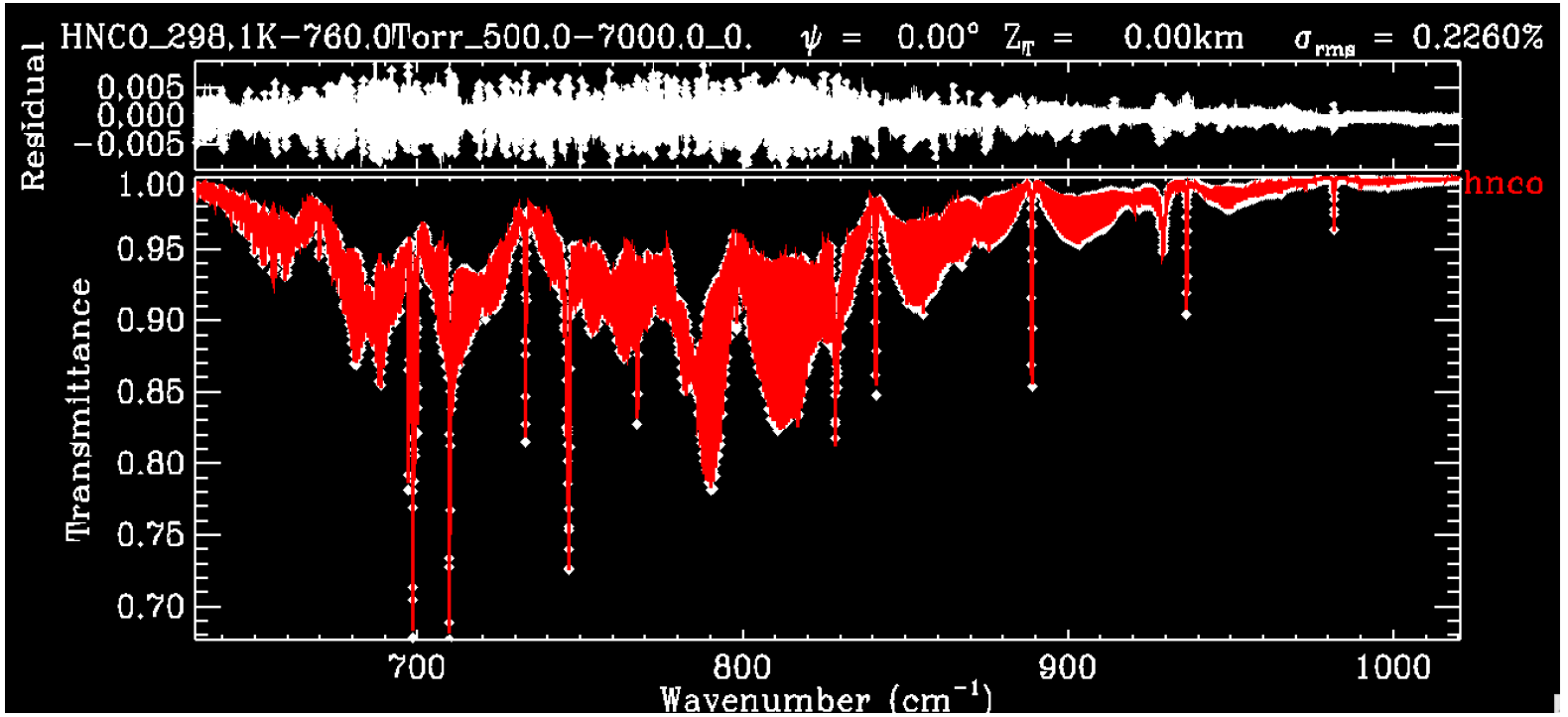
Fit to PNNL lab spectrum using HNCO Empirical Pseudo Line List

Below 630 cm^{-1} spectrum shows rotational structure with a line spacing of ~0.8 cm^{-1}, but absorption is weak (<12%)

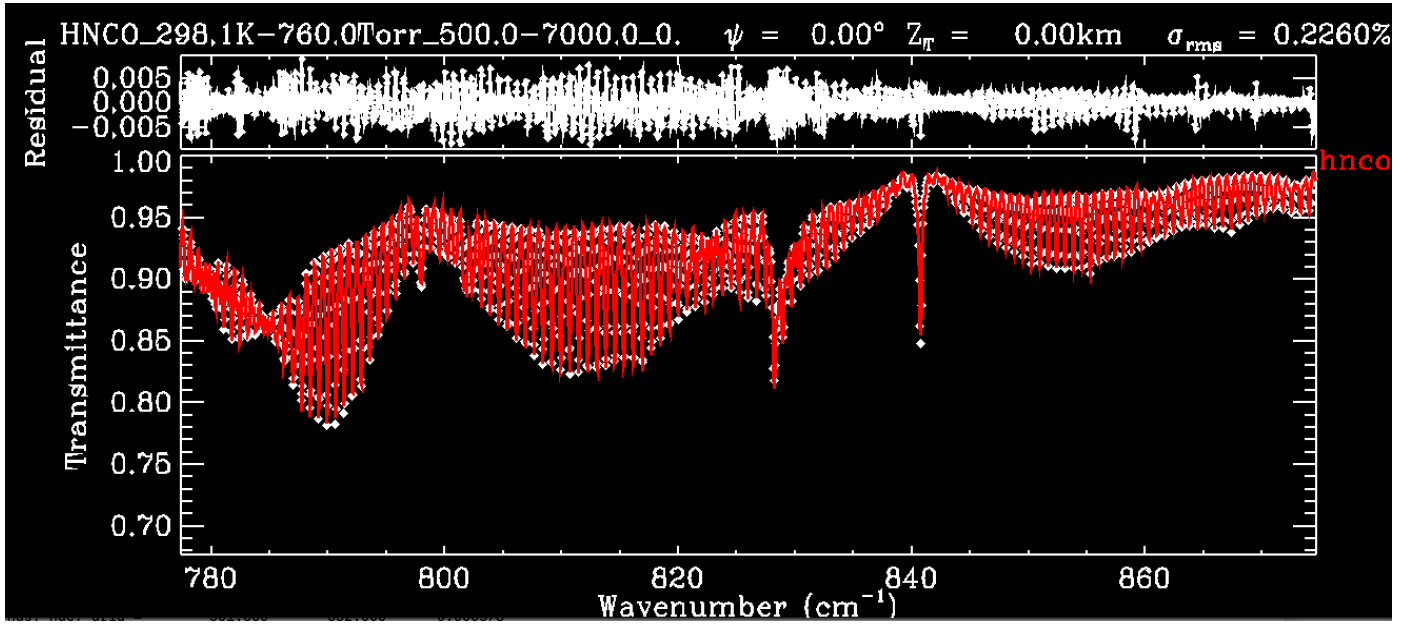


Fit to PNNL lab spectrum at 298K and 1 atm using HNCO Empirical Pseudo Line List

Above 630 cm-1 HNCO absorption is stronger (reaching 32%). HNCO seems to have several overlapping bands in this region all with Q-branches and well resolved P-and R-branch lines. A very distinctive absorption spectrum.



Lower panel zooms into the middle of the upper panel to illustrate the rotational structure, again with a spacing of 0.8 cm^{-1}.



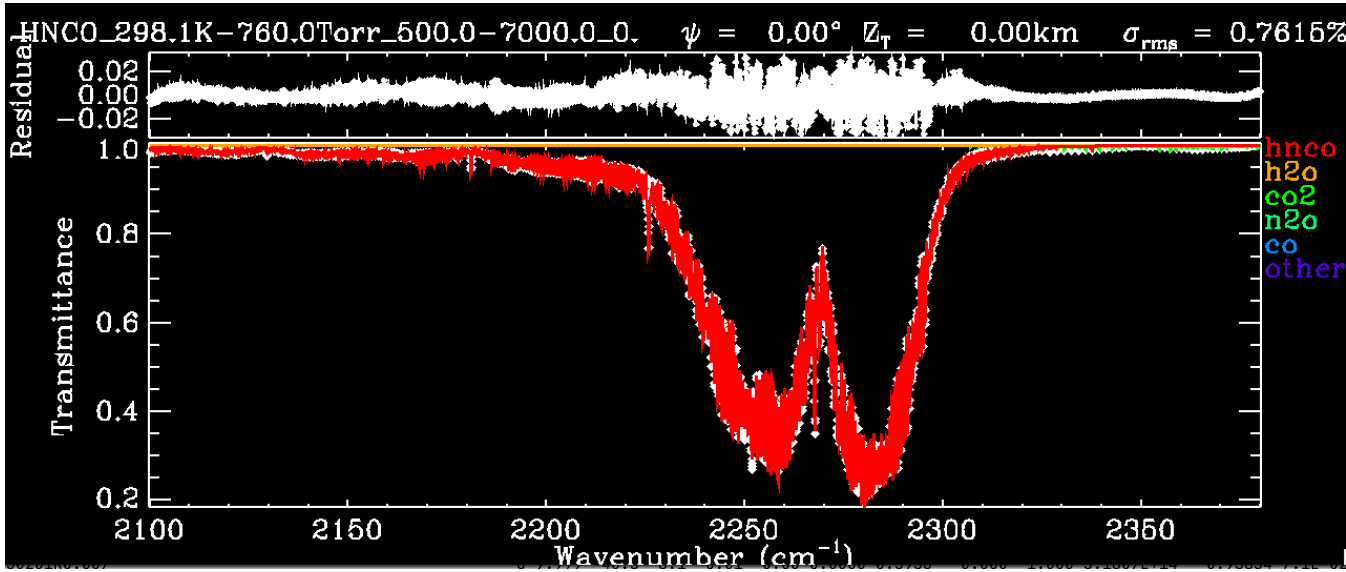
Fit to PNNL lab spectrum using HNCO Empirical Pseudo Line List

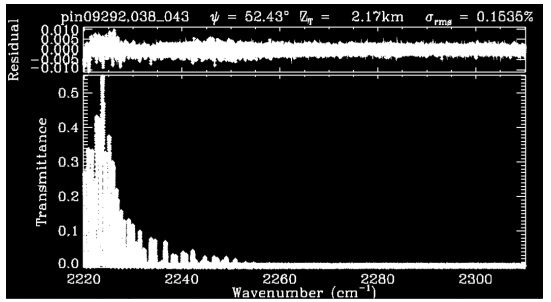
Top Panel: HNCO has its strongest band in the 2220-2300 cm^{-1} region. The main lines in the P- and R-branches are separated by 0.6 cm^{-1}. Q-branch is weak.

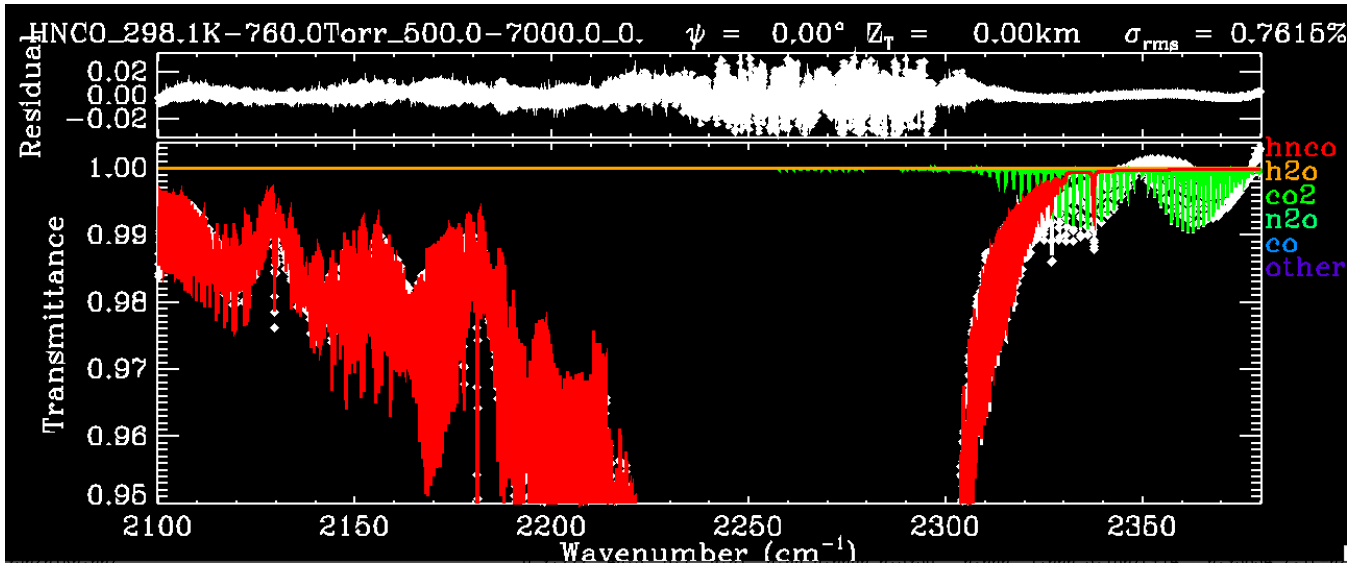
Middle Panel: Fit to ground-based atmospheric spectrum. The 2230-2290 cm^{-1} region is completely blacked out by CO_2 and N_2O; (weaker CO_2 bands than the $^{12}CO_2$ ν_3 band seen in lab spectra, but strong enough to black out the region).

Bottom Panel: Same spectral fit as the top panel, but with the y-scale zoomed in to better see the weak absorptions. Interfering absorption from the $^{12}CO_2$ ν_3 band can be seen (green) between 2310 and 2380 cm^{-1}. This had to be fitted out while the HNCO EPLL was developed to prevent CO_2 absorption being mis-attributed to HNCO when fitting atmospheric spectra.

If HNCO were lofted into the stratosphere, then this 2269 cm^{-1} band, being the strongest, would be the best band to detect it via limb viewing (e.g. solar occultation).

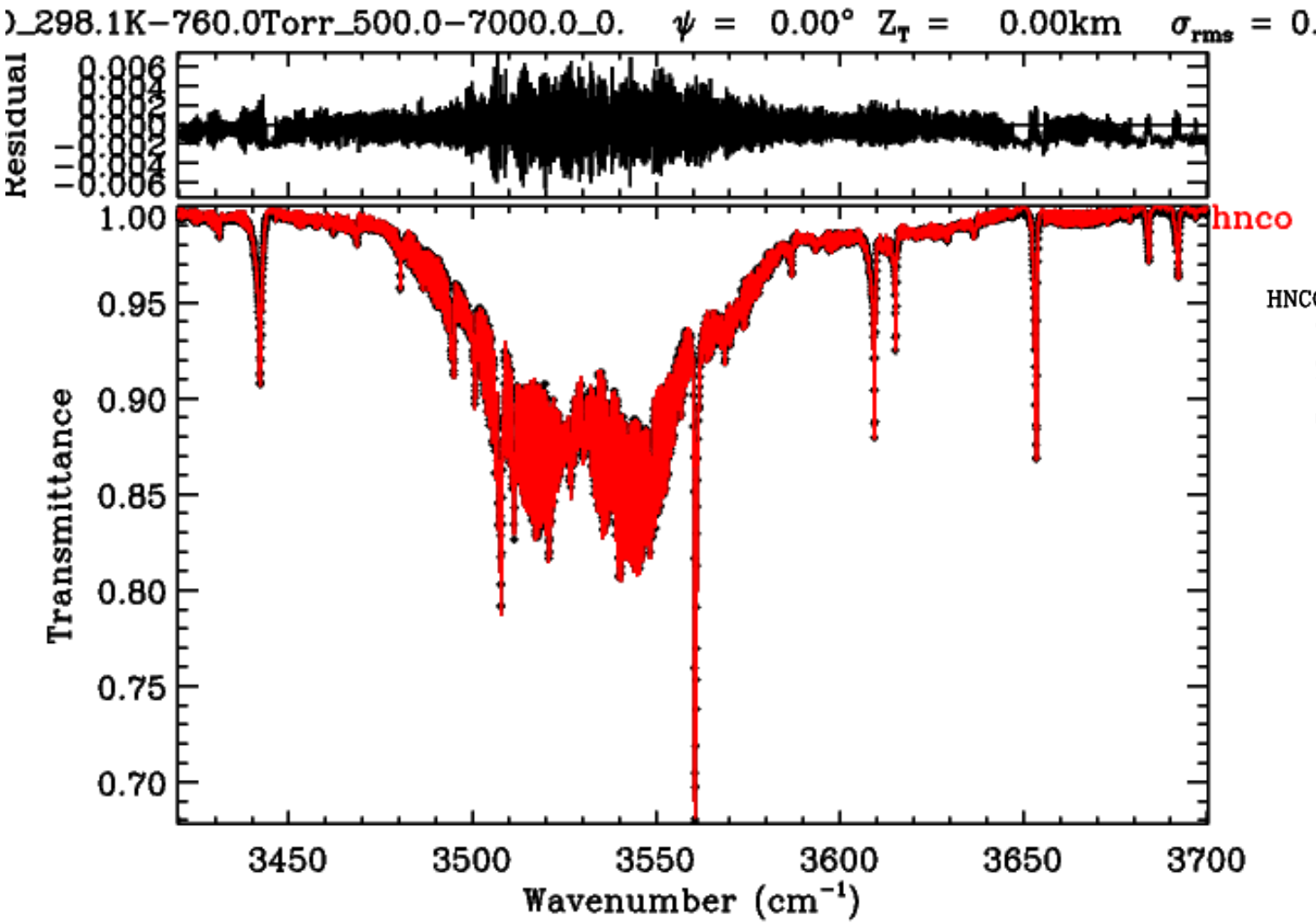




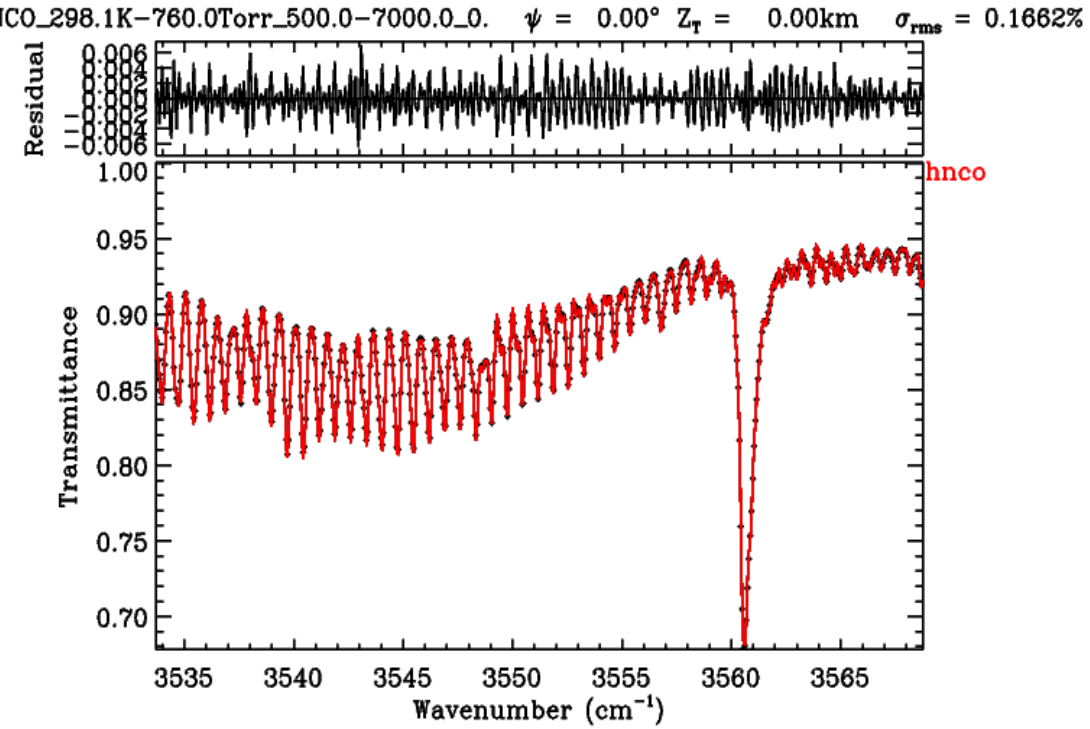


Fit to 3550 cm^{-1} region of PNNL lab spectrum using HNCO EPLL

Fit is very good because only one spectrum was available (PNNL). With more lines a perfect fit could have been achieved, but there is no point.



This region contains regularly-spaced lines of 0.75 cm^{-1} separation several Q-branches.



VSF_HNCO Consistency Across Lab Windows

The .cew file from the 28 spectra in the 6 fitted windows is below.

The window-to-window differences are not statistically significant.

The window centered at 545 cm^{-1} is clearly the worst, due to the weakness of the HNCO lines

Window	VSF	VSF_error	Chi2/N	CC_bar
hnco_545	0.8450	0.1501	0.9695	-0.5964
hnco_590	0.8762	0.0718	0.5481	0.6126
hnco_675	1.0020	0.0744	0.8879	0.6162
hnco_808	0.9932	0.0588	1.3128	0.5930
hnco_953	1.0237	0.0295	0.8419	0.6198
hnco_2240	1.0618	0.1288	0.1511	0.5414

VSF_HNCO Consistency Across Lab Spectra

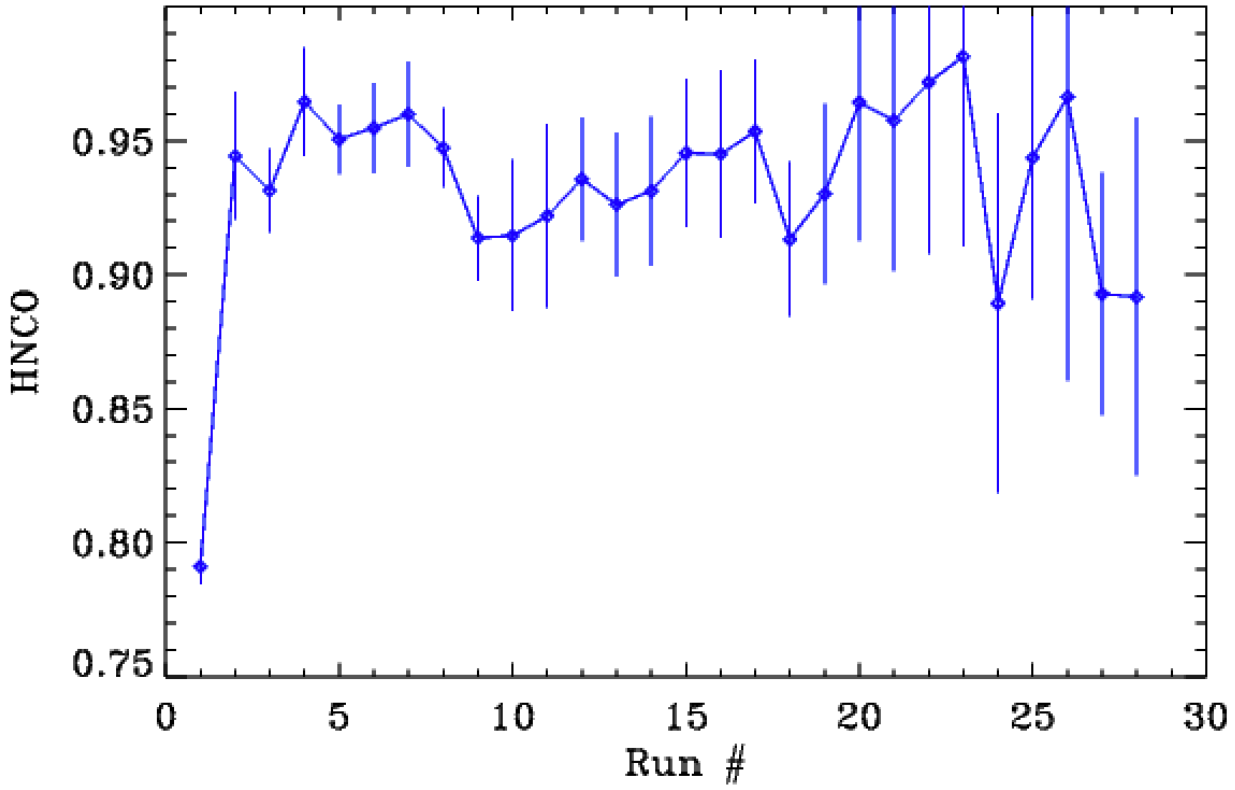
The PNNL spectrum was computed from the cross-sections, assuming a particular cell length and VMR. It is an absolute transmittance spectrum and can be well fitted with NCBF=0

In contrast, the Kitt Peak spectra have an unknown continuum component and therefore must be fitted with a rather large NCBF.

When the PNNL spectrum is fitted with NCBF=0 the resulting VSF values are larger (0.98) than when the spectrum is fitted with non-zero NCBF values (VSF=0.79).

The figure right shows the HNCO VMR Scale Factors for the 28 fitted spectra, using large NCBF values. Spectrum #1 is the PNNL spectrum. Spectra 2-28 are Kitt Peak.

The HNCO gas amounts are unknown for the Kitt Peak spectra, since these spectral are nominally of H_2O. So the fact that they are so consistent and so close to 1.0 is because they HNCO VMRs were adjusted.



HNCO Partition Function

Having 4 atoms, there are 3N-6 = 6 fundamental bands. In computing the vibrational partition function, these were assumed to have a degeneracy of 1 and be centered at wavenumbers:

550, 650, 700, 750, 2268, 3540 cm^{-1}

The rotational partition function was assumed to be $(296/T)^{3/2}$

The resulting entry in the isotopologs.dat file is:

80 1 HNCO Isocyanic Acid 1426 1.000000E-00 0 0 43 0.40 0.000 1.50 6 550 1 650 1 700 1 750 1 2268 1 3540 1

Summary and Conclusions

A linelist with 6117 lines was developed by fitting:

- a PNNL HNCO lab spectrum at 0.06 cm^{-1} resolution (8 cm OPD),
- 25 Kitt Peak spectra measured on 870402
- two KP spectra measured on 960131

In total, 28 spectra. The KP spectra were measured at 295-298K, 1-500 Torr pressure, and with 0.01 cm^{-1} resolution (48 to 94 cm max OPD). These spectra are nominally H_2O, but were found to be contaminated with HNCO, HCOOH, and CH_3COOH.

The HNCO Linelist covers:

- 501-1020 cm^{-1} (3753 lines)
- 2097-2338 cm^{-1} (704 lines)
- 3420-3700 cm^{-1} (1660 lines)

The linefinder program was used to find the positions and intensities of the lines, and the adjust_sf.f program refined these initial estimates after re-fitting the lab spectra using GFIT. This is not a pseudo-linelist of uniformly-spaced lines. The HNCO lines were only placed where needed.

Ground-State energies were all assumed to be 400 cm^{-1}.
ABHW values vary from 0.009 to 0.16 cm^{-1}/atm.
SBHW values vary from 0.40 to 0.50 cm^{-1}/atm.

Evidence of line-mixing was seen in the spectra, e.g. narrowing of Q-branch-like features, which was partially accommodated by narrowing the widths of strong overlapping lines.

Retrievals from MkIV ground-based spectra

Five windows were defined:

```
758.50  25.20  15 1 1 0  ncbf=3  fs  sg  cf  zo :  hnco  co2  h2o  o3  hno3  c2h2
780.95  18.90  15 1 1 0  ncbf=3  fs  sg  cf  zo :  hnco  co2  h2o  o3  clno3
812.25  35.10  15 1 1 0  ncbf=6  fs  sg  cf  zo :  hnco  co2  h2o  o3  chclf2  nh3  clno3  ho2no2
857.95  63.30  15 1 1 0  ncbf=7  fs  sg  cf  zo :  hnco  co2  h2o  hno3  ccl2f2  ccl3f  chclf2  nh3
914.45  49.70  15 1 1 0  ncbf=6  fs  sg  cf  zo :  hnco  co2  h2o  hno3  ccl2f2  nh3  f142b
```

These cover the best window regions in which HNCO absorption signature has distinctive features.

The 758 cm^{-1} window consistently produced negative column HNCO amounts and so was dropped. The remaining 4 windows give surprisingly self-consistent HNCO amounts (see .cew file below), all within 12% of 1.0

Window	VSF	VSF_error	Chi2/N	CC_bar
hnco_780	0.8852	0.7763	0.9912	0.8046
hnco_812	1.0686	0.4884	0.7701	0.8494
hnco_857	0.9314	0.4724	0.8346	0.8585
hnco_914	1.1123	0.7467	1.1502	0.8074

HNCO Retrievals from MkIV ground-based spectra

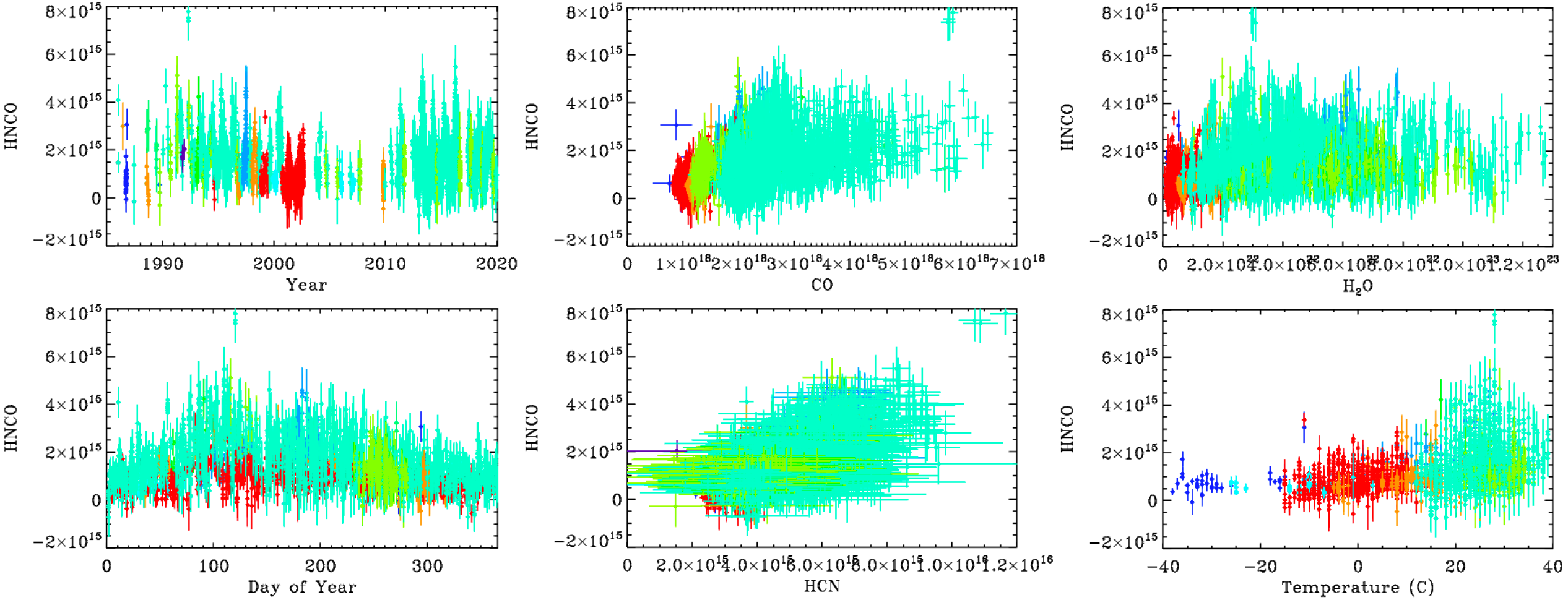


Figure shows retrieved HNCO columns. Points are color-coded by altitude (Blue=0 km, Green =1 km; Orange=2 km; Red=4 km). Columns are in the range 0-4 x 10^{15} molecules.cm^{-2} at JPL (green), with less at other sites. The sites above 2 km (Orange; red) have HNCO in the range 0-2 x10^{15}. There is a seasonal cycle at JPL with a winter minimum. HNCO is somewhat correlated with CO and HCN at JPL. HNCO appears **not** to be correlated with H_2O or temperature. At JPL the HNCO column is about 1/3 of the HCN column, which seems to much. Further sensitivity analyses are needed to determine whether these HNCO retrievals are reliable, or artifacts of the instrument or the spectroscopy.