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 in the cross-section folder (see figure below). The band centered at 2260 cm\(^{-1}\) is by far the strongest and is covered by InSb detectors, but there are lots of interfering absorbers (CO\(_2\), N\(_2\)O, etc.) in atmospheric spectra. The bands at 600-950 cm\(^{-1}\) are 4x weaker but in a better atmospheric window, at least above 740 cm\(^{-1}\). The band at 3450-3600 cm\(^{-1}\) is completely blacked out from the ground.
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).

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**Previous measurements of HNCO: Lab and Atmosphere**

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Article

**Diode Laser Spectrum of the Fundamental $\nu_2$ Band of HNCO**

B. Lemoine, Koichi Yamada, G. Winnewisser

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**Abstract**

Infrared spectrum of HNCO near 5 $\mu$m was measured by a diode laser spectrometer with source frequency modulation and Stark modulation methods. The subbands of the $\nu_2$ 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 $\nu_2$ band suggests that the levels are perturbed by accidental resonances.

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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$_2$O spectra but were found to be contaminated with HNCO. The cell pressures varied between 1 and 7 Torr of pure H$_2$O, 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.
For the 540-1400 cm\textsuperscript{-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 higher wavenumbers, the Kitt peak spectrum '950131R0.006','H2O 4.8torr 433m, 600-2750cm\textsuperscript{-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.

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 $\sim$0.8 cm$^{-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\(_2\)O; (weaker CO\(_2\) bands than the \(^{12}\)CO\(_2\) \(v_3\) 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\(_2\) \(v_3\) 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).
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

<table>
<thead>
<tr>
<th>Window</th>
<th>VSF</th>
<th>VSF_error</th>
<th>Chi2/N</th>
<th>CC_bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>hnco_545</td>
<td>0.8450</td>
<td>0.1501</td>
<td>0.9695</td>
<td>-0.5964</td>
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<td>hnco_590</td>
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<td>0.0718</td>
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<td>hnco_675</td>
<td>1.0020</td>
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<td>0.8879</td>
<td>0.6162</td>
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<tr>
<td>hnco_808</td>
<td>0.9932</td>
<td>0.0588</td>
<td>1.3128</td>
<td>0.5930</td>
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<tr>
<td>hnco_953</td>
<td>1.0237</td>
<td>0.0295</td>
<td>0.86419</td>
<td>0.6198</td>
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<tr>
<td>hnco_2240</td>
<td>1.0618</td>
<td>0.1288</td>
<td>0.1511</td>
<td>0.5414</td>
</tr>
</tbody>
</table>
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\textsubscript{2}O. So the fact that they are so consistent and so close to 1.0 is because they HNCO VMRs were adjusted.
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
A linelist with 4457 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\(_2\)O, but were found to be contaminated with HNCO, HCOOH, and CH\(_3\)COOH.

The HNCO Linelist covers:

- 501-1020 cm\(^{-1}\) (3753 lines)
- 2097-2338 cm\(^{-1}\) (704 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

<table>
<thead>
<tr>
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<th>Chi2/N</th>
<th>CC_bar</th>
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<tr>
<td>hnco_812</td>
<td>1.0686</td>
<td>0.4884</td>
<td>0.7701</td>
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<tr>
<td>hnco_857</td>
<td>0.9314</td>
<td>0.4724</td>
<td>0.8346</td>
<td>0.8585</td>
</tr>
<tr>
<td>hnco_914</td>
<td>1.1123</td>
<td>0.7467</td>
<td>1.1502</td>
<td>0.8074</td>
</tr>
</tbody>
</table>
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 $0-4 \times 10^{15}$ molecules.cm$^{-2}$ at JPL (green), with less at other sites. The sites above 2 km (Orange; red) have HNCO in the range $0-2 \times 10^{15}$. 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$_2$O 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.