ROTATIONAL SPECTRA OF THE MOLECULAR IONS $\text{H}_2\text{NCO}^+$ AND $\text{NCO}^-$

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The H, N, C, O system

✓ 4 main elements in the ISM; > 90 % molecules detected
✓ HNCO observed in over 60 galactic sources and 9 external galaxies
✓ Discovery of isomerization
✓ Cyanic acid and fulminic acid recently observed in interstellar gas
The NCO\(^-\) anion

✓ Closed-shell \(^1\Sigma\) ground state with a very large electron affinity (EA = 3.6 eV)

✓ Several studies on the solid state properties of cyanate ion

✓ IR laser spectroscopy work derived ground state rotational constant and CD quartic term; from CC study dipole moment of \(\mu = 1.5\) D

✓ No-detection search for NCO\(^-\) in dark cloud, L134N by Morisawa et al.

✓ New CCSD(T)/aug-cc-pwCV5Z calculations for nitrogen quadrupole coupling constant (eQq)
Protonated isocyanic acid, $H_2NCO^+$ & $HNCOH^+$

- Isocyanic acid large proton affinity (7.49 eV)
- $C_{2v}$ isomer more stable form by ~ 18 kcal/mol

($\mu_a = 1.3 \text{ D}$, $\mu_b = 1.7 \text{ D}$)

- In the gas phase protonation sequence is:
  $H_3^+ + HNCO \rightarrow H_2 + H_2NCO^+$

($\mu_a = 4.1 \text{ D}$)

- No lab/astro data
- New calculations:
  - $H_2NCO^+$:
    - CCSD(T)/cc-pwCV5Z - CCSD(T)/cc-pVQZ
  - $HNCOH^+$:
    - CCSD(T)/cc-pwCVQZ - CCSD(T)/cc-pVTZ

18 kcal/mol
Detection of the fundamental rotational transition by FTMW spectroscopy

5 - 42 GHz

6 Hz pulsed nozzle to inject the supersonic molecular beam (∼ Mach 2)

$T_{\text{rot}} \sim 1-3$ K

Synthesized isocyanic acid from KOCN + H$_3$PO$_4$

DC discharge of HNCO heavily diluted in a H$_2$ buffer
$J = 1 - 0$

- 4 consecutive scans
- 15 minutes each
- $2\sigma$ from IR rotational constant
- expected 3:5:1 hyperfine ratio

*Lattanzi et al., ApJ in press*
Experimental setup - mm-wave

✓ Mixture of H\textsubscript{2}O and (CN)\textsubscript{2} in an argon buffer, in a room temperature cell
✓ 6 lines detected with this conditions in the 161 - 368 GHz range
$MM$-wave spectrum

$J = 16 - 15$

Frequency (MHz)
### Table 1. Laboratory Frequencies of NCO

<table>
<thead>
<tr>
<th>Transition $J' - J$</th>
<th>Frequency $F' - F$ (MHz)</th>
<th>$O - C$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – 0 1 – 1</td>
<td>23027.659(2)</td>
<td>1</td>
</tr>
<tr>
<td>2 – 1</td>
<td>23027.969(2)</td>
<td>0</td>
</tr>
<tr>
<td>0 – 1</td>
<td>23028.432(2)</td>
<td>0</td>
</tr>
<tr>
<td>7 – 6</td>
<td>161189.304(20)</td>
<td>9</td>
</tr>
<tr>
<td>8 – 7</td>
<td>184214.146(20)</td>
<td>3</td>
</tr>
<tr>
<td>9 – 8</td>
<td>207238.157(20)</td>
<td>29</td>
</tr>
<tr>
<td>10 – 9</td>
<td>230261.101(20)</td>
<td>-21</td>
</tr>
<tr>
<td>13 – 12</td>
<td>299323.109(20)</td>
<td>7</td>
</tr>
<tr>
<td>16 – 15</td>
<td>368372.276(20)</td>
<td>-5</td>
</tr>
</tbody>
</table>

The estimated $1\sigma$ uncertainties are in parentheses.

Calculated from the spectroscopic constants in Table 2.


<table>
<thead>
<tr>
<th>Constant</th>
<th>This work</th>
<th>IR</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>11513.96789(50)</td>
<td>11516.3(13)</td>
<td>11507</td>
</tr>
<tr>
<td>$10^3D$</td>
<td>4.5588(16)</td>
<td>4.62(33)</td>
<td></td>
</tr>
<tr>
<td>$eQq$</td>
<td>-1.0307(37)</td>
<td>-1.00</td>
<td></td>
</tr>
</tbody>
</table>

H$_2$NCO$^+$ & HNCOH$^+$

✓ Under the same experimental conditions, search with FTMW for protonated isocyanic acid
✓ Fundamental rotational transition of H$_2$NCO$^+$ found at 0.02% from the predicted value!!
✓ Soon observed the J(2 - 1) $K_a = 0$ and $K_a = 1$ lower
✓ All the transitions with the expected hyperfine structure
✓ First two $K_a = 0$ rotational transitions of the higher energy isomer (18 kcal/mol) HNCOH$^+$
After the MW detection, mm-wave search

Better condition using the HNCO synthesized sample in a -50 °C cell

A total of 18 mm-wave transitions detected

Up to $K_a = 3$

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<table>
<thead>
<tr>
<th>Constant (MHz)</th>
<th>Laboratory</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>319339(33)</td>
<td>319690.8</td>
</tr>
<tr>
<td>$B$</td>
<td>10278.6785(19)</td>
<td>10280.3</td>
</tr>
<tr>
<td>$C$</td>
<td>9948.9010(14)</td>
<td>9951.8</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>0.381397(85)</td>
<td>0.386</td>
</tr>
<tr>
<td>$10^3 D_J$</td>
<td>3.0604(12)</td>
<td>2.96</td>
</tr>
<tr>
<td>$10^3 D_K$</td>
<td>25.3</td>
<td>25.3</td>
</tr>
<tr>
<td>$10^6 d_1$</td>
<td>$-108.8(16)$</td>
<td>$-96.6$</td>
</tr>
<tr>
<td>$10^6 d_2$</td>
<td>$-41.4(13)$</td>
<td>$-26.2$</td>
</tr>
<tr>
<td>$\chi_{aa}(N)$</td>
<td>3.6263(56)</td>
<td>3.205</td>
</tr>
<tr>
<td>$\chi_{bb}(N)$</td>
<td>1.369(14)</td>
<td>0.932</td>
</tr>
</tbody>
</table>
mm spectrum of $H_2NCO^+$

$J = 17 - 16$

$K_a = 3$

$K_a = 2$

Frequency (MHz)

343713  343718  343723  343728

20 mins
✓ B and D for the anion three orders of magnitude improvement
✓ The entire rotational spectrum can now be calculated well into the THz region to 1 km s$^{-1}$

✓ Two new molecular ions detected for the first time
✓ mm-wave spectrum of $H_2NCO^+$ good for radioastronomical search
✓ Isomer interstellar chemistry
✓ mm-wave search for $HNCOH^+$ in progress
Acknowledgments

✓ Harvard-Smithsonian Center for Astrophysics
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FTM spectrometer

discharge nozzle

Q ~ 40,000

FID ~100 µsec

cooled to 77 K

credit M. C. McCarthy