FIRST OBSERVATION OF THE N₂O-OC VAN DER WAALS COMPLEX AND NEW SET OF EXPERIMENTAL MEASUREMENTS ON THE N₂O-CO COMPLEX.

CLÉMENT LAUZIN, A. J. BARCLAY, S. SHEYBANI-DELOUI, NASSER MOAZZEN-AHMADI
Previous Works (I)

*The C-O Stretching Band of the CO-N₂O van der Waals complex*


First detection!!

Planar semi-rigid system

\[ R_{\text{dim}} = 3.878 \text{ Å} \]

CO stretch
Previous Works (I)

The C-O Stretching Band of the CO-N₂O van der Waals complex

First detection!!
Planar semi-rigid system

\[ R_{\text{dim}} = 3.878 \, \text{Å} \]

\textbf{a}-type transitions only

![Diagram of CO stretch with spectral analysis]
Previous Works (II)

The C-O Stretching Band of the CO-N_2O van der Waals complex

First detection!!
Planar semi-rigid system

\[ R_{\text{dim}} = 3.878 \text{ Å} \]

\( \theta_2 = 20^\circ \pm 5^\circ \)
\( \theta_1 = 80^\circ \pm 5^\circ \)

\[ \text{a-type} \]
transitions only

\[ \text{b-type} \]
transitions only

8 months later

High resolution spectroscopy and structure of CO-N_2O
Hai-Bo Qian and Brian Howard, JMS 184,156-161 (1997)

\( \text{CO stretch} \)
\( \text{NN stretch} \)
Previous Works (II)

The C-O Stretching Band of the CO-N₂O van der Waals complex


8 months later

High resolution spectroscopy and structure of CO-N₂O

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First detection!!
Planar semi-rigid system

\[ R_{\text{dim}} = 3.878 \, \text{Å} \]

\[ \theta_2 = 20° \pm 5° \]
\[ \theta_1 = 80° \pm 5° \]

\[ \tan(\theta) = \frac{\mu_{b_{N_2O}} \sin(\theta_1)}{\mu_{a_{N_2O}} \cos(\theta_1)} = \frac{\mu_{b_{CO}} \sin(\theta_2)}{\mu_{a_{CO}} \cos(\theta_2)} = \tan(\theta_2) \]

We estimated that any perpendicular component was at least 10 times weaker than the parallel component.

<table>
<thead>
<tr>
<th>( \theta (°) )</th>
<th>( \tan(\theta) )</th>
<th>Transition dipole moment ratio</th>
<th>Intensity ratio between the two types of transitions a,b</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.36</td>
<td>7.5 (0.13 )</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.27</td>
<td>14 (0.073)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.18</td>
<td>31 (0.032)</td>
<td></td>
</tr>
</tbody>
</table>
Rotational Spectroscopic investigation of the weak interaction between CO and \( \text{N}_2\text{O} \)
M. Ngarĩ, Y. Xu, W. Jäger, JMS 197,244-253 (1999)

Studied the microwave spectrum of five different isotopologues.

Structural parameters of the CO-N\(_2\)O complex

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effective</th>
<th>Pseudo-substitution</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{\text{dim}} )</td>
<td>3.863</td>
<td>3.879</td>
</tr>
<tr>
<td>( \theta_1 )</td>
<td>80.8</td>
<td>88.7</td>
</tr>
<tr>
<td>( \theta_2 )</td>
<td>10.8</td>
<td>15.7</td>
</tr>
</tbody>
</table>
Important conclusions and predictions:

1. In agreement with M. Ngari, Y. Xu and W. Jaeger about the structure of $N_2O-CO$

2. Evaluation of the intermolecular frequencies of $N_2O-CO$

3. Prediction of the existence of a second isomer O-bounded (Isomer 2, $N_2O-OC$)

4. Calculation of the intermolecular frequencies of $N_2O-OC$. 

Ab initio molecular orbital studies of the vibrational spectra of some van der Waals complexes. Part 3: Complexes of carbon monoxide with carbon dioxide, nitrous oxide, carbonyl sulphide and carbon disulphide

MP2/6-311 +G(d)
Geometry optimization (VERYTIGHT)
Harmonic evaluation of the frequencies
Ab initio molecular orbital studies of the vibrational spectra of some van der Waals complexes. Part 3: Complexes of carbon monoxide with carbon dioxide, nitrous oxide, carbonyl sulphide and carbon disulphide

**Important conclusions and predictions:**

1. In agreement with M. Ngari, Y. Xu and W. Jaeger about the structure of N₂O-CO
   - **Try to observe the missing lines on the fundamental bands**

2. Evaluation of the intermolecular frequencies of N₂O-CO
   - **Try to observe combination bands**

3. Prediction of the existence of a second isomer O-bounded (Isomer 2, N₂O-OC)
   - ?????????

4. Calculation of the intermolecular frequencies of N₂O-OC.
   - ???????
Experimental set-up
1. Trying to observe the missing lines on the fundamental bands


Hai-Bo Qian and Brian Howard, JMS 184, 156-161 (1997)
2. Trying to observe combination bands of $\text{N}_2\text{O-CO}$

a) $\text{N}_2\text{O} \nu_3$ stretch region
2. Measurement of the combination bands of N$_2$O-CO

a) N$_2$O $v_3$ stretch region
2. Measurement of the combination bands of N$_2$O-CO

a) N$_2$O $\nu_3$ stretch region

Experiment

OC-N$_2$O

a-type transitions
2. Measurement of the combination bands of N$_2$O-CO

\[ \tilde{\nu}_0 - \tilde{\nu}(V_{NN}=1) = 24.181 \text{ cm}^{-1} \]

a) N$_2$O $v_3$ stretch region

Experiment

OC-N$_2$O+N$_2$Odimer

N$_2$O dimer

OC-N$_2$O

a-type transitions

$T_{rot} = 2.5$ K

Gaussian line profile with a FWHM = 0.002 cm$^{-1}$
2. Measurement of the combination bands of N$_2$O-CO

b) CO stretch region
2. Measurement of the combination bands of $\text{N}_2\text{O-CO}$

$$\tilde{\nu}_0 - \tilde{\nu}_{(V_{CO}=1)} = 24.2568 \text{ cm}^{-1}$$

b) CO stretch region

b-type transitions
2. Measurement of the combination bands of N$_2$O-CO

\[ \tilde{\nu}_0 - \tilde{\nu}(V_{CO}=1) = 39.571 \text{ cm}^{-1} \]
• Vibrational assignment:

comparison with ab initio prediction and similarities with previous work on CO$_2$-CO
A. Barclay, S. Sheybani-Deloui, K.H Michaelain, A. R. W. McKellar, N. Moazzen-Ahmadi

<table>
<thead>
<tr>
<th>Intermolecular vibration</th>
<th>This work / cm$^{-1}$</th>
<th>Selection rules</th>
<th>$ab$-initio Venayagamoorthy et al.</th>
<th>OC-CO$_2$</th>
<th>$ab$-initio Venayagamoorthy et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO bend or geared motion + NN stretch</td>
<td>24.180</td>
<td>a-type</td>
<td>(29.13)</td>
<td>(24.343)</td>
<td>(24.3)</td>
</tr>
<tr>
<td>CO bend or geared motion + CO stretch</td>
<td>24.256</td>
<td>b-type</td>
<td>(29.13)</td>
<td>24.343</td>
<td>(24.3)</td>
</tr>
<tr>
<td>Out of plane rock + CO stretch</td>
<td>39.571</td>
<td>c-type</td>
<td>(48.51)</td>
<td>43.958</td>
<td>(42.81)</td>
</tr>
</tbody>
</table>

• Summary

More than 300 assigned lines fitted with a residuals of 0.0004 cm$^{-1}$ (12 MHz)--------Agreement for the structure intermolecular potential energy surface seem to be quite harmonic (relatively good agreement with ab initio values)
3. Prediction of the existence of a second isomer O-bounded (Isomer 2, N₂O-OC)

Predicted to be the same structure with the CO flipped by 180°.
3. Prediction of the existence of a second isomer, O-bounded

Experiment

CO-N$_2$O dimer + CO dimer

CO-N$_2$O dimer

CO dimer

CO stretch region

Wavenumber / cm$^{-1}$
3. Prediction of the existence of a second isomer, O-bounded

From the a-type/b-type ratio, $\theta_2$ is larger than for $\text{N}_2\text{O}-\text{CO}$. $22^\circ\pm5$ rather than $10-15^\circ$.

$\theta_1$ is the same as in isomer 1. $R_{\text{dim}}$ is smaller $3.51\,\text{Å}$ instead of $3.87\,\text{Å}$ for $\text{N}_2\text{O}-\text{CO}$. Also detected and assigned in the $\text{N}_2\text{O}$ range.
4. Measurement of the combination bands of N$_2$O-OC

$\tilde{\nu}_0 - \tilde{\nu}_{(v_{O=1})} = 14.502 \text{ cm}^{-1}$

**b-type transitions**
4. Measurement of the combination bands of $\text{N}_2\text{O-OC}$

\[ \tilde{\nu}_0 - \tilde{\nu}_{(V_{CO}=1)} = 21.219 \text{ cm}^{-1} \]

c-type transitions

Wavenumber / cm$^{-1}$
Conclusions

The second isomer exists!!!!

\[ \theta_2 \] is larger in N\(_2\)O-OC than in N\(_2\)O-CO and \( R_{\text{dim}} \) is smaller than for N\(_2\)O-CO.

We measured the intermolecular frequencies

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<th>Intermolecular vibration</th>
<th>This work / cm(^{-1})</th>
<th>Selection rules</th>
<th>Ab-initio Venayagamoorthy et al. /cm(^{-1})</th>
<th>CO-CO(_2)</th>
<th>Ab-initio Venayagamoorthy et al. /cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO bend or geared motion</td>
<td>14.502</td>
<td>a-type</td>
<td>(23.85)</td>
<td>14.19</td>
<td>15.45</td>
</tr>
<tr>
<td>CO stretch region</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Out of plane rock</td>
<td>21.219</td>
<td>c-type</td>
<td>(44.46)</td>
<td>22.68</td>
<td>36.32</td>
</tr>
<tr>
<td>CO stretch region</td>
<td></td>
<td></td>
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</table>

Not a good agreement between ab initio predictions and experimental measurements until now.....

Similarity between CO\(_2\) and N\(_2\)O gets stronger!
Thank you for your attention!!!!!!
3. Prediction of the existence of a second isomer O-bounded (Isomer 2, N₂O-OC)

Experiment

**CO-N₂O dimer+CO dimer**

**CO-N₂O dimer**

**CO dimer**

*He-CO-N₂O ?*

From the a-type/b-type ratio, θ₂ seem to be larger than for isomer 1. ~20° rather than 10-15°
Rotational Spectroscopic investigation of the weak interaction between CO and N$_2$O
M. Ngarĩ, Y. Xu, W. Jäger, JMS 197,244-253 (1999)