Fourier Transform NIR Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (FT-IBBCEAS) of HONO/DONO, HNO₃

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Motivation

a. Spectroscopy

<table>
<thead>
<tr>
<th>ν/cm⁻¹</th>
<th>HONO (cm⁻¹)</th>
<th>DONO (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis</td>
<td>trans</td>
<td>cis</td>
</tr>
<tr>
<td>ν₁</td>
<td>3426.1963(2)</td>
<td>3590.7704(1)</td>
</tr>
<tr>
<td>ν₂</td>
<td>1640.517(1)</td>
<td>1699.7602(1)</td>
</tr>
<tr>
<td>ν₃</td>
<td>1261</td>
<td>1263.2075(4)</td>
</tr>
<tr>
<td>ν₄</td>
<td>851.943(3)</td>
<td>790.171(3)</td>
</tr>
<tr>
<td>ν₅</td>
<td>621.224(2)</td>
<td>618</td>
</tr>
<tr>
<td>ν₆</td>
<td>469.7432(16)</td>
<td>543.8707(7)</td>
</tr>
</tbody>
</table>

High resolution Fourier transform spectra of DONO were first recorded by Halonen et al. [3], who analysed the ν₁, ν₂, ν₃ and ν₄ fundamental bands of tris DONO and the ν₅ fundamental of cis DONO. However, no absorption band of DONO has been measured full date in the NIR region. Detailed studies of the ν₁, fundamental band of tris and cis DONO [2] between 2530 and 3000 cm⁻¹ at 0.01 cm⁻¹ resolution showed that unlike the ν₁ band of HONO, no strong perturbations exist for either isomer of DONO.

b. Atmospheric chemistry

HONO is a precursor of the most important oxidising agent in the troposphere, the hydroxyl (OH) radical. In polluted urban areas, this in turn leads to the formation of green house gases like O₃ and CO₂. The hydrolysis of ONO₂ on heterogeneous surfaces is a well-known mechanism for formation of HONO, resulting in HNO₃, as a by-product. Simultaneous measurement of these species can thus help understand the production of the molecule and the reaction chemistry better.

Experimental Setup

FT-IBBCEAS [3, 4]

• Measures the Fourier transform of the transmitted light intensity through a stable optical cavity (length, d = 6.44 m) consisting of high reflectance mirrors
• All spectra were recorded at a resolution of 0.08 cm⁻¹ between 3500 and 8000 cm⁻¹
• NIR: Less spectral congestion, vibrational overtones’ detection
• The transmission signal strength is measured with and without the absorber present inside the cavity (T₀ and T(α), respectively). From the ratio of the wavelengths-dependent transmitted intensities, the reflectivity of the mirrors R(α) and the sample’s extinction coefficient ε(α) is calculated as

\[ ε(α) = \frac{1}{d} \left( \frac{T_0}{T(α)} \right) - 1 \]

where \( N \) is the number of passes, \( p \) is the path length per pass, \( d \) is the cavity, and \( R(α) \) is the cavity reflectance.

The reflectivity is determined by filling the chamber with a known concentration of CO₂ (pressure P = 6 mbar), and estimating the extinction coefficient based on the absorption cross-section of the sample at a particular wavelength.

Results

Simultaneous detection of HNO₂/HONO/NO₂ in the NIR

• Several rotationally resolved overtone bands of HONO, HNO₃ and NO₂ were detected simultaneously across the NIR spectral range, demonstrating the potential of FT-IBBCEAS to detect multiple trace gases simultaneously through their known line positions.

• Estimated particle densities

\( n_{HNO₂} \approx 2.4\times10^{10} \text{ molecule cm}^{-3} \)
\( n_{HNO₃} \approx 2.7\times10^{10} \text{ molecule cm}^{-3} \)
\( n_{NO₂} \approx 1.6\times10^{10} \text{ molecule cm}^{-3} \)

The NIR spectra of DONO

Experimental (top) and simulated [5] (bottom) spectra at 300 K, 0.08 cm⁻¹ resolution, and the table of spectroscopic constants obtained from PCGopher fit.

References


Acknowledgement

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