Spectroscopy for Industrial Applications: High-Temperature Processes

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Outline

• Hot flow gas cell and FTIR/UV optical set up
• A road to In Situ measurements:
  o NH3 spectroscopy at high-temperatures: band assignment and spectra modelling
  o NH3/H2O field measurements at a pilot scale 6MW gasifier
  o Phenol –major trace gas from PAH’s in low temperature gasification
  o Temperature-dependent UV absorption cross-sections
  o Why In Situ measurements are important: comparison with “standard” tools

• How planets meet the Earth

• Conclusions
Lab (Home work) NH3/Phenol: experimental set up

- 3-zones flow gas cell for corrosive gases;
- No internal windows;
- Stable uniform T-profile (±1.8°C);
- Tmax = 525°C
- L = 33.25 cm
- P = 1 bar
- suitable for UV-FIR optical measurements
- more details: H. Grosch et al. JQSRT 130 (2013) 392–399

- FTIR Spectrometer (Agilent 660), 0.09 cm⁻¹
- an IR light source (up to 1500°C)

- UV spectrometer (Acton 250i/CCD), 0.019 nm
- a highly stable D2-lamp
NH3 FTIR absorption spectra: changes with T

NH3=5% 0.25cm⁻¹ 1027C

NH3=0.983% 0.09cm⁻¹ 500C

NH3=1036 ppm 0.09cm⁻¹ 23C
**NH3 spectroscopy: line assignments, new results**

### Table 1: Lines assigned to previously observed bands

<table>
<thead>
<tr>
<th>Band</th>
<th>J&lt;sub&gt;max&lt;/sub&gt;</th>
<th>K&lt;sub&gt;max&lt;/sub&gt;</th>
<th>Frequency Range cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Number of Lines</th>
<th>J&lt;sub&gt;max&lt;/sub&gt;</th>
<th>K&lt;sub&gt;max&lt;/sub&gt;</th>
<th>Number of Lines</th>
<th>Reference</th>
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<tr>
<td>v&lt;sub&gt;4&lt;/sub&gt;</td>
<td>17</td>
<td>17</td>
<td>1290 - 1868</td>
<td>277</td>
<td>15</td>
<td>15</td>
<td>1663</td>
<td>Cottaz 2000</td>
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<tr>
<td>v&lt;sub&gt;2&lt;/sub&gt;</td>
<td>20</td>
<td>20</td>
<td>634 - 1333</td>
<td>385</td>
<td>23</td>
<td>20</td>
<td>177</td>
<td>Yu 2010</td>
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<tr>
<td>v&lt;sub&gt;2&lt;/sub&gt;+v&lt;sub&gt;4&lt;/sub&gt;-v&lt;sub&gt;2&lt;/sub&gt;</td>
<td>12</td>
<td>12</td>
<td>1412 - 1818</td>
<td>83</td>
<td>10</td>
<td>15</td>
<td>384</td>
<td>Cottaz 2001</td>
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<tr>
<td>2v&lt;sub&gt;2&lt;/sub&gt;</td>
<td>16</td>
<td>15</td>
<td>1407 - 1870</td>
<td>43</td>
<td>15</td>
<td>15</td>
<td>403</td>
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<tr>
<td>2v&lt;sub&gt;2&lt;/sub&gt;-v&lt;sub&gt;2&lt;/sub&gt;</td>
<td>18</td>
<td>18</td>
<td>607 - 1236</td>
<td>180</td>
<td>10</td>
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<td>12</td>
<td>1104 - 1652</td>
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<td>10</td>
<td>15</td>
<td>132</td>
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</table>

### Table 2: Lines assigned to previously unobserved bands* with 10 or more lines assigned in this work.

<table>
<thead>
<tr>
<th>Band</th>
<th>J&lt;sub&gt;max&lt;/sub&gt;</th>
<th>K&lt;sub&gt;max&lt;/sub&gt;</th>
<th>Frequency Range cm&lt;sup&gt;-1&lt;/sup&gt;</th>
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<td>11</td>
<td>622 - 1013</td>
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<td>5</td>
<td>1430 - 1792</td>
<td>10</td>
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<tr>
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<td>8</td>
<td>5</td>
<td>1420 - 1805</td>
<td>10</td>
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<tr>
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<td>13</td>
<td>680 - 1270</td>
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<td>12</td>
<td>9</td>
<td>628 - 743</td>
<td>12</td>
</tr>
</tbody>
</table>

*Have not found measurements in published works.
## NH₃ spectroscopy: line assignments, an example

### List of Assigned Lines

<table>
<thead>
<tr>
<th>BYTEe Frequency</th>
<th>Experimental Frequency</th>
<th>Obs - Calc</th>
<th>Upper Quantum Numbers*</th>
<th>Lower Quantum Numbers*</th>
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<tbody>
<tr>
<td>968.761998</td>
<td>968.825639</td>
<td>0.063641</td>
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<td>+0 1 0 0 0 0 16 16</td>
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<td>970.332898</td>
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<tr>
<td>971.871137</td>
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<tr>
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<td>-0 1 0 0 0 0 13 2</td>
</tr>
<tr>
<td>972.363167</td>
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<td>972.801729</td>
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<td>+0 1 0 0 0 0 18 18</td>
</tr>
</tbody>
</table>

*Parity v₁ v₂ v₃ v₄ l₃ l₄ J K
Can we use BYTe at 500C for practical apps?

- in general a good agreement
- some difficulties with strong line intensities
- some frequency shifts in line positions

More work to do at even higher $T (>500C)$
• Very complex producer gas composition (CO2, H2O, CO, H2, HC, PAH, tars) + particles
• Producer gas is fed into an industrial burner of a power plant

Why to do it? (examples):
• H2O (related to mass balance)
• NH3 (related to NOx formation)

How?: In Situ IR abs measurements: no gas extraction
• Tough: out of the building on a platform (safety) with limited space (practical issues);
• Tgas about 530C;
• optical measurements over 30 cm;
• very strong any (UV-IR) light attenuation.
Lab (Home work) | Phenol UV absorption cross-sections: experimental set up

1. Gas mixing unit
   - N₂ (industrial standard)
   - molten aromatic crystals in tube
   ⇒ concentration unknown
   - admixture of N₂ for different concentration

2. Gas cell and optics

3. Petersen column
   - sampling in acetone
   - Sampling time 30 min
   - analysis with GC/MS

Measurements strategy:
• At each T two phenol concentrations
• At each concentration two sample
• During each sampling three UV spectra and three double concentration determination
Lab (Home work) Phenol UV absorption cross-sections: temperature effects

• Not too many reference data available even at low T (about 23C)
• An excellent agreement with published data at low T
• Significant changes in the fine structure of the cross-section spectra with T

Low-temperature abs cross-sections: comparison

Abs cross-sections: from 23C to 500C
In Situ measurements on LT-CFB (100kW) gasifier

- Focus on trace gases in low- and high-temperature gasification processes;
- Producer gas issues:
  - corrosion (boilers)
  - reduced gas quality (fuel cells, gas grids)
- Phenol – major trace gas from PAH’s in the producer gas (LT-CFB process);
- \( T_{\text{gas}} = 300-500 \degree C \); In Situ UV abs measurements over 3 mm;
- Phenol measurements by various techniques:
  - GC/MS (Petersen column (30 min) 215 ppm (±5%)
  - Gas extraction, 150 C: 407 ppm (±5%) (3 min)
  - In Situ, 306 C (DOAS approach): 7700 ppm (±10%) (3 min)
Industry and Universities

How other planets meets the Earth

- Far away planets on a global scale (e.g. exoplanets, stars) and current Earth’s problems on a local scale (energy, emissions, taxes)

- Spectroscopy of hot planets and high-temperature processes: the same gases/temperatures of interest;

- DTU’s projects about optical measurements in combustion (SO2, SO3, NH3, etc), gasification (trace gases, Cl-compounds) and waste utilization in collaboration with industry (DONG Energy, Vattenfall and Babcock & Wilcox Vølund)

- UCL’s and DTU’s common PhD/postdocs projects: SO3/SO2 and Cl-compounds (KCl, HCl, CH3Cl, CH4, H2CO)
Conclusions

In general

- You can find a lot inspirations for the work on the Earth
- Different research areas can have the same origin
- Scientists can make industry guys happy

In particular:

- Excellent experimental tools are available for (VUV) UV-FIR optical measurements
- Temperature range can be also negative (e.g. gases at low T)
- New data/lines for NH3 BYTe extension and development
- New data for phenol
- Try always In Situ and avoid any Ex Situ (extraction) measurements
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• To MST.dk

• To DONG Energy and Vattenfall

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