Spectroscopy for Industrial Applications: High-Temperature Processes

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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
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

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NH3 spectroscopy: line assignments, new results

Table 1: Lines assigned to previously observed bands

<table>
<thead>
<tr>
<th>Band</th>
<th>$J_{\text{max}}$</th>
<th>$K_{\text{max}}$</th>
<th>Frequency Range cm$^{-1}$</th>
<th>Number of Lines</th>
<th>$J_{\text{max}}$</th>
<th>$K_{\text{max}}$</th>
<th>Number of Lines</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_4$</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>
</tr>
<tr>
<td>$v_2$</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>
</tr>
<tr>
<td>$v_2$+$v_4$-$v_2$</td>
<td>12</td>
<td>12</td>
<td>1412 - 1818</td>
<td>83</td>
<td>10</td>
<td>20</td>
<td>384</td>
<td>Cottaz 2001</td>
</tr>
<tr>
<td>$2v_2$</td>
<td>16</td>
<td>15</td>
<td>1407 - 1870</td>
<td>43</td>
<td>15</td>
<td>15</td>
<td>403</td>
<td>Cottaz 2000</td>
</tr>
<tr>
<td>$2v_2$-$v_2$</td>
<td>18</td>
<td>18</td>
<td>607 - 1236</td>
<td>180</td>
<td>10</td>
<td>10</td>
<td>32</td>
<td>Singh 1988</td>
</tr>
<tr>
<td>$3v_2$-$v_2$</td>
<td>12</td>
<td>12</td>
<td>1104 - 1652</td>
<td>18</td>
<td>10</td>
<td>10</td>
<td>132</td>
<td>Cottaz 2001</td>
</tr>
</tbody>
</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>$J_{\text{max}}$</th>
<th>$K_{\text{max}}$</th>
<th>Frequency Range cm$^{-1}$</th>
<th>Number of Lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_4$-$v_2$</td>
<td>11</td>
<td>11</td>
<td>622 - 1013</td>
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<tr>
<td>$2v_4$-$v_4$</td>
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<td>1430 - 1792</td>
<td>10</td>
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<tr>
<td>$2v_4$-$v_4$</td>
<td>8</td>
<td>5</td>
<td>1420 - 1805</td>
<td>10</td>
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<tr>
<td>$v_2$+$v_4$-$v_4$</td>
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<td>13</td>
<td>680 - 1270</td>
<td>77</td>
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<tr>
<td>$3v_2$-$2v_2$</td>
<td>14</td>
<td>12</td>
<td>628 - 1455</td>
<td>31</td>
</tr>
<tr>
<td>$3v_2$-$3v_2$</td>
<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>BYTE Frequency</th>
<th>Experimental Frequency</th>
<th>Obs - Calc</th>
<th>Upper Quantum Numbers*</th>
<th>Lower Quantum Numbers*</th>
</tr>
</thead>
<tbody>
<tr>
<td>968.761998</td>
<td>968.825639</td>
<td>0.063641</td>
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<td>+0100001616</td>
</tr>
<tr>
<td>970.332898</td>
<td>970.874628</td>
<td>0.54173</td>
<td>-020000143</td>
<td>+010000133</td>
</tr>
<tr>
<td>971.871137</td>
<td>971.868991</td>
<td>-0.002146</td>
<td>-01000021</td>
<td>+00000011</td>
</tr>
<tr>
<td>972.159794</td>
<td>972.456569</td>
<td>0.296775</td>
<td>+020000142</td>
<td>-010000132</td>
</tr>
<tr>
<td>972.363167</td>
<td>972.60723</td>
<td>0.244063</td>
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<td>-0100001717</td>
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<tr>
<td>972.801729</td>
<td>973.330403</td>
<td>0.528674</td>
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</tr>
<tr>
<td>974.317864</td>
<td>974.354898</td>
<td>0.037034</td>
<td>-01010131</td>
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</tr>
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<td>975.511534</td>
<td>975.530054</td>
<td>0.01852</td>
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<td>-00010122</td>
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<tr>
<td>976.392929</td>
<td>976.449086</td>
<td>0.056157</td>
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<td>+0100001818</td>
</tr>
</tbody>
</table>

*Parity v1, v2, v3, v4, l3, l4, J, K
Lab (Home work)  NH3: experiment (0.09cm-1) vs calculations (BYTe)

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)
From Lab to Field | In Situ measurements on Pyroneer (6MW) gasifier

- 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

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Phenol UV absorption cross-sections: temperature effects

- Not too many reference data available even at low T (about 23°C)
- 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 23°C to 500°C
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);

• \( T_{gas} = 300-500^\circ C \); 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:
  o Excellent experimental tools are available for (VUV) UV-FIR optical measurements
  o Temperature range can be also negative (e.g. gases at low T)
  o New data/lines for NH3 BYTe extension and development
  o New data for phenol
  o Try always In Situ and avoid any Ex Situ (extraction) measurements
Industry and Universities

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