Identifying and using advantages and limitations of laboratory and theoretical spectroscopy: $H_2O$ and $CO_2$ line lists for HITRAN and HITEMP

Iouli E. Gordon
Laurence S. Rothman
Pros and Cons of Experimental Data

• Advantages
  • Low uncertainty in determining parameters of relatively strong unblended lines
  • Direct observation of perturbations which often hard to account for with theoretical methods

• Disadvantages
  • Large uncertainty in determining parameters of weak or saturated lines
  • Sensitivity to impurities and congested spectra
  • Difficulties in controlling the conditions
  • Difficulties in covering large spectral and dynamic ranges simultaneously
Intercomparison of experimental measurements of water lines air-broadening in different laboratories

Data from different laboratories

![Graphs showing intercomparison of water lines air-broadening in different laboratories](image-url)
Intercomparison of experimental data

Pros and Cons of Theoretical and Semi-Empirical Data

**Advantages**
- Completeness, i.e. prediction of parameters that could not be measured by experiment
- Can be easily adjusted to match high quality experiments

**Disadvantages**
- Rarely can compete with experimental uncertainty
- Sometimes the model is oversimplified
- Semi-empirical methods often lead to large errors when used for extrapolating the data
CO$_2$ data assembly for HITRAN2008 in the operational region of GOSAT and OCO-2 satellites
Sources for CO$_2$ data (4300-7000 cm$^{-1}$)
## Assessment of Sources for CO$_2$ data (4300-7000 cm$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th><strong>Pros</strong></th>
<th><strong>Cons</strong></th>
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</table>
| **JPL-OCO (FTS experiments)** | • Very accurate observations for the strongest bands  
• Pressure shifts and self and air broadening coefficients | • Incomplete $< 10^{-26}$ cm$^{-1}$/(molecule cm$^{-2}$)  
• Extrapolations down to  
$4 \times 10^{-30}$ cm$^{-1}$/(molecule cm$^{-2}$) show large deviations  
• Traceability |
| **CRDS (Grenoble)**   | • Nearly complete above  
$5 \times 10^{-29}$ cm$^{-1}$/(molecule cm$^{-2}$) | • Typical accuracy $1 \times 10^{-3}$ cm$^{-1}$  
• (1250) - 1428 -1705 nm  
• (8000) - 7000 - 5850 cm$^{-1}$ |
| **CDSD (Effective Hamiltonian Calculations)** | • Complete (at least for 626, 636 and 628)  
• Excellent predictive abilities for positions and intensities | • Interpolyad coupling  
• Cannot reproduce JPL accuracy |
Algorithm for CO$_2$ assembly in HITRAN (4300-7000 cm$^{-1}$)

1. OCO, CRDS, CDSD line lists
   - Is $S_{OCO} > 10^{-26}$ for $^{17}$CO$_2$ or $S_{OCO} > 10^{-27}$ for other isotopologues? Yes → No → Does transition exist in CRDS and is not blended? Yes → Take OCO line position and intensity → Add pressure-induced parameters from OCO line list → HITRAN2008 CO$_2$ line list for 4300 to 7000 cm$^{-1}$ region
   - Is $S_{OCO} > 10^{-26}$ for $^{17}$CO$_2$ or $S_{OCO} > 10^{-27}$ for other isotopologues? No → Does transition exist in CDSD? Yes → Take CDSD position and intensity → Add pressure-induced parameters from OCO line list → HITRAN2008 CO$_2$ line list for 4300 to 7000 cm$^{-1}$ region
   - Does transition belong to $^{17}$O$^{12}$C$^{18}$O or $^{18}$O$^{13}$C$^{18}$O? Yes → Take CRDS experimental line positions and intensities and supplement with CDSD intensities if needed → Add pressure-induced parameters from OCO line list → HITRAN2008 CO$_2$ line list for 4300 to 7000 cm$^{-1}$ region
   - Does transition belong to $^{17}$O$^{12}$C$^{18}$O or $^{18}$O$^{13}$C$^{18}$O? No → Ignore transition → HITRAN2008 CO$_2$ line list for 4300 to 7000 cm$^{-1}$ region

Note: The flowchart diagram is a visual representation of the algorithm described above. Each decision point is connected to the next step based on the outcome of the previous decision.
H$_2$O data assembly for HITEMP2010 (reliable for up to 4000 K) in the 0-30,000 cm$^{-1}$ region
H$_2$O: BT2 line list

http://www.tampa.phys.ucl.ac.uk/ftp/astrodata/water/BT2/

- PES fit B of Shirin et al. (2003), based on *ab initio* surface with adjustments for electronic relativistic and adiabatic effects and fitted to the available experimental data
- File#1: 221,100 energy levels (up to J=50, E = 30,000 cm$^{-1}$)
  14,889 experimentally known
- File#2: 506 million transitions (PS list has 308m), references for upper and lower levels in File#1, provides Einstein-A coefficient for the transition
## Comparison with Experimental Levels

<table>
<thead>
<tr>
<th>Agreement:</th>
<th>BT</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within 0.10 cm$^{-1}$</td>
<td>48.7</td>
<td>59.2</td>
</tr>
<tr>
<td>Within 0.33 cm$^{-1}$</td>
<td>91.4</td>
<td>85.6</td>
</tr>
<tr>
<td>Within 1 cm$^{-1}$</td>
<td>99.2</td>
<td>92.6</td>
</tr>
<tr>
<td>Within 3 cm$^{-1}$</td>
<td>99.9</td>
<td>96.5</td>
</tr>
<tr>
<td>Within 5 cm$^{-1}$</td>
<td>100.0</td>
<td>97.0</td>
</tr>
<tr>
<td>Within 10 cm$^{-1}$</td>
<td>100.0</td>
<td>98.1</td>
</tr>
</tbody>
</table>

*Number of Experimental Levels: 14,889*
How to improve line positions?

• It is very time consuming to collect all the line positions directly measured in the high-temperature experiments. There are problems with ambiguous assignments and misassignments.

• The preliminary IUPAC effort has collected about 15,000 energy levels derived from numerous experiment. One can create a database of all allowed transitions (over 3.5 million) between these energy levels. These differences were used to replace the theoretical ones wherever possible.
New HITEMP Water List Assembly

List created using BT2 database
- for principal isotopologue, created at 296K
with lines that have significant intensity at up to
4000K, $J \leq 50$

Convert to HITRAN format

Based on quantum numbers, replace line positions with the ones generated from the
EXPERIMENTALY determined energy levels
(when available)

Einstein A-coefficients, Statistical weights

HITEMP Water Line List

Line-shape parameters (widths, shifts, etc)
Validation with High-Temperature Experiments

Comparison of new high-temperature laboratory data (1200K H$_2$O) from Stanford University with HITRAN2008, HITEMP1995, and HITEMP2010

Conditions: T = 1200 K, 25 Torr Neat H$_2$O, 152.4 cm path length

HITEMP 2010 revisions improve simulation at 7471.61 and 7472.05 cm\(^{-1}\) 1200K. Only minor differences between simulations and SU data remain.

Conditions: T = 1200 K, 25 Torr Neat H\(_2\)O, 152.4 cm path length

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- R. Barber, J. Tennyson (BT2 linelist water)
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