Updates for O₃ fundamentals spectroscopic database

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Initial Background/Introduction

- Atmospheric $O_3$ columns from IR 4% larger than from UV (Brewer)
- Either IR cross sections too small or UV cross sections too large
- DLR work: Intended measurement of FIR/MIR/UV of the same gas sample
- In the frame of ESA-funded project “SEOM - Improved Atmospheric Spectroscopy Databases (IAS)”, partners: Uni Reims, Uni Grenoble, LISA, KIT

Initial goal: Absolute line intensities of $O_3$ fundamentals
New MIR measurements

• Initial assumption: relative line intensities of ozone correct
• 2 measurements: pure ozone at 23 mbar, 293K and 11 mbar, 233 K, absorption path 22 cm, 700-1200 cm\(^{-1}\)
• Advantage of high ozone pressure:
  • Column amount can be determined to sub-percent level from pressure measurements – ozone decomposition <1%, leak and outgassing negligible
  • Significant Lorentzian broadening reduced instrumental lineshape error
• Disadvantage:
  • Strong lines saturated in \(\nu_3\), weak lines determine HITRAN scaling factor

Result: HITRAN \(\nu_3\) (980-1080 cm\(^{-1}\)) 1.8% too weak
Are the relative line intensities in HITRAN correct?

What is the status of the relative line intensities in HITRAN?

- Relative intensities were introduced in 1992 (Flaud Atlas)
- Last update: Scaling fundamental line intensities by 0.96, based on work of three labs (Uni Reims, Uni Paris, DLR) in HITRAN2004
- Surprisingly, we found disagreement of relative intensities measured at DLR in 1998 (Wagner et al., JGR 2002) and HITRAN

Solution

- Multispectrum fit of old (Wagner et al., JGR 2002) and new measurements, old measurements had smaller column amount and covered strong lines, too
- Multispectrum fitting features “linefit” ILS treatment (Frank Hase, KIT), pCqSDHC lineshape (Ngo, Tran) + line mixing (Rosenkranz)
Example of multispectrum fitting, residuals(green)x10
Results

- Average line intensity ratios with HITRAN16 were calculated for line intensity ranges
- **Pronounced dependence of ratio on intensity for \( \nu_3 \)** (new results larger than HITRAN 1.5% - 2.7%)
- New \( \nu_1 \) intensities about 2% larger than HITRAN
- New \( \nu_2 \) intensities about 1.5% larger than HITRAN
- New spectroscopic databases: Substitution of fitted line positions and intensities in HITRAN, published on ZENODO

<table>
<thead>
<tr>
<th>-Log(S) range</th>
<th>( \frac{S_{\text{exp}}}{S_{\text{HIT}}} \nu_1 )</th>
<th>( \chi )</th>
<th>( n )</th>
<th>( \frac{S_{\text{exp}}}{S_{\text{HIT}}} \nu_2 )</th>
<th>( \chi )</th>
<th>( n )</th>
<th>( \frac{S_{\text{exp}}}{S_{\text{HIT}}} \nu_3 )</th>
<th>( \chi )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>19 - 20</td>
<td>1.02149(79)</td>
<td>2.68</td>
<td>34</td>
<td>1.0150(10)</td>
<td>1.55</td>
<td>30</td>
<td>1.02710(70)</td>
<td>1.21</td>
<td>471</td>
</tr>
<tr>
<td>20 - 21</td>
<td>1.01907(35)</td>
<td>2.31</td>
<td>620</td>
<td>1.01355(43)</td>
<td>2.17</td>
<td>667</td>
<td>1.01699(41)</td>
<td>2.70</td>
<td>723</td>
</tr>
<tr>
<td>21 - 22</td>
<td>1.0241(16)</td>
<td>1.73</td>
<td>585</td>
<td>1.0208(23)</td>
<td>1.68</td>
<td>456</td>
<td>1.0176(37)</td>
<td>1.71</td>
<td>228</td>
</tr>
</tbody>
</table>
Why are the results different analysing the same spectra?

• Analysis of four old and two new spectra (one at 230 K)
• Multispectrum fitting analysis instead of single spectrum fitting
• Different ILS treatment, especially crucial for nearly Doppler-limited pure O$_3$ measurements – old analysis relied on simple sinc x box ILS
• Speed dependence was found to be of importance even for 0.2 mbar measurements
Further data reduction

- Jean-Marie Flaud carried out an effective Hamiltonian fit of line positions and intensities of the $\nu_1/\nu_3$ region
- Predictions for line positions/intensities of $\nu_1/\nu_3$ fundamentals and intensities for hot bands
- Predictions are significant improvement over experimental data, especially in the $\nu_3$ region with many blended lines
- Line intensity weighted averages of $S_{\text{JMF}}/S_{\text{HIT}}$

Opacity 0.1 Doppler: Column $9 \times 10^9$ cm$^{-2}$ (limb s.) $9 \times 10^8$ cm$^{-2}$ (NADIR)

$S_{\text{JMF}}/S_{\text{HIT}}$ $\nu_3$ Av 1.023 $\nu_1$ Av 1.020
Results

- Intercomparison with ab initio results (only ca. 50 strong lines) by V. Tyuterev et al. (JCP 2017): **Average intensity difference 0.3%!**

\[
\frac{S(\text{Eff. Ham.})}{S(\text{ab initio})} - 1, \ K_a=0, \text{ vs. } J''
\]
Background

- Four new $\nu_3$ measurements available:
  - Barbe, Uni Reims
  - Jacquemart, Janssen, Uni Sorbonne
  - Drouin, JPL
  - Birk, Wagner, DLR

- General consent: New data 2.3-3.3% above HITRAN

But: simple scaling of HITRAN not sufficient for $\nu_1$ and $\nu_3$
Broadening problems with O₃ database?

- Up to 8% more O₃ at 30-40 km in AB
- Similar results for MIPAS-B
- Increasing $\gamma_{\text{air}}$ by 6% for AB reduced the bias significantly
- Conclusion in paper: Spectroscopy wrong!

This motivated the spectroscopists 😊 who provided the O₃ broadening data (in HITRAN04/08/12/16, basis for PF4.45) to investigate whether this is true
Re-analysis of old RT O$_2$- and N$_2$-broadened spectra

- Improved line intensity available
- Improved self-broadening data from pure O$_3$ fits
- Improved ILS available
- Multispectrum fitting available
- Influence of speed dependence investigated

Example of multispectrum fitting, residuals(green)x10

MW: 27 0: pp=0.21 pTot=20.15 T=297.90 l=25.0

1: pp=0.60 pTot=49.41 T=297.24 l=25.0

2: pp=8.76 pTot=25.38 T=293.36 l=25.0

3: pp=8.27 pTot=53.75 T=293.36 l=25.0
Comparison of new air-broadening parameters with HITRAN

\[ \gamma_{0\text{air}}(\text{new})/\gamma_{0\text{air}}(\text{HITRAN}), \quad 1\sigma \text{ error bars} \]
Comparison of new air-broadening parameters with HITRAN

$\gamma_{0\text{air}}(\text{new})/\gamma_{0\text{air}}(\text{HITRAN}) - 1$ vs $J'', K_{a''}=7$, R-branch, $1\sigma$ error bars
Comparison of new air-broadening parameters with HITRAN

- Intercomparison on single line basis only for $\nu_3$ – 20 times stronger lines than $\nu_1/\nu_2$
- On average changes small
- For single lines $\nu_3$ up to 5% significant differences
- No room for global 6% systematic differences between $\nu_2$ and $\nu_3/\nu_1$ – Note broadening of all fundamentals analysed from same measurements

<table>
<thead>
<tr>
<th>Band</th>
<th>S range</th>
<th>% Error limit $\text{N}_2/\text{O}_2$</th>
<th>Mean $\gamma_{0\text{air}}$ ratio new/HITRAN</th>
<th># of lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_3$</td>
<td>$S &lt; 1\text{e}-20.5$</td>
<td>4/8</td>
<td>0.99598 (43)</td>
<td>1175</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>$1\text{e}-20.5 &lt; S &lt; 1\text{e}-20.0$</td>
<td>4/8</td>
<td>1.01355 (39)</td>
<td>323</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>$S &gt; 1\text{e}-20.0$</td>
<td>4/8</td>
<td>1.01091 (18)</td>
<td>442</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td></td>
<td>4/8</td>
<td>1.00938 (15)</td>
<td>1940</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>10/10</td>
<td>1.0006(16)</td>
<td>468</td>
<td></td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>10/10</td>
<td>0.99636(95)</td>
<td>514</td>
<td></td>
</tr>
</tbody>
</table>
Pressure-induced line shifts

- Not relevant for MIPAS, only for tropospheric $\text{O}_3$
- Shifts could be fitted but may exhibit a bias error due to missing calibration
- Bias determined from comparison of shifts for two lines with results from Minissale et al. [First pressure shift measurement of ozone molecular lines at 9.54 $\mu$m using a tunable quantum cascade laser, Journal of Molecular Spectroscopy Volume 348, June 2018, Pages 103-113]
- $\delta$ values were fitted in polynomial vs. $\gamma_{\text{air}}$
- Single line values used in output database when error <0.001 cm$^{-1}$/atm – for other $\nu_3$: polynomial output
Impact of speed dependence

- In case of opaque lines the real Lorentzian broadening is needed, laboratory measurements using Voigt only deliver an effective value valid for non-opaque lines.
- The difference between real and effective Lorentzian broadening is around 2%.

### Speed dependence influence for N2 broadening in the $\nu_3$

<table>
<thead>
<tr>
<th>$\sigma$</th>
<th>$S$</th>
<th>$\gamma_0$</th>
<th>$\gamma_2$</th>
<th>$\gamma_{\text{eff}}$</th>
<th>$(\gamma_{\text{eff}} - \gamma_0)$ in %</th>
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</thead>
<tbody>
<tr>
<td>1029.0784</td>
<td>2.276e-020</td>
<td>0.0869</td>
<td>0.0104</td>
<td>0.0850</td>
<td>-2.2</td>
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<tr>
<td>1029.0954</td>
<td>3.850e-020</td>
<td>0.0841</td>
<td>0.0100</td>
<td>0.0825</td>
<td>-1.8</td>
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<tr>
<td>1029.1457</td>
<td>1.017e-021</td>
<td>0.0794</td>
<td>0.0076</td>
<td>0.0783</td>
<td>-1.4</td>
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<tr>
<td>1029.1683</td>
<td>6.516e-021</td>
<td>0.0863</td>
<td>0.0102</td>
<td>0.0844</td>
<td>-2.3</td>
</tr>
</tbody>
</table>
New databases

- All new databases were based on HITRAN12
- $\nu_2$: intensities scaled by 1.01355, bugfix for polynomials in $\gamma_{\text{air}}$ with $J''=K_a''$ – bugfix so far not implemented in HITRAN
- $\nu_1$: JMF line positions and intensities where available, experimental value for isolated lines with intensity error <10%, same bugfix as $\nu_2$
- $\nu_3$: JMF line positions and intensities where available, experimental value for isolated lines with intensity error <10%, individual $\gamma_{\text{air}}$ values with uncertainties <4%, pressure-induced line shifts
Conclusions/Outlook

- New databases for the $O_3$ fundamentals created with significant updates for the line positions and intensities in $v_1$ and $v_3$
- Re-analysis of broadening showed validity of HITRAN data
- Strong lines in the $v_3$ were updated with broadening data on single line basis (without polynomials)
- Errors in broadening data as cause for $O_3$ differences in $A$ and $AB$ are unlikely
- Impact of new databases on MIPAS will be investigated by Norbert Glatthor
- Validation is planned with solar occultation (Frank Hase), ACE (Chris Boone), Kitt Peak spectra (Geoff Toon)
- In order to cover the intensity range relevant for limb sounding new measurements are required, especially air broadened