IMPACTS OF NEW MEASUREMENTS OF OXYGEN COLLISION-INDUCED ABSORPTION ON ESTIMATES OF SHORTWAVE ATMOSPHERIC ABSORPTION

Júlio C. S. Chagas¹*
David A. Newnham²
Kevin M. Smith²
Keith P. Shine¹

¹ Dept of Meteorology, Reading University, UK
2 Space Science and Technology Dept, Rutherford Appleton Laboratory, Didcot, UK
* Permanent affiliation: Centro de Previsão do Tempo e Estudos Climáticos – CPTEC, Cachoeira Paulista, SP, Brazil.
(Center for Weather Forecast and Climate Studies).
<table>
<thead>
<tr>
<th>(a)</th>
<th>0.98</th>
<th>0.16</th>
<th>-</th>
<th>0.78</th>
</tr>
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<tbody>
<tr>
<td>(b)</td>
<td>0.94</td>
<td>0.17</td>
<td>-</td>
<td>0.78</td>
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<tr>
<td>(c)</td>
<td>0.93-1.31</td>
<td>-</td>
<td>0.29-0.42</td>
<td>0.42</td>
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<tr>
<td>(d)</td>
<td>0.87-1.22</td>
<td>-</td>
<td>0.19-0.30</td>
<td>0.42</td>
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Solomon et al. (1998)

<table>
<thead>
<tr>
<th>(e)</th>
<th>0.84</th>
<th>-</th>
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<tr>
<td>(f)</td>
<td>0.42</td>
<td>-</td>
<td>0.29</td>
<td>0.10</td>
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<tr>
<td>(g)</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
<td>0.37</td>
</tr>
<tr>
<td>(h)</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
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Blacker et al. (1998)

<table>
<thead>
<tr>
<th>(i)</th>
<th>0.7-1.7 µm</th>
<th>-</th>
<th>1.8-2.1 µm</th>
<th>1.27-1.7 µm</th>
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</thead>
</table>

Kersten et al. (1997)

<table>
<thead>
<tr>
<th>Band</th>
<th>VIS 0.6-1.0 µm</th>
<th>1.27-1.7 µm</th>
<th>1.8-2.1 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2O</td>
<td>2.9 ± 0.5 mm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O2</td>
<td>2.9 ± 0.5 mm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N2O+</td>
<td>2.9 ± 0.5 mm</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Kersten et al. (1997)

| Mx-2 | - | - | - |

Blank et al. (1998)

| Table 4 | Globally averaged short-wave absorption by oxygen collision complexes in all sky. |

From different studies. (V= visible/ near-ultraviolet band; c= clean sky; a= all sky.)
How the Solomon et al.'s binary cross-sections for the 1.27-μm band were obtained:

O₂-O₂:
has same shape as 1.06-μm band,
band intensity ranges from 1 to 1.6 times the 1.06-μm band intensity.

O₂-N₂:
efficiency of nitrogen as a collision partner if compared to oxygen itself ranges from 0.1 to 0.3.

So... the “range” of values.

Our work main advantage:
Use high resolution measurements of 1.27-μm band to do the estimates of atmospheric absorption (measurements of the 1.06-μm band too).
Recent laboratory measurements

Maté et al. 1999:
(JGR, 104, 30585-30590)
1.27-μm band

Smith and Newnham 1999, 2000:
(Chem. Phys. Lett., 308, 1-6, 1999;
JGR, 105, 7383-7396)
Both bands.
The experiments

**Spectrometer:** Bruker IFS 120HR Fourier transform spectrometer.

**Source:** 150 W quartz-tungsten-halogen (Osram Type HLX61640).

**Beam-splitter:** silica-coated calcium fluoride (near-infrared).

**Spectral resolution:** spectra originally recorded at 0.05 cm$^{-1}$ and subsequently re-processed to a resolution of 0.5 cm$^{-1}$.

**Gas cell:** short path length absorption cell set to 12.94 m.

**Samples:**

21 % oxygen in nitrogen, $T \equiv 230, 260$ and 295 K,

\[ p \equiv 1, 1.5, 2.5, 3.5 \text{ and 5 atm.} \]

21 % oxygen in argon, $T \equiv 280$ K,

\[ p \equiv 1, 1.5, 2.5, 3.5 \text{ and 5 atm.} \]

Pure oxygen, $T \equiv 230, 295$ K,

\[ p \equiv 1, 1.5, 2.5, 3.5 \text{ and 5 atm.} \]
Figure 5.2: The procedure to convert the raw single-channel oxygen measurements of arbitrary intensity units to binary absorption cross-sections (reproduced from Smith and Newbome 2000). (a) oxygen absorption spectrum and empty cell background spectrum; (b) transmittance spectrum calculated as the ratio of the sample to background spectra; (c) cubic spline fitted to data points in regions of zero absorption to correct to the 100% transmittance level; (d) corrected transmittance spectrum; (e) Napierian absorbance spectrum obtained from the corrected transmittance spectrum; (f) rms baseline noise data points and best fit polynomial; (g) binary absorption cross-section; (h) standard deviation of the binary cross-sections.

(JGR, 105, 7383-7396, 2000)
**Error analysis**

Standard deviation associated with the binary cross-sections calculated taking into account uncertainties in:

- Pressure
- Temperature
- Oxygen volume fraction
- Path length
- Absorbance

Standard deviation in absorbance includes the root mean square error associated to the noise in the measured spectra.
Manganese (cm⁻¹)

Wave number (cm⁻¹)

binary cross-section (cm² mg⁻¹ cm⁻¹)

F 1  a  E  a  6  F  a

Onset

Gaussian-distribution

difference

427 cm⁻¹

120 bar

O₂⁻ + N₂ = 2N₂, 261 K, 5.0 bar
Table 5.6: Peak binary cross-sections and integrated binary intensity for the 1.06-μm oxygen collision-induced absorption band according to different studies. Integrated binary intensity for Greenblatt et al calculated here from spectrum provided by J. Burkholder (personal communication). Peak absorption and integrated binary intensity for Smith and Newnham are mean values for different oxygen-nitrogen mixtures at different temperatures. Values for this work are an average of different pure oxygen measurements.

<table>
<thead>
<tr>
<th></th>
<th>Peak absorption $(10^{-46} cm^6 molecule^{-2})$</th>
<th>Integrated binary intensity $(10^{-13} cm^3 molecule^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenblatt et al. (1990)</td>
<td>12(±1)</td>
<td>3.5</td>
</tr>
<tr>
<td>Mlawer et al. (1998)</td>
<td>13.8</td>
<td>2.4(±0.5)</td>
</tr>
<tr>
<td>Smith &amp; Newnham (2000)</td>
<td>14.61(±0.46)</td>
<td>2.61(±0.17)</td>
</tr>
<tr>
<td>This work</td>
<td>14(±1)</td>
<td>3.14(±0.97)</td>
</tr>
</tbody>
</table>
Relay measurements at 2.0 bar and different temperatures. All mixtures are 21% oxygen.

Figure 8.4: Binary cross-section of the oxygen 1.06-mm-band absorption band for bler...
Figure 5.15: Binary cross-sections of the oxygen 1.27-μm collision-induced bands for halogen mixtures at 5.0 bar and different temperatures. All mixtures are 21% oxygen.
Radiative transfer code

- Delta-Eddington code of Slingo & Schrecker (1982) modified to include the 220-band structure of Edwards & Slingo's (1996) code and its Rayleigh, water vapour and ozone coefficients;
- Water vapour and ozone absorption;
- Clear sky;
- Oxygen collision-induced absorption enters as grey absorption (cross-sections averaged over appropriate bands of the code).

Climatological atmospheric profiles

- From observations
- 10-degree-latitude belts zonal averages
- Monthly averages

1.27-μm band → 7 bands of model.
1.06-μm band → 4 bands of model.
Increase in solar absorption due to O\textsuperscript{2} collision continua.
the 1.27-$\mu$m and 1.06-$\mu$m bands are included (estimates for clear skies).

Behind these (a) the 1.27-$\mu$m collision-induced absorption band of oxygen and (b) water vapor are mid-season monthly climatological conditions averaged over 10-degree

Figure 5.20: Percent impact of the solar irradiance absorbed by atmospheric ozone and
<table>
<thead>
<tr>
<th>Complex:</th>
<th>( \text{O}_2 \bullet \text{O}_2 )</th>
<th>( \text{O}_2 \bullet \text{N}_2 )</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band:</td>
<td>Vis 1.06-( \mu \text{m} ), 1.27-( \mu \text{m} ), 1.38-( \mu \text{m} ), 1.27-( \mu \text{m} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pfeilsticker et al. (1997)</td>
<td>0.53</td>
<td>-</td>
<td>0.53 (c)</td>
</tr>
<tr>
<td>Mlawer et al. (1998)</td>
<td>0.57</td>
<td>0.10</td>
<td>0.67 (c)</td>
</tr>
<tr>
<td>Solomon et al. (1998)</td>
<td>0.42</td>
<td>0.19</td>
<td>0.61 (c)</td>
</tr>
<tr>
<td>Zender (1999)</td>
<td>0.45</td>
<td>0.20</td>
<td>0.65 (c)</td>
</tr>
</tbody>
</table>

\[ \text{Our study:} \quad \frac{0.42}{\text{Vis, Salo et al.}} + \frac{0.58}{\text{Mlawer, 1.38-\( \mu \text{m} \)}} \approx \frac{1.03}{\text{km}^2 \text{molec}^{-2}} \approx \frac{1.00}{\text{km}^2 \text{molec}^{-2}} \]
SUMMARY

Main improvements:
- Measurements of 1.27-μm band used
- Global estimates from observed climatology

Some results:
- Nitrogen efficiency $\sim 0.2$
- Argon nearly as efficient as nitrogen
- Only oxygen in the 1.06-μm band

Problems:
- Small signal-to-noise, especially at low pressures, due to the short path length
- Temperature dependence of cross-sections still unclear