

Parameterization of the 1.27 micron O₂ continuum absorption

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With help from Paul, I have finally figured out how to represent the O₂ continuum absorption in a fashion that gives consistent results with both atmospheric and laboratory spectra. As a bonus, the spectral fits are better too. So I thought that I'd better write it up before I forget what I did.

The Laboratory Spectra of Smith and Newnham

I acquired the absorption cross-sections from their FTP site. The spectra were acquired through a 513 m cell using a Bruker 120HR. Each spectrum covers the 7500-8600 cm⁻¹ region at 0.25 cm⁻¹ point spacing and 0.50 cm⁻¹ resolution, which is enough to separate the underlying continuum absorption from the discrete lines. I first had to calculate the transmittance spectra from Smith and Newnham's absorption coefficients. But this was easy, given the T, P, vmr and path length.

Table 1. Lists the 7 S&N spectra and their experimental conditions

FILE	T_K	P_mbar	vmr
"o2_ral_127_295_21"	295.1	1002.3	0.21
"o2_ral_127_229_21"	229.0	1002.0	0.21
"o2_ral_127_228_50"	228.2	1009.1	0.50
"o2_ral_127_229_75"	228.5	1002.4	0.75
"o2_ral_127_199_50"	198.7	1002.1	0.50
"o2_ral_127_199_21"	198.5	919.0	0.21
"o2_ral_127_198_75"	198.4	1002.2	0.75

These spectra appear to correspond to the first 7 rows of Table 4 in Smith and Newnham [2000], but in reverse order. I don't know why the penultimate spectrum was acquired at 10% lower pressure than the others, nor why they made the 295K measurement at only one O₂ vmr (0.21).

Theory

The O₂ absorption can be represented by

$$\text{Total Absorption} = a.[\text{O}_2].[\text{O}_2] + b.[\text{O}_2].[\text{N}_2] + c.[\text{O}_2]$$

where

a represents the cross-section for O₂-O₂ collisions

b represents the cross-section for O₂-N₂ collisions

c represents the discrete line absorption.

I will assume that the third term, representing the discrete absorption lines, is correctly handled by the Goldman linelist, so that it need not be considered further here.

If $[\text{O}_2] = V_{\text{O}_2} \cdot \rho$ (i.e. vmr * number_density), then Collision Induced Absorption (CIA)

$$\text{CIA} = \rho^2 \cdot (a \cdot V_{\text{O}_2}^2 + b \cdot V_{\text{N}_2} \cdot V_{\text{O}_2})$$

If there are no other gases present, $V_{O_2}+V_{N_2}=1$, and so

$$\begin{aligned} \text{CIA} &= \rho^2 \cdot (a \cdot V_{O_2}^2 + b \cdot V_{O_2} \cdot (1 - V_{O_2})) \\ \text{CIA} &= \rho^2 \cdot ((a-b) \cdot V_{O_2}^2 + b \cdot V_{O_2}) \end{aligned}$$

Note that the first term is quadratic in V_{O_2} whereas the second term that is linear in V_{O_2} . Well, I now believe that S&N [2000] denoted the former $((a-b) \cdot V_{O_2}^2)$ as "binary" absorption and the latter $(b \cdot V_{O_2})$ as "monomer" absorption. Fig 4b of S&N shows the monomer absorption peaking $\sim 7890 \text{ cm}^{-1}$ and the binary absorption peaking $\sim 8010 \text{ cm}^{-1}$.

If you now look at figure 6 in Mate et al [1999] you will see that their O_2 - O_2 absorption cross section peaks at 7900 cm^{-1} , but with a tail to higher frequencies. Their O_2 - N_2 absorption is narrower, more symmetrical, with a peak at 7890 cm^{-1} . If you now mentally subtract these two curves, the difference peaks around 8000 cm^{-1} . This is completely consistent with S&N's "binary" absorption.

Implementation

So now it becomes clear how to parameterize the continuum absorption. Instead of monomer and binary linelists, we need Foreign Collision Induced Absorption (FCIA) and Self Collision Induced Absorption (SCIA) linelists. For O_2 , these look just like the upper and lower curves in Fig. 6 of Mate et al. [1999].

So the new version of GFIT will read the linelists fcia.101 and scia.101 and compute

$$\begin{aligned} \text{CIA} &= \rho^2 \cdot [S_{\text{SCIA}} \cdot V_X^2 + S_{\text{FCIA}} \cdot V_X \cdot (1 - V_X)] \\ \text{where } S_{\text{SCIA}} &= a \text{ and } S_{\text{FCIA}} = b \text{ in units of } \text{cm}^{-1}/(\text{molecules}^2/\text{cm}^5) \end{aligned}$$

Note that in abscof.f, the quantity $SX=D \cdot S \cdot V_X$ is already calculated the same way that that it would for any normal spectral line. The statements

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if(scia) SX=SX*\rho*Vx
if(fcias) SX=SX*\rho*(1-Vx)
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then apply the additional density & vmr dependences for the lines from the CIA linelists.

Integrated band intensities

Table 1. Comparison of integrated band intensities obtained from the S&N spectra, with those obtained by Mate et al. All values in units of $\times 10^{-43} \text{ cm}^{-2}/(\text{molec.cm}^{-3})^2$

	This Work	Mate et al.[1999]	Smith & Newnham [2000]
a= O_2 - O_2	4.504	4.847(22)	N/A
b= O_2 - N_2	1.277	0.941(50)	N/A
a-b	3.227	3.906	2.31 to 3.38 for "binary"

Interestingly, the sum of the O_2 - O_2 and O_2 - N_2 intensities (5.78) is extremely similar between this work and Mate et al.,[1999]. This is because you are fitting the total absorption as the sum of two similarly shaped contributions. If one is over-estimated, the other will be under-estimated by a roughly equal amount.

Results: Lab Spectra.

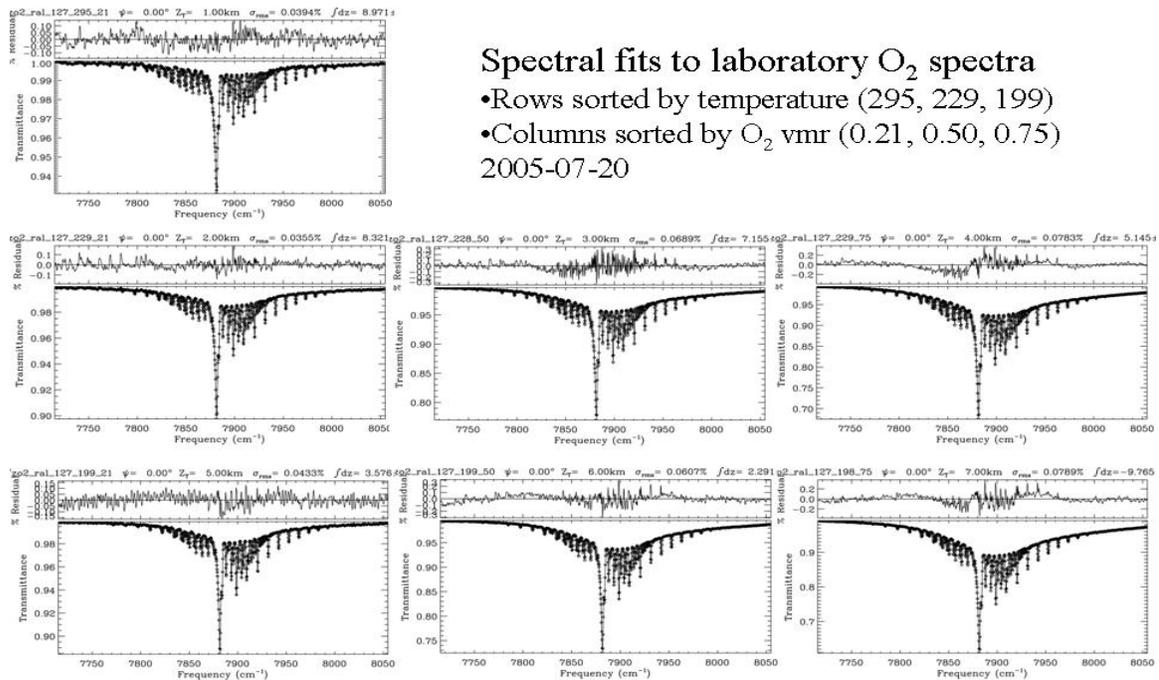
So how well does this new linelist/approach work? I can now fit all 7 S&N lab spectra with a VF_o2 that varies from 0.98 to 1.01 (see Table 2). The previous linelist produced results that varied from 1.9-2.3, and the linelist before that from 1.85-5.3.

As before, the VF_O2 values obtained by fitting the discrete lines in the S&N spectra are also close to 1.0. [Note that the strengths of the discrete o2 lines have been multiplied by 0.89 for the latest analyses. VF_o2 values must therefore be multiplied by 0.89 to make them comparable with earlier results]

Table 2: Information from fitting S&N spectra

Spectrum	RMS/CI	AM_o2	VF_o2	VF_0o2
o2_ral_127_295_21	0.0394	-----	$1.0186 \pm 1.1E-02$	$1.0011 \pm 3.5E-02$
o2_ral_127_229_21	0.0355	-----	$1.0124 \pm 7.1E-03$	$1.0079 \pm 1.5E-02$
o2_ral_127_228_50	0.0689	-----	$1.0095 \pm 6.8E-03$	$0.9762 \pm 1.0E-02$
o2_ral_127_229_75	0.0782	-----	$1.0100 \pm 6.1E-03$	$1.0083 \pm 7.4E-03$
o2_ral_127_199_21	0.0433	-----	$1.0115 \pm 7.9E-03$	$1.0044 \pm 1.4E-02$
o2_ral_127_199_50	0.0607	-----	$1.0023 \pm 5.4E-03$	$0.9878 \pm 6.4E-03$
o2_ral_127_198_75	0.0789	-----	$1.0166 \pm 5.6E-03$	$1.0134 \pm 5.4E-03$

The spectral fits to these 7 S&N spectra are below. The columns represent different O2 vmrs, and the rows different temperatures. Average RMS/CL = 0.057816%



Results: Atmospheric spectra

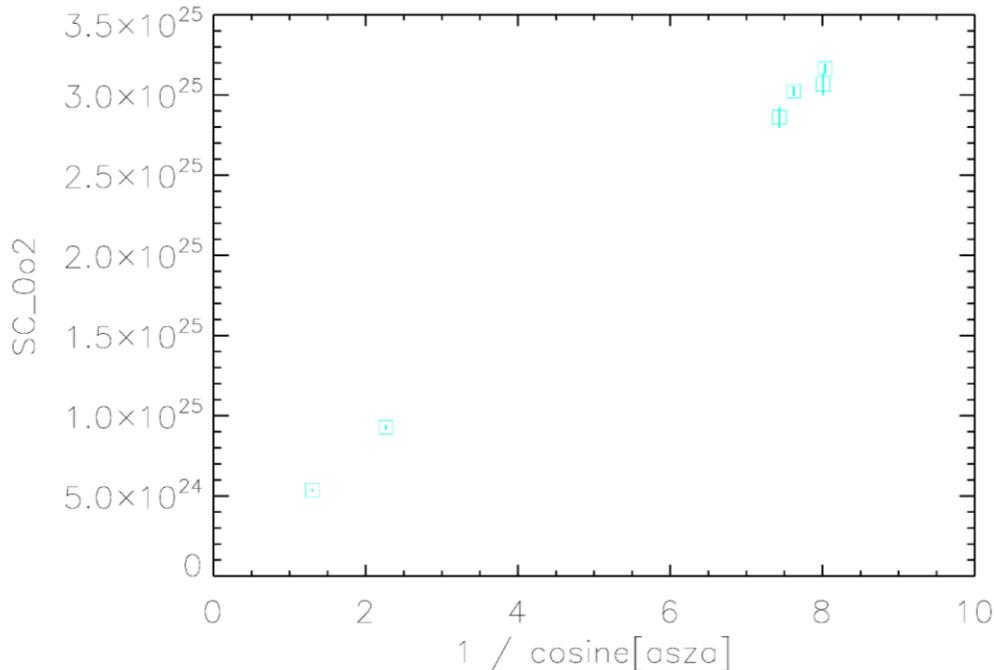
I next fitted a selection of Park Falls spectra from July 21 2004 and Dec 22 2004, using the exact same linelists and gfit version. All fits were made using Voigt lineshape (i.e. no super-lorentzian). The results are summarized below. The increase in VF_o2 with airmass on 20040721 is likely due to neglect of super-Lorentzian far line wings. The difference in VF_o2 between 20040721 (+28°C) and 20041222 (-23°C) is due to neglect of H₂O dilution.

Table 3: Information from fitting selected Park Falls spectra

Spectrum	RMS/Cl	AM_o2	VF_o2	VF_0o2
pa20040721saaaaa.049	0.4220	1.298	0.9942 ± 1.3E-02	1.1791 ± 1.3E-02
pa20040721saaaaa.125	0.5000	2.252	0.9970 ± 1.5E-02	1.1180 ± 1.5E-02
pa20040721saaaaa.182	0.7298	6.974	1.0018 ± 2.2E-02	1.0686 ± 2.2E-02
pa20040721saaaaa.185	0.7418	7.444	1.0064 ± 2.2E-02	1.0650 ± 2.2E-02
pa20041222saaaaa.021	0.3435	7.498	1.0141 ± 1.0E-02	1.0687 ± 1.0E-02
pa20041222saaaaa.022	0.3404	7.155	1.0154 ± 1.0E-02	1.0698 ± 1.0E-02

Average RMS/CL = 0.47882%

I believe that the inverse airmass dependence of the VF_0o2 in the Park Falls data is likely due to concavity of the continuum in the 7900 cm⁻¹ region. This has a bigger fractional impact when the airmass is small than when large. I have plotted the 0o2 slant column versus airmass (attached). It's linear, but doesn't go through the origin. The offset represents the apparent additional 0o2 slant column due to the continuum curvature.



Outstanding Questions

- 1) Why were the previous VF_0o2 values so bad? The main reason is I assumed that the monomer absorption was ∝ D, when in fact it is ∝ D².

2) Why does the O₂-O₂ absorption have a tail toward higher frequencies? What we term the O₂-O₂ CIA probably includes direct O₄ absorption. Since O₄ has an electric dipole, and since [O₄]∝[O₂]², the direct O₄ absorption will have a very similar pressure- and vmr-dependencies to that of the O₂-O₂ CIA and will therefore be folded into the SCIA.

3) Why not define an air-collision induced absorption coefficient

$$S_{ACIA} = 0.21 * S_{SCIA} + 0.79 * S_{FCIA}$$

such that the CIA in air could have been represented with a single linelist (instead of two)? This would have prevented me fitting the laboratory spectra with enriched O₂. (I think that it is important to fit all available lab spectra)

Summary

I think that we now have a good parameterization of the O₂ CIA in the 1.27 micron band. I doubt that it will have a discernable effect on the VF_O2 retrieved from the discrete lines. But at least we won't have to worry about the O₂ CIA for the foreseeable future.

Is it still necessary to fit the 0o2, given that the VF_0o2 factors are now much close to 1.0? Yes. Although the CIA parameterization is much improved, there are departures of up to 20% due to continuum curvature. So fitting the 0o2 not only improves the fits, it also “protects” the discrete lines from the effects of continuum curvature.