Reinvestigation of the $^{16}O_2$ atmospheric A band by high-resolution Fourier transform spectroscopy

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SUMMARY

- ✓ WHAT? Line parameters of the oxygen atmospheric A band $b^1\Sigma^+_g$ (v'=0) ← X $^3\Sigma^-_g$ (v"=0) (12800-13400 cm^{-1} or 780-745 nm).
- ✓ HOW ? A Fourier transform spectrometer (FTS) coupled to a T°-controlled multipass cell → 5 pure O_2 & 2 O_2+N_2 mixtures spectra @ room T°.
- ✓ HOW MANY ? A linelist of 58 lines including calibrated wavenumbers and linestrengths, also with self- and N_2-broadenings and shifts for most of them.
- ✓ CONCLUSIONS:
  - Interesting results for self- and N_2- broadenings at high J"
  - Still questionable results due to weakness and overlap of lines
  - Large error bars and scatter of results → precision and accuracy are not improved compared to existing data.

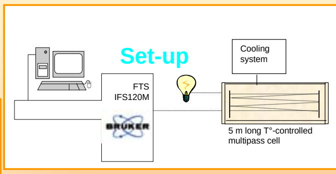
INTRODUCTION : THE PROBLEM ?

The scatter among published O_2 line parameters is significantly larger than the sub-% precision required to improve spaceborne CO_2 measurements by photon paths lengths retrievals [1, 2, 3]. Also, cloud retrievals results from satellite measurements can vary up to 20% depending on the chosen O_2 dataset [4].

INTRODUCTION : THE AIM OF THIS WORK ?

- ✓ Contribute to spectroscopic parameters improvements needed for atmospheric remote sensing applications.
- ✓ Attempt to validate reported values.
- ✓ Fulfill the need for new laboratory measurements in case of sparse existing data like pressure-shifts.

EXPERIMENTAL



Experimental conditions

Spectral range (cm^{-1})	8000-16000
Resolution (cm^{-1})	0.02
Path length (m)	61
Temperature (K)	293 & 220
O_2 pressure (hPa)	20, 40, 80, 200, 400
N_2 pressure (hPa)	320, 800
Lamp & detector	W & Si diode
Co-added scans	8 x 64

Procedure & data processing

- ✓ 8 x Postzerofill
- ✓ Spectrum divided by Blank to eliminate the atmospheric contribution
- ✓ Spectrometer alignment regularly checked
- ✓ Voigt line shape and baseline fitting using WSpectra [5]
- ✓ Wavenumber calibration using I_2 [6, 7] and atmospheric O_2 lines
- ✓ Careful examination of spectroscopic data → weak, unresolved, saturated lines excluded, outliers eliminated
- ✓ Line parameters determination using conventional equations [8] and linear least-squares fits [9]

RESULTS

Set of Measurements

Fig. 1: Overview of the oxygen A band absorption (arb. units) at the highest and the lowest pressure of pure oxygen (see table for experimental details).

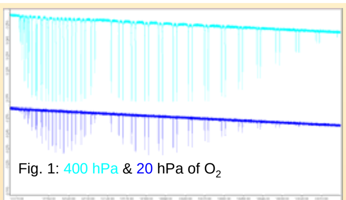


Fig. 1: 400 hPa & 20 hPa of O_2

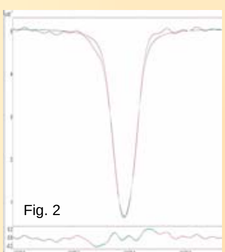


Fig. 2

Voigt versus Galatry line profile ?

Fig. 2: Comparison of line fitting obtained with Voigt (blue) and Galatry (green) line profiles. The observed spectrum @ 80 hPa (divided by blank) is in black. The Observed - Fitted residual is shown below (amplitude +/- 5%). This line corresponds to 88% of absorption.

- Voigt and Galatry fits are undistinguishable;
- The characteristic w-shaped residual due a Galatry profile modeled with a Voigt lineshape is not observable, and the line is not perfectly fitted neither by a Voigt, nor by a Galatry lineshape.
- Line intensity ratio Voigt / Galatry = 99.3% for this line, but values down to 97.1% have been measured for intense (Absorption> 85%) neighboring lines.

P-induced effects

Fig 3: Pure O_2 spectra at different pressures (0.02, 0.04, 0.08, 0.2, 0.4 hPa) clearly showing **self-broadening and shifting**. Also shown is a blank spectrum containing the external atmospheric O_2 contribution.

Fig 4: N_2-broadening and shift. Note the lineshape 'degradation' at the highest O_2+N_2 pressure explaining the difficulty of obtaining high precision parameters.

Fig. 5: Examples of good (**RR(1), RR(3)**) & less good (**PP(17)**) results for the pressure dependence of the Lorentzian linewidth.

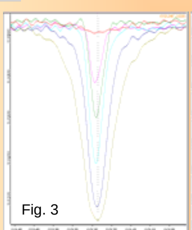


Fig. 3

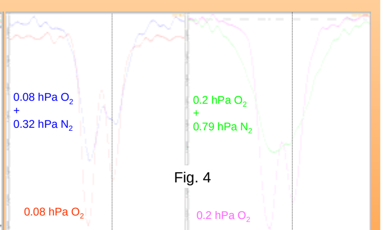


Fig. 4

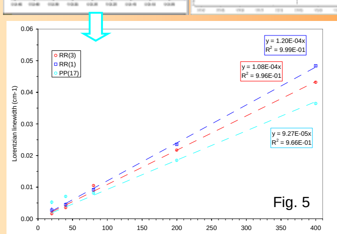


Fig. 5

DISCUSSION: Comparison with literature data

	n	Wvnb	Intensity	gL self	gL air	Pshift self	Pshift air
Hitran '04	91	91	91	91	91	0	91
Brown & Plymate, '00	44	44	44	44	42	42	41
Schermaul & Learner, '99	67	67	65	65	0	0	0
Cheah et al., '00	61	61	59	0	0	0	0
Ritter & Wilkerson, '87	54	0	54	54	0	0	0
O'Brien et al., '01	80	80	0	0	0	0	0
Hill et al., '03	37	0	0	0	0	37	0
Philips& Hamilton, '95	53	0	0	0	0	53	37
van Leeuwen et al., '04,	12	12	12	12	0	0	0
Yang et al., '00	11	0	11	3	4	0	0
This work	58	58	58	53	49	53	48

Positions

Nu(HITRAN) – nu(literature)	Average	±	Std dev
Brown & Plymate, '00	0.0004	±	0.0013
Schermaul & Learner, '99	0.0010	±	0.0018
Cheah et al., '00	0.0028	±	0.0078
O'Brien et al., '01	-0.0042	±	0.0100
O'Brien + Brown	-0.0022	±	0.0095
van Leeuwen et al., '04,	0.0082	±	0.0079
This work	-0.0015	±	0.0011

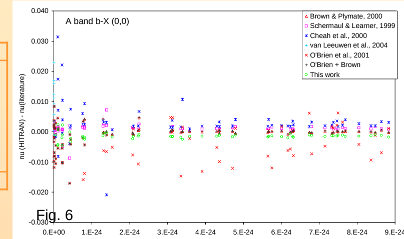


Fig. 6

Fig. 6 & table:

- This work shows a slight negative but systematic difference with HITRAN, inferred to the multi-step calibration procedure
- The absolute difference is of the same order of magnitude of the uncalibrated positions given by Schermaul
- The scatter logically increases for decreasing line intensities

Intensities

Fig. 7:

- Average ratios are written in ( )
- Similarly to wavenumbers differences, the scatter logically increases for decreasing line intensities

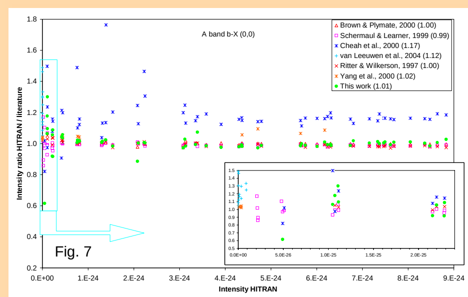


Fig. 7

Self broadenings

Fig. 8:

- Still large errors for some lines
- This work extends Brown's data at high J"
- The divergence from the Hitran values is confirmed, in agreement with the data from Yang and Ritter & Wilkerson, also as well as with Yang's fit.
- Similar trends are observed for the PQ and RQ-type transitions as well as for the N_2-broadenings although fewer literature data exist in the latter case.

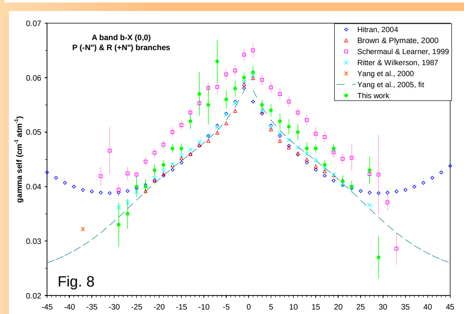


Fig. 8

N_2-shifts

Fig 9:

- Few literature data
- This work gives new data at high J"
- Good agreement between Brown, Hill and this work, and similar trend

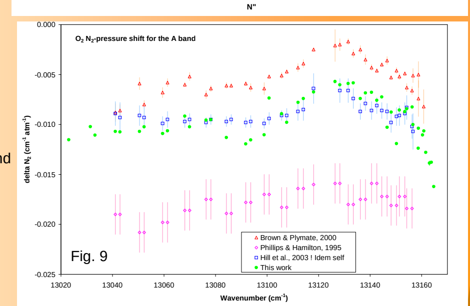


Fig. 9

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