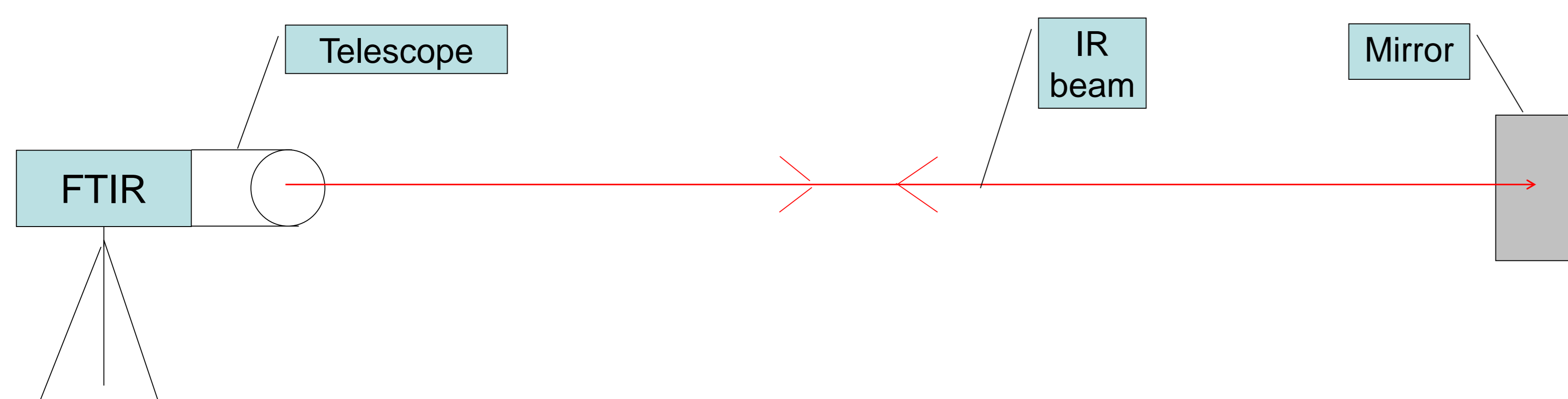


How to quantify gases in air with an open-path FTIR or a variable pathlength cell

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Since the middle of the 90's several FTIR instruments are available to measure and quantify gases in the open atmosphere. A typical setup (monostatic) looks like this :



Before going outside, it is easier to get spectra in the lab and make sure of the results. So, spectra were taken with a Bruker IFS66 FTIR at 0,5 cm⁻¹ resolution (aperture of 2,5 mm) and a Wilks « variable path » cell (0,75-21,75 m) equipped with BaF₂ windows.

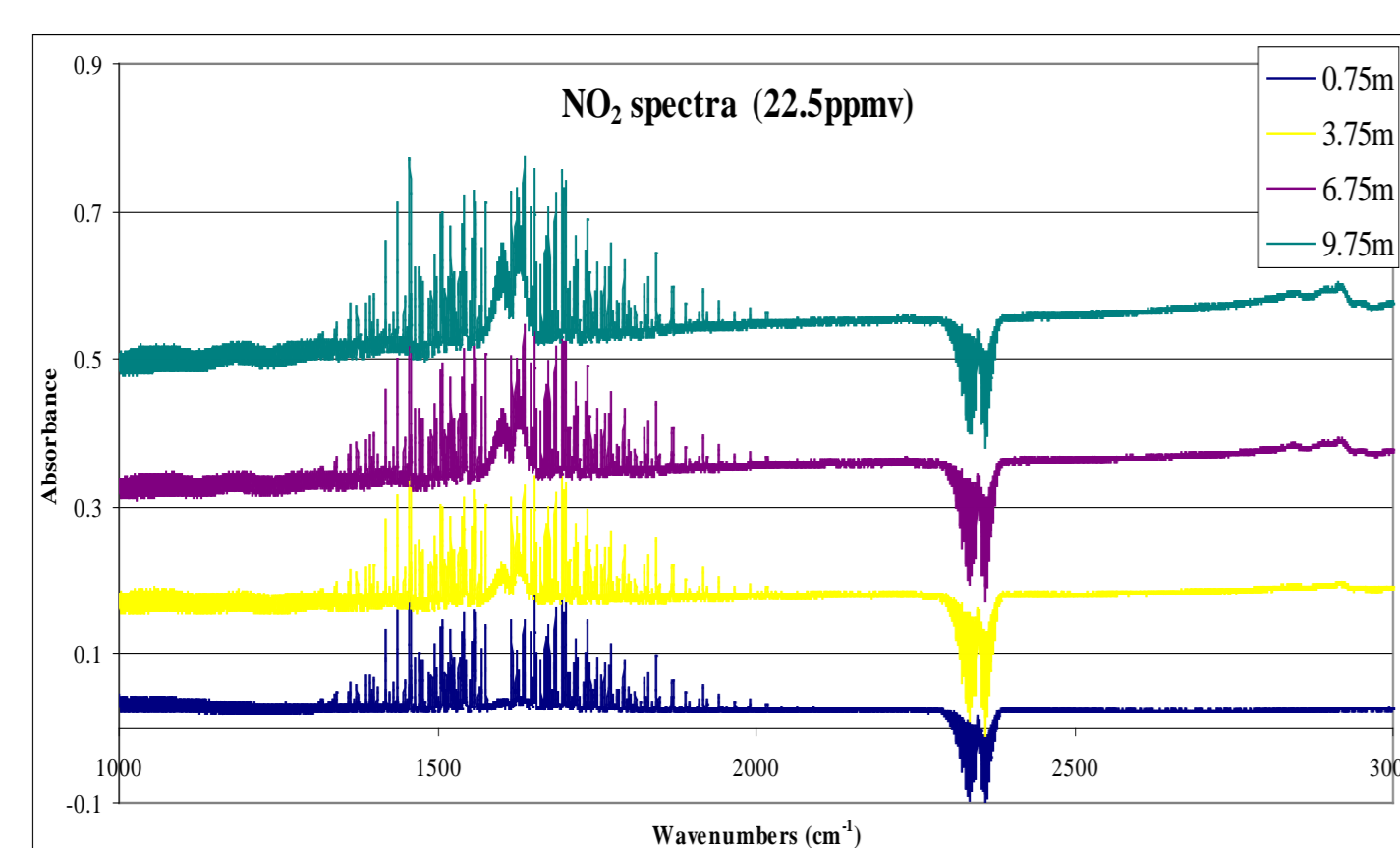


Figure 1.

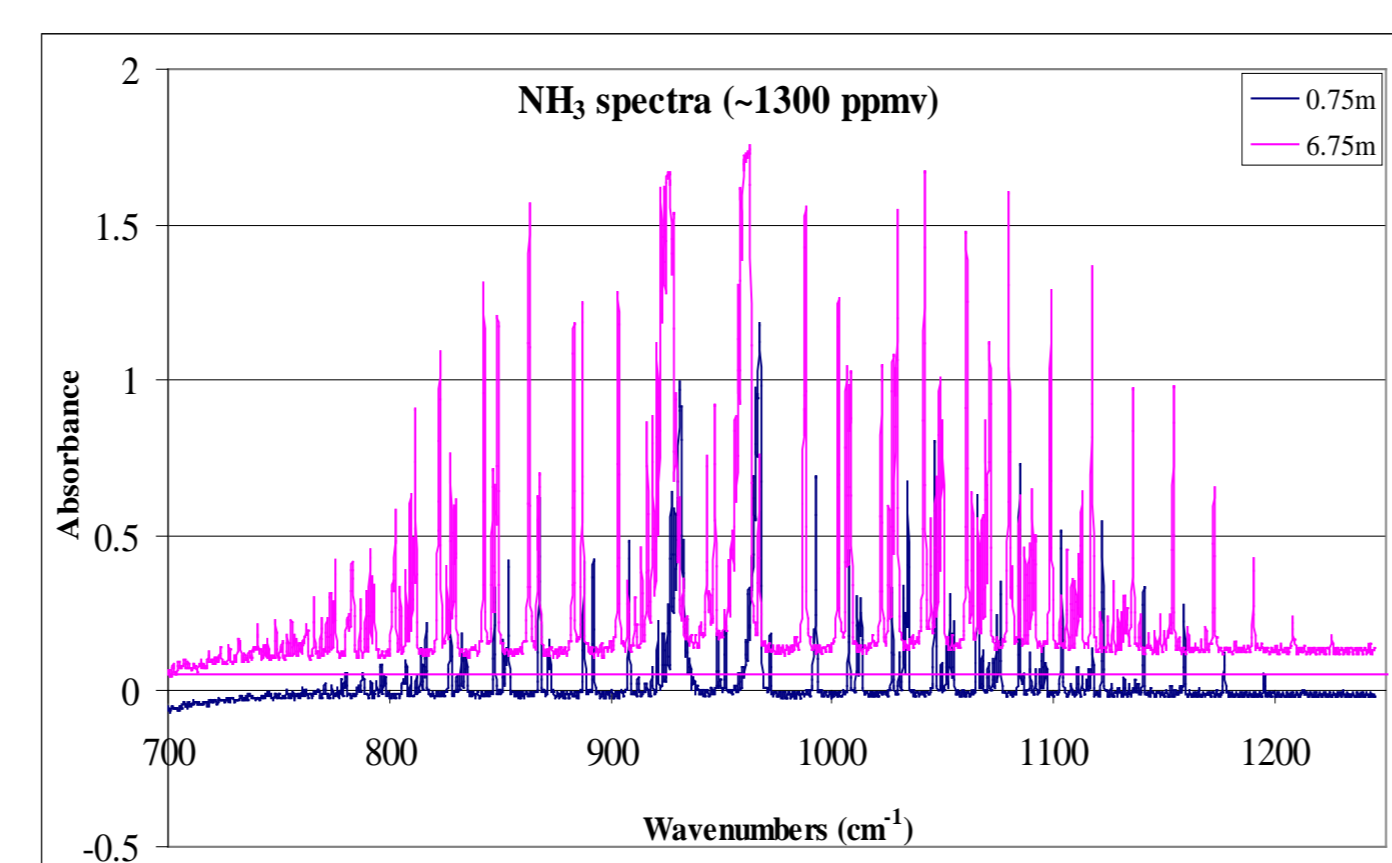


Figure 2.

The way the spectra were taken, the reference spectrum was made with the cell empty (pressure < 1 Torr) then the gas inserted into the cell and completed to atmospheric pressure with N₂.

By doing so, a series of spectra were taken by varying the optical pathlength in the cell (from 0,75 to 11,25 m). These spectra showed a moving baseline due to pathlength difference between the gas spectrum and the reference spectrum (see Figure 1).

When not respecting the Beer-Lambert law⁽¹⁾ (see Figures 1 and 2), spectra may be distorted and care was taken to avoid it.

A usual feature in open atmosphere spectra is the presence of bands in the 1400-1800, 2250 and 3500-4000 cm⁻¹ regions (see Figure 6). These bands are due to the ubiquitous presence of H₂O and CO₂ which were avoided in the lab setup.

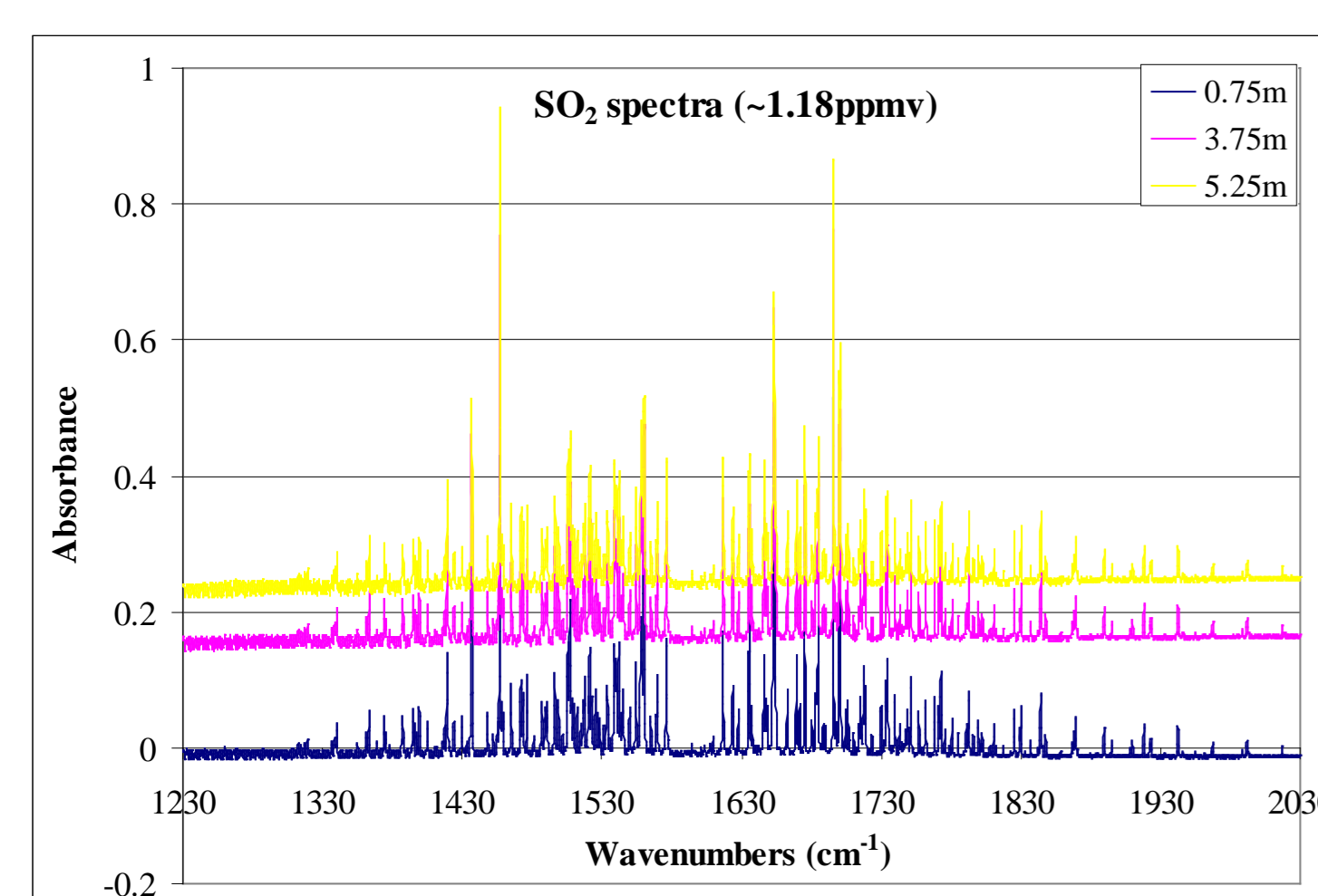


Figure 3.

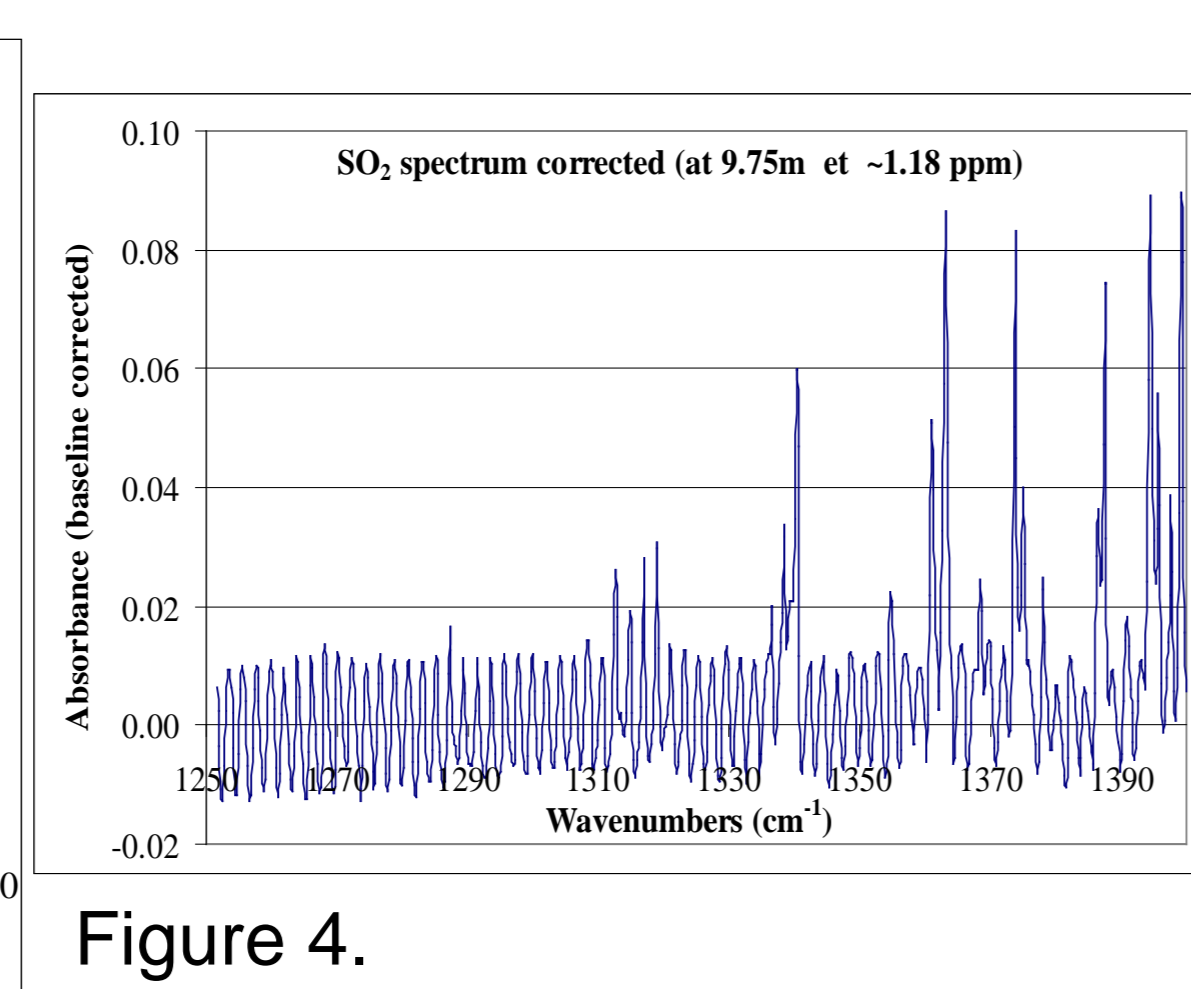


Figure 4.

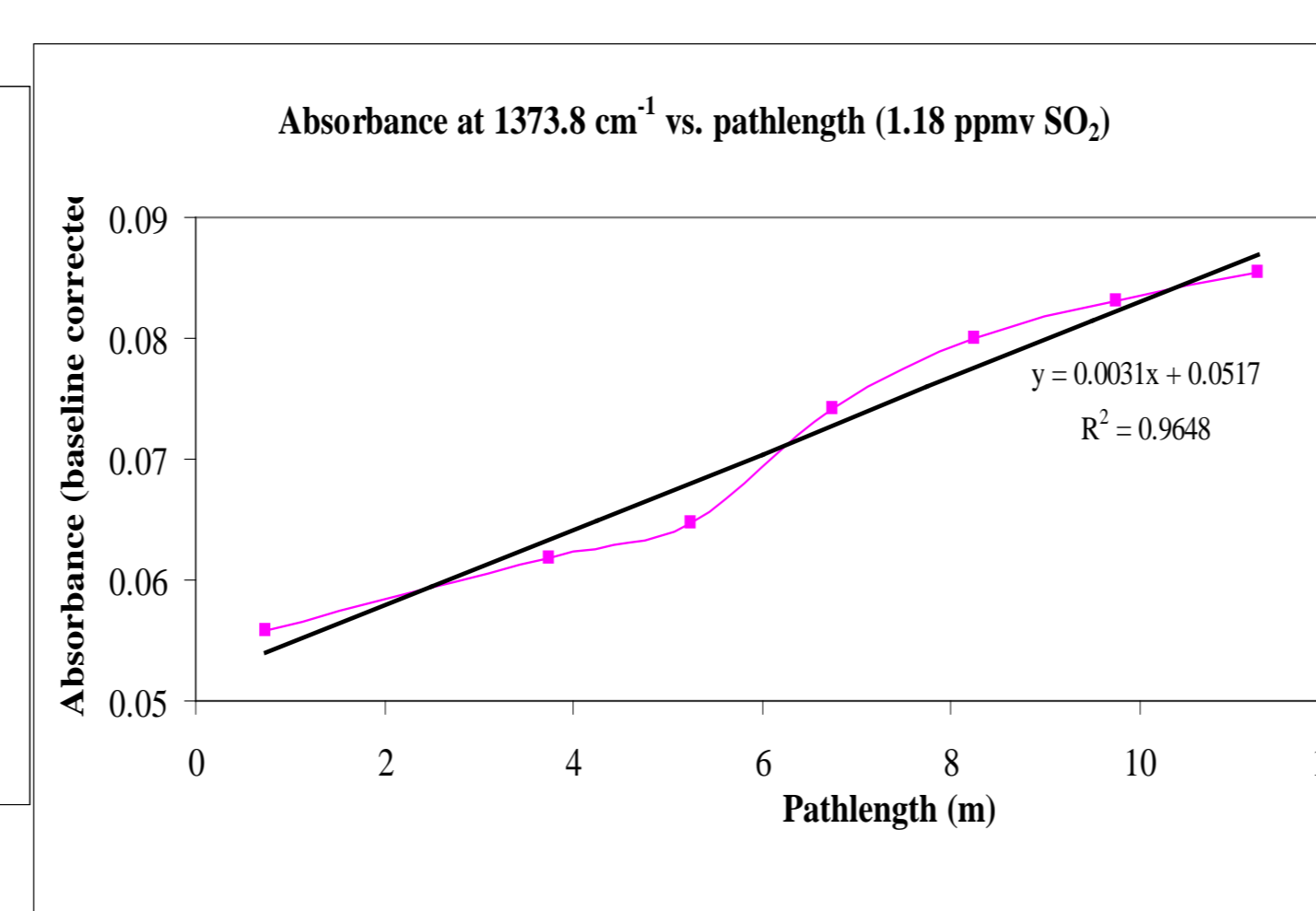


Figure 5.

The baseline was flattened close to zero absorbance by taking reference points on each side of the region of importance and assuming a linear variation with the wavenumbers. As a simple verification, the mean baseline absorbance value between 1260 and 1270 cm⁻¹ had a value lower than 1 milliabsorbance (see Figure 4).

One peak of SO₂, at 1373.8 cm⁻¹, is shown in Figure 5 to increase linearly with optical pathlength as expected.

From the good old Beer-Lambert's law⁽²⁾ : **Abs = ε n l**

Where ε is in units of cm² molec⁻¹
n in units of molec cm⁻³
l in units of cm

The sum of the line intensities over a whole band has to be done to get a comparable value⁽³⁾ :

$$\sum \epsilon \times \text{FWHM} (\text{cm}^{-1}) \rightarrow \sum S (\text{cm molec}^{-1})$$

Here the FWHM was used instead of the Doppler halfwidth for a matter of availability (medium resolution spectra).

Table 1.

	Σ S (cm molec ⁻¹)		Difference
	Hitran database	This work	
NH ₃ (630-1244 cm ⁻¹)	8.78 x 10 ⁻²⁰	6.49 x 10 ⁻²⁰ *	-26 %
SO ₂ (1311-1400 cm ⁻¹)	3.08 x 10 ⁻¹⁷	2.71 x 10 ⁻¹⁷	-12 %
NO ₂ (1429-1837 cm ⁻¹)	5.69 x 10 ⁻¹⁷	4.72 x 10 ⁻¹⁷	-17 %

* From 700 cm⁻¹ only

Then the line intensities (S) is related to the Einstein A coefficient⁽⁴⁾ :

$$\sum S = \frac{A g_u}{g_l 8 \pi n_r^3 c v^2}$$

where A : Einstein A coefficient (spontaneous emission)

g_u and g_l : degeneracies of upper and lower states (assumed to be ~1)

n_r : refraction index (taken as 1.00027) c : speed of light (2.9979x10¹⁰ cm s⁻¹)

v : mean wavenumber of the transition (950, 1362 and 1617 cm⁻¹ respectively)

Table 2.

	Einstein A coefficient (s ⁻¹)		Difference
	Hitran database	This work	
NH ₃	33	0.044	- 99.9 %
SO ₂	47	38	- 9 %
NO ₂	161	93	- 30 %

Respecting the Beer-Lambert law allows the quantification of gases in agreement with accepted values (HITRAN). Ammonia result is three orders of magnitude off the reference value because of a distorted spectrum by too high absorbance.

A warm car exhaust sample (Volvo 2000) was aspirated into the cell (through 5μ filter) and diluted with N₂ to give spectra in Figure 6.

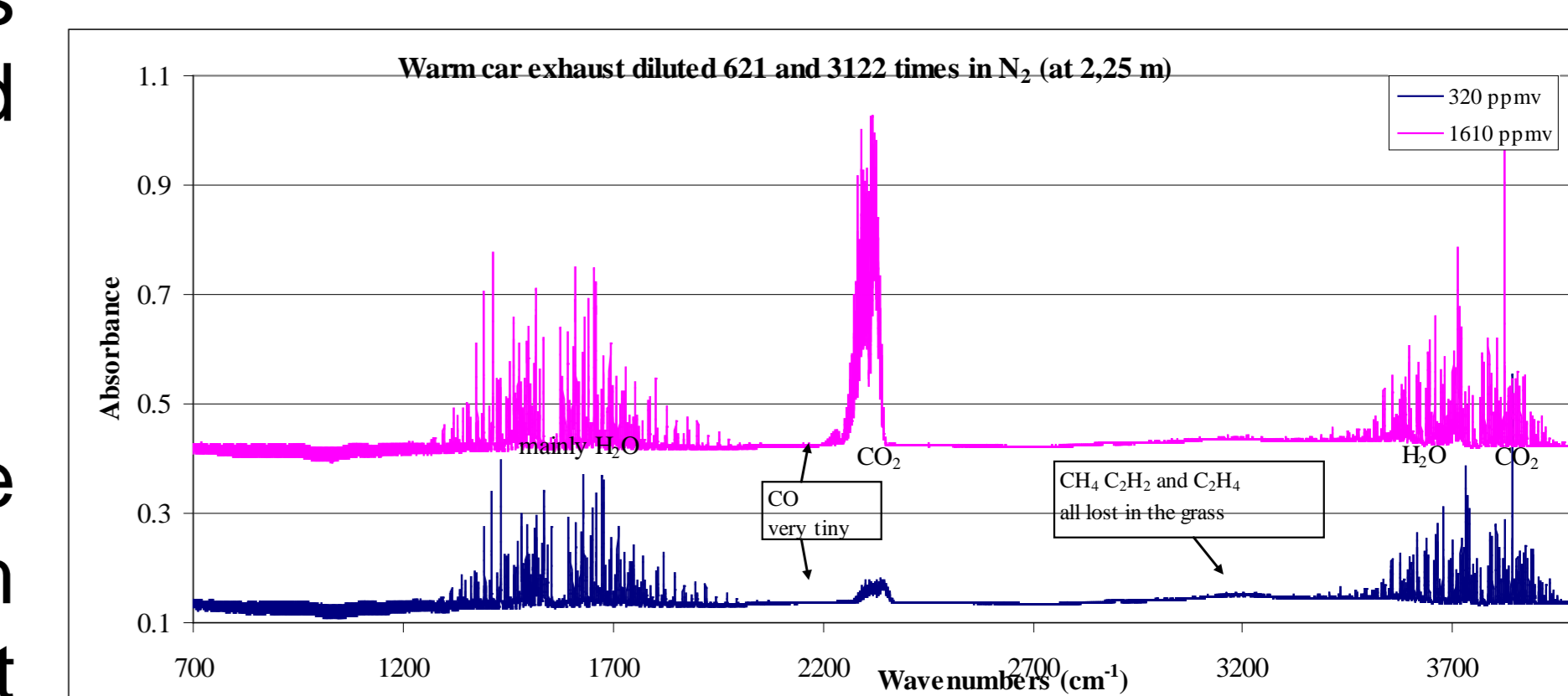


Figure 6.

Spectra of H₂O and CO₂ with the exact same treatment would be needed to subtract them from the ones on Figure 6 to be able to get the trace contaminant in the exhaust.

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