

How to be sure to measure all the ammonia in the original samples by infrared spectroscopy

Denis Bussi eres^a, A. Leclerc^a, L-M Gilbert^a, A. St-Gelais^a, D. Mass e^a, R. Larouche^b et S. Bourgault-C ot e^b.

^aD ept. Sc. Fondamentales, Universit e du Qu ebec   Chicoutimi ^bC egep de Jonqui ere

Infrared (IR) spectroscopy is used more and more to quantify different substances. Quantitative analysis puts some particular challenges when working with gas samples such as being sure of a calibration, the value of pressure and temperature, the amount of analyte with good precision.

While working with different gases, we have observed that ammonia, NH_{3(g)}, showed a variable signal with time (Fig.1 and 2). Some others^{1,2} observed the same phenomenon.

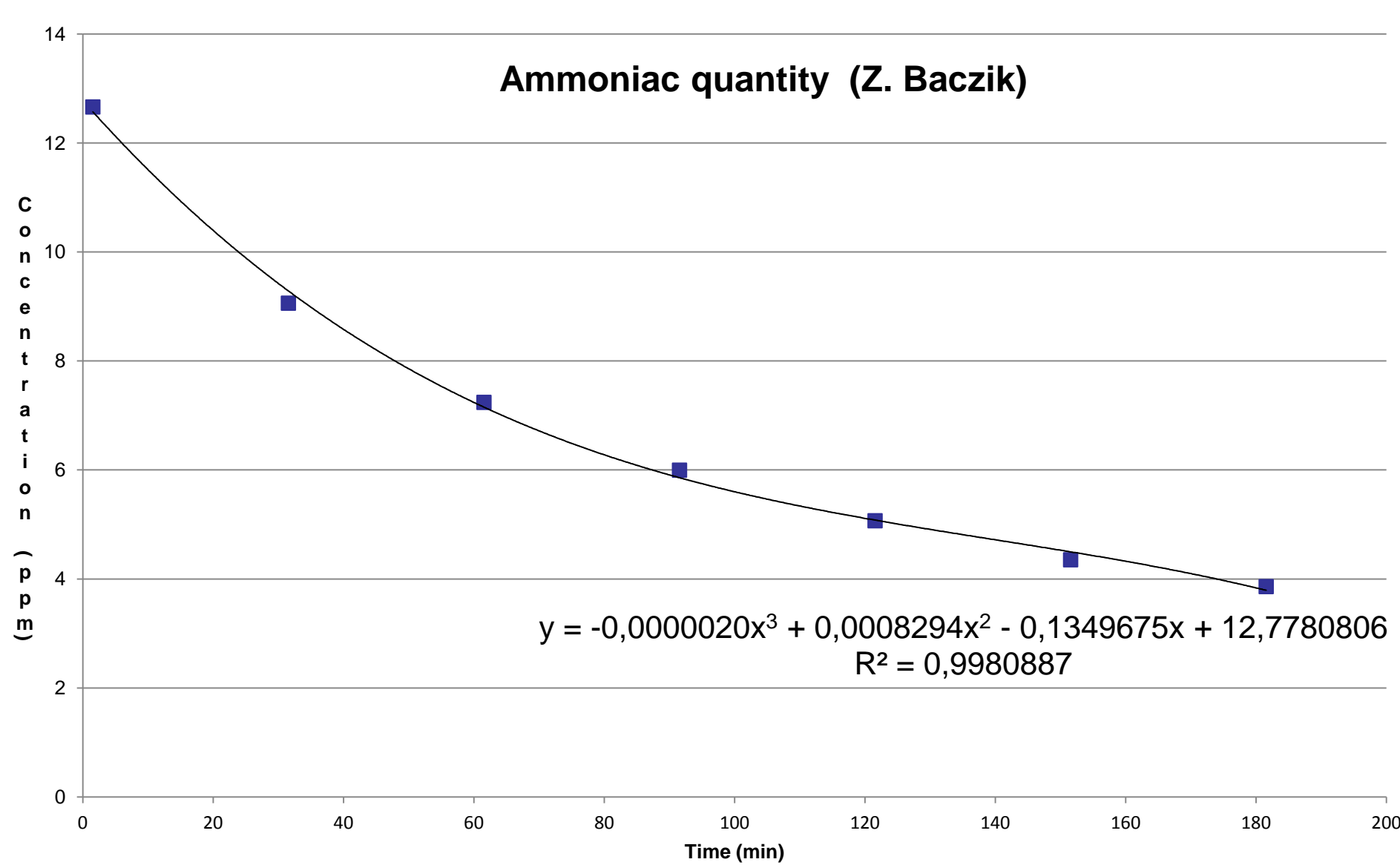


Figure 1. Ammoniac concentration by FTIR as a function of time of measurement (Z. Baczik¹).

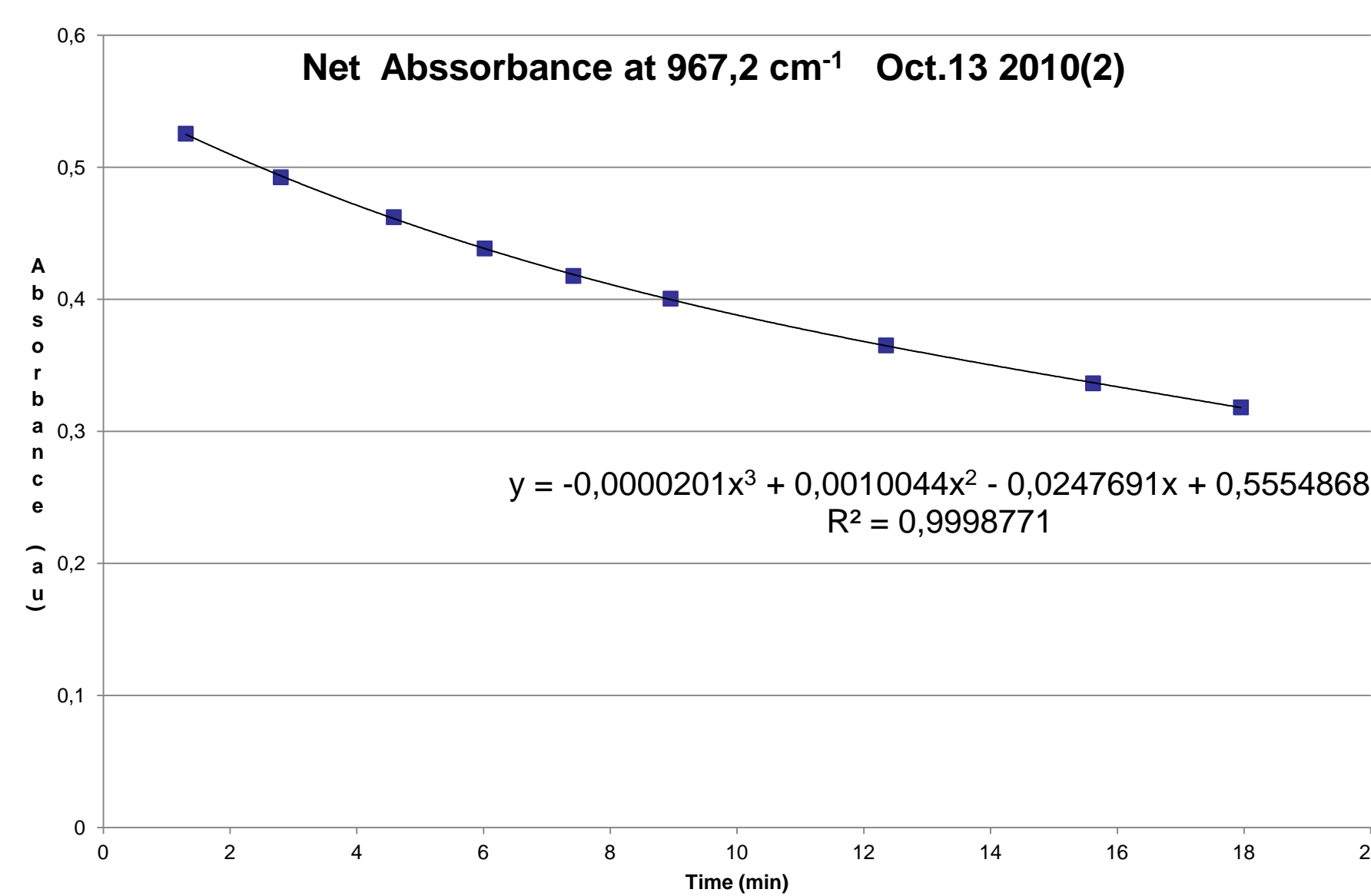


Figure 2. Net absorbance of ammonia at 967,2 cm⁻¹ (3600ppm in 1 atm dry N₂) as a function of time.

Our spectra were taken with an ABB (Bomem) infrared spectrophotometer with Fourier Transform (FTIR) model FTLA2000-104 (nominal resolution 1cm⁻¹ which means one data point every 0,5 cm⁻¹) with a DTGS detector.

We used a homemade glass cell with BaF₂ or ZnS windows and an optical path of 17 cm (volume 138,9 cm³). The ammonia gas had a purity of 99,995% and was sampled through Drierite with a gas-tight 500 L Hamilton syringe then injected into the cell through a rubber septum; the pressure in the gas cell was brought up to one atmosphere with dried N₂.

All spectra were recorded as single-beam files, for 4, 6, 16 or 64 scans depending on the need; a new background spectrum was recorded with only dried N₂ every time before a series of sample spectra. Spectra were manually transformed into Absorbance units upon verification of stable signal and baseline.

Ammonia presents a particular challenge for quantification with a decreasing signal. We consider this phenomenon as adsorption on the inside walls of the cell; this is not surprising when one considers the polarity of the molecule and the literature based on this behaviour for this gas.

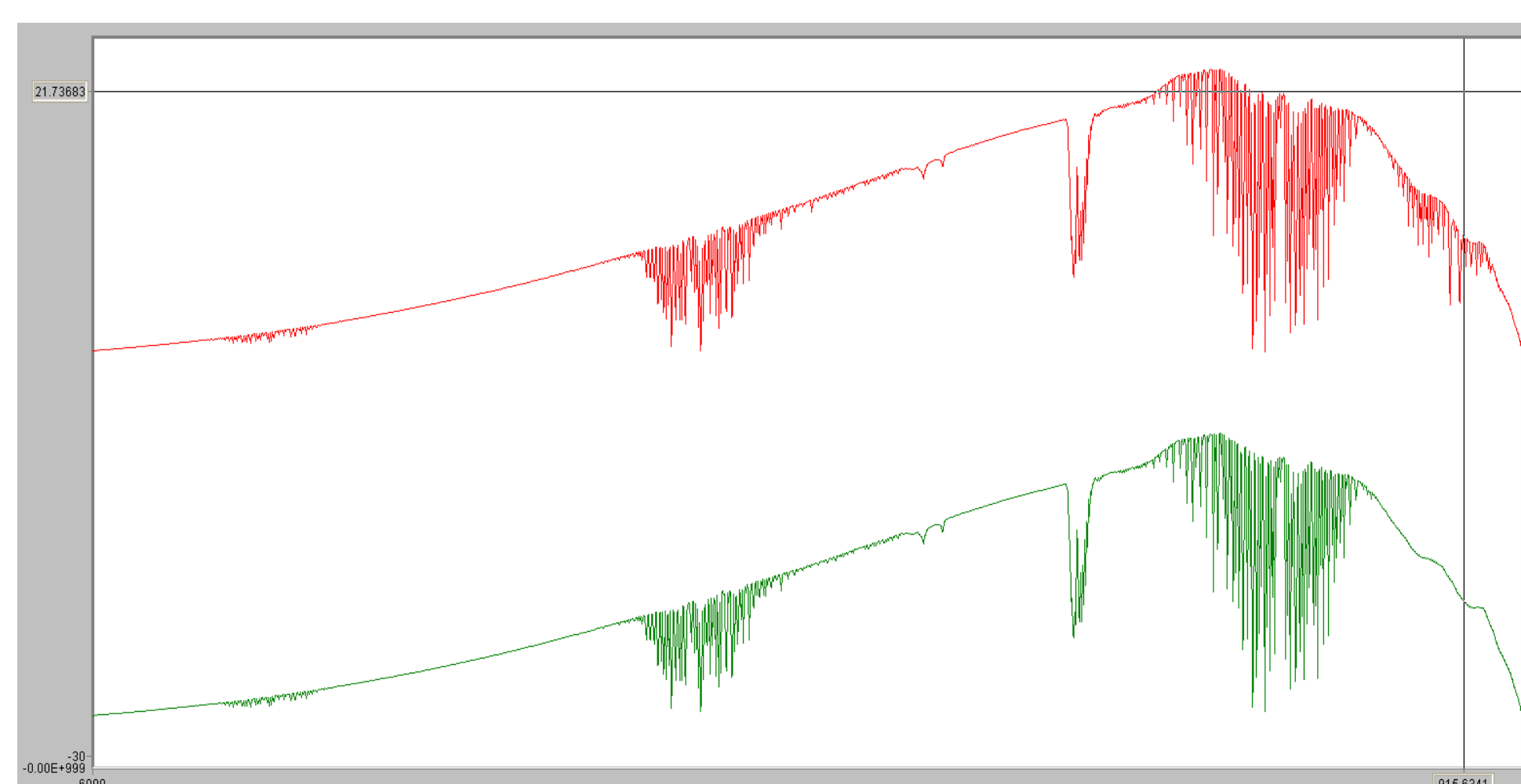


Figure 3. Single-beam spectra of ammonia (upper) with 6 scans and background (lower) with N₂ cell (October 13, 2010).

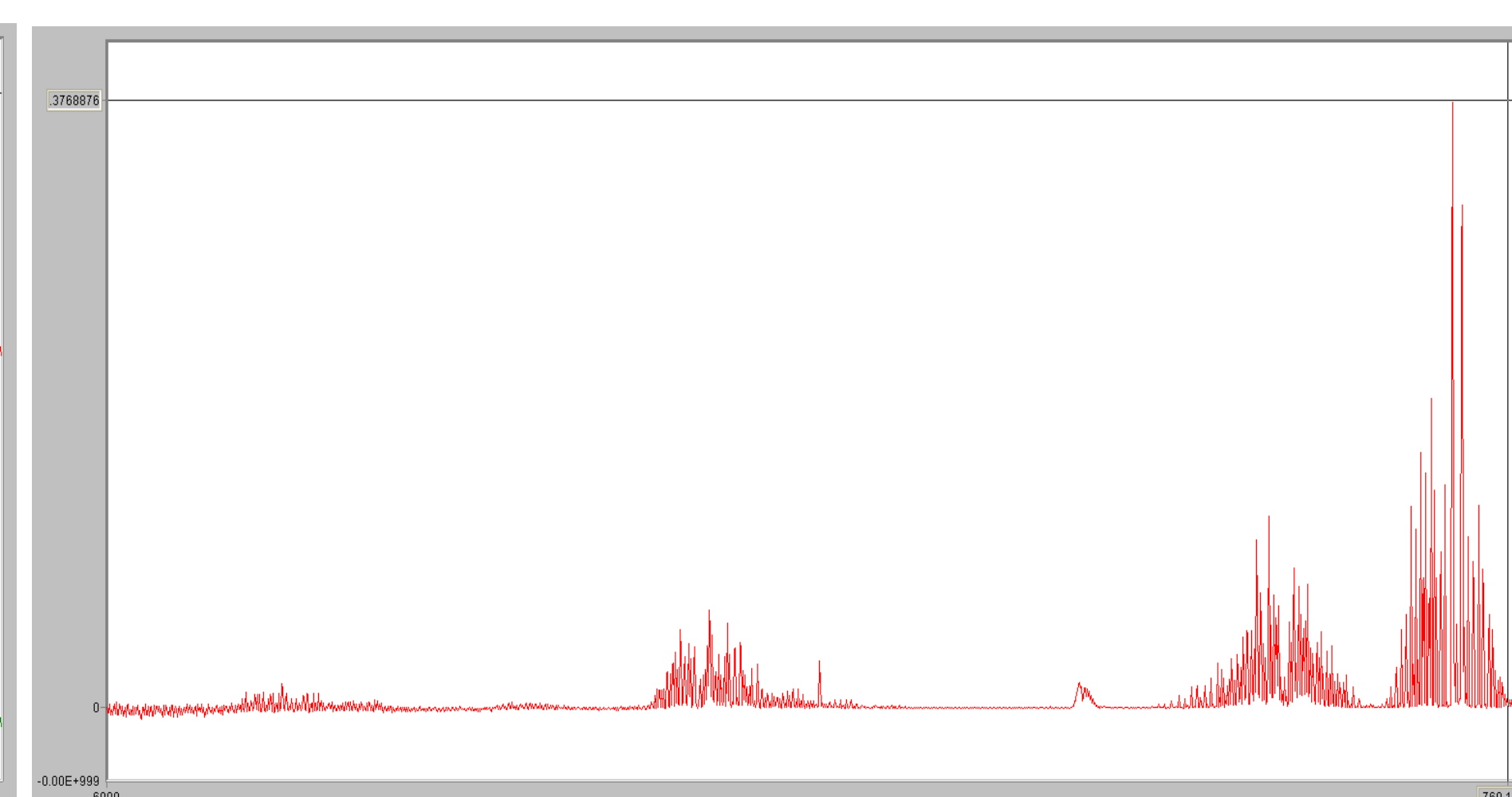


Figure 4. Absorbance spectrum of ammonia in 17 cm gas cell (October 13, 2010).

To quantify gas, one looks at the strongest absorbing peak in the spectrum. We choose the transition line at 967,2 cm⁻¹.

The best comparison available may come from a vast repertory of validated data and incorporated into a public database called HITRAN³. One finds a myriad of absorption lines identified with specific parameters for 41 different molecules; for ammonia, there are 1704 lines identified. The parameters of interest to us are the line intensities, S (cm⁻¹ molec⁻¹), the air-broadened halfwidth,  _{air} (cm⁻¹ atm⁻¹), the air-broadened pressure shift,   (cm⁻¹ atm⁻¹) and a relative uncertainty interval on these parameters.

To be able to relate such "Line Intensity" or "S" to the Absorbance given by an instrument, one has to apply (multiply by) a normalised line shape function, like a Lorentz profile, to "S". Then, one has to consider what is seen by the spectrometer (its detector), this referring to the point to be compared with these calculations. In our case, as two data points were measured by cm⁻¹, we considered that the spectrometer had a "window" of 0,5 cm⁻¹(this was verified by deconvoluting some small single peaks to check its full width at half maximum, FWHM).

The sum of the line intensities times the normalised line shape function has to be done to get a value comparable to the "usual extinction coefficient"   (3).

Table 1. Different transition lines considered and their parameters, centered at 967,2 cm⁻¹.

Datasheet for NH₃ at 296 K

| γ (cm ⁻¹) | Intensity S (cm molec ⁻¹) | γ_{air} (air broaden.) (cm ⁻¹) | δ Press. Broadening (cm ⁻¹ atm ⁻¹) | Sum of "S x f" (cm ² molec ⁻¹) |
|---------------------------------|---|---|--|--|
| 966,269 | 1,51E-19 | 0,1012 | 0,0000 | 2,45E-21 |
| 966,380 | 1,48E-19 | 0,0946 | 0,0000 | 3,63E-21 |
| 966,474 | 2,97E-20 | 0,0893 | 0,0000 | 1,10E-21 |
| 966,533 | 7,00E-21 | 0,0859 | 0,0000 | 2,50E-22 |
| 966,660 | 1,829E-34 | 0,0582 | 0,0000 | 6,99E-36 |
| 966,815 | 3,069E-19 | 0,1073 | 0,0000 | 8,29E-20 |
| 966,895 | 2,030E-24 | 0,0921 | 0,0000 | 1,37E-24 |
| 966,905 | 3,000E-19 | 0,1009 | 0,0000 | 1,94E-19 |
| 966,929 | 3,649E-35 | 0,0544 | 0,0000 | 3,30E-35 |
| 966,981 | 6,032E-20 | 0,0957 | 0,0000 | 4,00E-20 |
| 967,031 | 1,420E-20 | 0,0923 | 0,0000 | 1,15E-20 |
| 967,168 | 2,897E-30 | 0,0586 | 0,0000 | 2,88E-30 |
| 967,250 | 1,440E-20 | 0,1069 | 0,0000 | 1,15E-20 |
| 967,329 | 6,905E-27 | 0,0905 | 0,0000 | 5,64E-27 |
| 967,346 | 5,675E-19 | 0,1062 | 0,0000 | 4,39E-19 |
| 967,397 | 8,413E-31 | 0,0905 | 0,0000 | 5,72E-31 |
| 967,407 | 1,169E-19 | 0,1018 | 0,0000 | 7,54E-20 |
| 967,449 | 2,753E-20 | 0,0977 | 0,0000 | 1,81E-20 |
| 967,738 | 2,260E-19 | 0,1052 | 0,0000 | 2,67E-20 |
| 967,775 | 5,319E-20 | 0,1019 | 0,0000 | 3,45E-21 |
| 967,998 | 1,17E-19 | 0,1048 | 0,0000 | 5,05E-21 |

Sum 8,99E-19

This sum is equivalent to " " in Beer-Lambert law

One just multiplies this by "c x l" to get the Absorbance

So, these calculations give a theoretical Absorbance = 0,588 au

In our experiences, we had an Absorbance after zero time « extrapolated » to 0,55 au.

Considering the uncertainty of 10-20% on the « S » parameter and on the Lorentz line profile, these values agree very well and our quantification is good.

Unfortunately, we cannot be more precise than the reference data used.

Sincere thanks to Dr. S. Allaire, Laval University, for the use of her FTIR.

(1) Paczik, Zoltan, Private comm. (2008).

(2) Aroui, H., Private comm. (2011).

(3) Rothman, L.S. et al., HITRAN public database with associated documentation (2011) : <http://www.cfa.harvard.edu/HITRAN/>

Beer-Lambert law : **Abs =   n l**

Where   is our extinction coefficient =

8,99E-19 cm² molec⁻¹

n is our number of molecules =

3600ppmv = 8,85E16 molec cm⁻³

l is our cell optical path = 17 cm