

Physikpraktikum für Vorgerückte

Laser Spectroscopy

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1 Summary

Various experiments with a gas spectrometer using a tunable infrared diode laser are made, including measurement of device properties such as spectral and intensity response of the detectors, quantitative analysis of a gas mixture, and examination of the pressure dependence of absorption lines. A great part of the work consists in processing and analyzing the gathered data, which is done on a computer using the programs Matlab, Pro Fit, and Gnuplot.

2 Experimental Setup

The main parts of the setup used are:

- an external cavity infrared diode laser which can be tuned to any wavelength between 1540 and 1660 nm with a resolution of 0.001 nm at powers between 0.20 and 6.32 mW,
- a multipass gas analysis cell, which is a glass tube holding the gas to analyze in which the laser beam is folded using mirrors to achieve a longer absorption path length,
- a photodiode measuring the transmitted laser intensity.
- To eliminate environmental influences, the amplitude of the laser beam is modulated using a mechanical chopper, whose control signal is fed together with the measurement signal from the photodiode to a lock-in amplifier, which detects the signal with the right frequency and discards all the rest.
- The whole installation is operated by a computer that automatically adjusts the laser wavelength and records the measurement from the lock-in amplifier together with some other quantities.
- To control the beam path in the multipass cell, the visible beam of a He-Ne laser can be overimposed on the invisible infrared beam.

Details of the setup are described in the lab manual.

3 Laser Power and Detector Response

To measure the maximal laser power as a function of the wavelength as well as the spectral and intensity response of the photodiode, the following measurements were made with the multipass cell fully evacuated:

laser power [mW]	wavelength interval [nm]	wavelength step [nm]	wavenumber interval [cm^{-1}]	# of data points
0.20	1540–1660	2.0	6024.1–6493.5	61
0.40	"	"	"	"
0.60	"	"	"	"
0.80	"	"	"	"
1.00	"	"	"	"
1.20	"	"	"	"
1.40	"	"	"	"
1.60	"	"	"	"
2.00	"	"	"	"
2.50	"	"	"	"
4.00	"	"	"	"
6.32	"	"	"	"

The raw results of these measurements are shown in figure 1. The marked points are those where the laser current limitation was in effect, i.e. the laser was delivering less than the requested power.

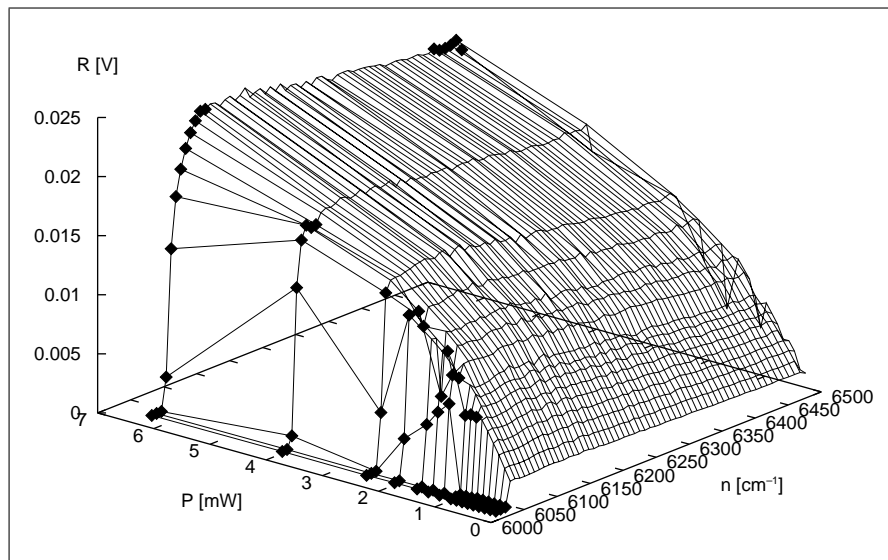


Figure 1: Raw measurement results

3.1 Maximal Laser Power

The maximal laser power can directly be taken out of the measurement at (requested) 6.32 mW, because a voltage signal proportional to the laser power is recorded during the measurements. It is shown in figure 2. Again, black marked points indicate current limitation.

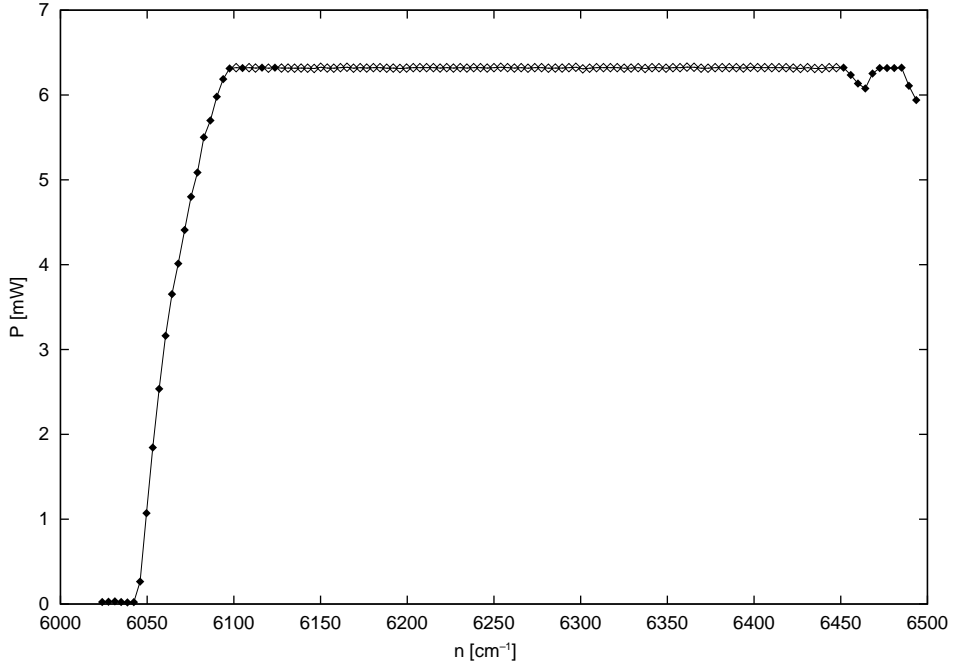


Figure 2: Maximal laser power as a function of the wavenumber

3.2 Spectral and Intensity Response of the Detector

As one can see in figure 1 (ignoring the points with current limitation), the detector signal has a slight dependence on the wavenumber and a nonlinear dependence on the laser power. It seems reasonable to model this total response function R as a product of a spectral response R_S and an intensity response R_I :

$$R(n, P) = R_S(n) \cdot R_I(P)$$

To find these two functions, the following algorithm was applied to the data shown in figure 1:

- Discard all garbage data points at the borders.
- Choose one reference wavenumber n_R . For every wavenumber n , do the following: calculate the quotient $R(n, P)/R(n_R, P)$ for every power P . Average this over all P to get the spectral response $R_S(n)$.
- For every power P , average the quotient of measured value and spectral response $R(n, P)/R_S(n)$ over all n to get the intensity response $R_I(P)$.
- Divide R_I by its value at $P = 1$ mW and multiply R_S by the same number to get the spectral response normalized to 1 mW.

The results of these calculations are shown in figure 3 and 4. Multiplying these two functions yields the function shown in figure 5, which differs from the original mea-

sured values by 2.1% (root mean square of $(R_{calc}/R_{meas} - 1)$). This is a clear confirmation that the product model was good.

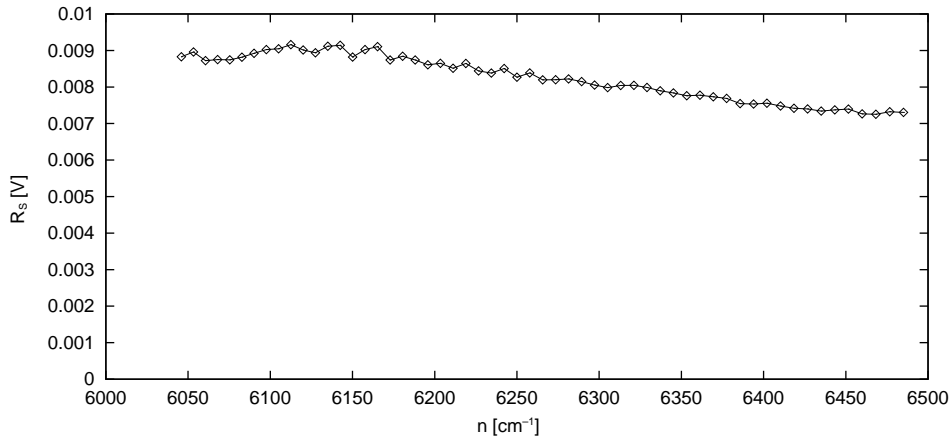


Figure 3: Spectral response (normalized to $P = 1$ mW)

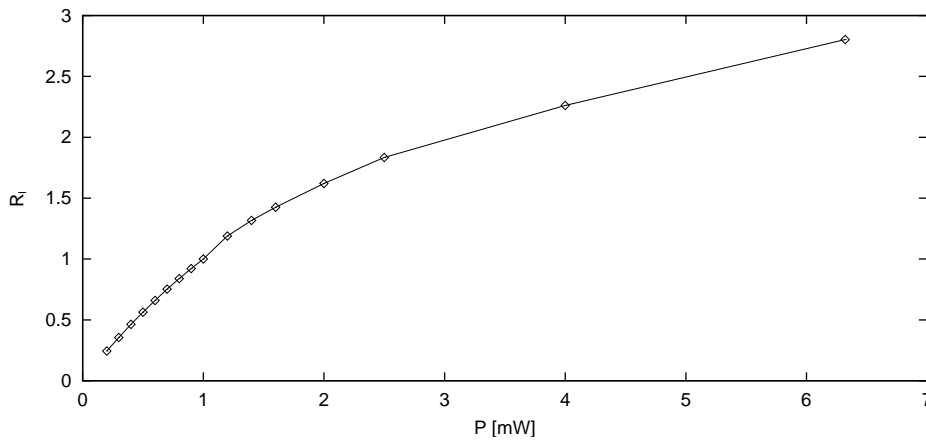


Figure 4: Intensity response

One disturbing thing about this spectral response curve is the bumps that it exhibits especially around 6150 cm^{-1} . These are caused by interference between the relatively coarse sampling and the high frequency variation caused by the Fabry-Perot etalon effect of the cell windows that is discussed in detail in [section 4.4](#). Because of their strong dependence on the phase of the variation, they cannot easily be systematically corrected. One can however get rid of them by just smoothing them out: convolution with $[1.5, 4, 5, 4, 1.5]/16$ has shown to generate a nice smooth curve. Together with the intensity response, one gets the final total response function shown in [figure 6](#). This function differs from the original measured values by 2.2% (RMS of $(R_{calc}/R_{meas} - 1)$), so the smoothing didn't add much error.

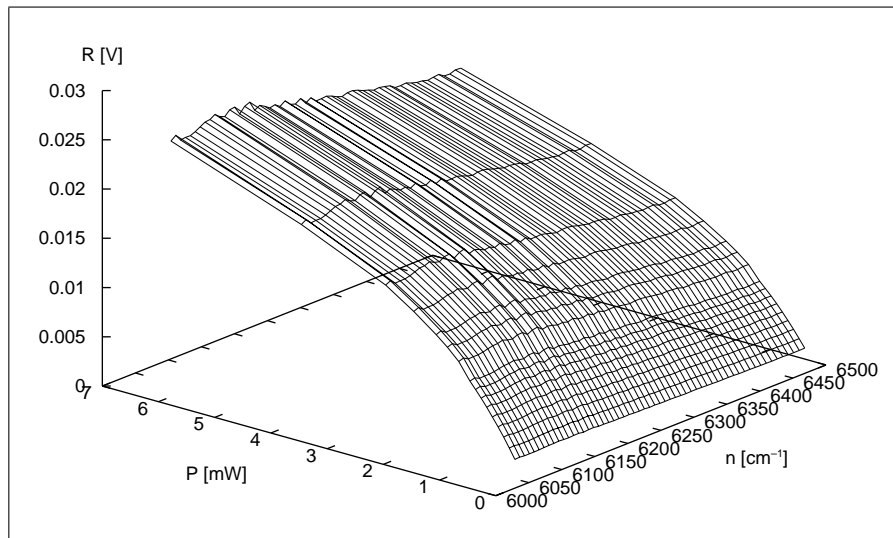


Figure 5: Calculated total response

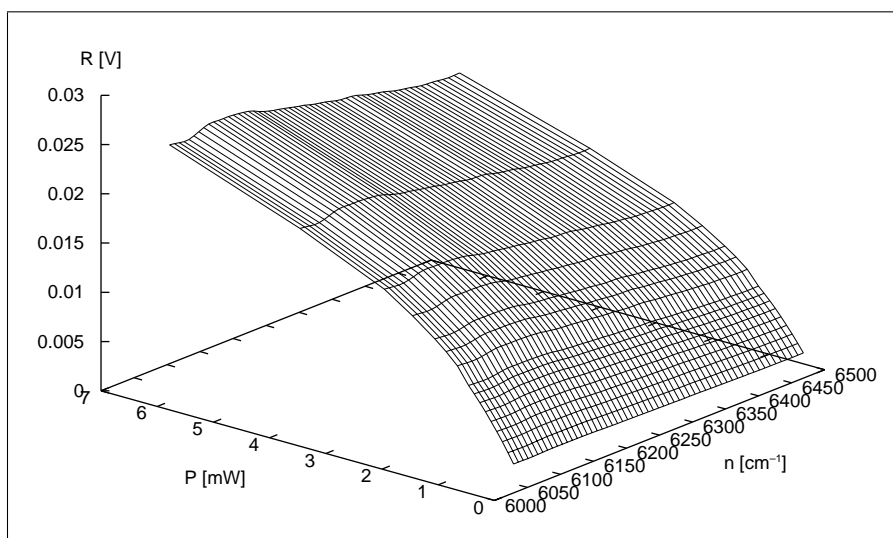


Figure 6: Final smoothed total response

4 Quantitative Gas Analysis

4.1 Multipass Cell

For quantitative gas analysis, the multipass cell is used. According to the lab manual, its mirrors have a reflectivity of 0.986, and the distance between them is 1.36 m. The windows through which the laser beam enters and leaves are made of KCl with a refractive index of 1.54. To calculate the total path length and the transmittance, it is necessary to know how many times the beam is reflected until it leaves the cell. This can be determined by using the He-Ne laser and counting the visible dots it makes on the field mirror. I counted 22 dots on the upper row and 23 on the lower one, which means that the beam passes through the cell $4 \cdot 23 = 92$ times and is reflected 91 times. Thus, the total path length is $92 \cdot 1.36 \text{ m} = 125.12 \text{ m}$, and the combined reflectivity of all mirrors $0.986^{91} = 0.28$. One face of a window has a reflectivity (for perpendicular incidence) of

$$R = \left(\frac{1.54 - 1}{1.54 + 1} \right)^2 = 0.045.$$

Because the window has two parallel faces within small distance, waves can be reflected between the two faces multiple times and interfere with each other, making the window act as a Fabry-Perot etalon. Its transmittance

$$\frac{1}{1 + \frac{4R}{(1-R)^2} \sin^2(kd)}$$

varies between 1 and 0.83 for different wave vectors k . At this small R , the transmittance as a function of k is approximately sine-shaped, thus the mean transmittance is approximately 0.92. For the mean total transmittance of the multipass cell, we get $0.28 \cdot 0.92^2 = 0.23$.

4.2 Reference Spectra from the HITRAN Database

Using the program Molspec, the HITRAN Database (version 2k), which lists 1 080 000 absorption lines of 36 gases, was searched for gases with absorptions in the available wavelength interval of 1540–1660 nm ($\hat{=}$ wavenumber interval 6024–6494 cm^{-1}). Lines were found for H_2O , CO_2 , CO , CH_4 , OH , HI , for which reference spectra were calculated by Molspec. As calculation parameters, the real values from the experiment were used: pressure 946 mbar, temperature 293 K, path length 12512 cm, Lorentz line shape. The concentrations were chosen so that the absorption lines are clearly visible without being clipped. These reference spectra are shown in figure 7.

4.3 Spectrum Measurement

To analyze the composition of a gas mixture that is provided in a gas cylinder in the lab, the multipass cell was filled with the gas up to the atmospheric pressure of 946 mbar, and the following measurements were taken with a laser power of 1 mW:

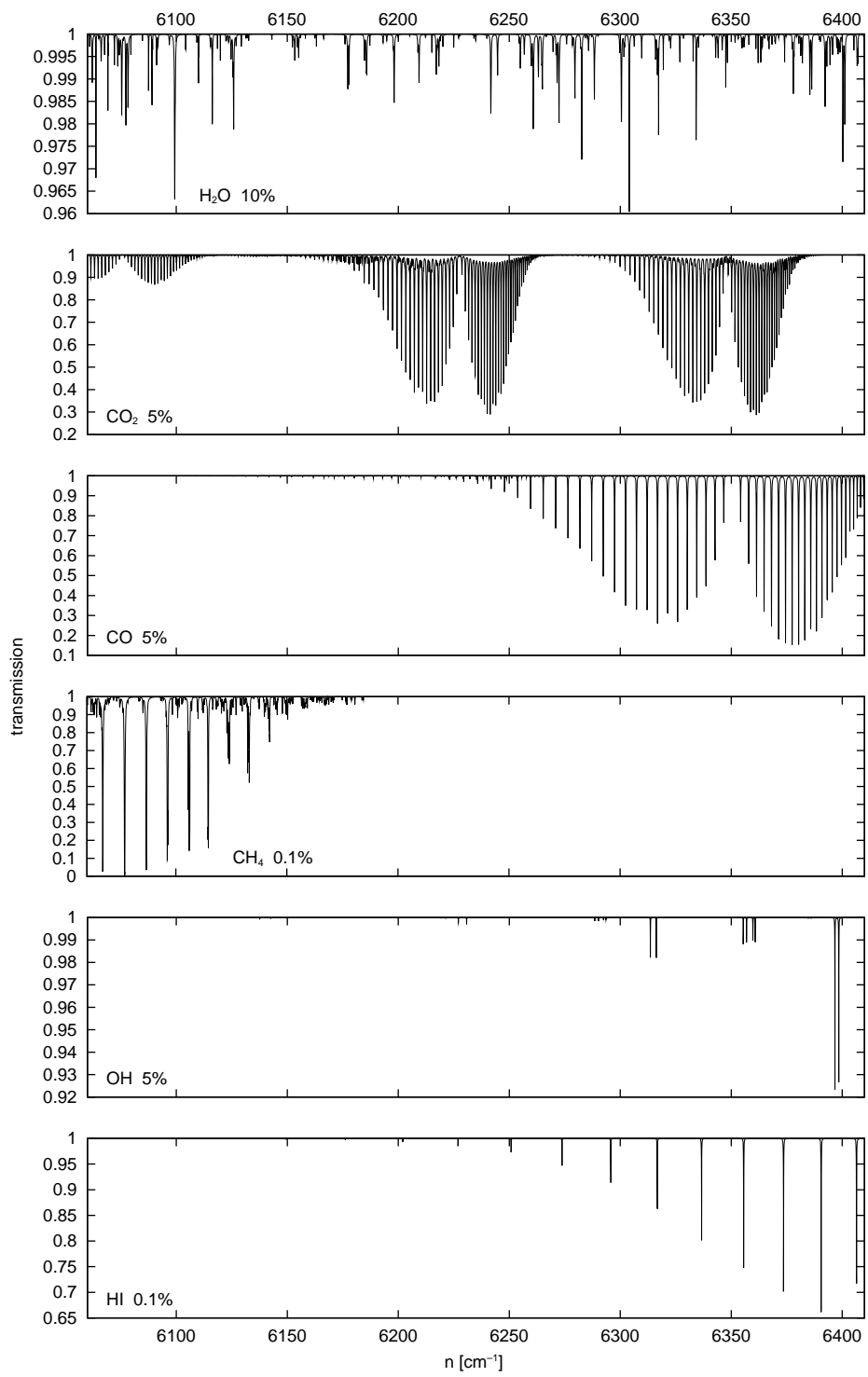


Figure 7: Reference spectra

	wavelength interval [nm]	wavelength step [nm]	wavenumber interval [cm ⁻¹]	# of data points
full spectrum	1560.00–1650.00	0.02	6060.6–6410.3	4501
CH ₄ detail	1645.400–1645.800	0.001	6076.069–6077.550	401
CO ₂ detail	1602.400–1603.200	0.001	6237.525–6240.640	801
CO detail 1	1568.000–1568.300	0.001	6376.331–6377.551	301
CO detail 2	1567.200–1567.600	0.001	6379.178–6380.807	401

Because the measurements take very long (0.5 seconds per data point), the full spectrum was not taken over the whole range 1540–1660 nm and with the best resolution of 0.001 nm.

Figure 8 shows the raw full spectrum.

4.4 Cleaning up the Spectrum

Fabry-Perot Effect

The first thing to catch one's eye about this spectrum is a consistent periodic variation with a period of about 0.8 cm⁻¹. As already discussed before, such a variation is caused by the cell windows acting as Fabry-Perot etalons. The period of the transmittance of an etalon of thickness d is π/d in wave vectors k or (with $k = 2\pi n$) $1/(2d)$ in wavenumbers n , so a period of 0.8 cm⁻¹ corresponds to a thickness of 6.25 mm, which seems quite a reasonable guess (unfortunately the window thickness can't be measured directly without taking apart the whole installation).

To correct this systematic error, it has to be modeled. As mentioned before, the transmittance of an etalon is roughly sine-shaped for small reflectivities.

- The frequency of the oscillation can easily be determined by following it over many periods. Measuring over 300 periods with an accuracy of 1/4 period gives a period of (0.8133 ± 0.0007) cm⁻¹.
- The amplitude of the oscillation shows no clear regularity, it seems to be approximately constant in the first third of the spectrum, then it diminishes and seems to vanish altogether towards the end. To get a quantitative measure of this behavior, some periods at several exposed places (around 6072, 6175, and 6294 cm⁻¹) were chosen and a sine fit to them to get the amplitude at that point (2.2, 2.2, and $0.94 \cdot 10^{-4}$ V, respectively), the amplitude at the end of the spectrum at 6420 cm⁻¹ was assumed to be 0, then that amplitude was linearly interpolated over the whole spectrum.
- The phase of the oscillation can also be taken from the local sine fits done in the previous step. One finds a shift of the sine by (0.43 ± 0.05) cm⁻¹.

Everything taken together, the etalon transmission is modeled as

$$T(n) = 1 - A(n) \left(\sin \left(\frac{2\pi}{8.133 \text{ cm}^{-1}} (n - 0.43 \text{ cm}^{-1}) \right) + 1 \right)$$

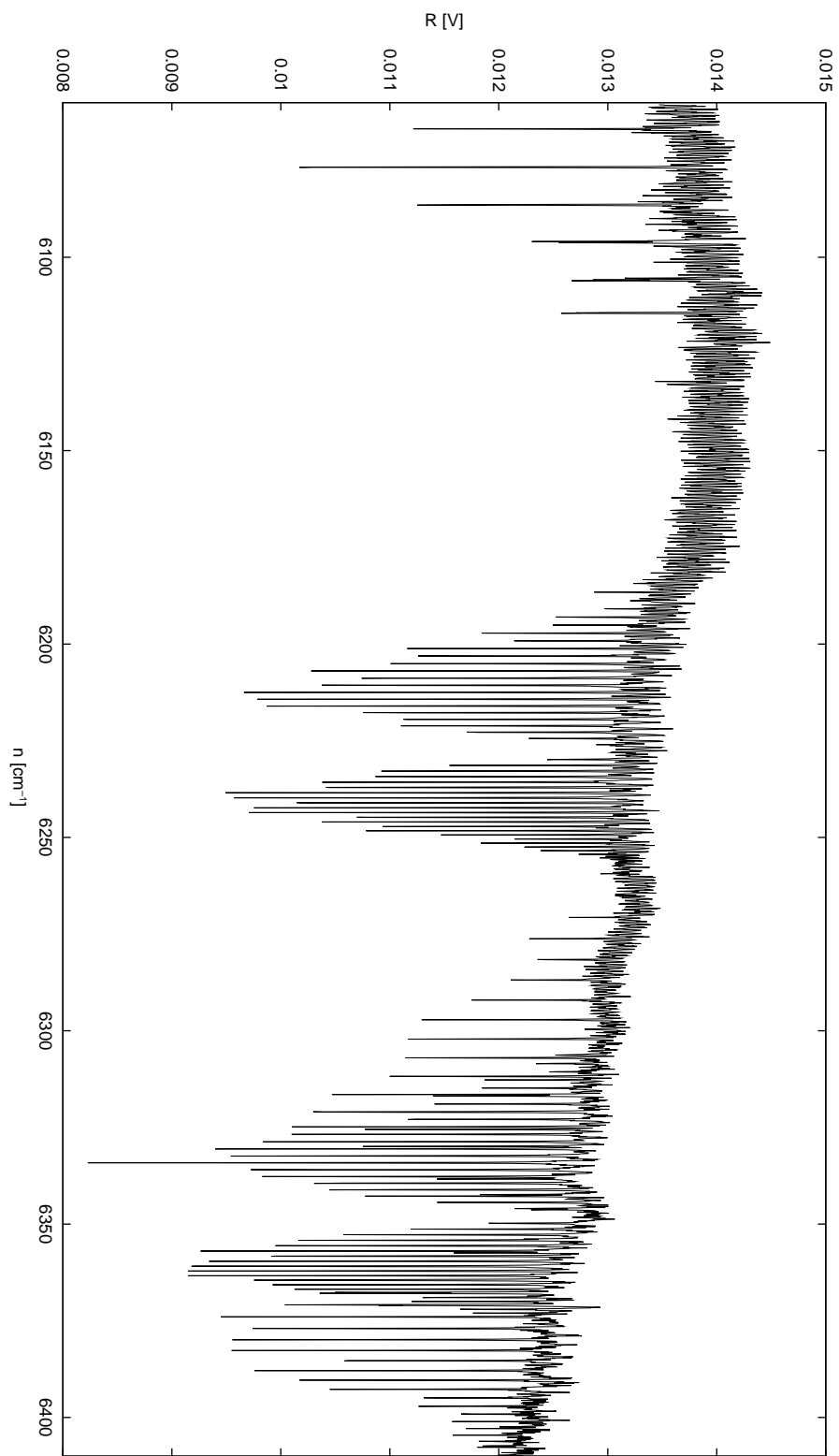


Figure 8: Raw full gas spectrum

where $A(n)$ is the linear interpolation of the points

$$\begin{aligned} &(6072.3 \text{ cm}^{-1}, (0.0157 \pm 0.0008)) \\ &(6175.6 \text{ cm}^{-1}, (0.0157 \pm 0.0008)) \\ &(6294.4 \text{ cm}^{-1}, (0.0072 \pm 0.0006)) \\ &(6420.0 \text{ cm}^{-1}, 0) \end{aligned}$$

which were calculated from the local sine fits.

Dividing the spectrum by this correction function indeed manages to get most of the oscillation away. Between 6090 and 6140 cm^{-1} , there is a slight phase shift between the measured oscillation and the correction function, so that the corrected spectrum oscillates just as much as before. Other than that however, all variation that's still left looks like noise and doesn't exhibit any distinguished frequencies. Correcting that phase shift, which probably comes from an inaccuracy in the laser tuning, as well would require much greater effort, and since there are no important absorption lines in that area, it doesn't seem worth it.

Detector Response

Second, the signal falls for higher wavenumbers. This is obviously the spectral response of the detector that was determined in [section 3.2](#), which can easily be corrected together with the intensity response (which mainly affects the depth of the lines) using the total response surface from [figure 6](#): project the curve from the signal-wavenumber plane onto the surface and from there down on the intensity-wavenumber plane to get a curve that is proportional to the intensity. This cleaned up spectrum is shown in [figure 9](#).

4.5 Quantitative Analysis

Comparing the cleaned up spectrum to the reference spectra, one clearly sees that the gas sample contains CO_2 , CO , and CH_4 . It might also contain some H_2O , but the in reference spectrum, even with the high concentration of 10%, the lines are so weak and so randomly distributed that one wouldn't notice them in the measured spectrum.

To find out the concentration of these components, the detail spectra taken from prominent lines (marked in [figure 9](#)) are used. First, the detector response is taken into account by projecting the data through the response surface as above. Then a sine with a period of 0.8133 cm^{-1} is fitted to the background of the line and the data divided by it to correct the etalon effect and normalize the background to 1, yielding the effective transmission $T(n)$. Because the absorption is exponential, the line strength S can then be found by integrating $-\ln(T(n))$ over the line: $S = -\int \ln(T(n))dn$. The same thing is done to the same line in the reference spectrum, and because the line strength is proportional to the gas density (and thus the concentration), the effective concentration C is found by multiplying the reference spectrum concentration with the ratio of measured line strength to reference line strength. The results of these calculations are as follows:

	reference		measurement	
	S [cm^{-1}]	C [%]	S [cm^{-1}]	C [%]
CH_4	1.488 ± 0.002	0.1	0.1166 ± 0.0002	$(7.84 \pm 0.02) \cdot 10^{-3}$
CO_2	0.266 ± 0.002	5	0.1019 ± 0.0004	1.92 ± 0.02

CO ₂ 2	0.273 ± 0.002	5	0.1138 ± 0.0004	2.08 ± 0.02
CO 1	0.338 ± 0.003	5	0.081 ± 0.003	1.20 ± 0.05
CO 2	0.332 ± 0.003	5	0.099 ± 0.003	1.50 ± 0.05

So, the final result is: (78.4 ± 0.2) ppm CH₄, $(2.00 \pm 0.08)\%$ CO₂, and $(1.3 \pm 0.1)\%$ CO. For comparison, a spectrum calculated by Molspec with these parameters is shown in figure 10.

5 Pressure Dependence of Spectral Lines

To analyze how the line width and the line strength of absorption lines depend on the pressure, the following measurements with laser power 1 mW were made on a CO₂ absorption line from the gas mixture analyzed in the previous section:

pressure [mbar]	wavelength interval [nm]	wavelength step [nm]	wavenumber interval [cm ⁻¹]	# of data points
0.3	1609.500-1609.800	0.002	6211.95-6213.11	151
10.1	"	"	"	"
21.2	"	"	"	"
50.2	"	"	"	"
98	"	"	"	"
200	"	"	"	"
300	"	"	"	"
399	"	"	"	"
508	"	"	"	"
652	"	"	"	"
801	"	"	"	"
946	"	"	"	"

The raw results of these measurements are shown in figure 11.

A surprising feature of this measurements is that the signal seems to decrease as the pressure is lowered. I have not found a good explanation for this, especially as the dependence seems to be somewhat irregular. What one would expect is that more light gets through when there's less gas in its way.

Cleaning up the data goes the usual way: projection through the detector response surface (at this small wavenumber interval, the spectral response can be assumed as constant, only the intensity response is relevant) yields a signal proportional to the intensity. Fitting sines with frequency and phase constant over all pressures to the background and dividing by them eliminates the etalon effect and normalizes the background transmission to 1 (also eliminating the strange pressure dependence of the background). Taking the negative logarithm gives the absorption strength curves shown in figure 12 (thin curves).

Experimentation shows that this data can be approximated very closely by Lorentz functions (much better than by Gauss functions). Fitting Lorentz functions to the curves gives the thick curves in figure 12.

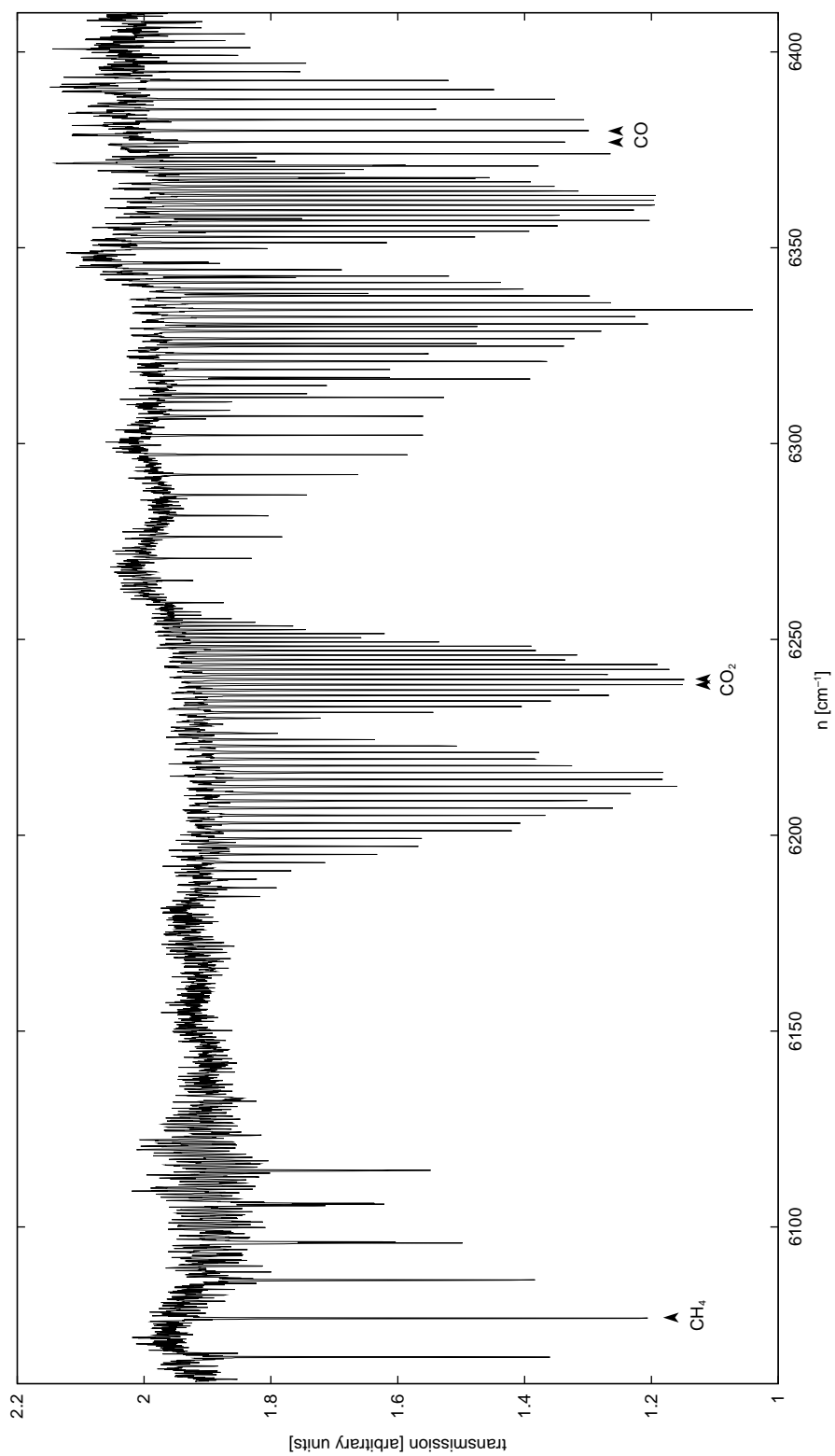


Figure 9: Cleaned up gas spectrum

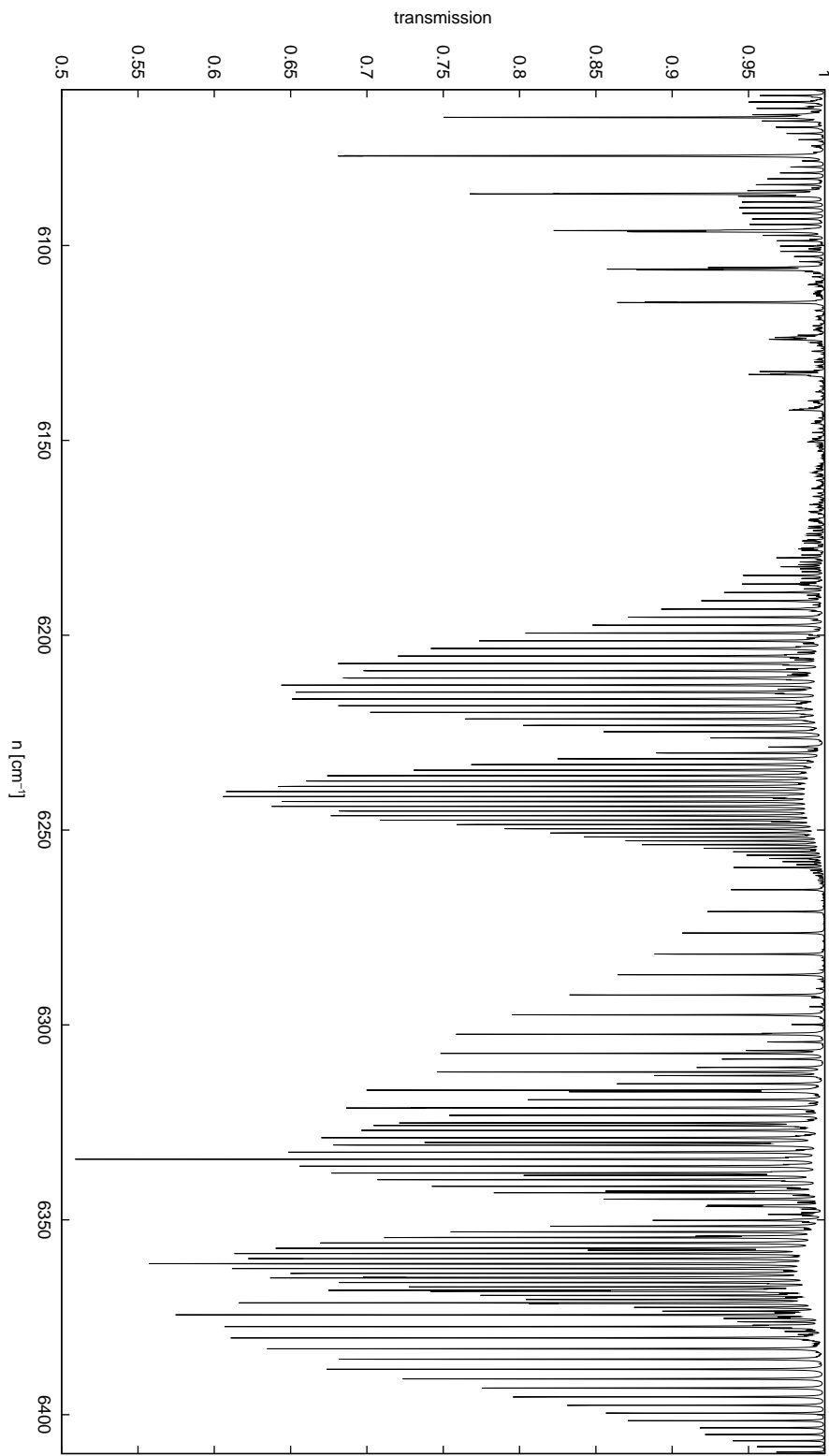


Figure 10: Spectrum calculated by Molspec

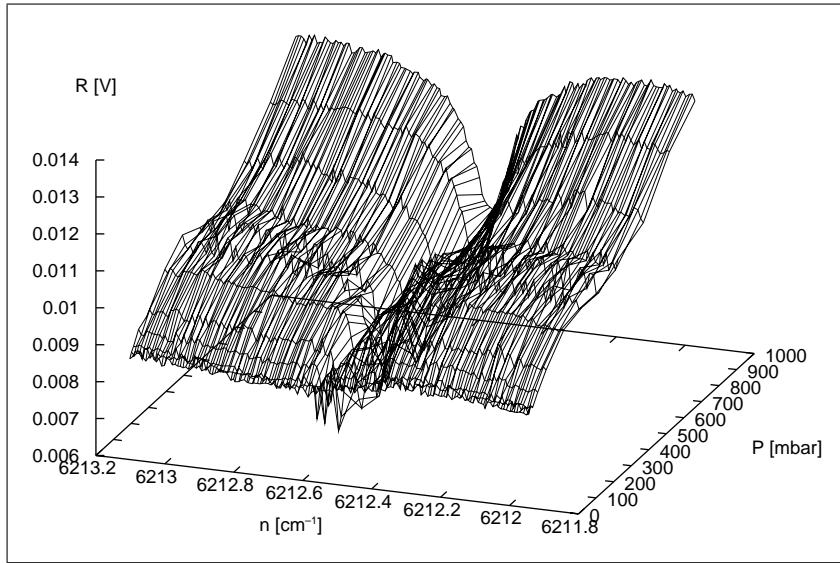


Figure 11: Raw measurement results

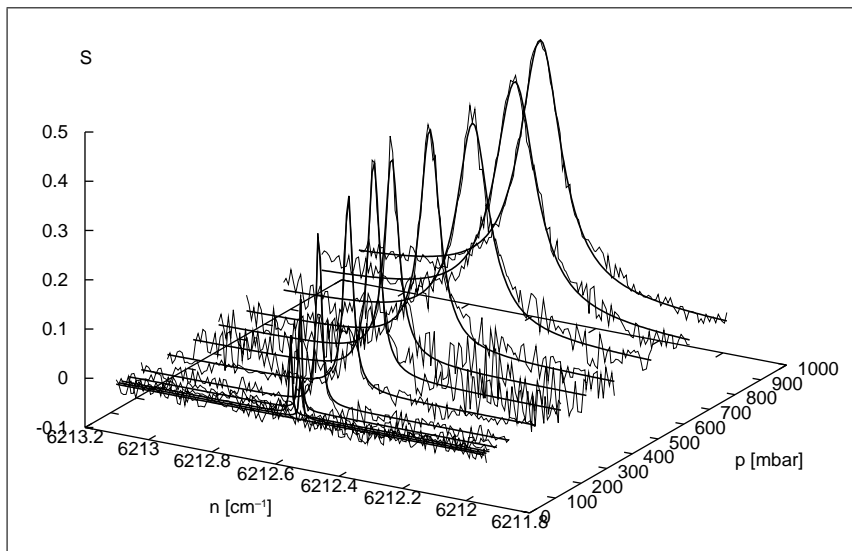


Figure 12: Absorption strength data with Lorentz fits

The fit parameters A (height) and K (sharpness) from the Lorentz functions

$$f(n) = \frac{A}{1 + K \cdot (n - n_0)^2}$$

can be used to calculate the line width (FWHM) $\delta n = 2/\sqrt{K}$ and the line strength $\int_{-\infty}^{\infty} f(n)dn = A\pi/\sqrt{K}$. The results of these calculations are shown in figures 13 and 14.

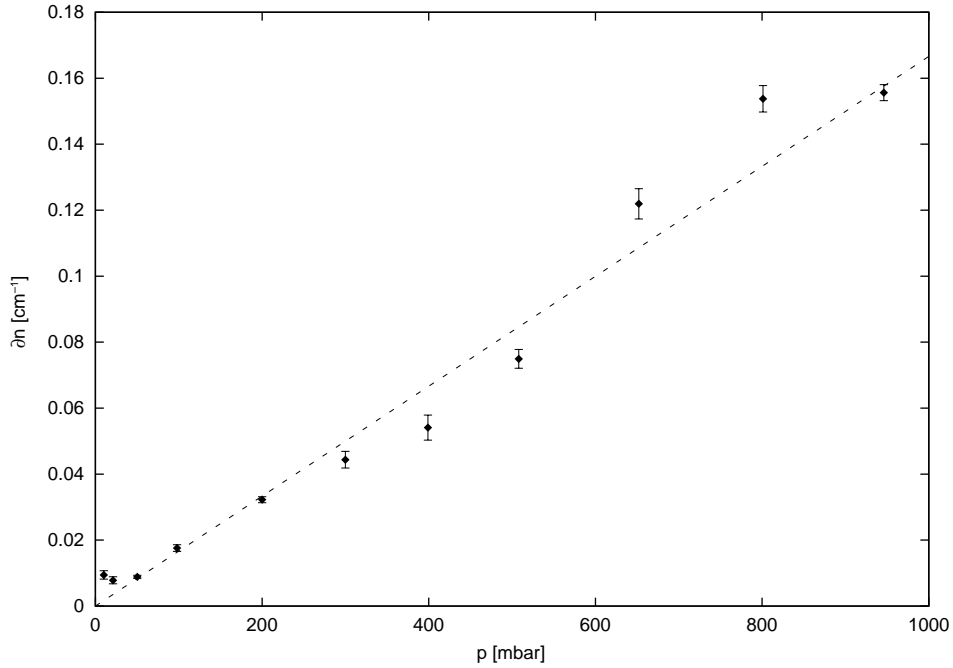


Figure 13: Line width as a function of pressure

Conclusions: The Lorentzian line shape and the line width roughly proportional to pressure, except for very small pressures, are a clear indication that the dominant line widening effect is pressure widening. The line strength being proportional to pressure is predicted by the absorption model which says that the probability of a photon being absorbed is proportional to the number (density) of gas molecules present.

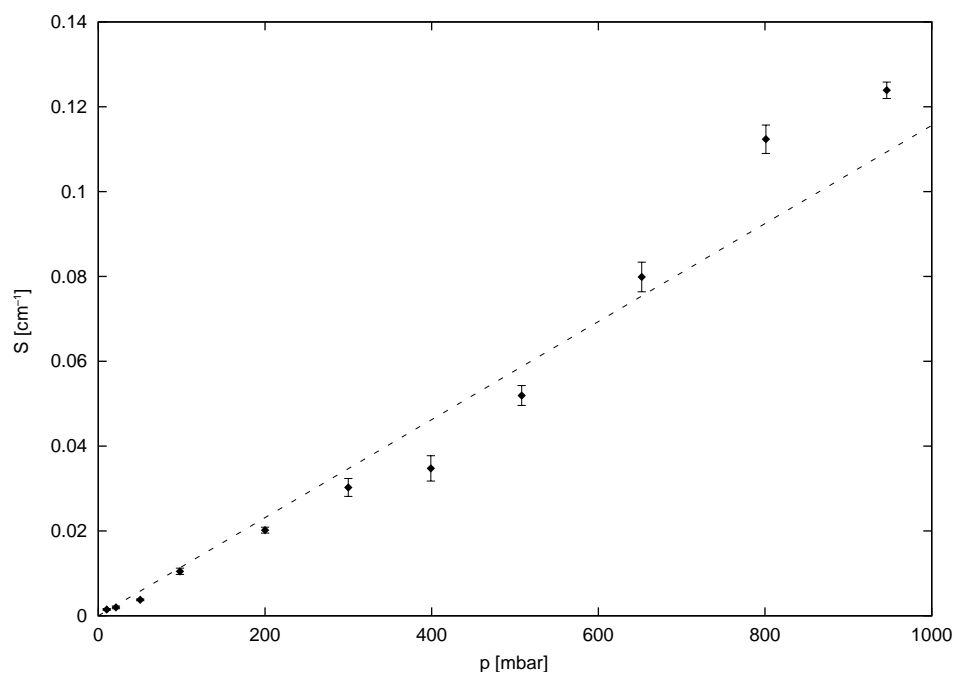


Figure 14: Line strength as a function of pressure