B2

Accurate measurements of CO_2 line

DLS LAB

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Introduction

Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). Several TDLS applications require measurement accuracy at level 0.1 %. In [1, 2] we've considered possibility to achieve this level. Present paper is next step (see also A1).

Measurements of green house gases in atmosphere require accurate measurement of their absorption. CO_2 was selected as molecule under investigation.

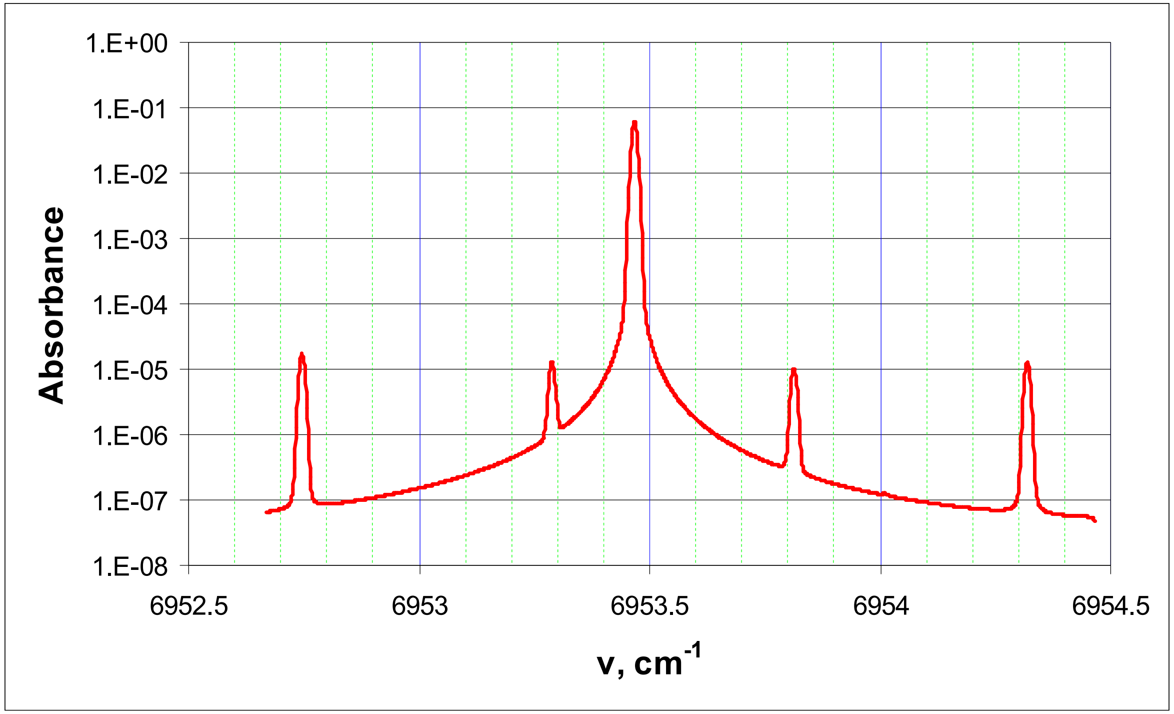
Goals of present work: select analytical CO_2 line for high accurate measurements; develop TDLS technique for high accurate absorption measurement; develop data processing for high accurate analytical line parameters determination; determine optimal experimental parameters of this determination.

[1] L.Konopelko, A.Nadezhdinskii, Accuracy in TDLS. TDLS as gas mixtures primary standard, Abstracts of TDLS 2009, Zermatt, Switzerland, p.76.

[2] http://www.dls.gpi.ru/rus/conf/TDLS2009/Posters/D2_TDLS%20primary%20standart.pdf

Analytical line selection

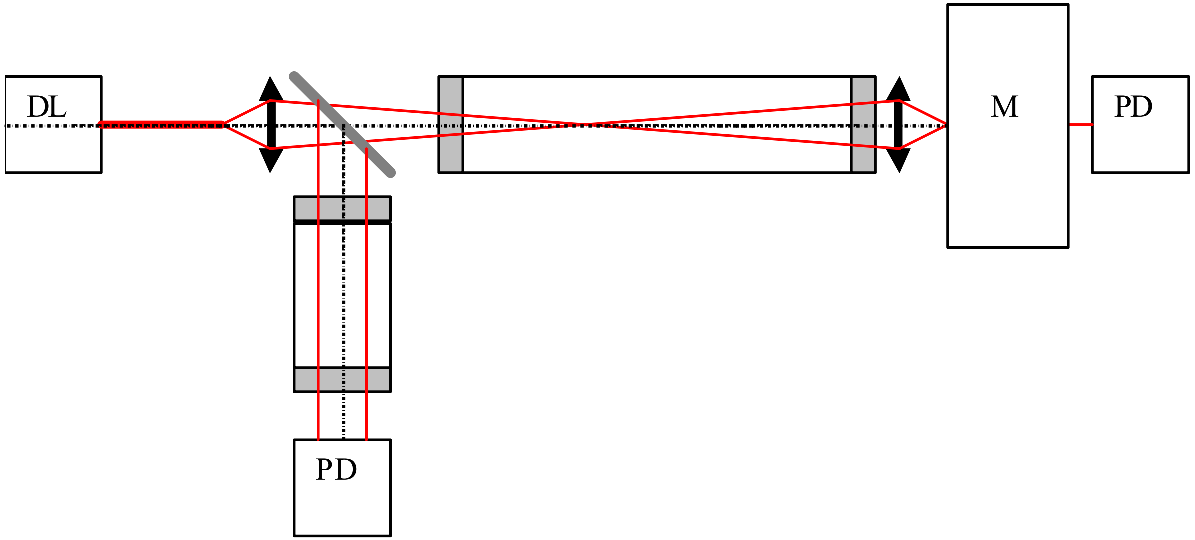
Requirements: isolated line. After modeling based on HITRAN 2008 P(20) 0 0 0 31 - 0 0 0 01 line was selected.
CO_2 absorbance in spectral range under consideration: L = 2 m, P_{CO2} = 2 mBar. Weak lines near analytical one are separated from it. They are due to $^{16}O^{12}C^{17}O$, no hot bands.



Parameter	Value	Accuracy
v, cm^{-1}	6953.46708	10^{-5}-10^{-4} cm^{-1}
S, $cm^{-1}(mol\ cm^{-2})$	5.27E-23	1-2%
γ_{air}, cm^{-1}/atm	0.0742	1-2%
γ_{self}, cm^{-1}/atm	0.099	1-2%
E'', cm^{-1}	163.8684	
n	0.71	2-5%
δ, cm^{-1}/atm	-0.008716	10^{-4}-10^{-3} cm^{-1}/atm

Left table – analytical line parameters from HITRAN 2008.

Experiment block-scheme



DL (NEL SN 537819) beam was focused inside analytical cell (200 cm) to prevent interference. Monochromator M was used to suppress DL broad spontaneous emission. Signal from reference channel with cell filled with low pressure CO_2 was used to stabilize DL frequency tuning.

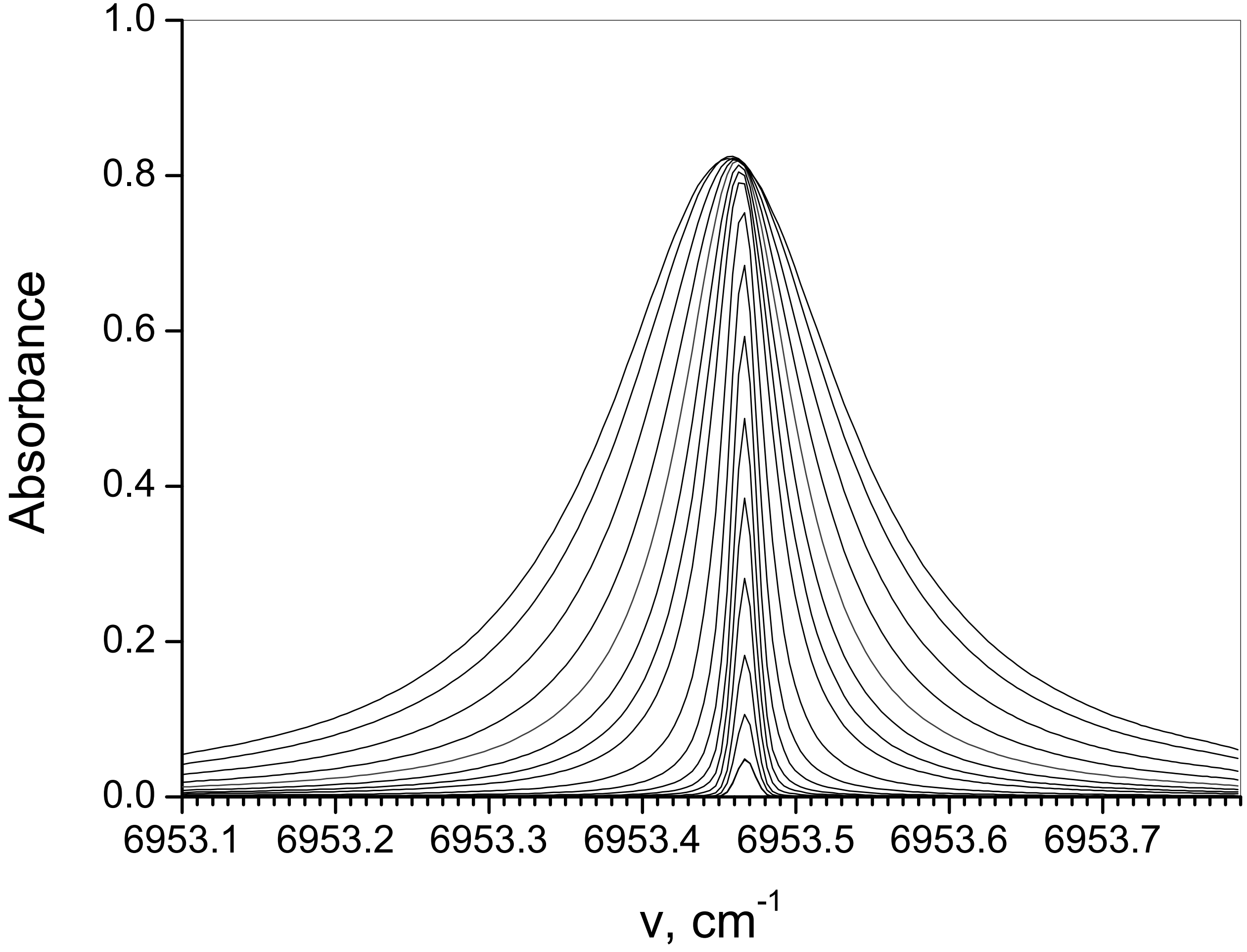
DL frequency tuning was calibrated with 1 10^{-4} cm^{-1} accuracy as described in A2. CO_2 sample preparation as well as other experimental details were considered in A1.

	Value	Error	Error %
L, cm	200.0	0.2	0.1
T, °C	20 - 25	0.2	0.007
P, mBar	0 - 100	0.07	0.07
	0-1000	0.7	0.07
CO_2 sample purity, %	99.98	0.02	0.02
PD non-linearity			0.02

Experimental accuracy estimate. For details see A1.

Absorbance spectra

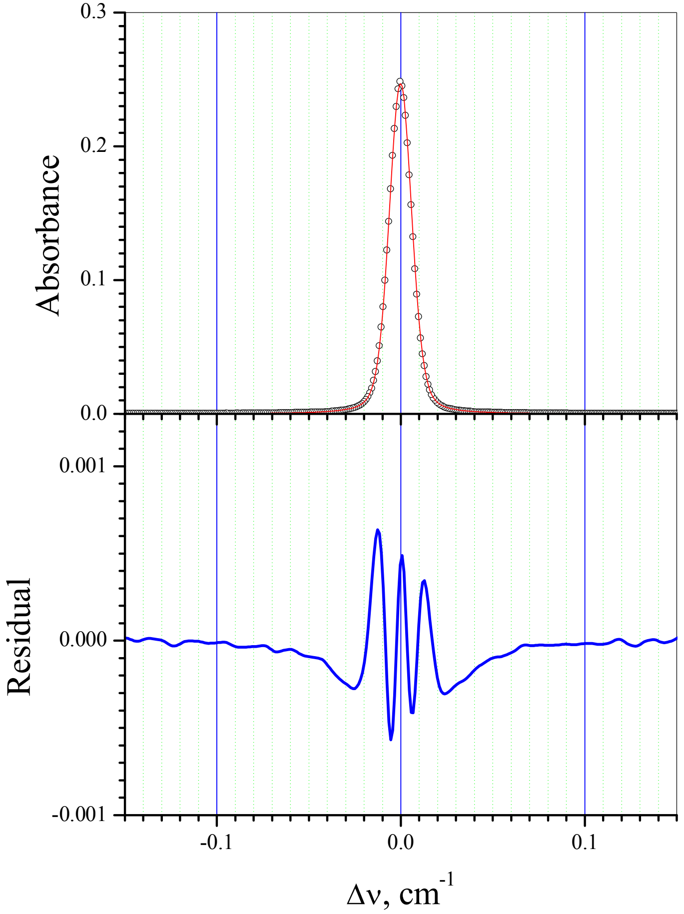
Many (~ 200) CO_2 analytical line spectra were recorded for different pressures of pure CO_2 sample. Cell temperature was measured simultaneously.



Examples of absorbance spectra obtained for different pressures.
CO_2 analytical line pressure broadening and shift can be observed.

Spectral line fitting

Software in use records gas pressure, cell temperature, signals, calibrates frequency scale, and calculates absorbance (see previous slide). In real time recorded line shape was fitted by Voigt (5 free parameters) and hard collision (6 free parameters) profiles. Pressure is corrected to 296 K.



Parameters of line fitting for P = 16.48 mBar.

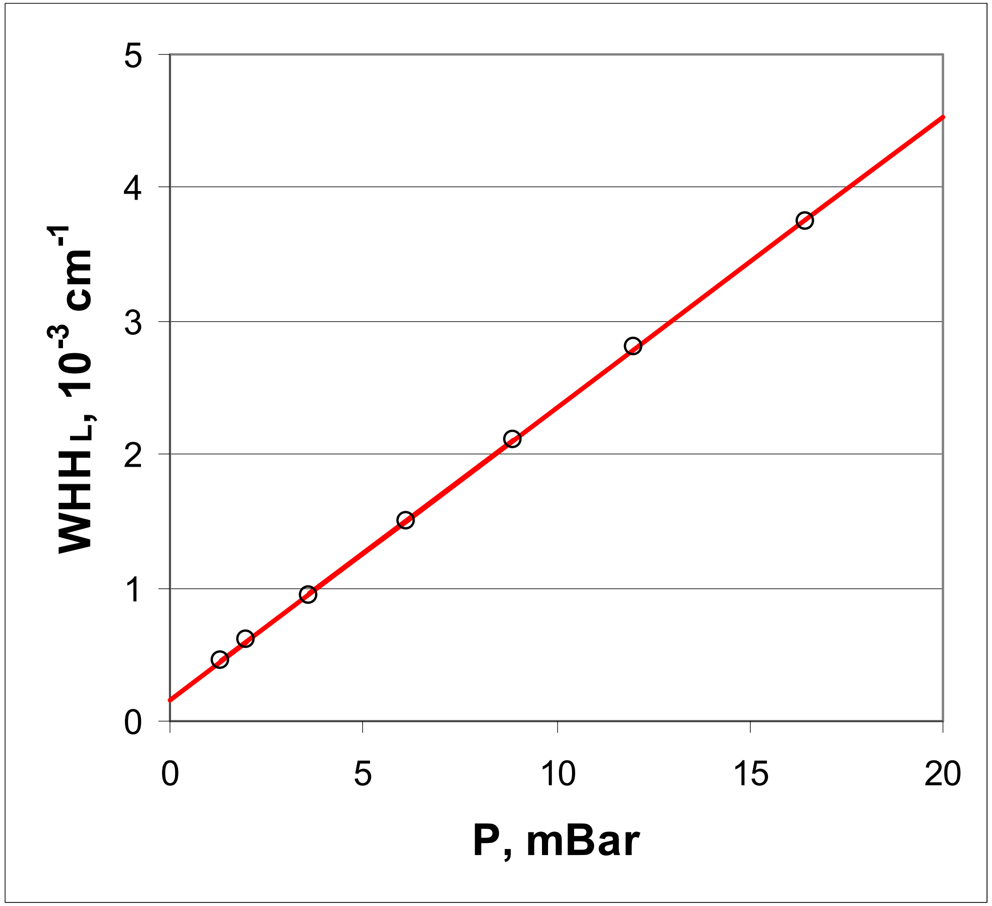
Hard			Viogt	
A	0.0041		A	0.004132
v	-0.00011		v	-0.00011
Γ	0.00155		2Γ	0.003692
b	4.51E-04		WHHG	0.012084
y0	1.91E-04		y0	0.00008
slope	1.29E-04			

Recorded line shape (black), its fitting by Voigt profile (red) and residual (blue) for P = 16.48 mBar.

Parameters of fitting and residual are subjects of further analysis.

Line shape model for low pressures

Recorded signal in TDLS is convolution of real signal with DL spectrum. DL spectrum has Lorentz shape with WHH_{DL}. Hence, for low pressures (small absorbance and small pressure broadening) Voigt profile is best model for experimental line shape fitting.



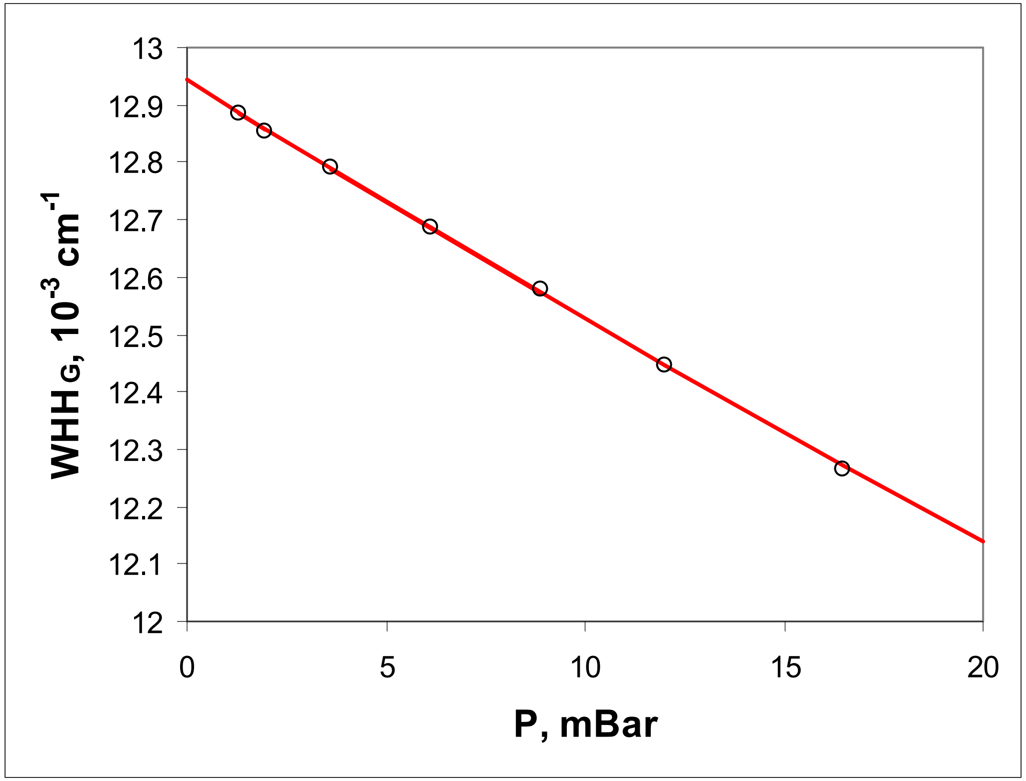
Pressure dependence of Voigt profile Lorentz width WHH_L.

Slope is determined by line pressure broadening.

Intercept is due to DL line width and can be obtained from experimental data:

$WHH_{DL} = 1.6\ 10^{-4}\ \text{cm}^{-1} = 4.8\ \text{MHz}$

Line shape model for low pressures



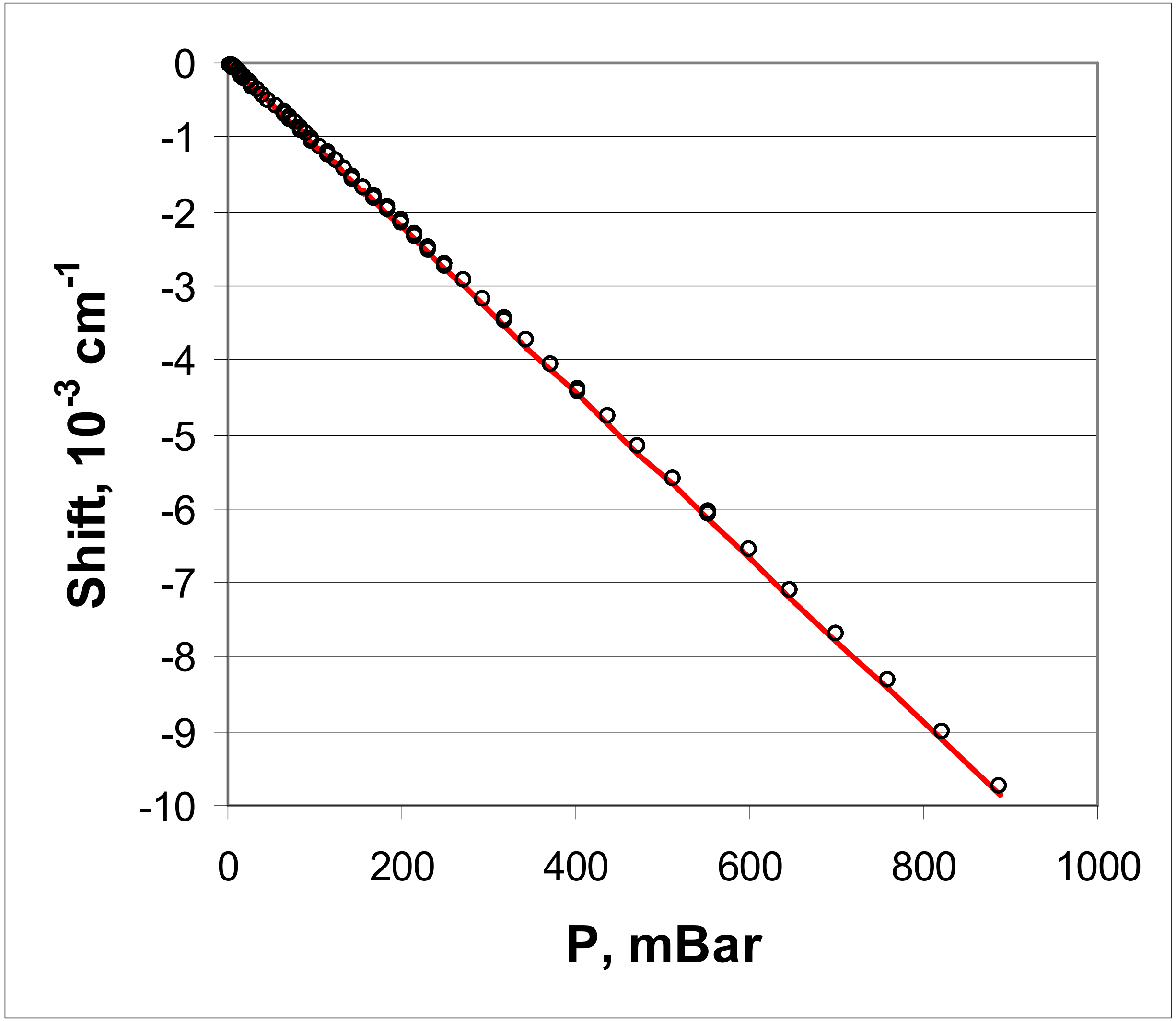
Pressure dependence of Voigt profile Gaussian width - WHH_G.
Intercept is Doppler width without collisions. It can be calculated for known temperature and wave number.
Comparison of measured and calculated Doppler widths of analytical line :

Measured	0.0129428(37)
Calculated	0.0129442

Presented values coincide within experimental accuracy.

Slope is due to Dicke narrowing.
Voigt profile is the best model of line shape fitting in TDLS if:
Absorbance is small. If “No” convolution with DL spectrum has to be taken into account during fitting (see D2).
Pressure broadening and narrowing are small with respect Doppler width of analytical line.

Pressure shift



Pressure dependence of analytical line self shift.

Within experimental accuracy both fitting models in use (hard collision and Voigt profiles) demonstrated the same results.

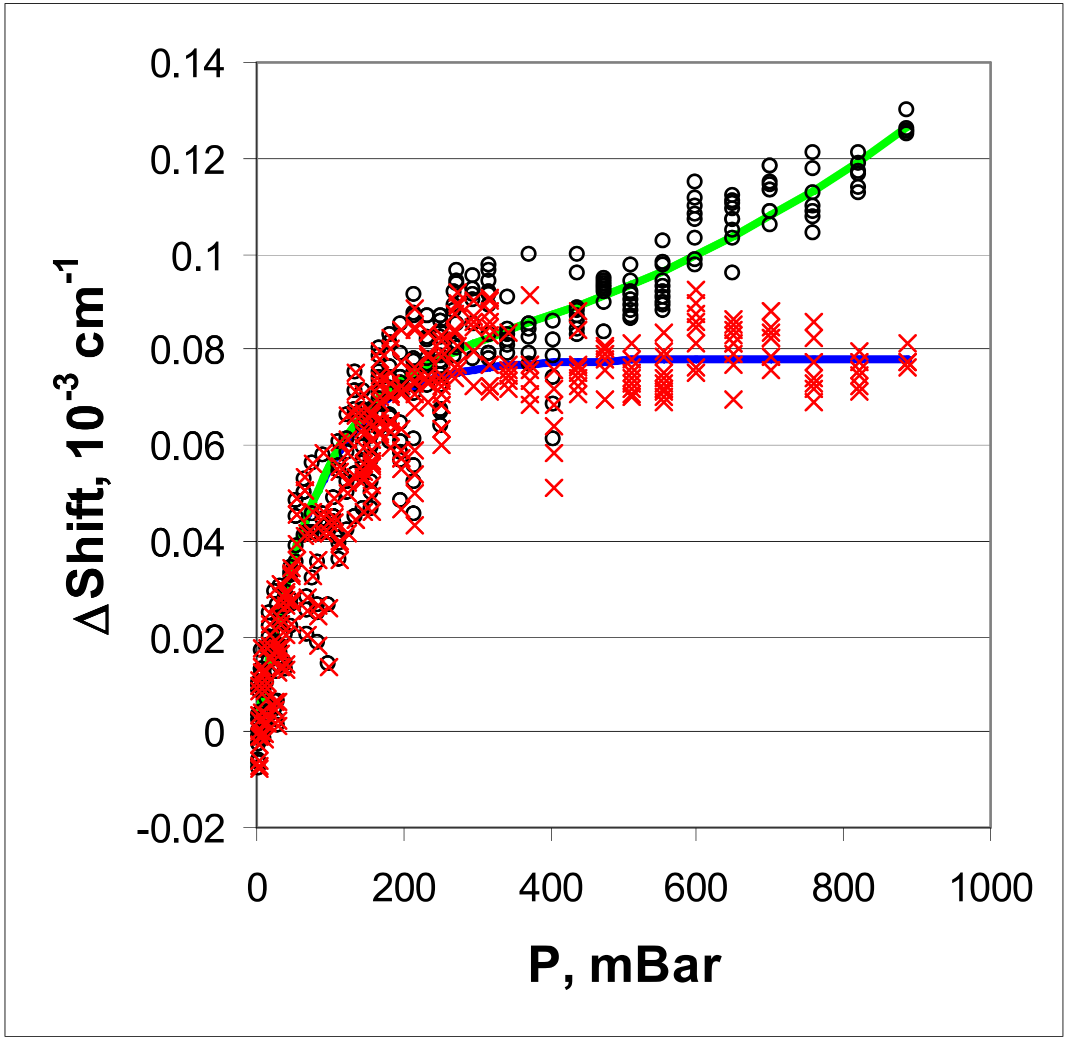
CO_2 pressure self shift coefficient was determined (see next slide for details):

$$\delta_{self} = 11.09(2)\,\frac{cm^{-1}}{mBar}$$

Pressure shift

Significant difference between experimental spectral line frequency and its linear pressure dependence (black circles, green curve) can be observed. This difference is due to two physical effects.

$$\Delta Shift = Shift(P) - \delta_{self} P$$



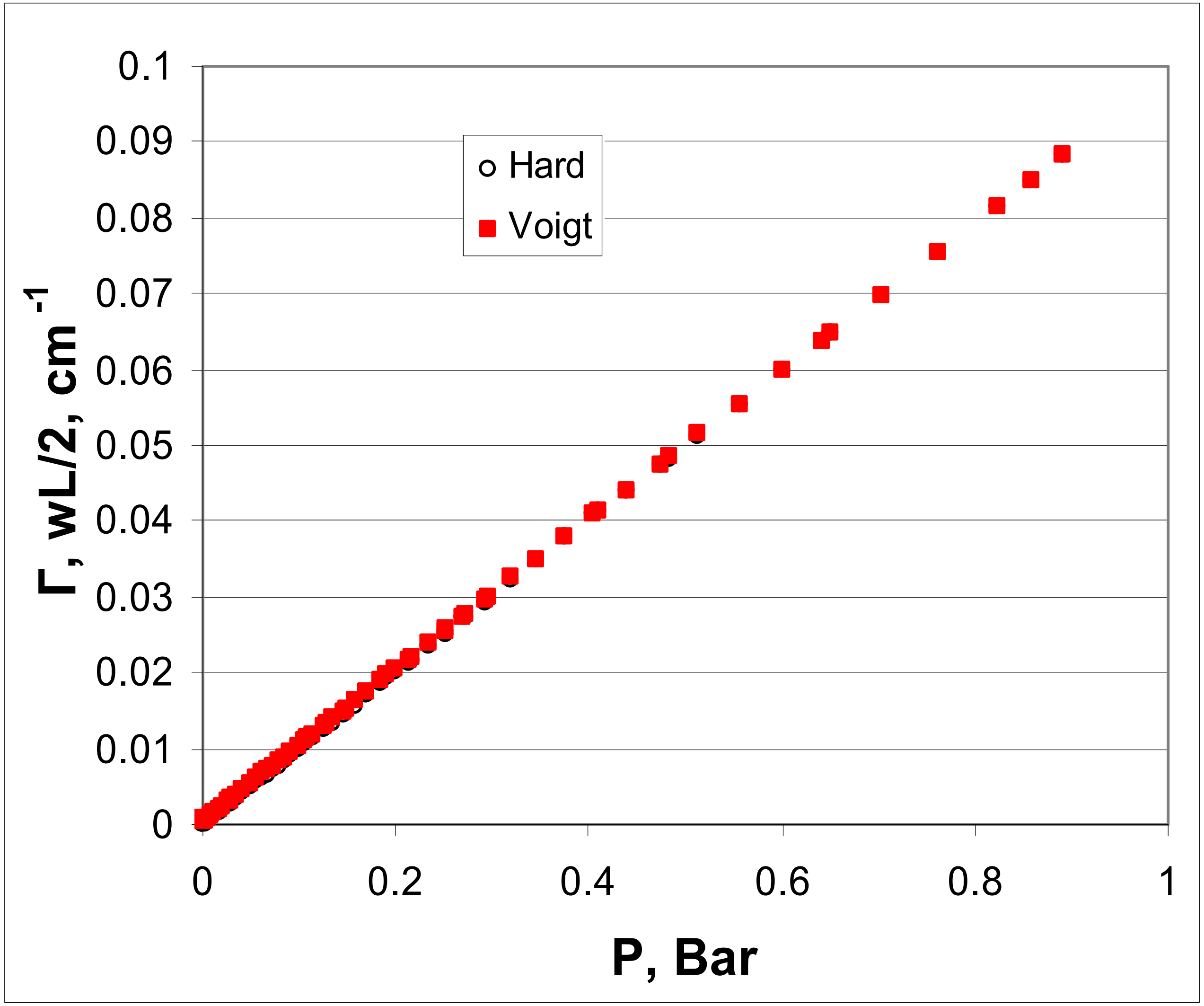
CO_2 is not ideal gas (second virial coefficient B = -123 cm^3/mol). This was taken into account (red crosses). Correction to δ_{self} due not ideal CO_2 gas behavior is around 0.6 %.

<u>Conclusion: Not ideal CO_2 gas behavior has to be taken into account.</u>

Final difference (red crosses and blue curve) is due to spectral line anisotropy (see slide 6).

<u>Pressure shift coefficient has to be measured above 300 mBar.</u>

Pressure broadening



Pressure dependence of analytical line self broadening.

Experimentally significant difference for fitting models in use (hard collision and Voigt profiles) was observed (see next slide).

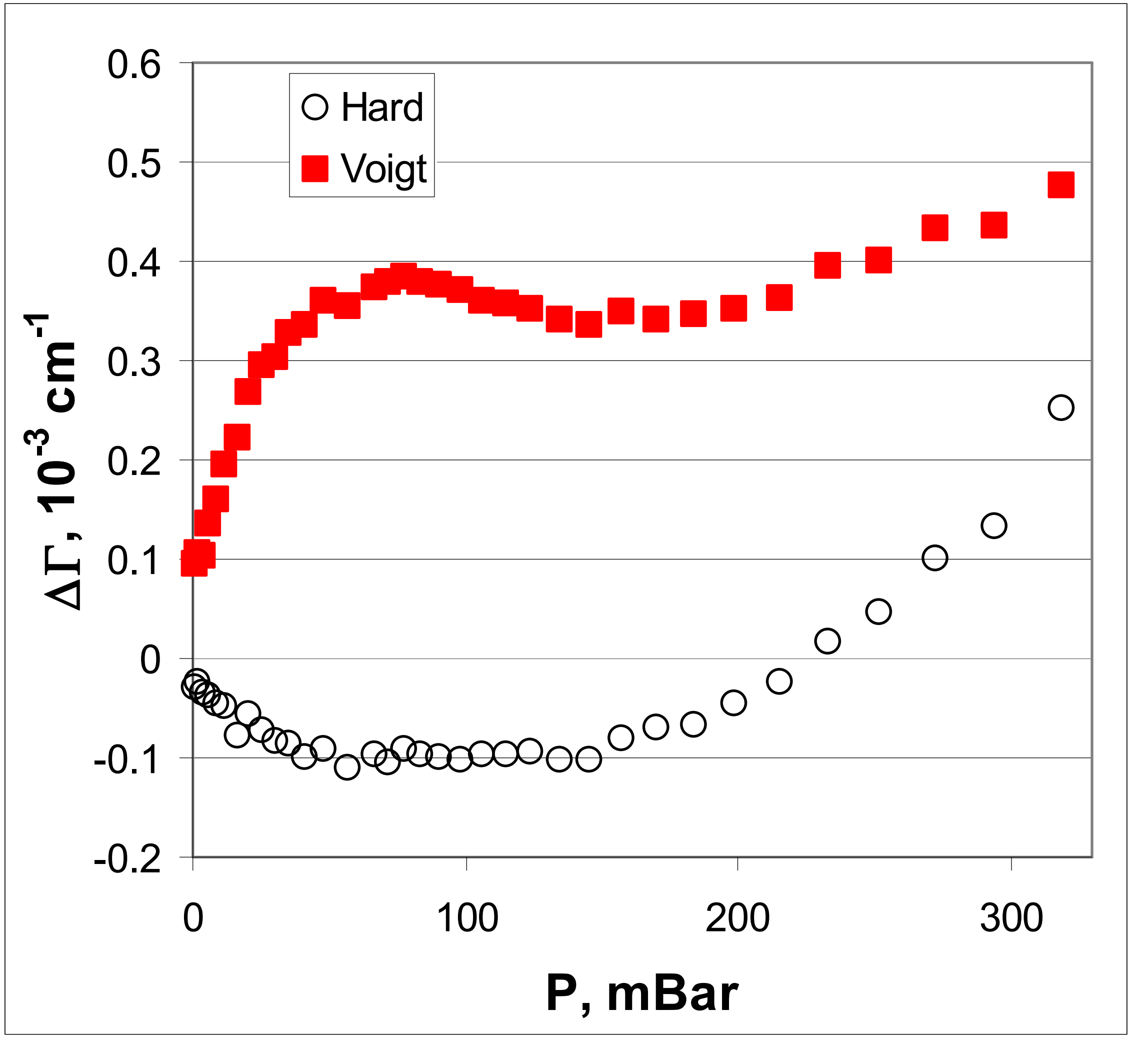
CO_2 pressure self broadening coefficient was determined (see next slide for details):

$$\gamma_{self} = 0.1003(2)\,\frac{cm^{-1}}{Bar}$$

Pressure Broadening

Significant difference between measured line width and its linear pressure dependence for two fitting models in use (hard collision and Voigt profiles) can be observed.

$$\Delta\Gamma = \Gamma(P) - \gamma_{self} P$$

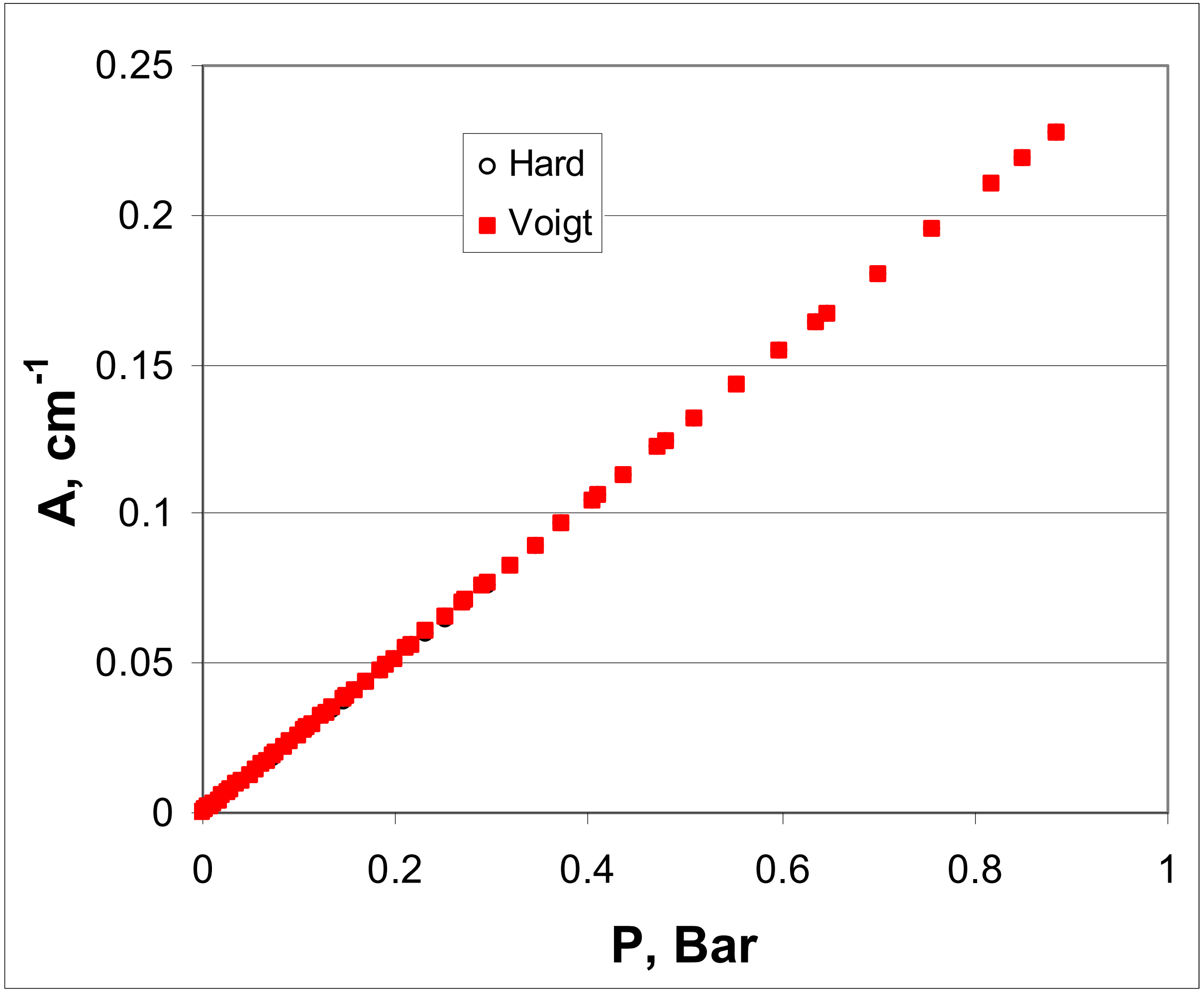


Both models are not good above 200 mBar. Hard collision profile is not valid for small pressures below 50 mBar.

Voigt profile is good for low pressures to determine DL line width. For real pressures it demonstrates significant non linear behavior at accuracy level under consideration.

Hard collision profile has to be used in pressure range 50 -150 mBar to determine pressure broadening.

Line intensity



Pressure dependence of analytical line integral intensity.

Experimentally significant difference for fitting models in use (hard collision and Voigt profiles) was observed (see next slide).

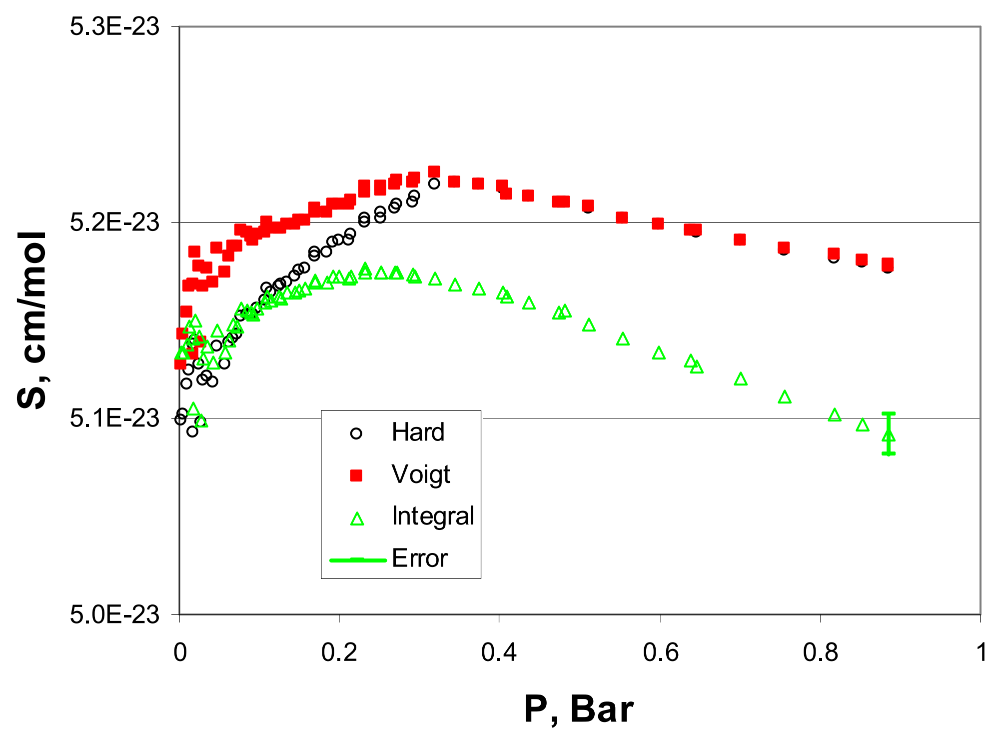
CO_2 analytical line intensity was determined (see next slide for details):

$$S = 5.172(33)10^{-23}\ \frac{cm}{mol}$$

Spectral line integral intensity - S

$$S = \frac{A(P)}{n_0 \, L \, P}$$

Here L – cell length; P – gas pressure for 296 K, corrected to CO_2 gas non ideal behavior; $n_0 = 2.47936 \; 10^{19}$ mol/cm^3 molecules number density for P = 1 Bar and T = 296 K.



Pressure dependence of analytical line intensity – S obtained from fitting by hard collision (black) and Voigt (red) profile models. Direct integration (Integral) of spectra recorded (green) was also used. For low pressures Voigt and integral coincide (see slides #7, 8).
Significant difference (about 1%) between S obtained using different methods can be observed. Experimental accuracy is shown by green vertical error.

Conclusion: S pressure dependence - spectral line can’t be considered as isolated one (line mixing);
Question: What method is correct for S determination?

Comparison with HITRAN

CO_2 analytical line parameters

	HITRAN	Error, %	Present work	Dif, %
S, 10^{-23} cm/mol	5.27	1-2	5.172(33)	-1.9
γ_{air}, cm^{-1}/Bar	0.0742	1-2		
γ_{self}, cm^{-1}/Bar	0.099	1-2	0.1003(2)	1.3
δ_{air}, cm^{-1}/Bar	-0.0087	5-10		
δ_{self}, cm^{-1}/Bar			0.01109(2)	

HITRAN data coincide with analytical line parameters measured in present work within HITRAN accuracy declared. Accuracy achieved in present work is order of magnitude better with respect to HITRAN accuracy declared.

Conclusion

1. Isolated CO_2 P(20) 00031-00001 line was selected as analytical one.
2. TDLS technique was develop for absorbance measurement with accuracy better than 0.1 %.
3. Recorded spectra were analyzed using different models to determine line intensity, shift, and broadening.
4. Effect of non ideal CO_2 gas behavior was observed and corrected.
5. Line intensity pressure dependence was found: line can not be considered as isolated one even for low pressures.
6. Difference obtained using different models is significantly larger than experimental error.
7. Models in use applicability was analyzed.
8. Optimal model and pressure range to obtain particular line parameter were selected.
9. Analytical line parameters were determined with accuracy 0.2-0.6 %.
10. They were compared with HITRAN 2008 being in agreement with it within 2 %. Declared HITRAN accuracy is 1-2 %.

Line shape