Investigation of isolated CO_2 line shape

DLS LAB

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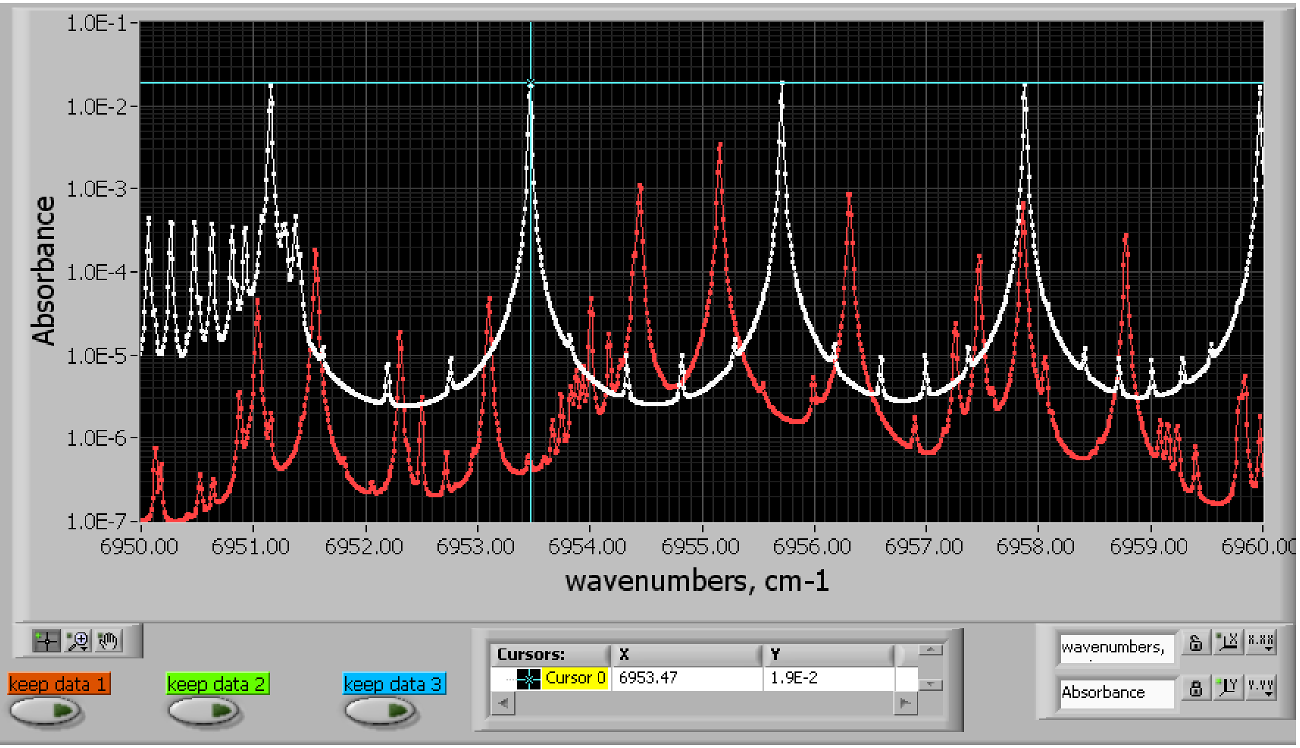
Introduction

Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). Several TDLS applications require measurement accuracy at level 0.1 %. This accuracy level was recently achieved in TDLS (A2). High accurate spectra of several gas mixtures were obtained for different pressures (C2, C3). Spectral line shapes obtained were fitted using procedure developed (B1).
Subject of present paper is to try to understand physical meaning of fitting parameters and their accuracy.

Analytical line selection

In present paper CO_2 molecule (representative of greenhouse gases) was chosen for investigation in near IR spectral range.



HITRAN 2008 based modeling of CO_2 and H_2O absorbance in selected spectral range white and red, respectively.

$L = 39$ m, $P_0 = 100$ mBar,

$C_{CO2} = 1000$ ppm,

$C_{H2O} = 10$ ppm.

Isolated CO_2 line P(20) of 00031 - 00001 band was selected as analytical one. Analytical line requirements: strong absorbance, absence of interference with water. Analytical line is marked by blue$_3$ cursor. Weak lines near analytical one are due to $^{16}O^{12}C^{17}O$.

Accuracy estimation

Possible error mechanisms during accurate spectral line recording using TDLS were analyzed, investigated, measured, and calibrated.

	Value	Error	Error %
L, cm	99.95	0.05	0.05
T, ^{o}C	20 - 25	0.1	0.03
P, mBar	0 - 100	0.07	0.07
CO_2 sample purity, %	99.98	0.02	0.02
PD non-linearity			0.02
v, 10^{-3} cm^{-1}		0.03	0.04
Optical zero			0.04
Baseline			0.01
DL Spectrum, MHz	2.5		0.07
Total			**0.13**

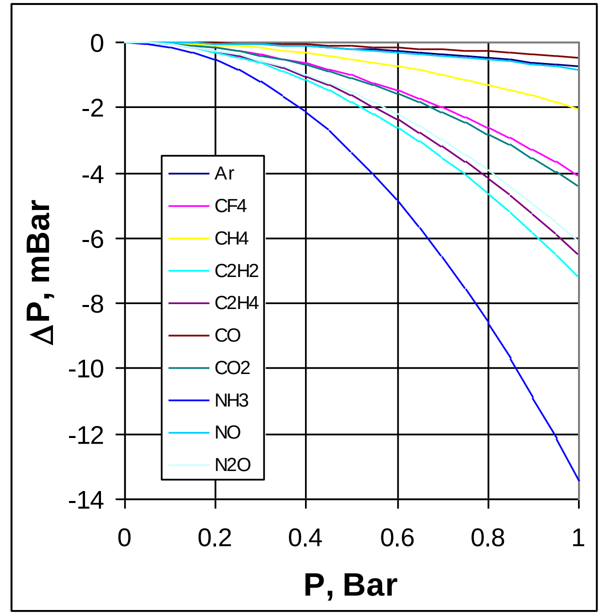
Results presented above were used to estimate accuracy of spectral line accurate measurements – 0.13 % (see A2).

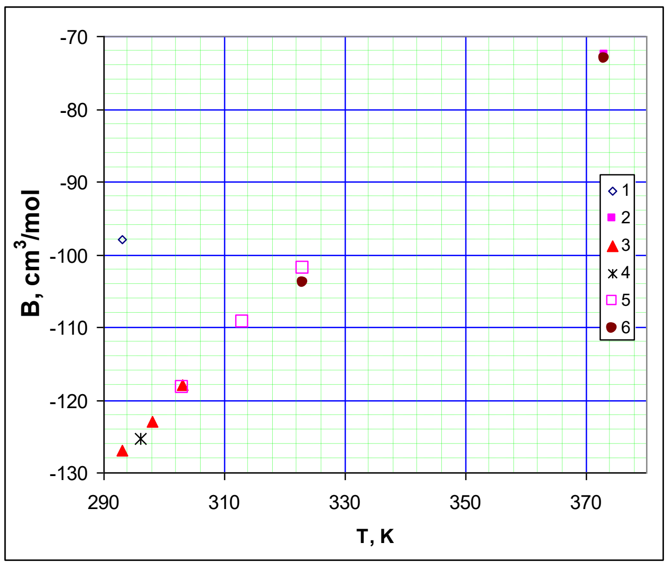
Real gas

Real gas equation, V – volume of 1 mole, B – second virial coefficient

$$P = \frac{RT}{V}\left[1 + \frac{B}{V} + \dots\right]$$

For real gas pressure has not linear dependence with respect to molecules number density. Correction is of the order 0.1 – 1 % for 1 Bar.



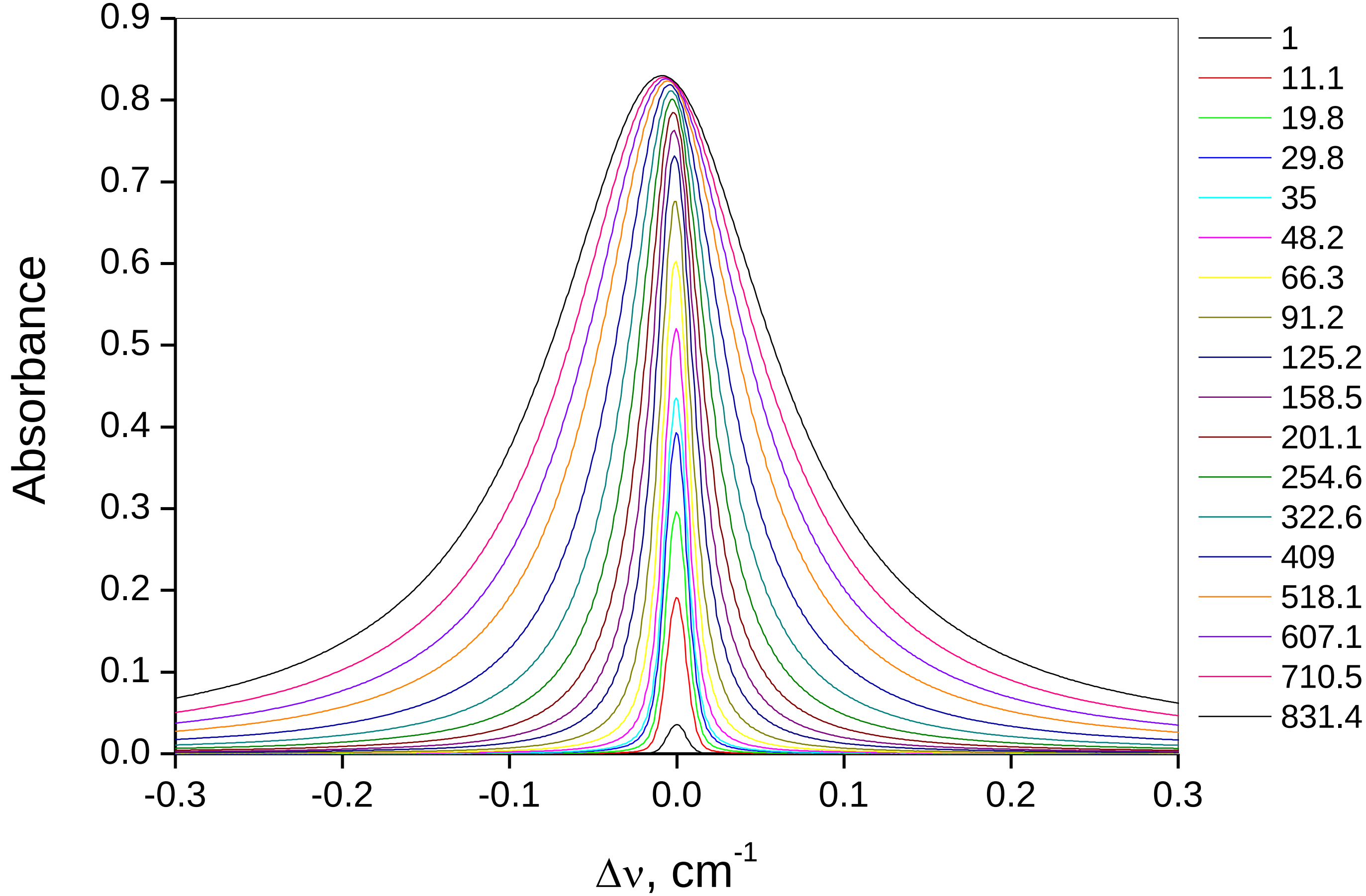


Second virial coefficient temperature dependence for CO_2.

For high accurate TDLS measurements real gas properties have to be taken into account – pressure correction using second virial coefficient.

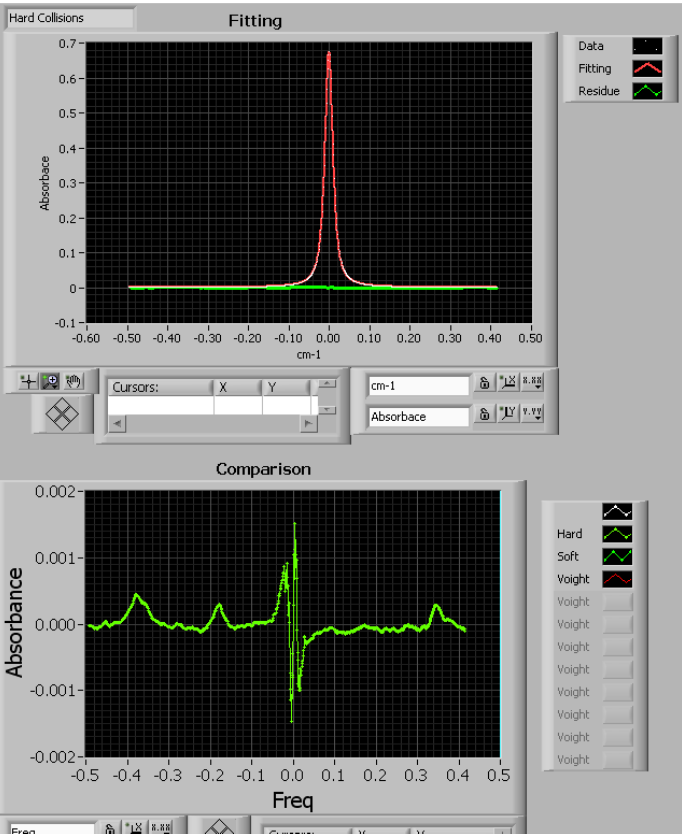
Experiment

High accurate spectra of CO_2 isolated line were obtained for different pressures.



Shapes of analytical CO_2 line for different pressures (mBar). Pressure broadening and shift can be observed.

Fitting



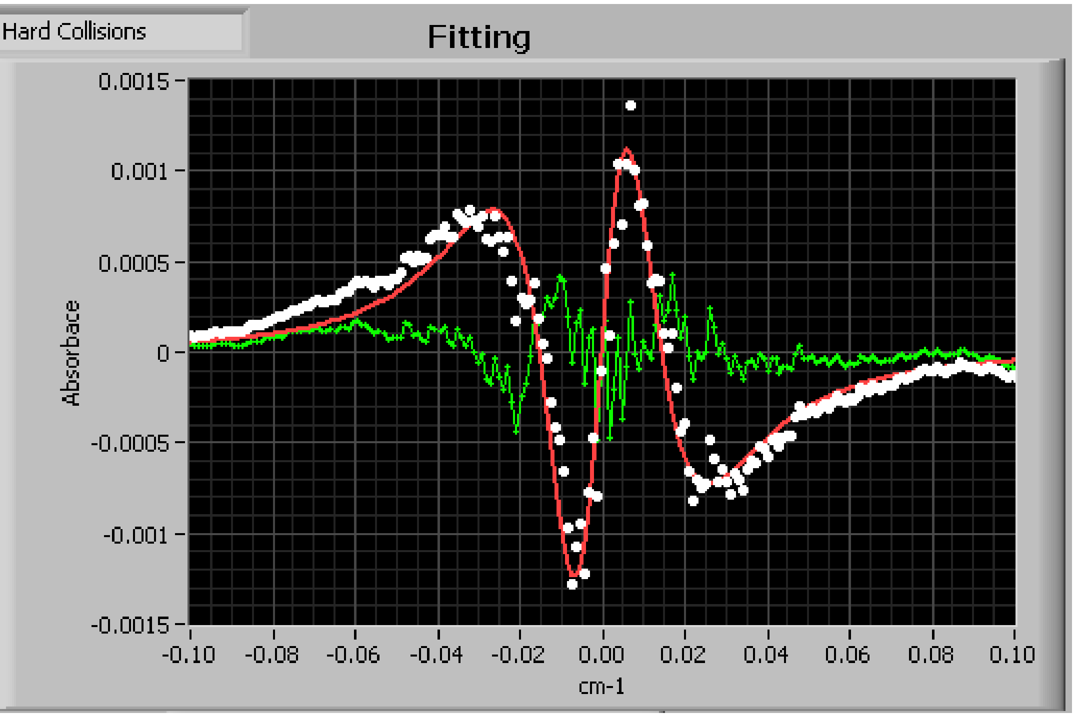
Experimental data were fitted using software developed (see B1). Fitting used following parameters set of line shape.

4.3772E-2	S	Integral intensity
-4.0341E-1	v0	Frequency
5.8159E-3	wG	Gauss width
1.7170E-2	WL	Lorentz width
6.1668E-3	beta	Narrowing parameter
4.8059E-4	Offset	Baseline

Experimental data were fitted using both soft and hard models of Doppler profile. Fitting results for both models will be compared. Residual demonstrates line asymmetry (see B2) as well as presence of weak lines. In present case, left is water line, two others are $^{16}O^{12}C^{17}O$ lines.

Line shape asymmetry

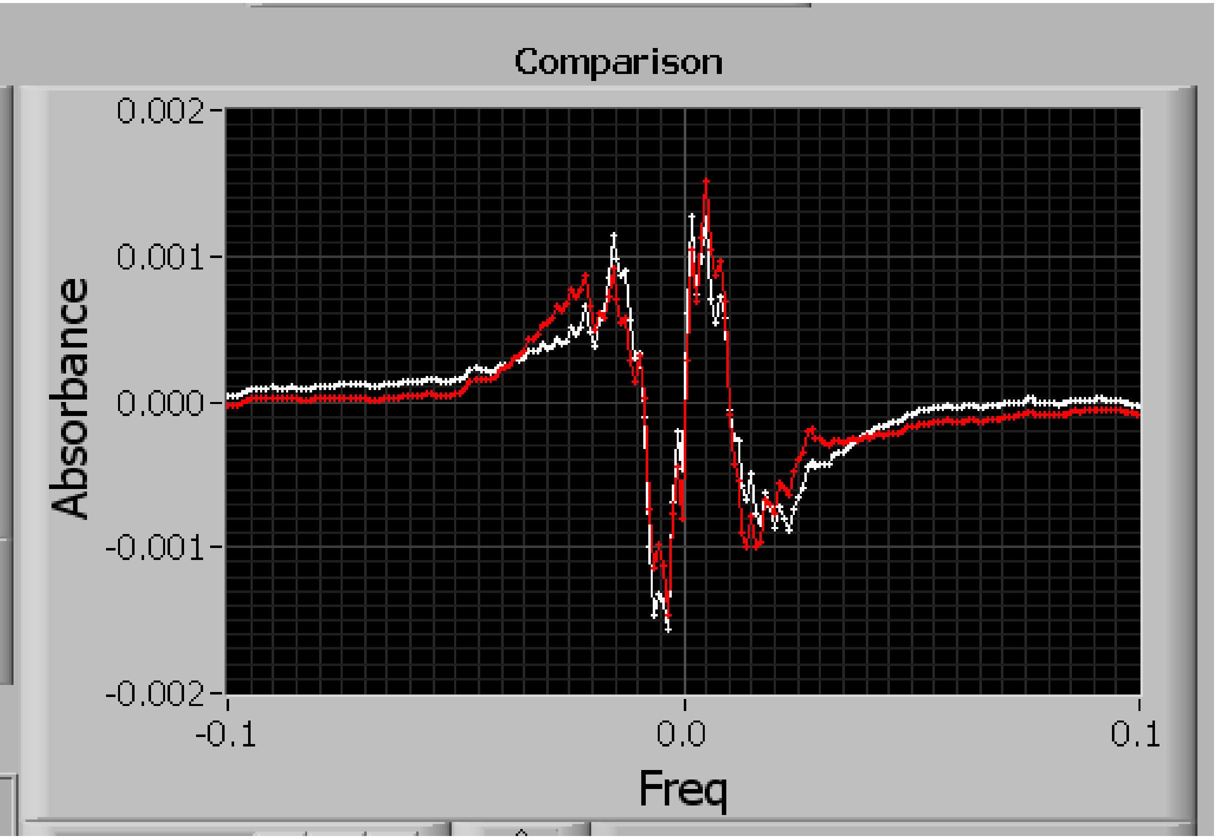
For all cases, asymmetry of analyzed spectral line was observed. White circles – CO_2 line residual for 171.4 mBar normalized to line maximum demonstrating spectral line asymmetry (3 roots).



To measure asymmetry, empirical model function was developed. Asymmetry model function is determined by derivatives of line under consideration shape. Using this function asymmetry can be fitted (red curve). This approach was tested for all pressures in use and gave ability to measure asymmetry value.

Final residual (green) was reduced to 0.04 % of line maximum. It is due to present experimental precision.

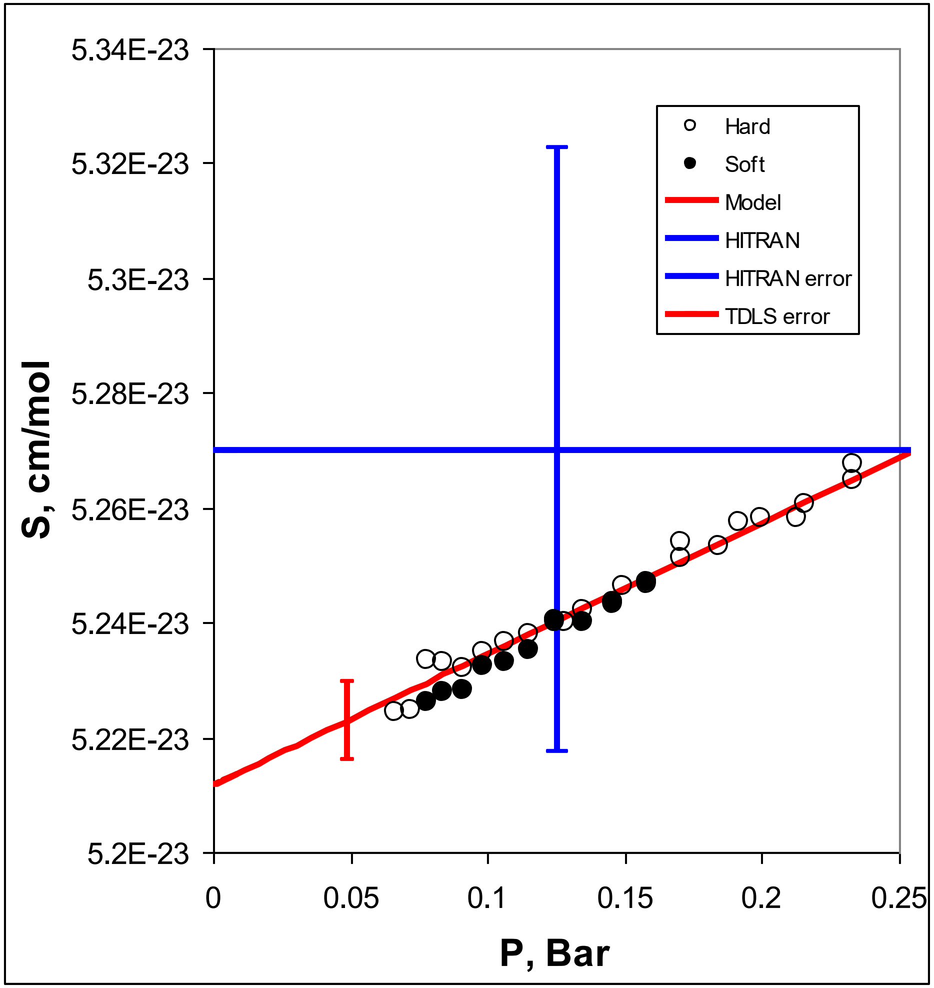
Asymmetry



Residual for fitting using hard (red) and soft (white) models.
The residual has 3 roots – asymmetry (previous slide and B2).

Asymmetry amplitude is 0.15 %. Difference between hard and soft is below level of experimental precision - 4 10^{-4} (see previous slide).

Spectral line integral intensity

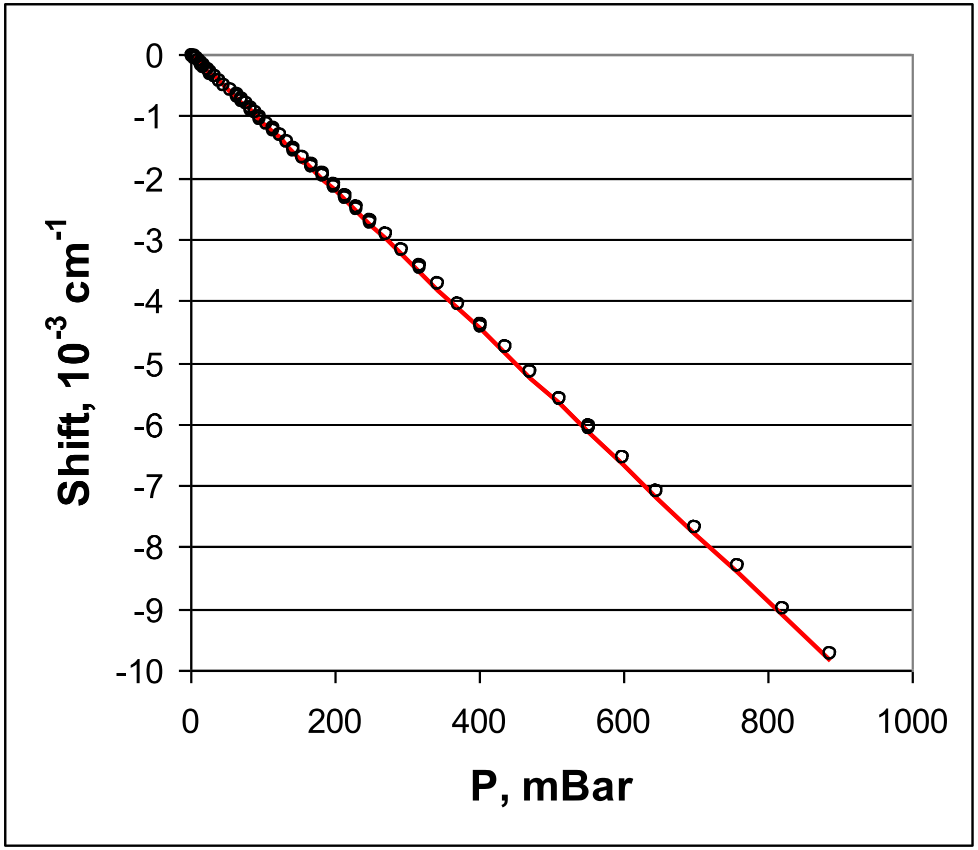


Both Soft and Hard give close results for integral intensity – S (circles).
S pressure dependence can be observed. Probably it is due to line mixing – the line can not be considered as isolated one.
Data obtained are in agreement with HITRAN 2008 data (blue constant) within HITRAN accuracy (blue vertical line).

S = 5.2117(52) 10^{-23} cm/mol

<u>For accuracy levels better than 1 %, measurements have to be done at low pressures and pressure dependence of spectral line integral intensity has to be taken into account.</u>

Pressure shift



Pressure shift of CO_2 line does not depend of fitting model in use (Hard or Soft).

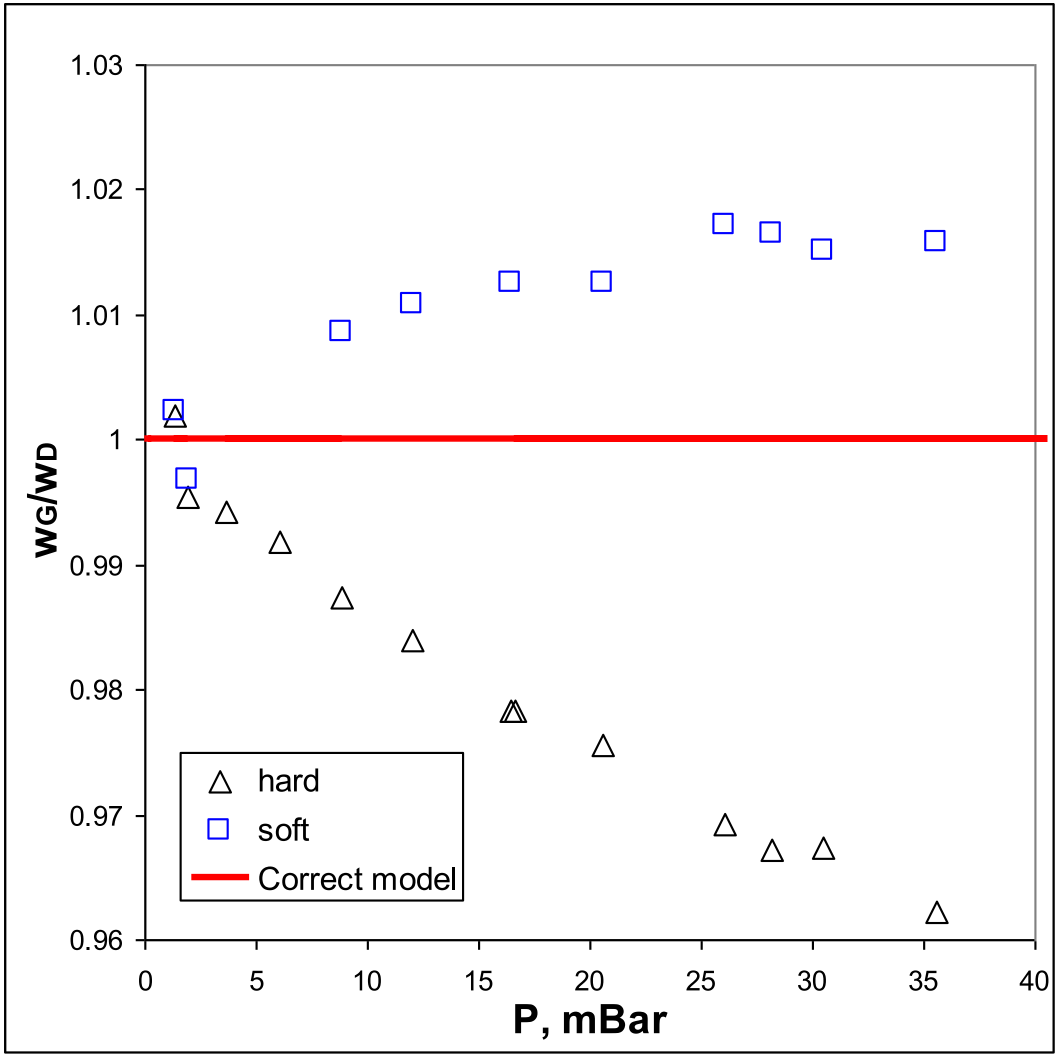
Line asymmetry presence leads to the line position shift from real value. When asymmetry was taken into account (see B2), correct line center values can be obtained and and self shift coefficient can be determined,

$$\delta = -0.010998(23)\ cm^{-1}/Bar$$

Precision of line frequency determination is 10^{-4} and $1.0\ 10^{-5}\ cm^{-1}$, without and with taking into account asymmetry, respectively.

For pressure shift, accuracy is 3 % and 0.21 % without and with taking into account asymmetry, respectively.

Gauss width

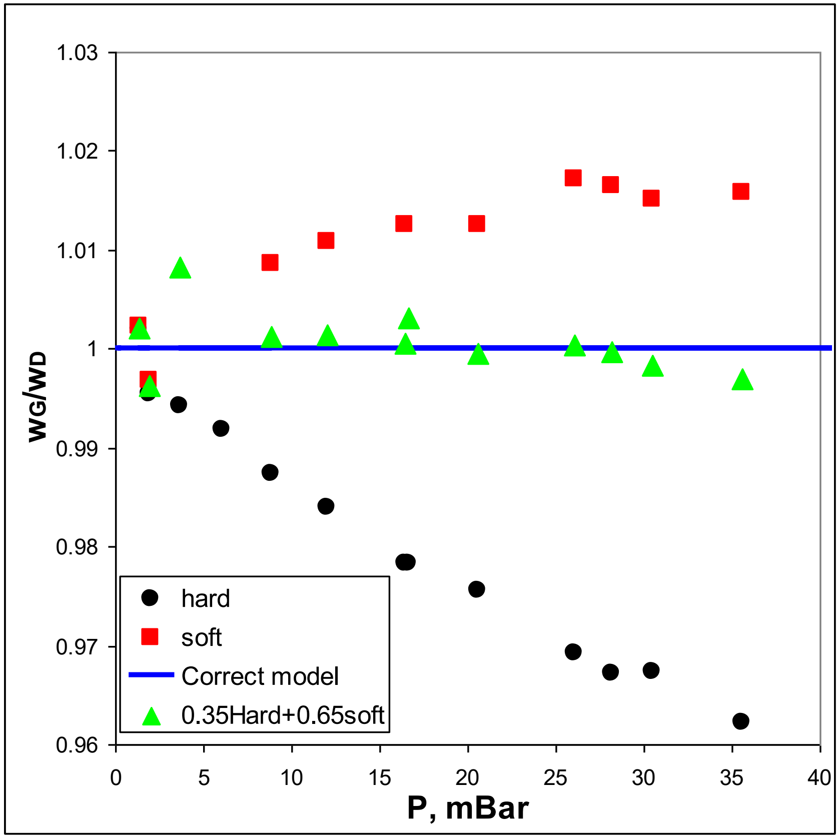


Pressure dependence of fitting parameter - w_G/w_D for CO_2 line for Hard (triangles) and Soft (squares) Doppler profile models. For correct model w_G/w_D has to be equal to 1 (red constant). Both models demonstrate correct value for P = 0 (no collisions) – check of experimental accuracy. Both Soft and Hard models are not correct for non zero gas pressure (presence of collisions). This result can be expected for CO_2 molecules collision.

For CO_2 we have intermediate case between Soft and Hard Doppler profile models.

Intermediate case

Soft and hard Doppler profile models linear superposition can be considered as model for intermediate case.

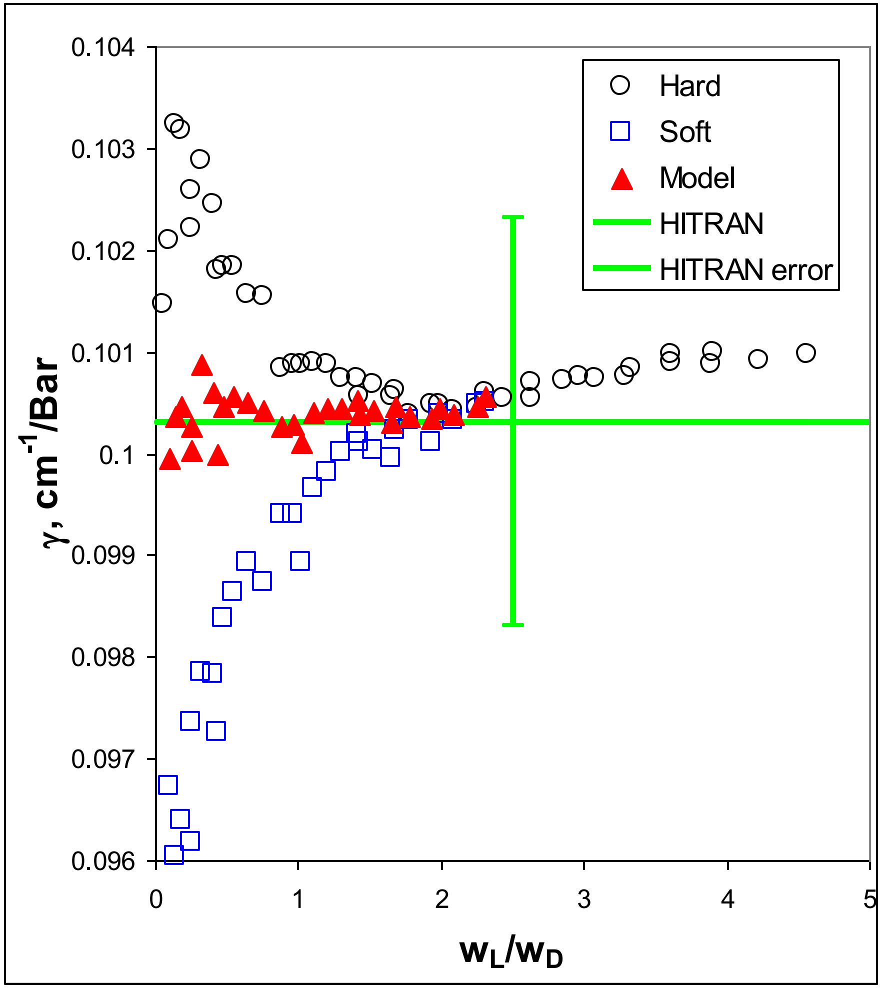


$$\text{Model} = \alpha \text{ soft} + (1 - \alpha) \text{ hard}$$

Above mentioned approach test (left) for CO_2:CO_2. For $\alpha = 0.35$ linear superposition of Soft and Hard is close to correct model.

α is measure of collisions number required to achieve equilibrium velocity distribution: 0 – infinite collisions number (soft); 1 – one collision (hard).

Self broadening



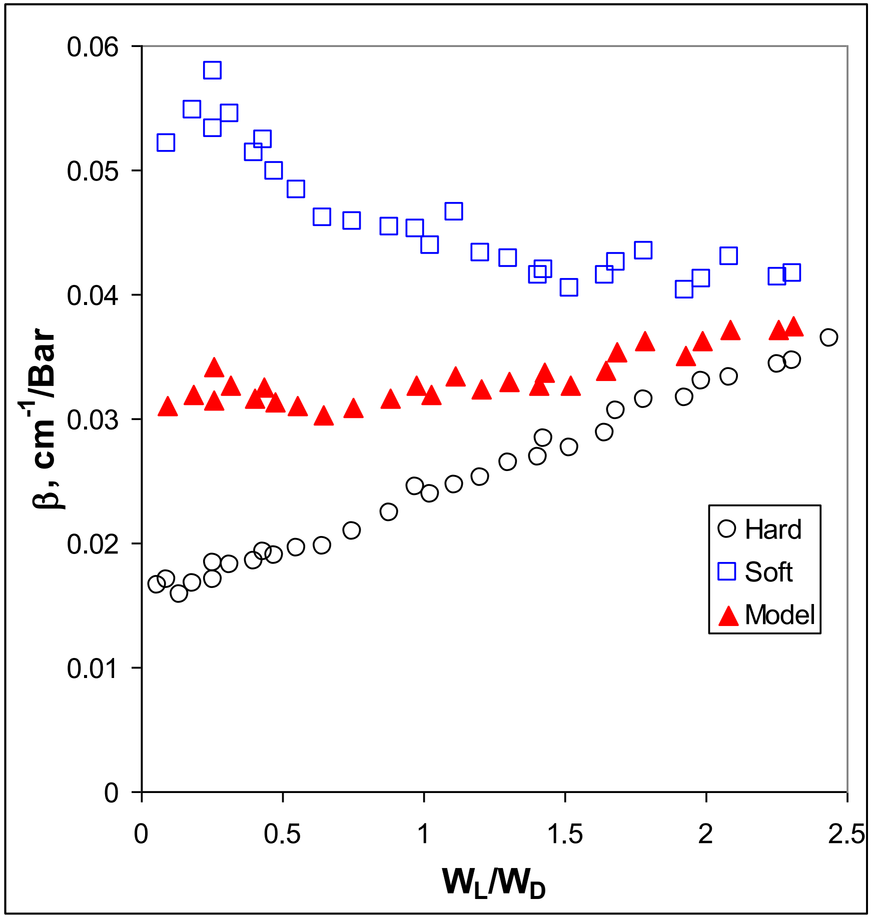
Self broadening coefficient vs. normalized Lorentz width for fitting using Hard and Soft models. Significant difference (8%) and pressure dependence can be observed. Data obtained are in agreement with HITRAN (green constant) and its error (green vertical line).

Both Soft and hard Doppler profile models are not correct for CO_2. Their linear superposition ($\alpha = 0.6$) can be considered as model for intermediate case (red triangles).

Self broadening coefficient can be determined with precision 0.21 %.

$$\gamma = 0.10008(18)\ cm^{-1}/Bar$$

Narrowing



Narrowing coefficient vs. normalized Lorentz width for fitting using Hard and Soft models. Significant difference (4 times) and strong pressure dependence (known in literature) can be observed. Both Soft and hard Doppler profile models are not correct for CO_2. Their linear superposition (with the same α = 0.6) can be considered as model for intermediate case (red triangles). For this linear superposition narrowing coefficient is close to constant.

Now narrowing coefficient can be determined with precision 11 %.

$$\beta = 0.046(11)\ cm^{-1}/Bar$$

Conclusions

- High accurate isolated CO_2 line shapes were recorded.
- Data obtained were fitted using fitting procedure developed and Hard and Soft Doppler profiles.
- Line asymmetry, pressure shift, and integral intensity do not depend on Doppler profile model.
- Integral intensity demonstrate pressure dependence.
- Gauss width as well as broadening and narrowing coefficients demonstrate significant dependence on Doppler profile model in use.
- The same linear superposition of Soft and Hard Doppler profile models was used to treat data obtained.
- The line parameters set was obtained with high accuracy.