B2

DL SPECTROMETER: INTEGRAL INTENSITY TEST

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1. Abstract

Diode Laser (DL) spectrometer for high accurate measurements was developed (A1).

The spectrometer subsystems were calibrated. Absolute accuracy of spectral line integral intensity measurements was estimated – 0.06 %.

Test of DL spectrometer frequency tuning accuracy was performed. It was based on comparison of TDLS measurements with HITRAN data. Results obtained are in agreement with accuracy estimations (B1).

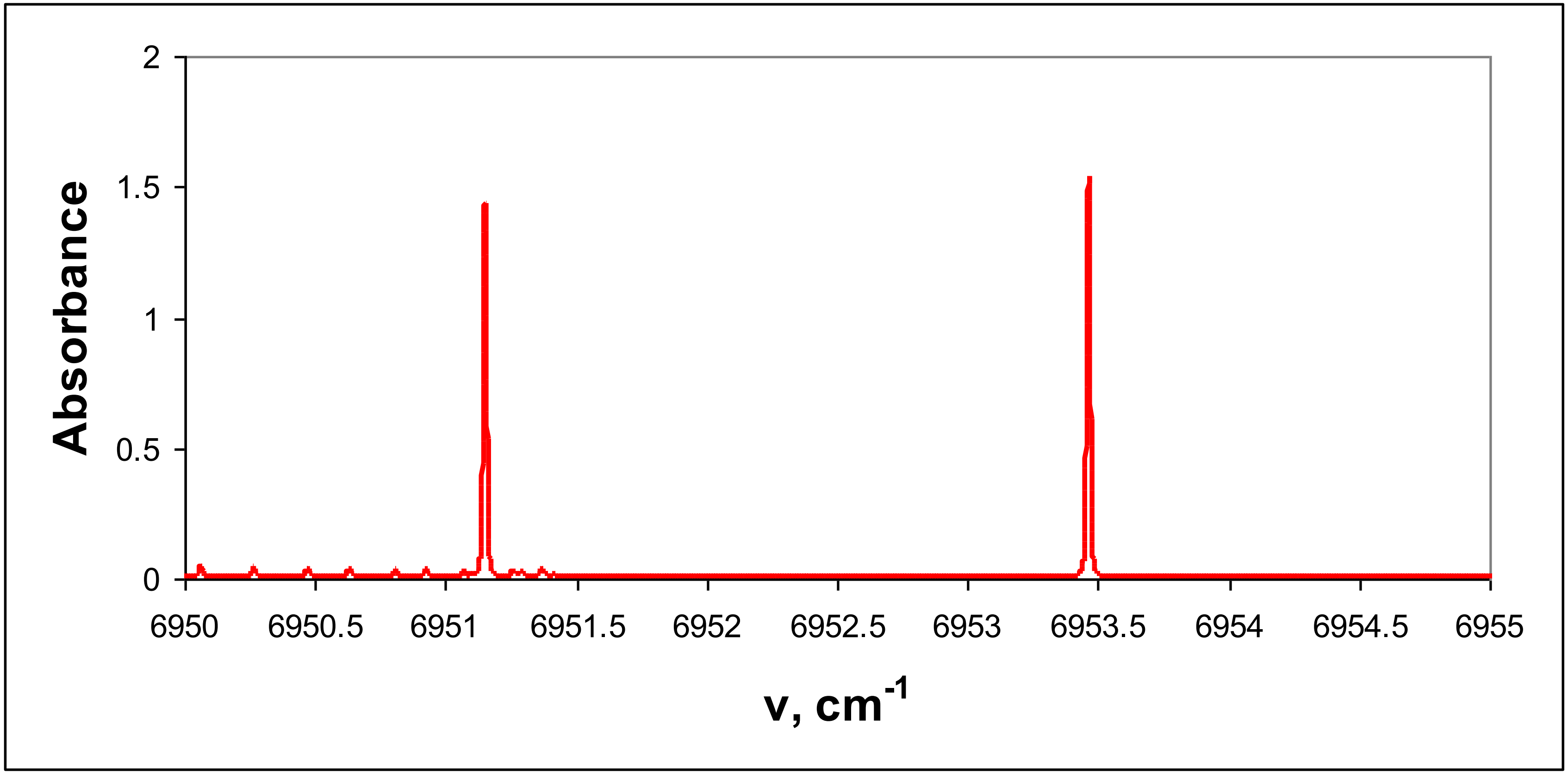
Test of spectral line integral intensity measurements is subject of present paper.

For this test HITRAN can not be used as standard. Its estimated accuracy 1 – 2 % is far above required accuracy level.

For this test additional physical axiom was used: for isolated spectral line integral intensity has to be constant with pressure change.

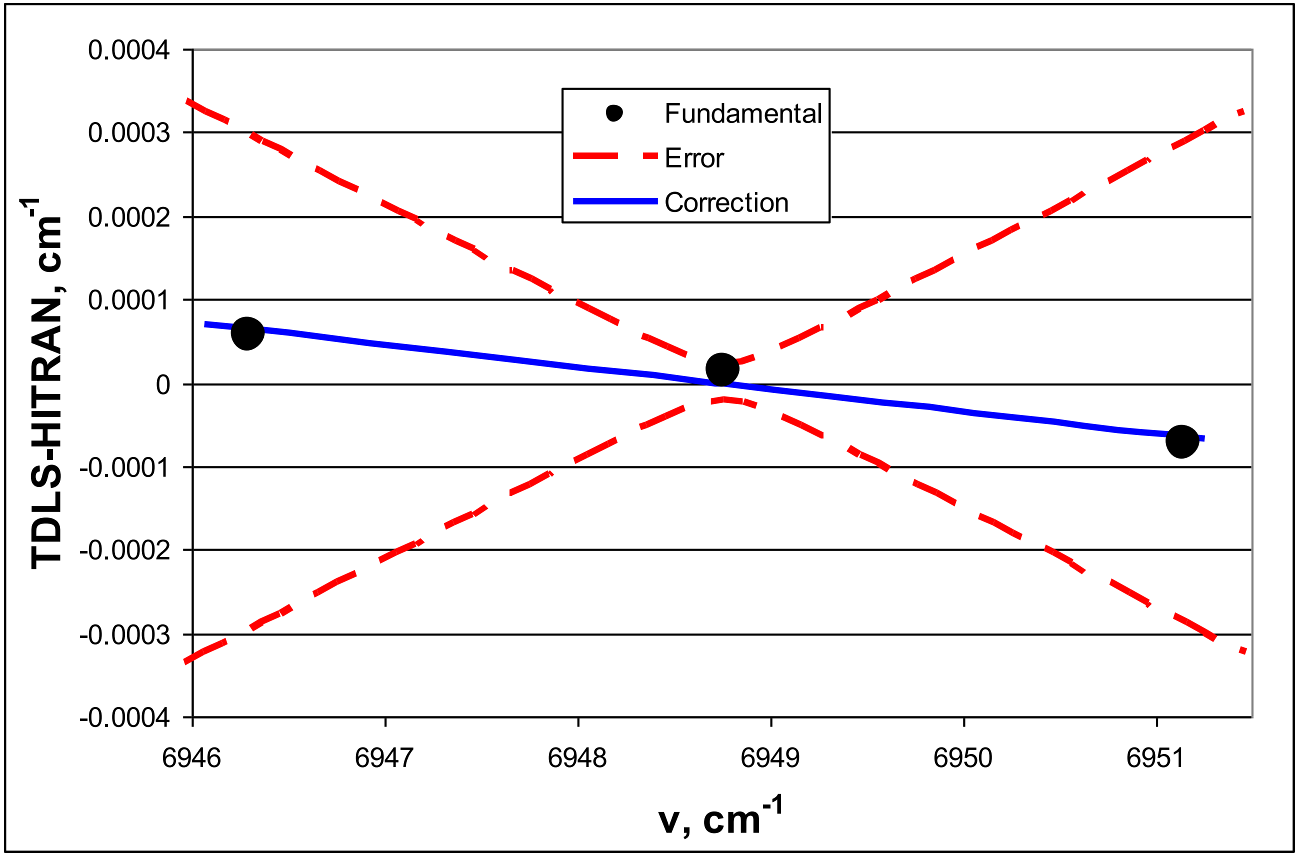
2. Analytical line selection

CO_2 molecule was selected for present test. CO_2 freezing at LN2 temperature and its evaporation provides its purification as well as simplify usage of the pure sample for numerous experiments.



Isolated CO_2 line 6953.467 cm^{-1} (P20e of 00031-00001 fundamental band) was selected as analytical one for this test.

3. DL frequency calibration accuracy



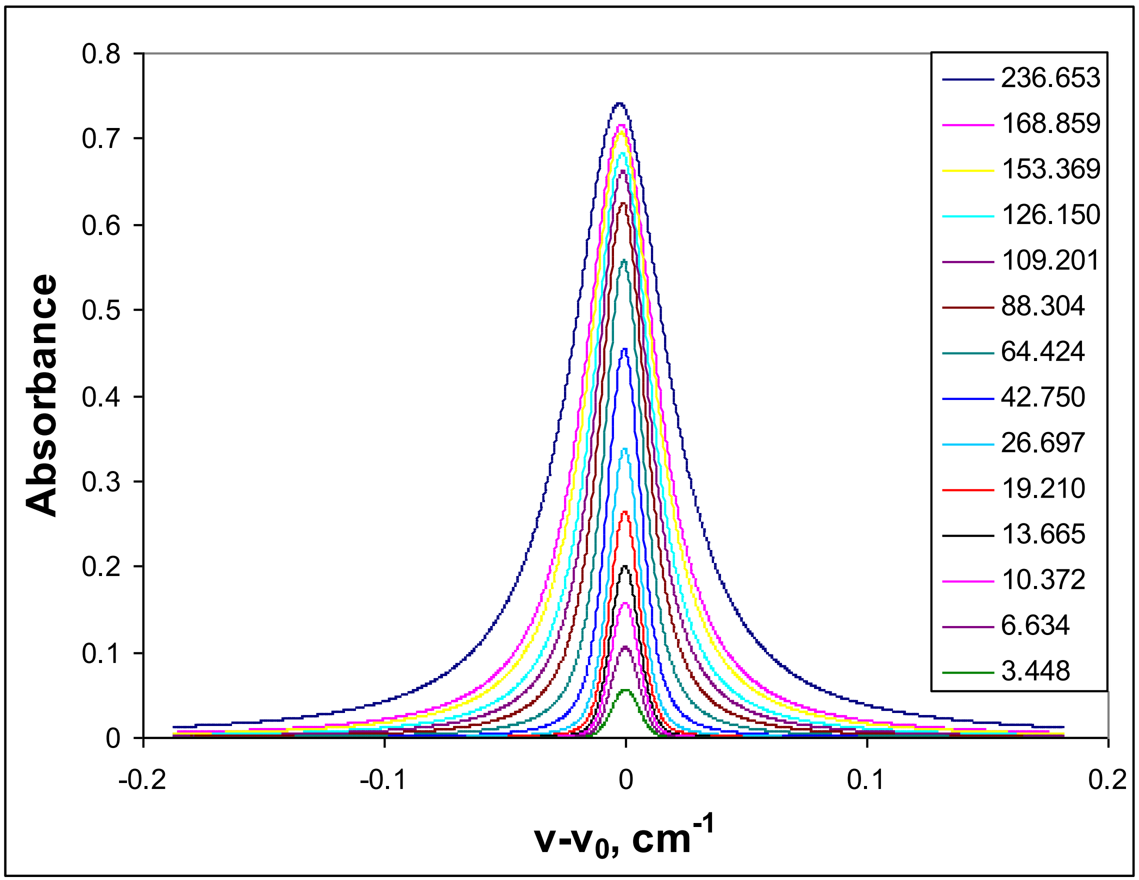
Frequencies of three CO_2 lines of 00031-00001 fundamental band were determined.
Solid black circles – difference between present measurements and HITRAN 2012.

Red dashed lines – TDLS accuracy estimation. Slope – accuracy of FP FSR determination (0.012 %).

Experimental results are within TDLS accuracy estimation.

4. Test procedure

Cell #2 (L2 = 183.50(4) cm) and cell #3 (L3 = 1519(1) cm) were filled with pure CO_2 (purity better 99.98 %) at different pressures. Simultaneously with spectra recording, gas pressure and temperature were measured. Accuracy of pressure and temperature measurements is 0.02 % and 0.05 ^oC, respectively.



For each pressure, two spectra were recorded. Eight measurement series were performed during 20 days period using different cells and PDs to check reproducibility of results obtained.

Example of one of the series experimental results. Here v_0 is line center position for zero pressure.

5. Fitting

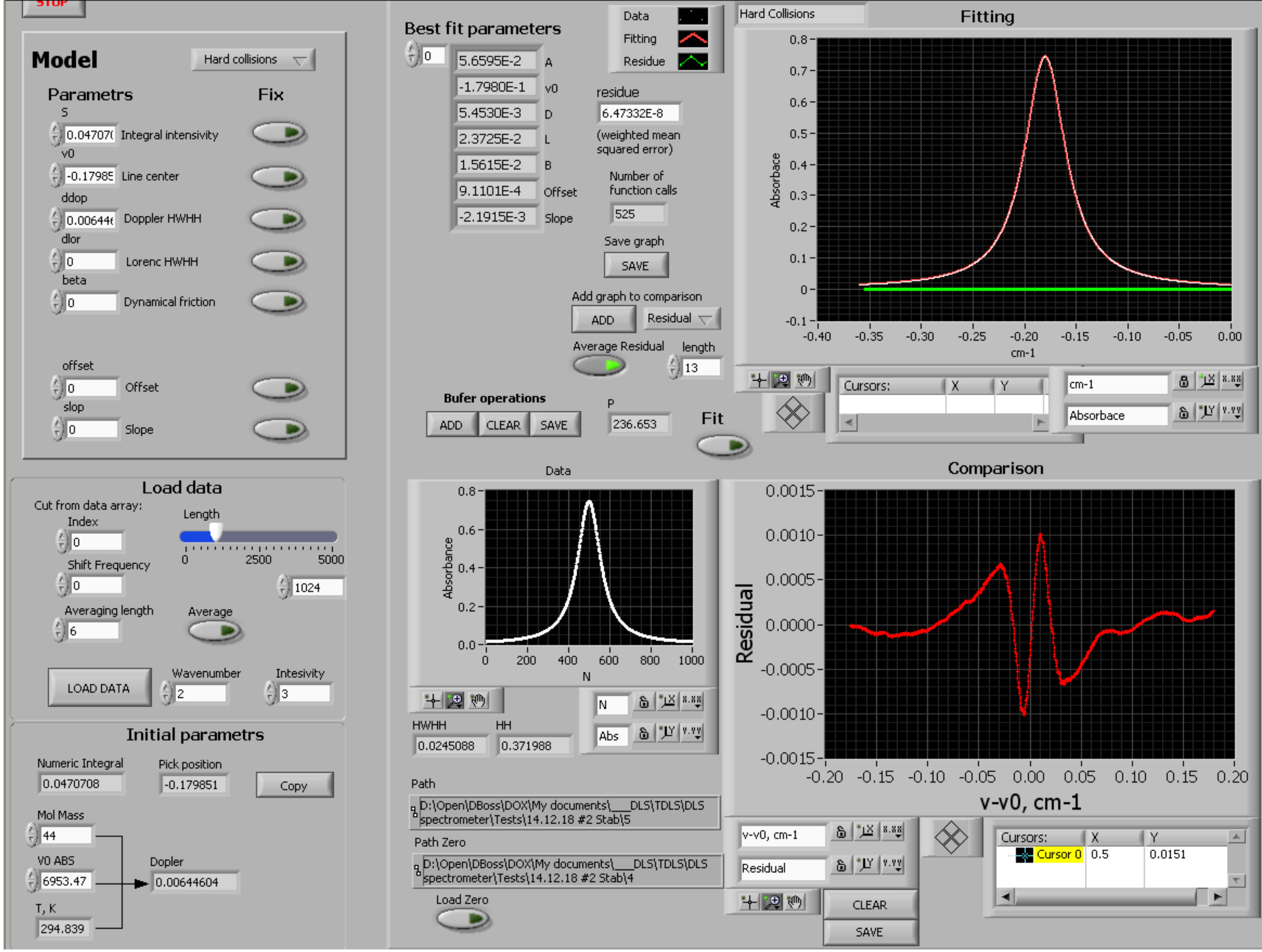
Next step is experimental line shape fitting by some model profile.
In general any smooth curve can be fitted with any accuracy with high order polynomial. However it has no physical meaning.
It is necessary to use physical models of spectral line shape. Spectral line shape is convolution of Doppler and collision broadening profiles. Sometimes it is not true (see C1).
To determine Doppler profile kinetic equation has to be solved [1]. Solutions for two limit cases Hard and Soft were obtained: molecule needs one or infinite number of collisions to achieve equilibrium velocity distribution. Reality is between these two limit cases.
Collision broadening profile has Lorentz shape if time of collision << time between collisions. Sometimes it is not true (see C1).

[1] S. G. Rautian and I. I. Sobel'man, "Effect of collisions on Doppler broadening of spectral lines," Sov. Phys. Usp. 9, 701–716 (1967).

Fitting goal - achieve best agreement between experiment and model (minimum residual) with minimum number of parameters (see A2).

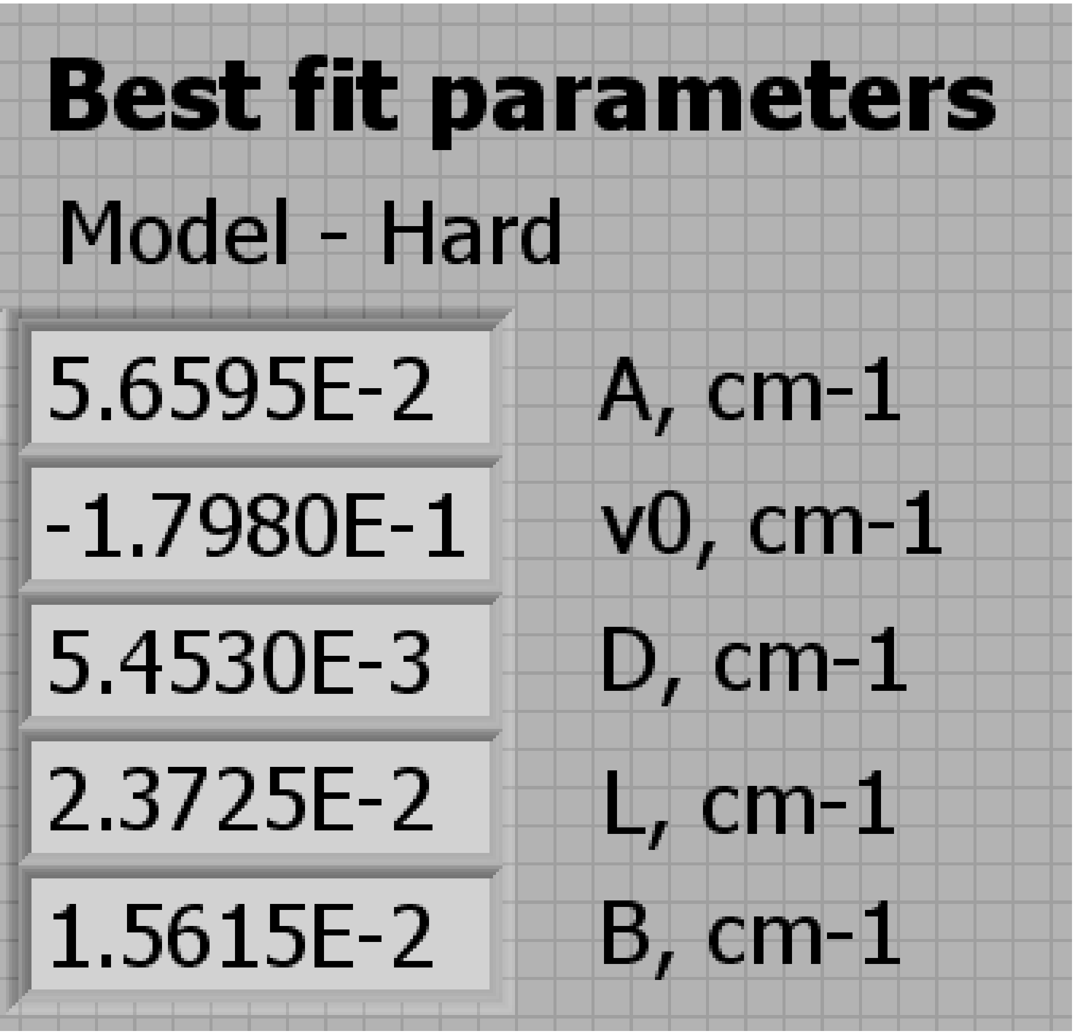
6. Fitting software

Interface of program developed for high accurate experimental spectra fitting (A2).



The program provides high accurate experimental spectra fitting (in present case CO_2 line for 236.65 mBar) using Soft and Hard models of Doppler profile. Fitting parameters: A, v0, D, L, B, offset и slope – baseline and its slope, respectively.

7. Results of fitting

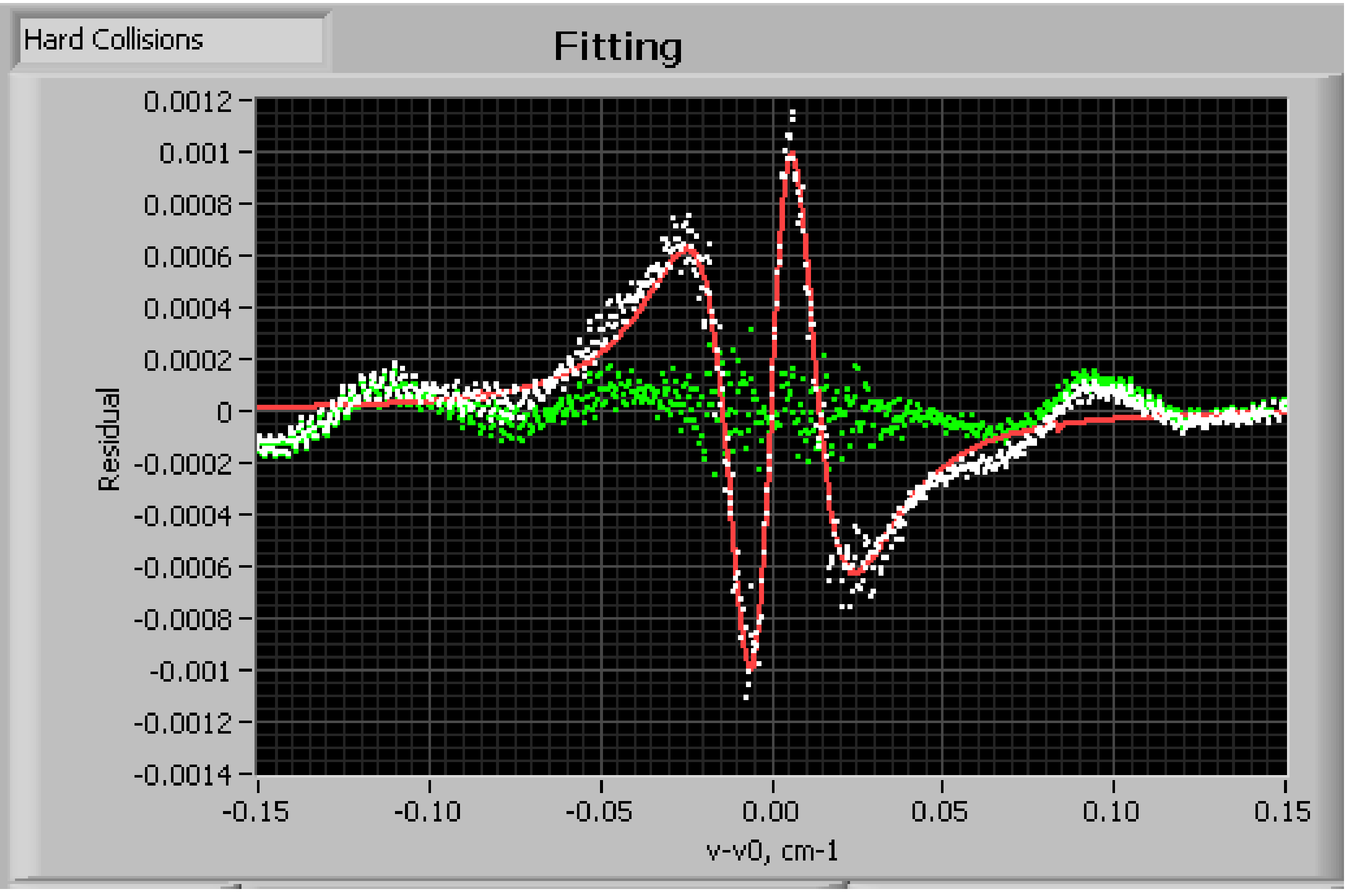


After fitting, following list of best fit parameters is available for model in use: A – absorbance integral, v0 – line center, D – Doppler width, L – Lorentz width, B – narrowing parameter.

It is necessary to mention that fitting parameters have above mentioned physical meaning only for correct model of spectral line under investigation.

8. Residual

White circles – CO_2 line residual for 153.31 mBar (Hard) demonstrating spectral line asymmetry (see A2).



This asymmetry (red curve) can be calculated using line parameters determined experimentally and independently (C1).

Final residual (green) was reduced to 0.02 % of line maximum subject of present experimental precision.

9. Integral intensity determination

Integral absorbance A [cm^{-1}] of spectral line is determined in present fitting. To obtain final result several steps are necessary. For non-ideal molecule, relation between pressure P and molecules number density – N is given by following:

$$P = kNT\left[1 + \frac{N}{N_A}B...\right]$$

Here k – Boltzmann constant, T – temperature, N_A – Avogadro number, B – second virial coefficient. From literature for CO_2 B = -125 cm^3/mole (296 K).

Relation between line integral absorbance – A [cm^{-1}] and integral intensity – S [cm/mol]. Here L is optical cell length.

$$S = \frac{A}{NL}$$

Finally, to be compared with HITRAN, integral intensity was recalculated to 296 K. It was done using CO_2 statsum temperature dependence, level of line under consideration energy (HITRAN 2012), and known temperature of the spectrum recording.

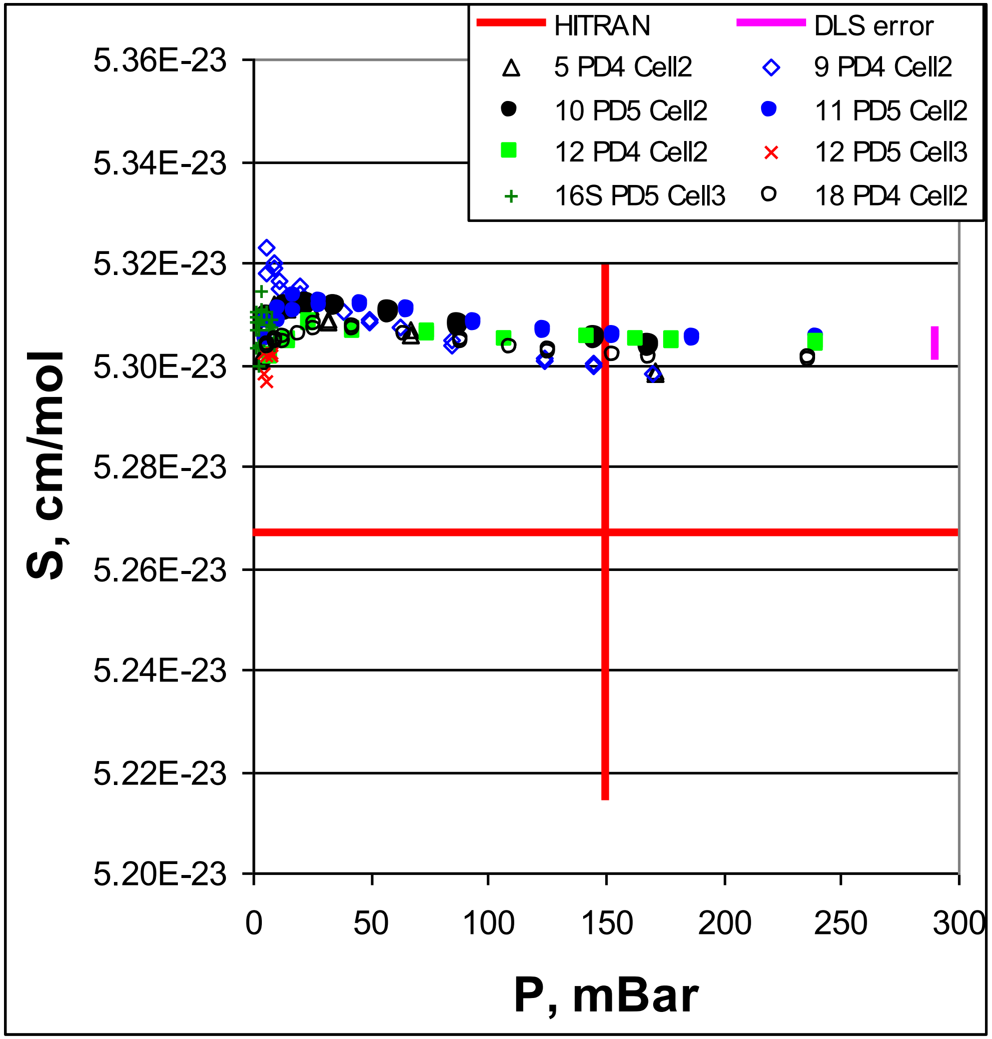
10. Error budget

Error budget for spectral line integral intensity measurements (see A1)

	Value	Error %
L, cm	183.5	0.022
DT, oC	20 - 25	0.017
P, mBar	100	0.036
CO2 sample purity, %	99.98	0.020
Subtotal		0.050
PD non-linearity		0.023
Dv, 10-3 cm-1	800	0.012
Baseline		0.003
Optical zero		0.004
DL Spectrum, MHz	0.5	0.014
Subtotal		0.030
Total		0.058

Absolute accuracy of integral intensity measurements is 0.06 %.

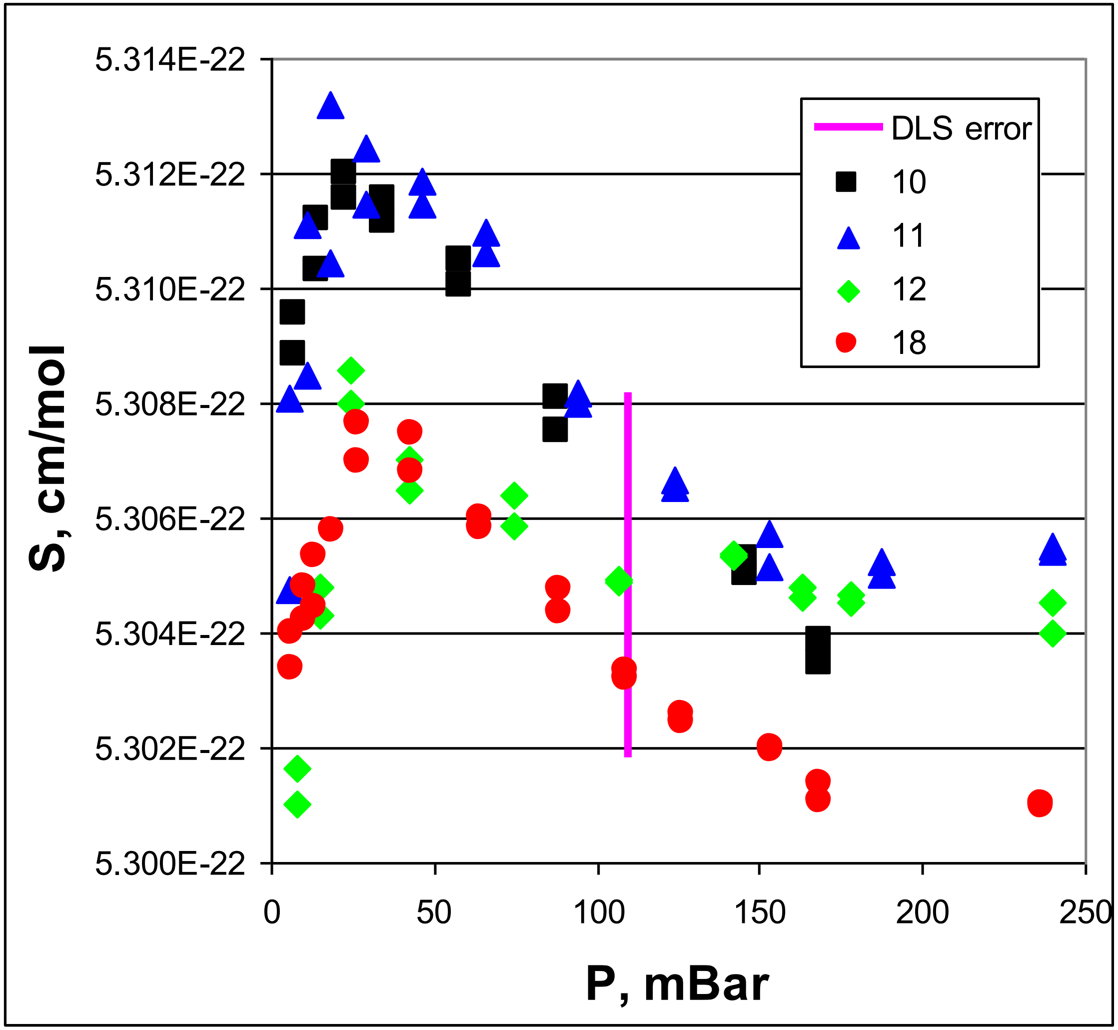
11. TDLS - HITRAN



Horizontal red constant is HITRAN integral intensity for analytical line. HITRAN accuracy estimation for this line is 1 – 2 %. Vertical red line corresponds 1 %. Our data can confirm HITRAN accuracy estimations. The reverse is not valid.

Spread of experimental data is in agreement with vertical bar - our accuracy estimation (0.06 % - A1).

12. Integral intensity

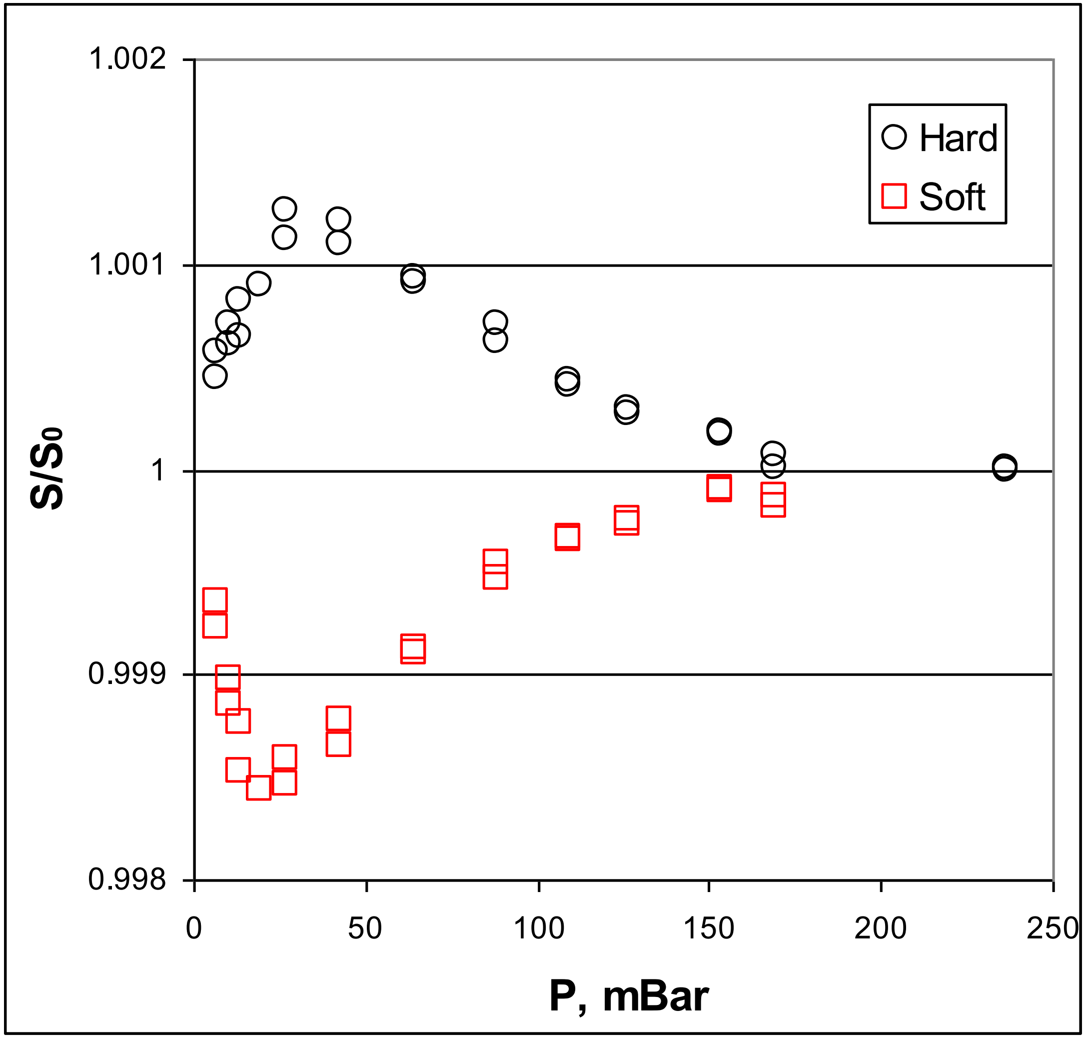


More accurate integral intensity measurements were obtained with cell #2 subject of more accurate the cell length and pressure measurements and Hard model.

Experimental data spread is within TDLS accuracy estimation - 0.06% (vertical bar).

Reproducible S pressure dependence can be observed.

13. S pressure dependence



Finally data obtained were fitted both by Hard and Soft models.

Normalized integral intensity is presented. Here S_0 is integral intensity at high pressure.

Both Hard and Soft are approaching to 1 for zero and high pressures.

Significant (0.015 %) difference can be observed in intermediate pressure range.

More careful analysis of the line shape models has to be done.

14. Phase and velocity correlation

Observed difference has important characteristics: it is negligible both for low and high pressures.

In [1] line shape was considered for model when phase and velocity are changing in the same collision and hence have correlation (**COR)**. It was predicted theoretically and main characteristics were analyzed.

COR: Its influence is negligible both for low (no collisions) and high pressures (for high number of collisions, the process is normal – no correlation). Line shape is not convolution of Doppler and Lorenz profiles. Author has no information that this effect was observed experimentally.

Conclusion: Correlation between phase and velocity changes during collision was experimentally observed for the first time. CO_2 molecule is good candidate for this effect observation because both broadening and narrowing cross sections have close values.

[1] S. G. Rautian and I. I. Sobel'man, "Effect of collisions on Doppler broadening of spectral lines," Sov. Phys. Usp. 9, 701–716 (1967), УФН, 90, 209-236 (1966) (in Russian).

15. Conclusions

1. Integral intensity test: eight measurement series were performed during 20 days period using different cells and PDs to check reproducibility of results obtained.
2. Estimated integral intensity measurements accuracy is 0.06 %.
3. Results obtained are in agreement with HITRAN (accuracy 1 – 2 %). Our data can confirm HITRAN accuracy estimations. The reverse is not valid.
4. Spread of measurement series results is within our estimated accuracy - 0.06 %.
5. Reproducible integral intensity pressure dependence was observed.
6. It looks like that theoretically predicted correlation between phase and velocity changes during collision was experimentally observed for the first time.

Test procedure

Cell #2 (L = 183.50(4) cm) was filled with pure CO_2 (purity better than 99.98 %) at different pressures. Simultaneously with spectra recording, gas pressure and temperature were measured. Accuracy of pressure and temperature measurements is 0.02 % and 0.05 ^{o}C, respectively. Five measurement series were performed during 20 days period to check reproducibility of results obtained.

Experimental spectra were fitted by software developed (A2 Hard).

Fitting procedure