B1

Spectral line fitting for high accurate experimental data

DLS LAB

A.Nadezhdinskii, Ya.Ponurovskii, V.Semenov

A. M. Prokhorov General Physics Institute of RAS, 38 Vavilov str., 119991, Moscow, Russia, E-mail: Nad@nsc.gpi.ru

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 (see A2).
Next step is fitting of experimental spectral line shape by some model profile. At the moment three model profiles are in use: Voigt, Galatry, and Rautian. Traditionally residual is measure of fitting quality. After fitting, some spectral line parameters can be obtained. Subject of present paper is to analyze what information can be obtained from such fitting for high accurate data. What is obtained parameters meaning and accuracy.

Spectral line shape

For accurate experimental data, correct spectral line shape model has to be used. It is determined by correlation function of molecule polarization:

$$P(t) \sim \exp\left[i2\pi\nu x(t) - i\varphi(t)\right]$$

Here v is wave number (cm^{-1}), x(t) – molecule under consideration trajectory, $\varphi(t)$ – the polarization phase shift due to molecular collisions. The first term determines Doppler profile, second one - collision broadening profile.

If there is no correlation between the molecule translation motion and phase shift during collisions, spectral line shape is convolution of Doppler and collision broadening profiles.

Doppler profile

No collisions: Doppler profile is determined by Maxwell distribution of molecules velocity.

In [1] Doppler profile line shape in presence of collisions was analyzed. It was shown that Doppler profile determination needs solution of kinetic equation. Solutions for two limit cases were obtained.

Soft collision (diffusion approximation of kinetic equation): molecule needs infinite number of collisions to achieve equilibrium velocity distribution.

Hard collision: molecule needs one collision to achieve equilibrium velocity distribution.

Reality is between these two limit cases.

[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).

Soft collisions model

Galatry analyzed Doppler profile of heavy molecule in buffer gas of light molecules. Correlation function of Galatry profile is:

$$C_{soft}(t) = \exp\left[-\frac{(kV_0)^2}{2}\left(\frac{|t|}{\beta P} + \frac{1}{(\beta P)^2}\left[\exp(-\beta P|t|) - 1\right]\right)\right]$$

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Soft collision (diffusion approximation of kinetic equation): molecule needs infinite number of collisions to achieve equilibrium velocity distribution. Soft model is more general in comparison with Galatry model.

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Hard collisions model

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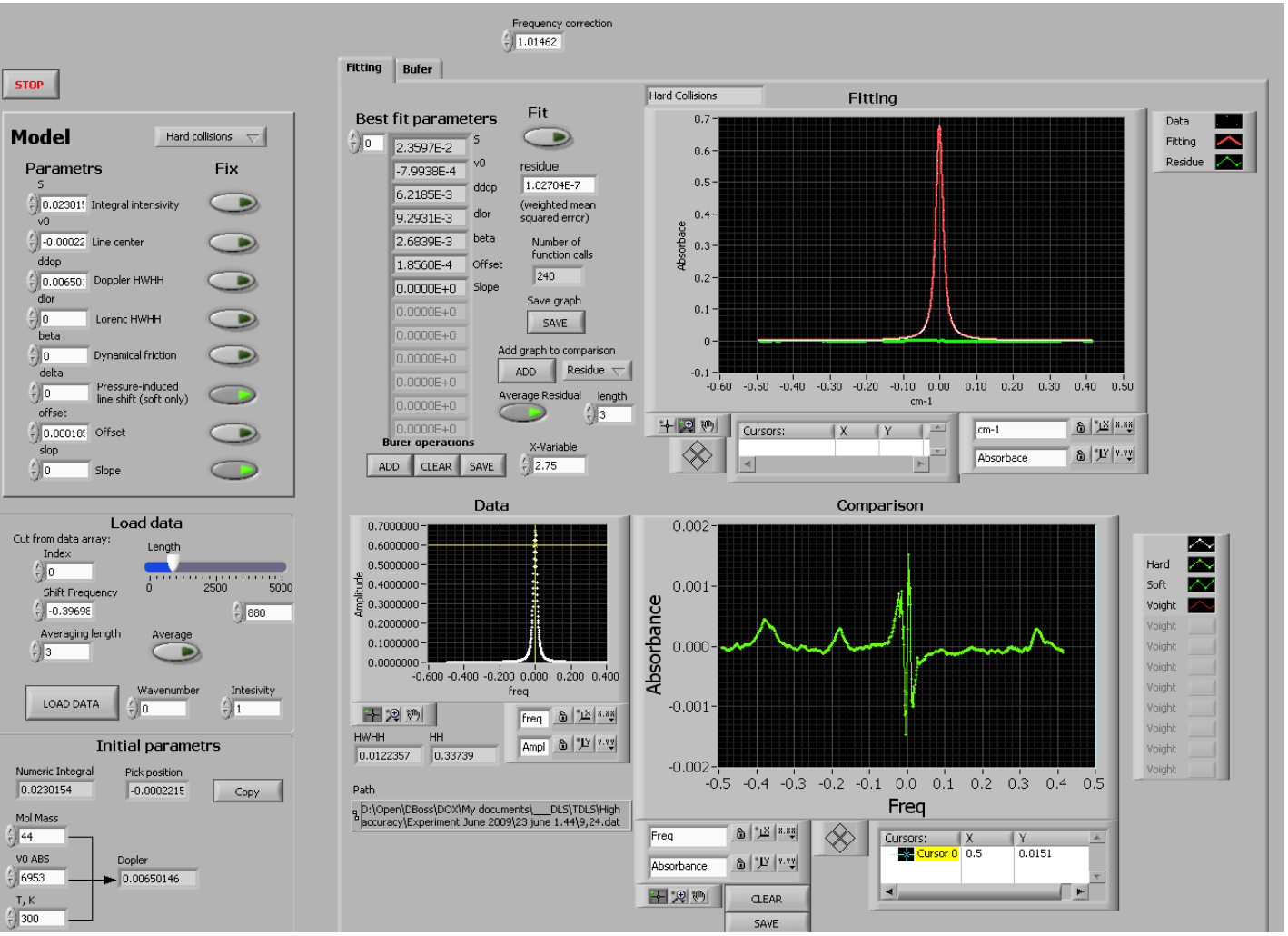
$$K_{hard} = \mathrm{Re}\frac{\frac{1}{\pi}\int \frac{W(\vec{V})d\vec{V}}{\beta P + i\left(\omega - \vec{k}_0\vec{V}\right)}}{1-\beta P\int \frac{W(\vec{V})d\vec{V}}{\beta P + i\left(\omega - \vec{k}_0\vec{V}\right)}}$$

Fitting software



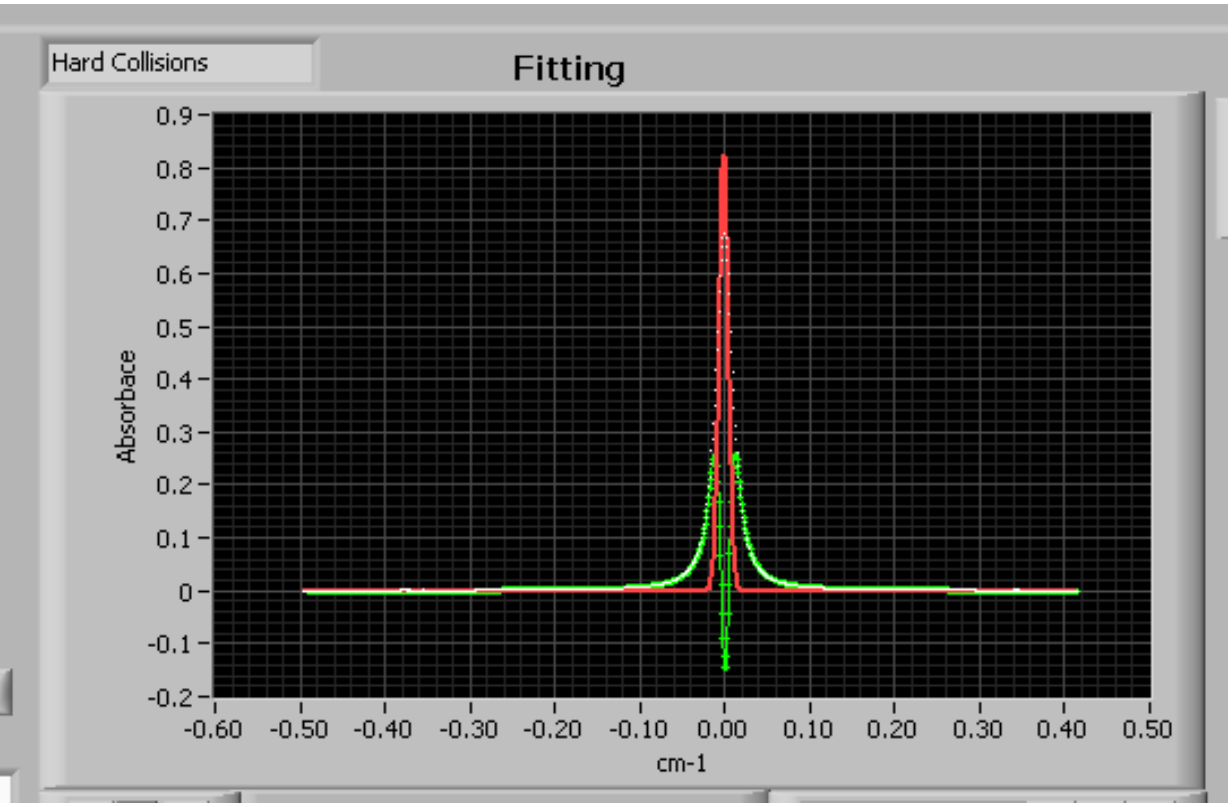
Software was developed to fit high accurate spectral line shape.

The software can fit experimental line shape using soft or hard models of Doppler profile (see C1). In present case CO_2 line for P = 92.4 mBar was analyzed.

Following line parameters were fitted: integral intensity – S, line center - v0, Doppler width – ddop, Lorenz width – dlor, narrowing parameter – beta, offset and slope of baseline. Each parameter can be selected as fixed one or to be included in fitting.

Fitting (S, v0)

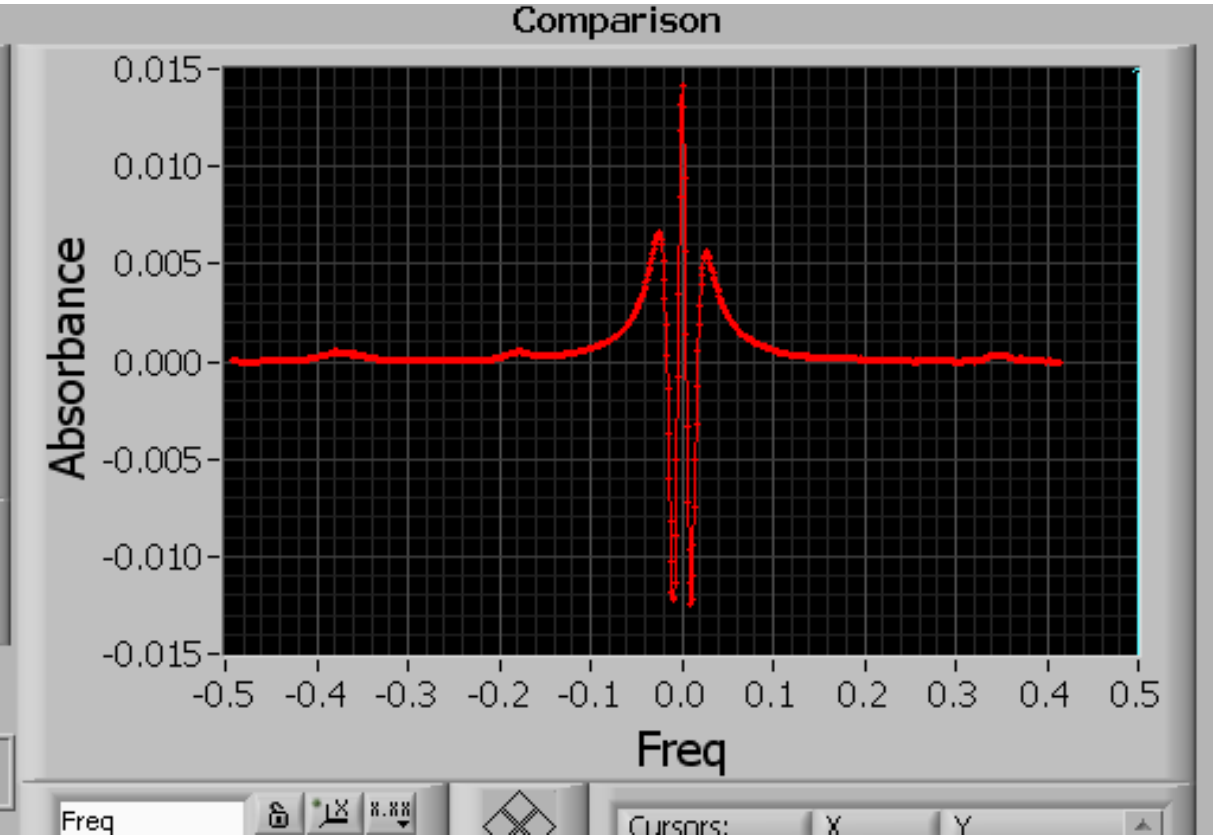
Let us consider fitting procedure step by step.



Result of fitting when only integral intensity – S and line center – v0 were included in the fitting procedure. Line was assumed to have Gauss shape with width determined by molecules Maxwell velocity distribution.

S removes line integral intensity, v0 removes first line shape derivative. Hence residual looks like second derivative of line shape (2 roots). This fitting doesn't consider the line Lorenz wings and its residual is at level of 30 %.

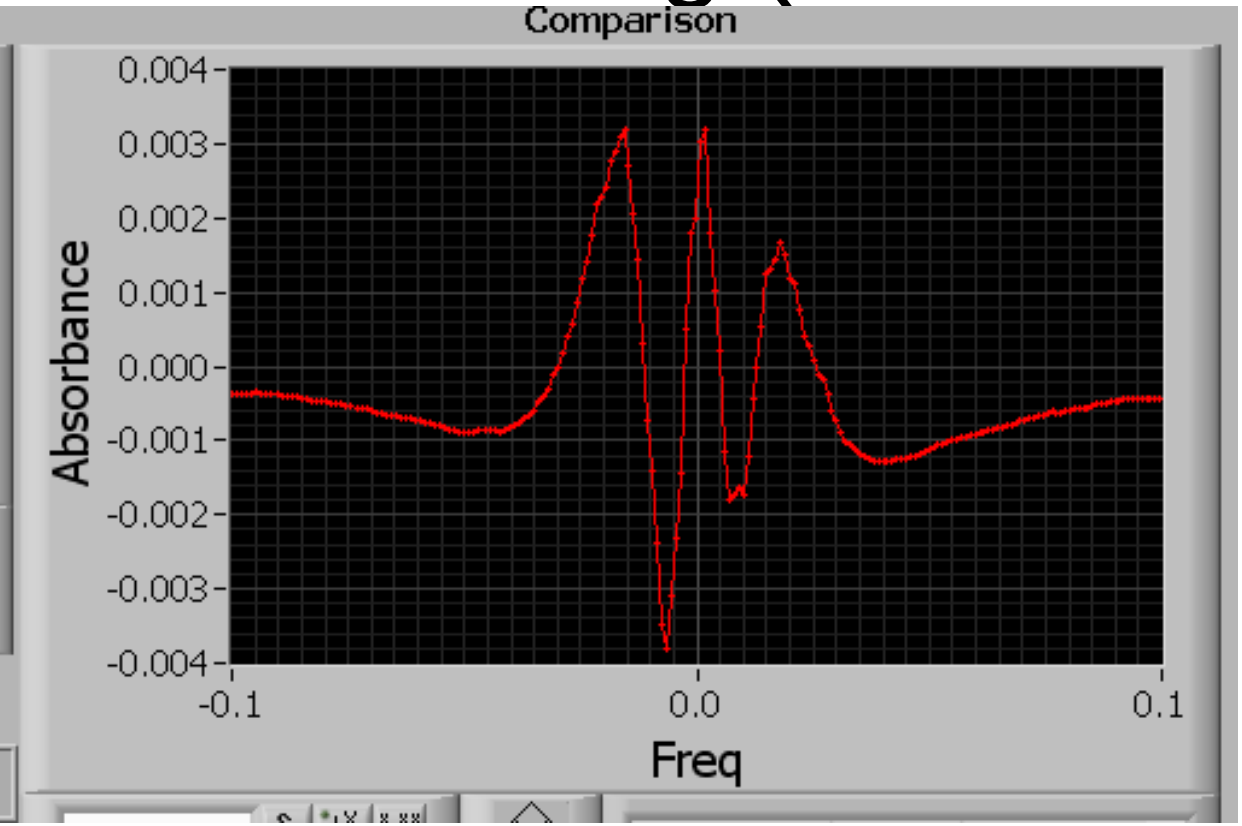
Fitting (S, v0, vlor)



When Lorenz width was included in fitting for fixed Doppler width second derivative was removed.

Significant residual improvement to 1.5 % level can be achieved. Here one can see 4 roots (4th line shape derivative). Here we have Foigt profile with fixed Doppler width.

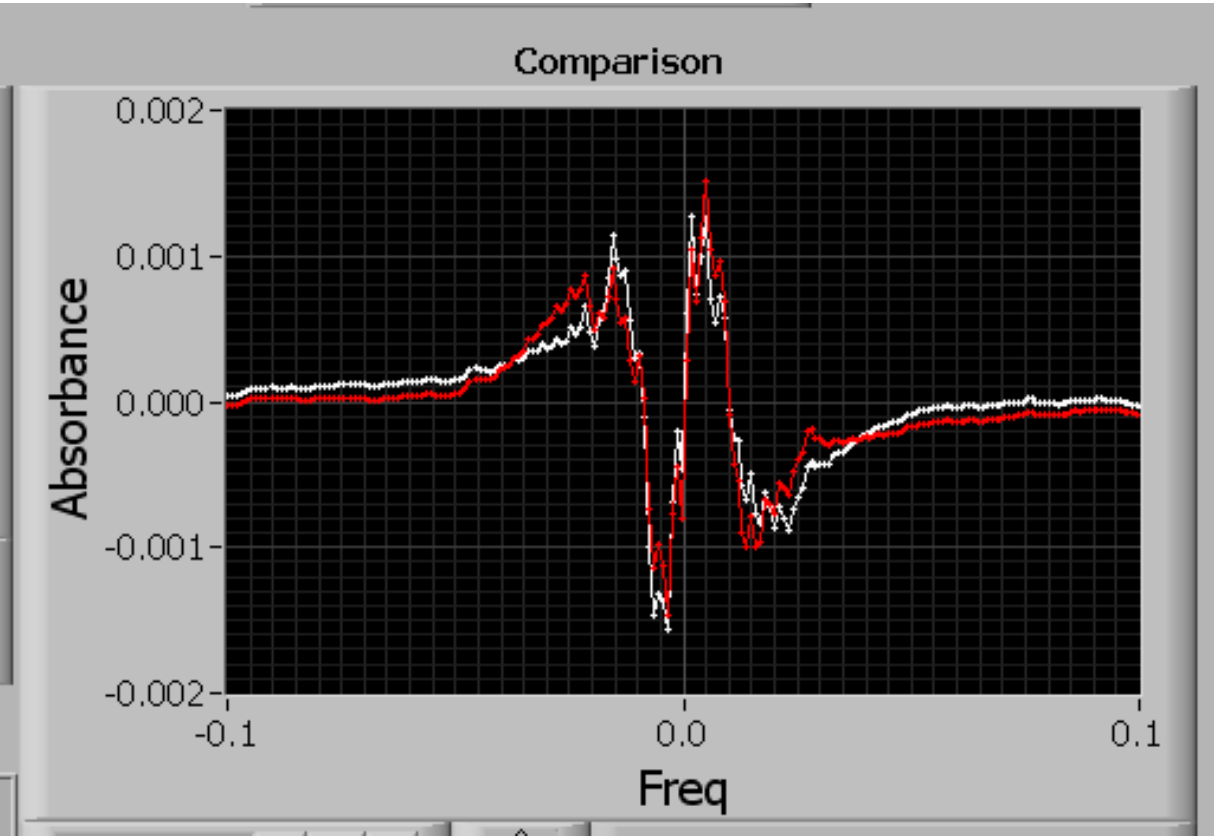
Fitting (S, v0, vlor, vdop)



Previous model didn't take in to account Dicke narrowing. As first approximation we can include in fitting Doppler width – vdop.

The residual was improved 5 times and 4^{th} derivative was removed. Such counter one will have for both soft and hard models with narrowing parameter fixed to 0. It is Voigt profile with variable Doppler width. For present model residual is determined by 6^{th} derivative (six roots). The residual asymmetry can be also observed – influence of odd derivatives.

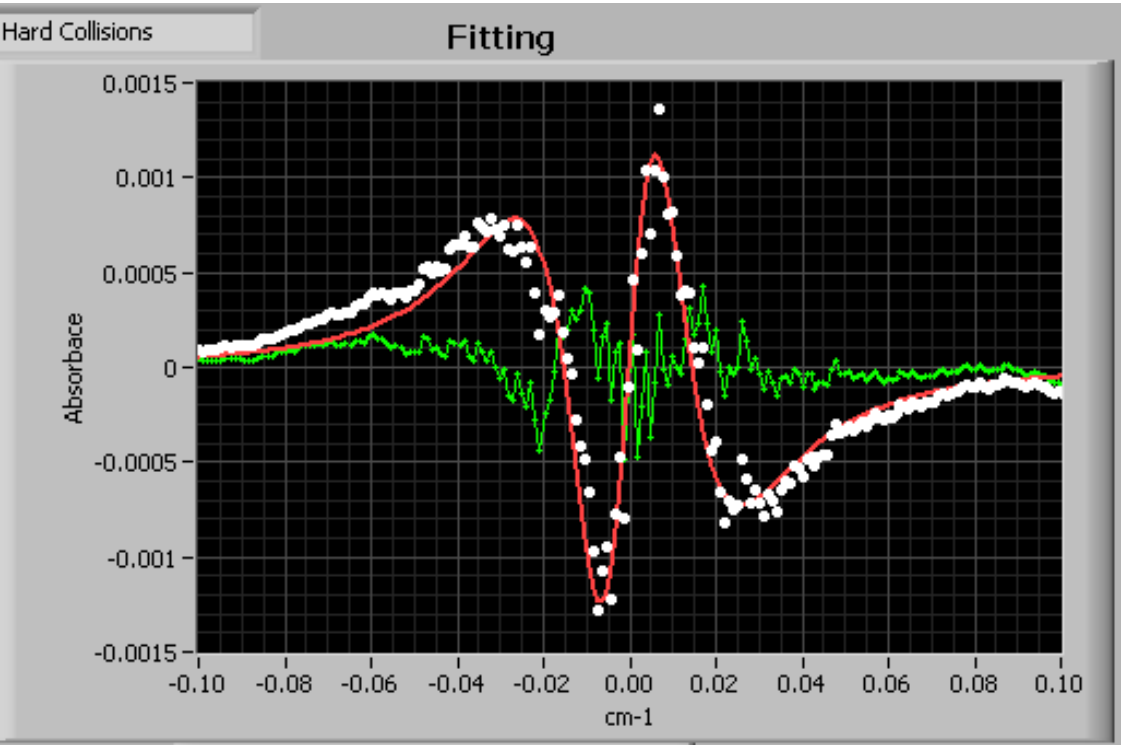
Fitting (S, v0, vlor, vdop, beta)



Previous model did not take into account correct Doppler profile (see above). Let us include in fitting narrowing parameter beta. Residual for fitting using hard (red) and soft (white) models.

The residual was reduced to 0.15 %. Difference between hard and soft is at the level of experimental precision - 4 10^{-4} (see below). The residual has 3 roots – asymmetry (see next slide and B2).

Asymmetry

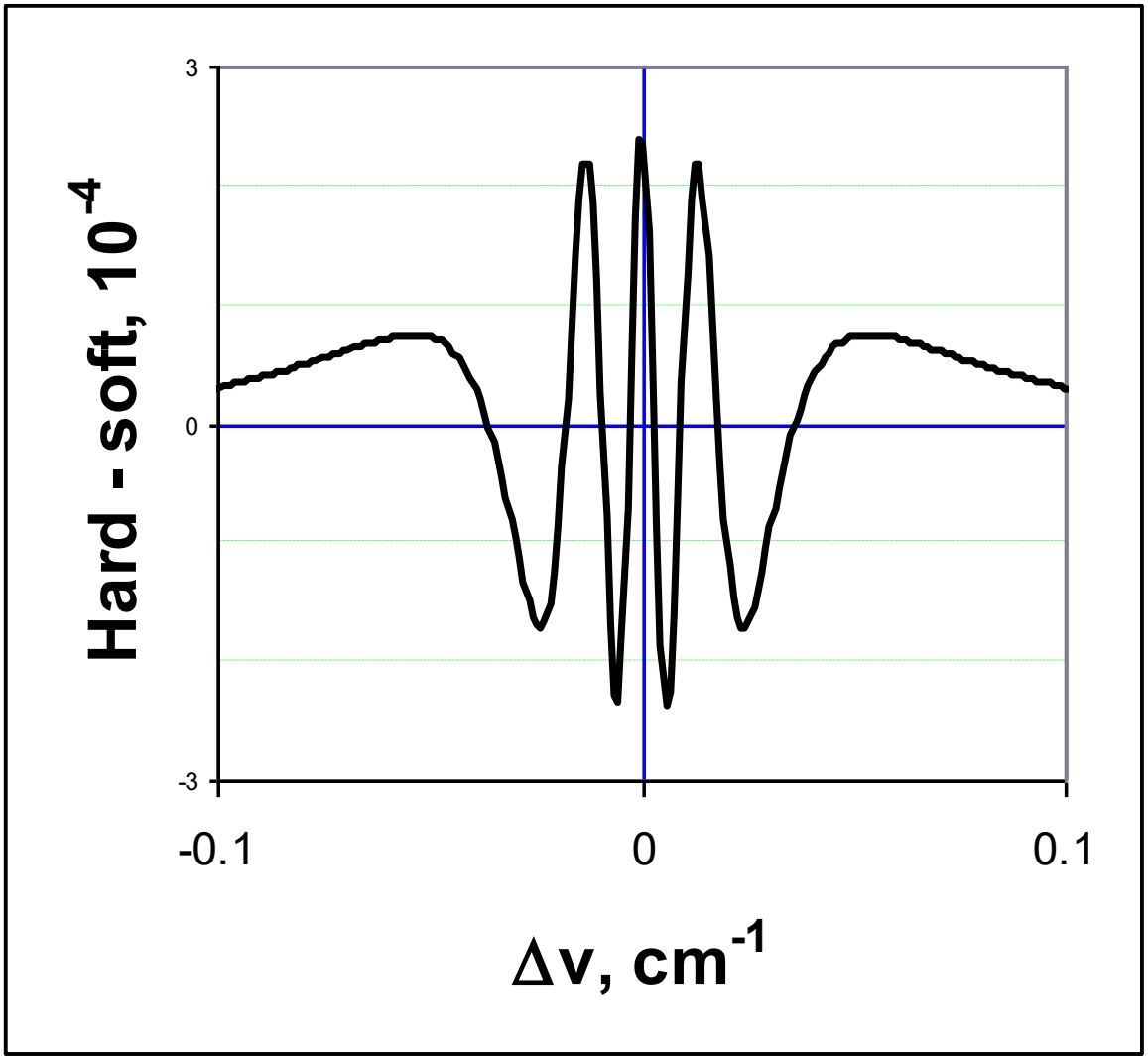


White circles – CO_2 line residual for 171.4 mBar normalized to line maximum demonstrating spectral line asymmetry (3 roots).
To measure asymmetry, empirical model function was developed. Asymmetry model function is determined by shape of line under consideration. Using this function asymmetry can be fitted (red curve). This approach was tested for all pressures in use.

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

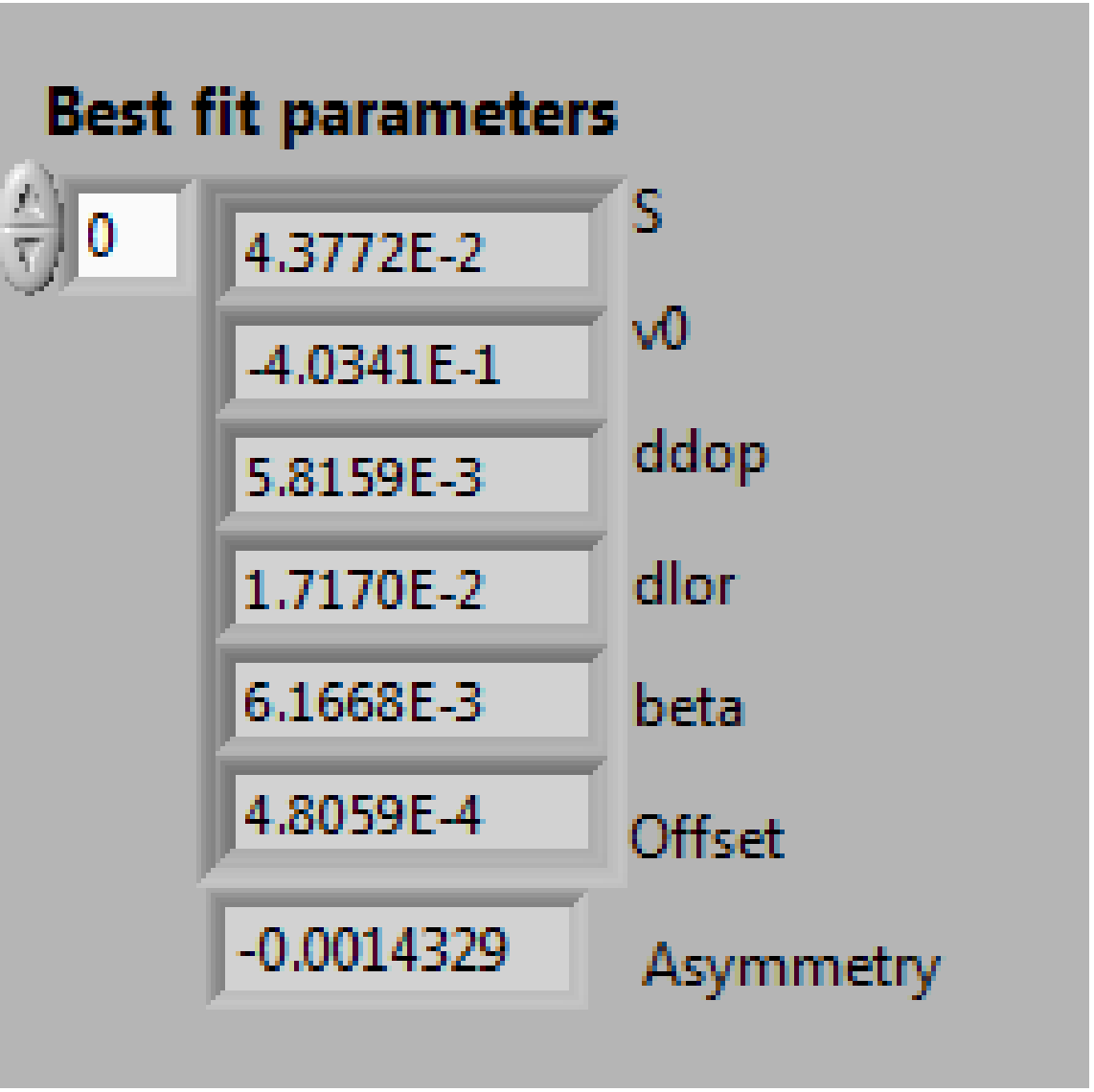
Soft - hard models difference

Next question: what is real difference between hard and soft?



The same CO_2 line (92.4 mBar) was fitted using hard and soft models.
Difference between these two fittings looks like 8th line shape derivative (8 roots) and is of the order of $2\ 10^{-4}$.
It is below experimental accuracy mentioned above.
Conclusion: if residual is using as measure of fitting quality, it is impossible to distinguish between soft and hard collisions models.

Line parameters



Finally after fitting particular experimental line using fitting procedure developed one have following set of the line under consideration parameters.

This set can be obtained both for hard and soft collision models.

These data analysis is subject of separate papers (B2, C1, C2).

Conclusions

- Spectral line shape fitting software using both hard and soft models was developed
- The software operation was analyzed
- Residual value of $4\ 10^{-4}$ was achieved! It is determined by present precision of our high accurate TDLS measurements.
- If residual is using as measure of fitting quality, it is impossible to distinguish between soft and hard collisions models.