A2

Fitting of high accurate experimental data

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1. Introduction

DL spectrometer for high accurate measurements was developed.

Motivations:
1. Traditional spectroscopy – accurate measurements of molecule under investigation spectral line frequency and intensity.
2. Spectral line shape – accurate measurements of spectral line shift, broadening, and shape.
3. Concentration accurate measurements of gas mixture under investigation.

Accuracy level 0.06 % was recently achieved in TDLS (see A1). Next step is high accurate experimental spectral line shape fitting.

Recent experimental accuracy improvement requires reanalysis of fitting procedure. Fitting has several goals: to fit experimental line shape with experimental accuracy (measure is residual normalized to line maximum) and to determine line parameters having physical meaning.

2. 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 - to achieve best agreement between experiment and model (minimum residual) with minimum number of fitting parameters.

3. Spectral line shape models

From K.Osipov presentation at A.M.Prokhorov All-Russian TDLS seminar.

[1] J. Tennyson, P. Bernath, A Campargue and etc. Recommended isolated-line profile for representing high-resolution spectroscopic transitions (IUPAC Technical Report). 10.2014

Abstract: … The Task Group recommends that the partially Correlated quadratic-Speed-Dependent Hard-Collision (pCqSDHC) should be adopted as the appropriate model for high resolution spectroscopy.

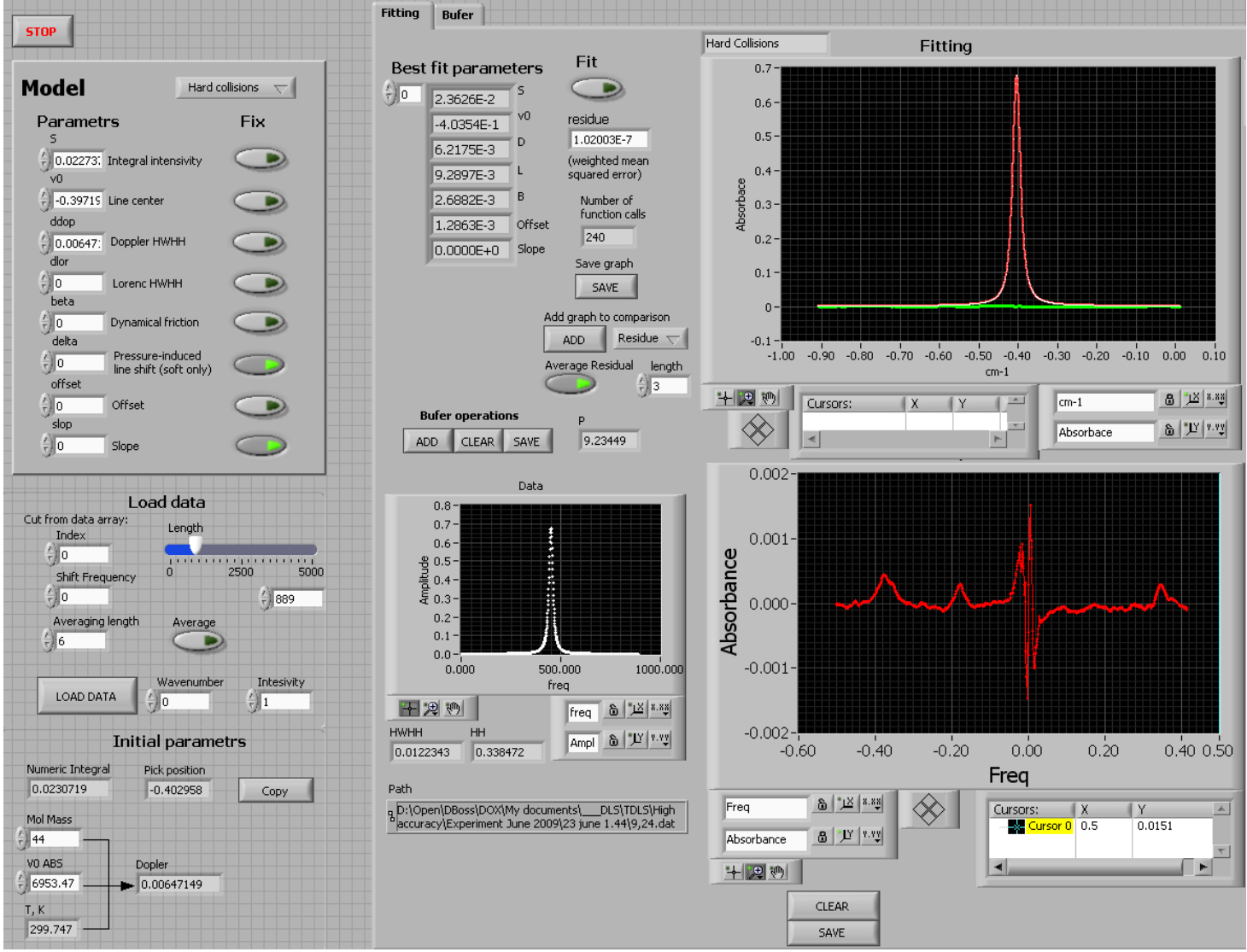
Acronym	Profile name	Parameters	Mechanism		
		N	SD[a]	VC[a]	Correlation
DP	Doppler	1 Γ_D	No	No	No
LP	Lorentz	2 Γ, Δ	No	No	No
VP	Voigt	3 Γ_D, Γ, Δ	No	No	No
GP	Galatry	4 Γ_D, Γ, Δ, ν_{VC}	No	Soft	No
RP	Rautian	4 Γ_D, Γ, Δ, ν_{VC}	No	Hard	No
NGP	Nelkin–Ghatak	4 Γ_D, Γ, Δ, ν_{VC}	No	Hard	No
SDVP[b]	speed-dependent Voigt	5 Γ_D, Γ_0, Δ_0, Γ_2, Δ_2	Yes	No	No
SDGP[b]	speed-dependent Galatry	6 Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}	Yes	Soft	No
SDNGP[b]	speed-dependent Nelkin–Ghatak	6 Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}	Yes	Hard	No
SDRP[b]	speed-dependent Rautian	6 Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}	Yes	Hard	No
HTP	Hartmann–Tran	7 Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}, η	Yes	Hard	Yes
CSDaRSP[b]	correlated SD asymmetric Rautian–Sobelman	8 Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}, χ, η	Yes	Combination	Yes
pCSDKS[b]	partially correlated SD Keilson-Storer	8 Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}, γ_{KS}, η	Yes	Combination	Yes

[a] SD = speed–dependent; VC = velocity changes due to collisions.

Real number of parameters is N+1 (integral intensity has to be included).

4. Fitting software

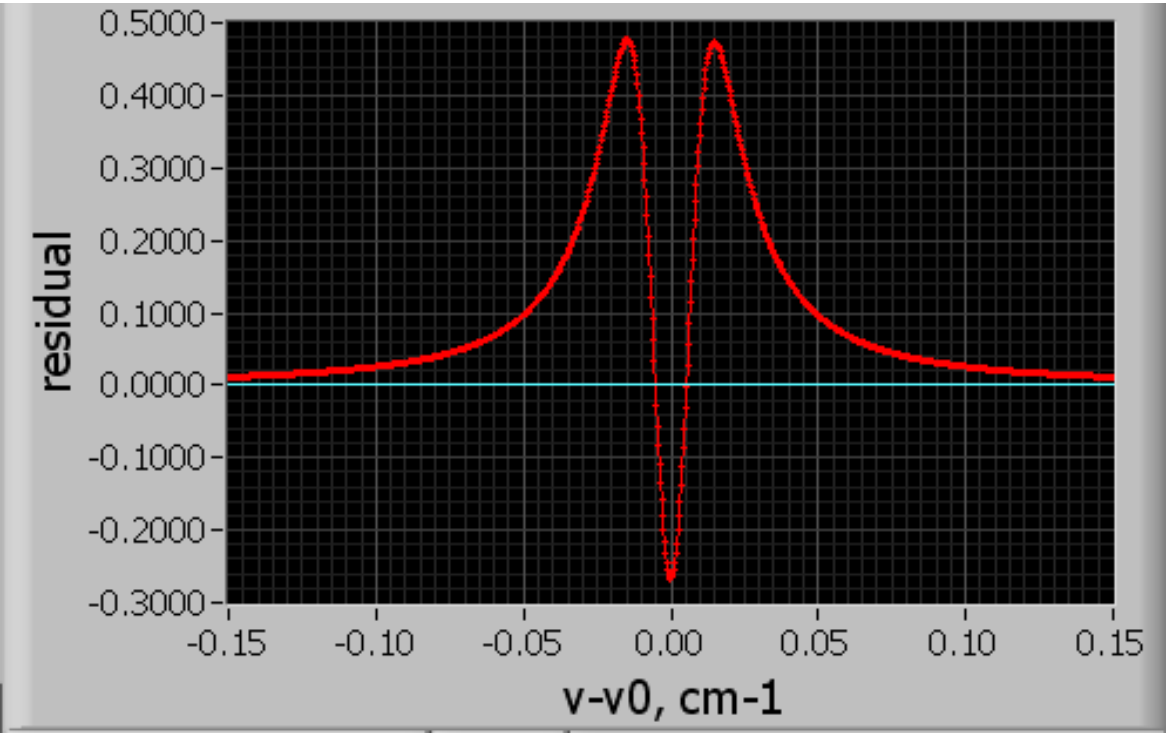
Interface of program developed for high accurate experimental spectra fitting.



The program provides high accurate experimental spectra fitting (in present case CO_2 line for 92.4 mBar) using soft and hard models of Doppler profile. Fitting parameters: S – integral intensity, v0 – line center, D – Doppler width, L – Lorentz width, B – narrowing parameter, offset и slope – baseline and its slope, respectively. All parameters can be fixed or included in fitting.

5. Fitting (S, v0)

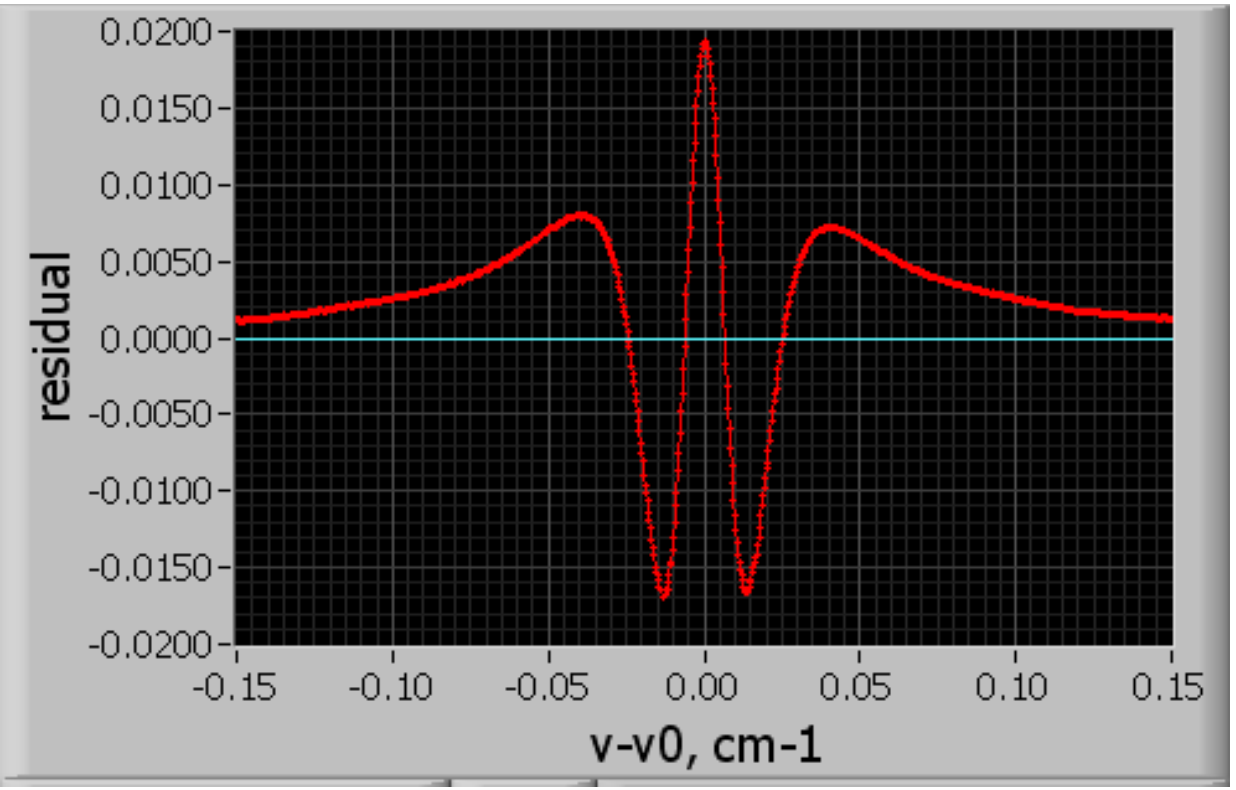
Let us consider fitting procedure step by step.
CO_2 line (6953.46708 cm^{-1}), P = 153.31 mBar is analyzed.



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 50 %.

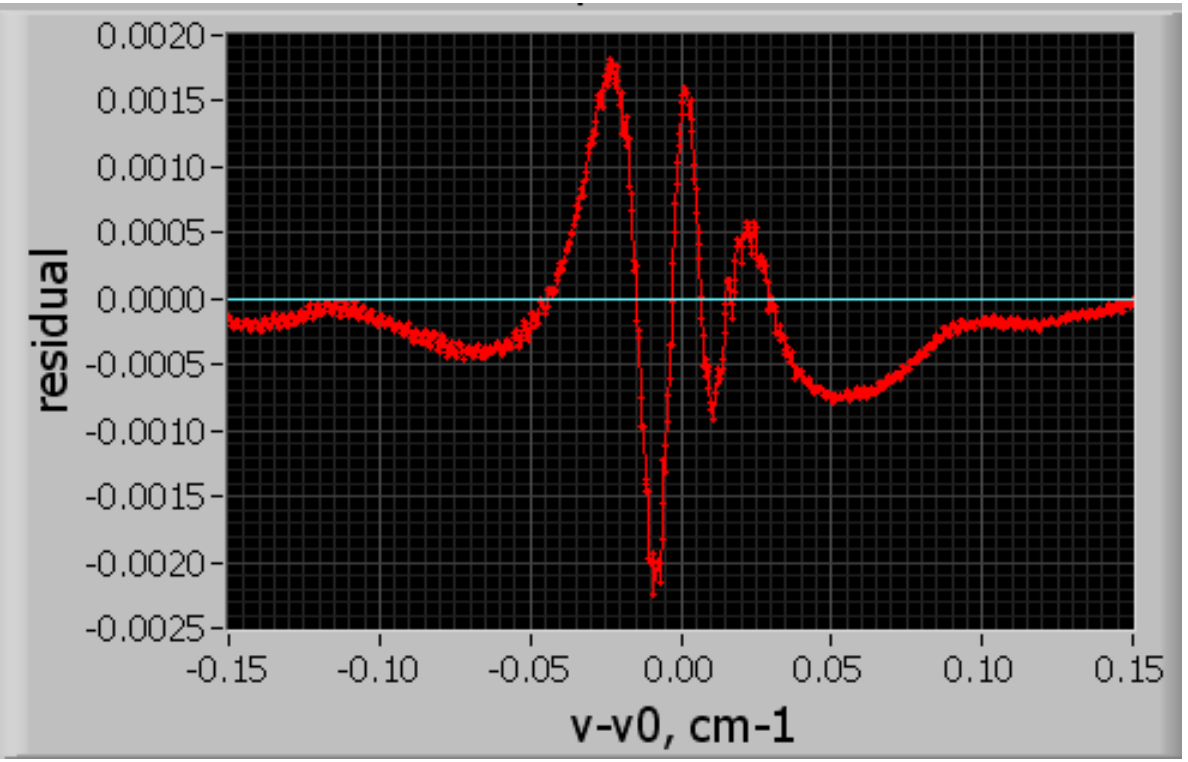
6. Fitting (S, v0, L)



When Lorenz width was included in fitting second derivative was removed.

Significant residual improvement to 1.9 % level can be achieved. Here one can see 4 roots (4th line shape derivative). Here we have Voigt profile with fixed Doppler width.

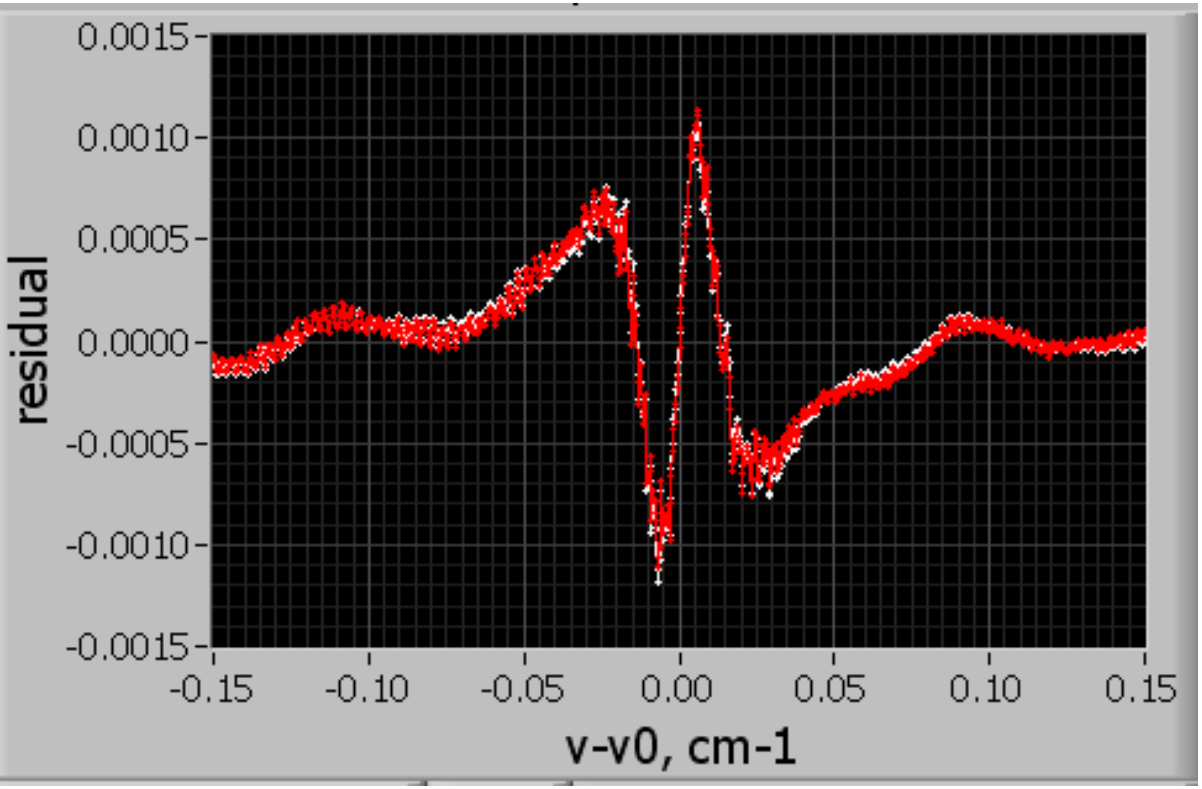
7. Fitting (S, v0, L, D)



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

The residual was improved 10 times and 4^{th} derivative was removed. This profile one will have for both soft and hard models with narrowing parameter B 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.

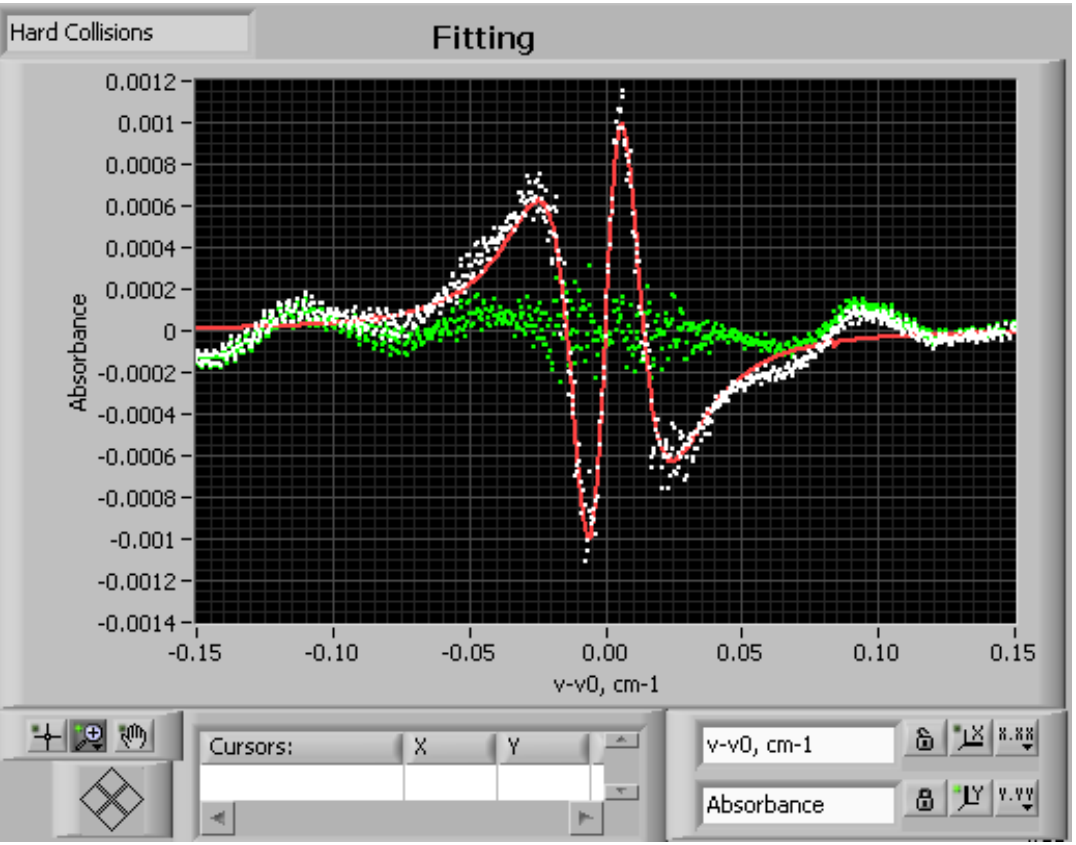
8. Fitting (S, v0, L, D, B)



Previous model did not take into account correct Doppler profile (slide 2). Let us include in fitting narrowing parameter B. Residual for fitting using hard (red) and soft (white) models.

The residual was reduced to 0.1 %. Difference between hard and soft is at the level of experimental precision - 2 10^{-4} (see below). Using only residual, it is impossible to distinguish between Soft and Hard.
The residual has 3 roots – asymmetry (see next slide).

9. Asymmetry

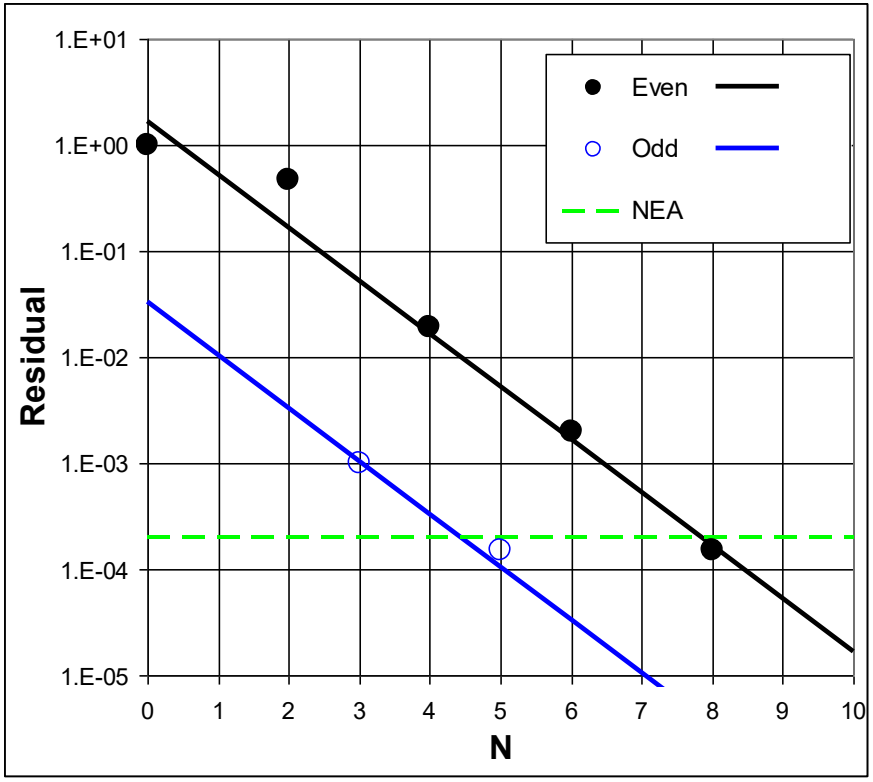


White circles – CO_2 line residual for 153.31 mBar demonstrating spectral line asymmetry (3 roots). To measure asymmetry, empirical model function was developed. Asymmetry model function is determined by shape of line under consideration. Using this function asymmetry can be measured (red curve).

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

It is not fitting – in C1 it will be demonstrated that asymmetry can be calculated using line parameters determined experimentally and independently .

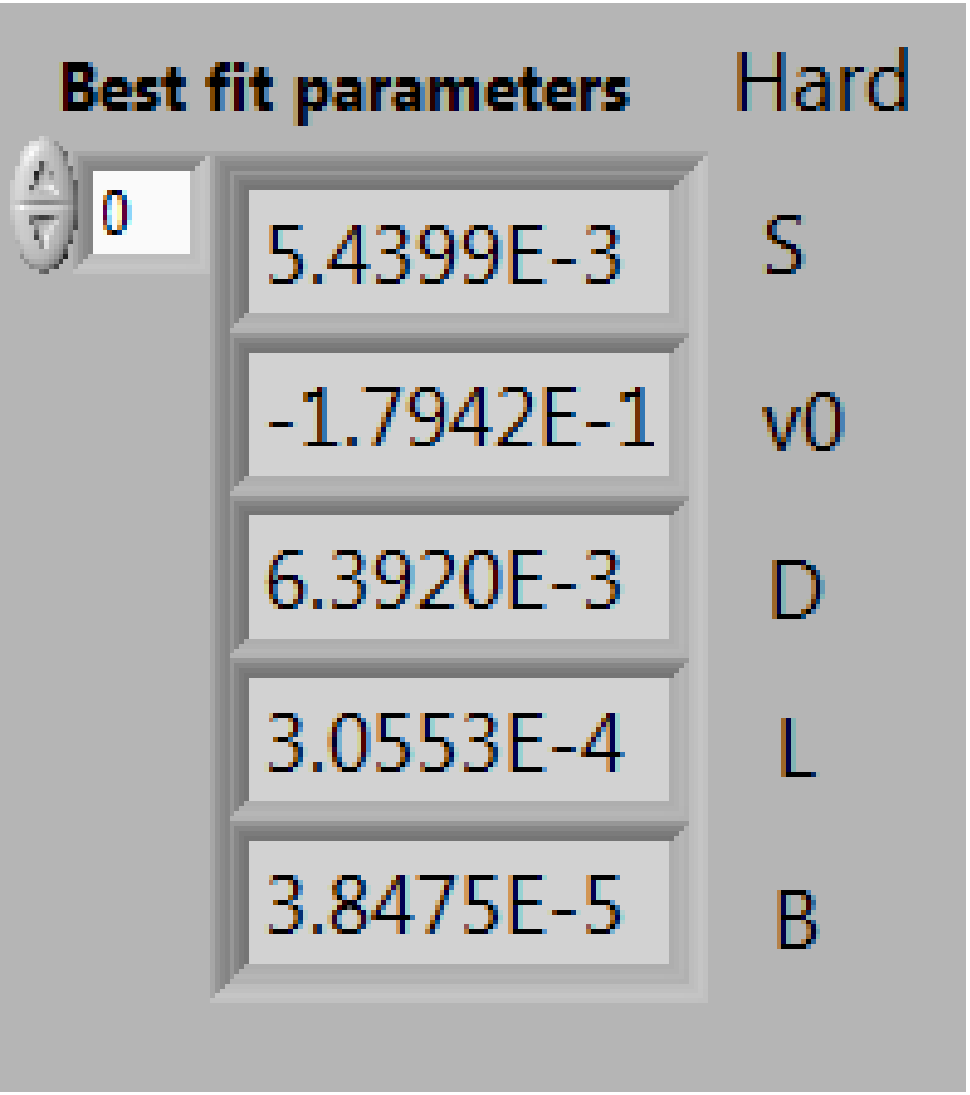
10. Fitting procedure



Let us consider fitting procedure from other side. Fig. presents residual as function of residual roots – N. Odd components are 50 times smaller than even ones. When new fitting parameter is adding, N is increasing by 2 and residual is decreasing by order of magnitude. It is good. It means that fitting procedure is correct.
Green dashed line represents NEA.

Conclusion 1: Line shape fitting with NEA = $2\ 10^{-4}$ (I do not think that anybody in the world has similar NEA) can be done using Soft or Hard models with 5 parameters: S, v_0, D, L, B. Usage of other parameters list has to be investigated similar to this slide depending on NEA available.
Conclusion 2: Usage of more fitting parameters (slide 3) is not correct. It leads to parameters correlation and their physical meaning loosing.

11. Results of fitting

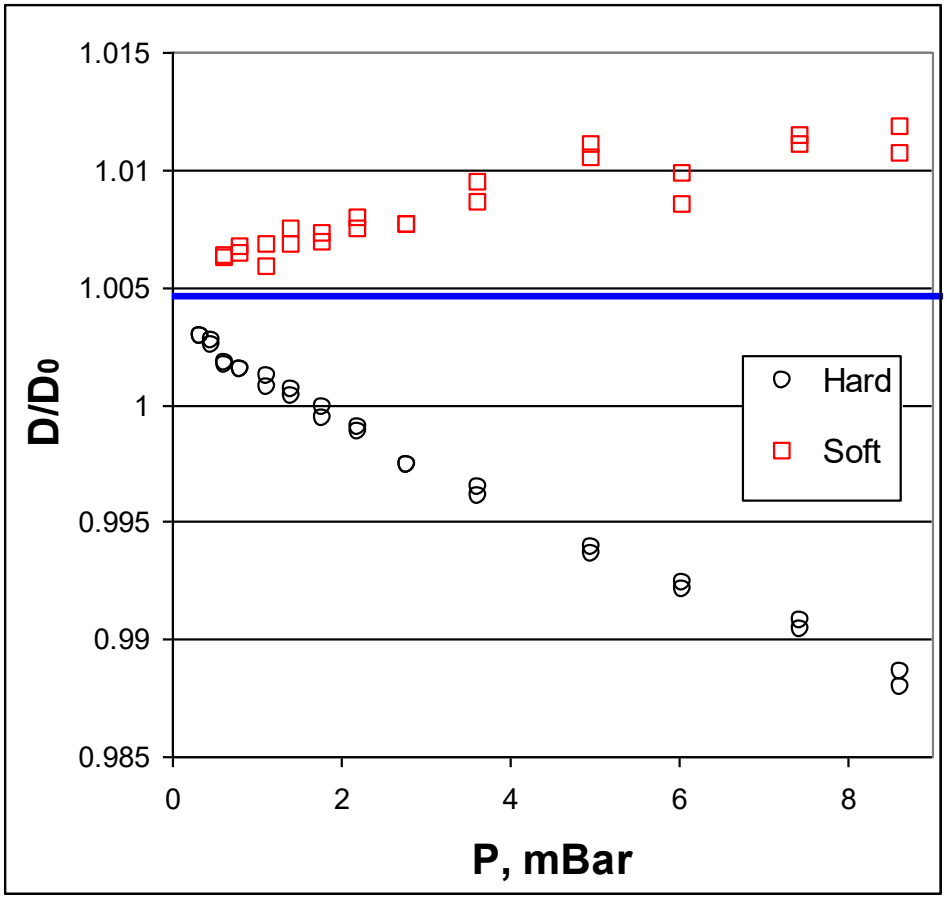


After fitting, following list of best fit parameters is available for fitting model in use: S – integral intensity, v0 – line center, D – Doppler width, L – Lorentz width, B – narrowing parameter.

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

12. Doppler width

Both Soft and Hard models contain D_0. It can be calculated from Maxwell distribution. What means including Doppler width – D in fitting. There are several motivations.



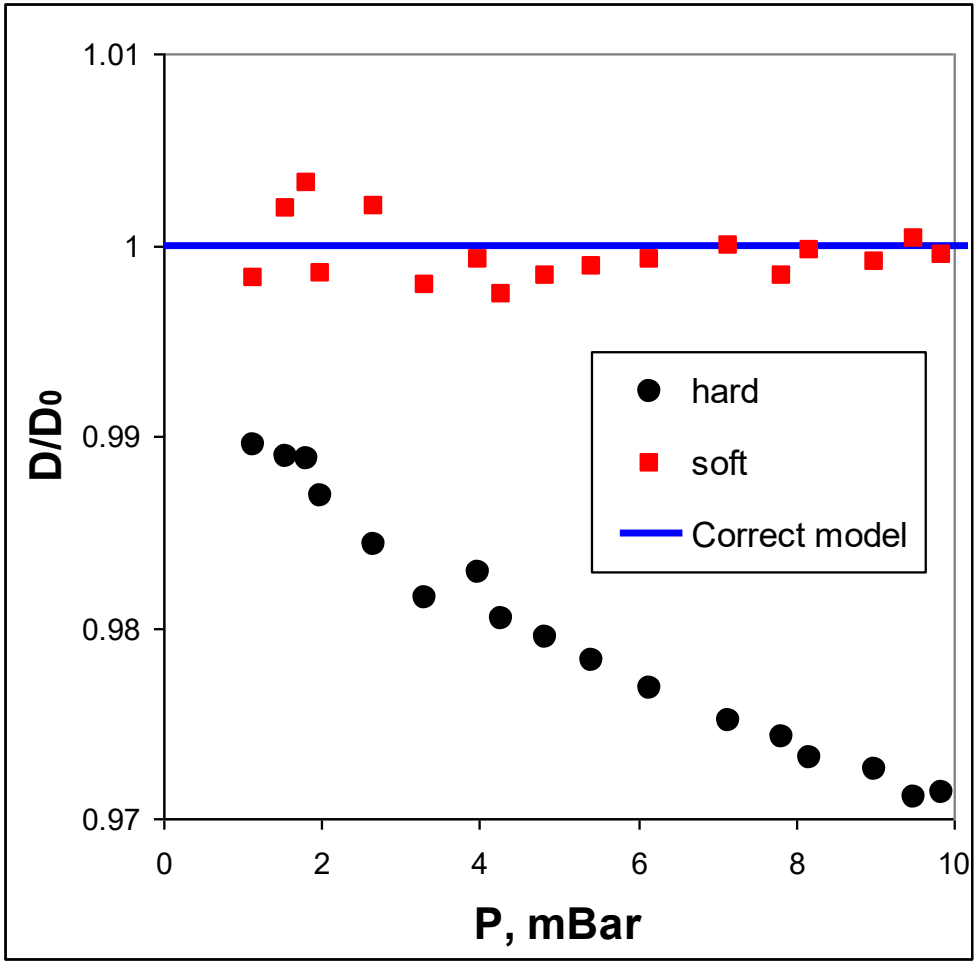
Results of CO_2 line (6953.46708 cm^{-1}) fitting using Hard and Soft models.

1. Both models give similar result for P=0, and its value is above 1. It is due to DL radiation characteristics (noise, optical feedback, etc.). This value (blue constant) has to be used in fitting as D_0.
2. Soft and Hard demonstrate totally different behavior being out of blue constant. Both models are not correct for CO_2.
3. For correct model results of fitting has to be close to blue constant.
4. Doppler width fitting can show model in use correctness.

Conclusion: Only for correct model results of fitting have physical meaning.

13. Soft collision model

Due to elastic scattering theory, scattering amplitude for dipole-dipole interaction has pole for zero scattering angle. It means small angle scattering. In other words it is soft collision model.

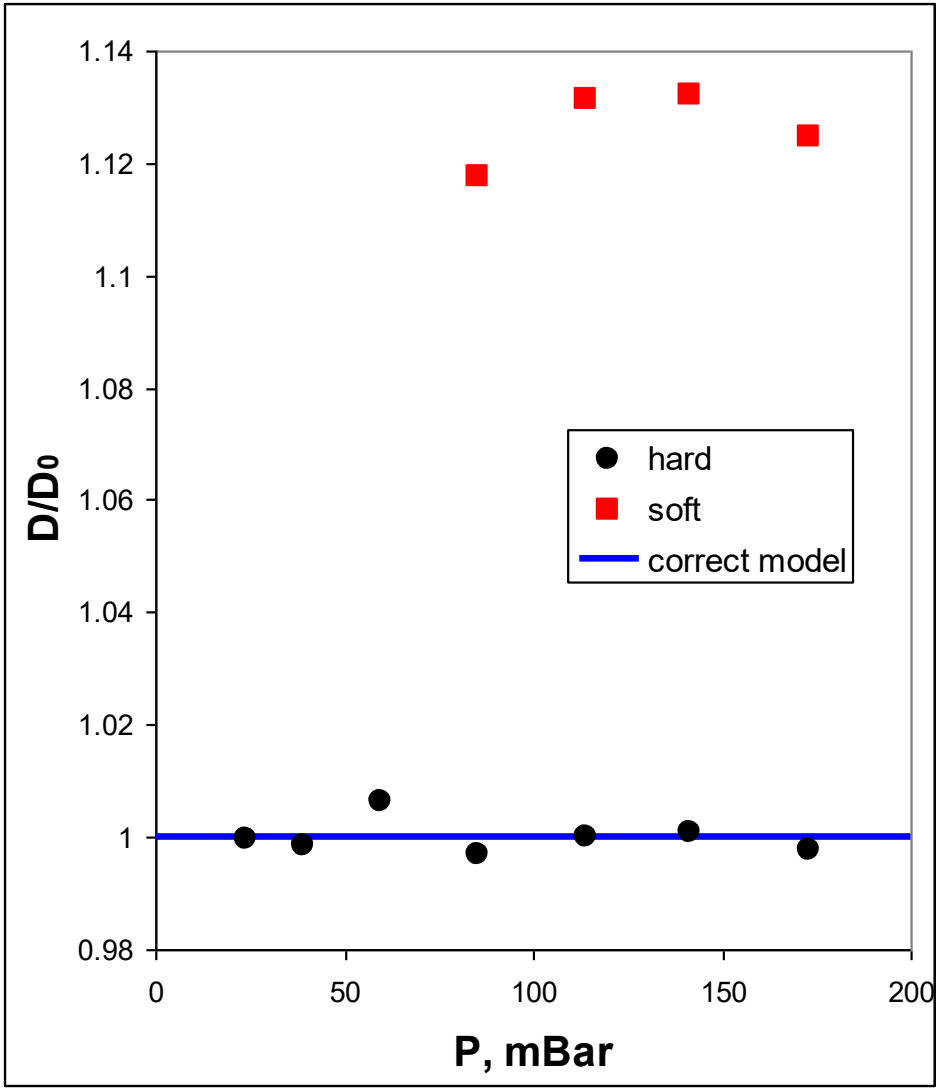


Hence, for collisions of dipole molecules, Doppler profile is described by soft model.

Pure water vapor investigation. In this case dipole – dipole interaction dominates and correct model is soft one.

14. Hard collisions model

Opposite situation is relate to light molecule in heavy buffer gas.



Investigation of water line in H_2O : Xe gas mixture.

In present case velocity orientation will relax during one collision. However, velocity module will not be changed significantly after collision. Hence, it is not totally true situation for hard model.

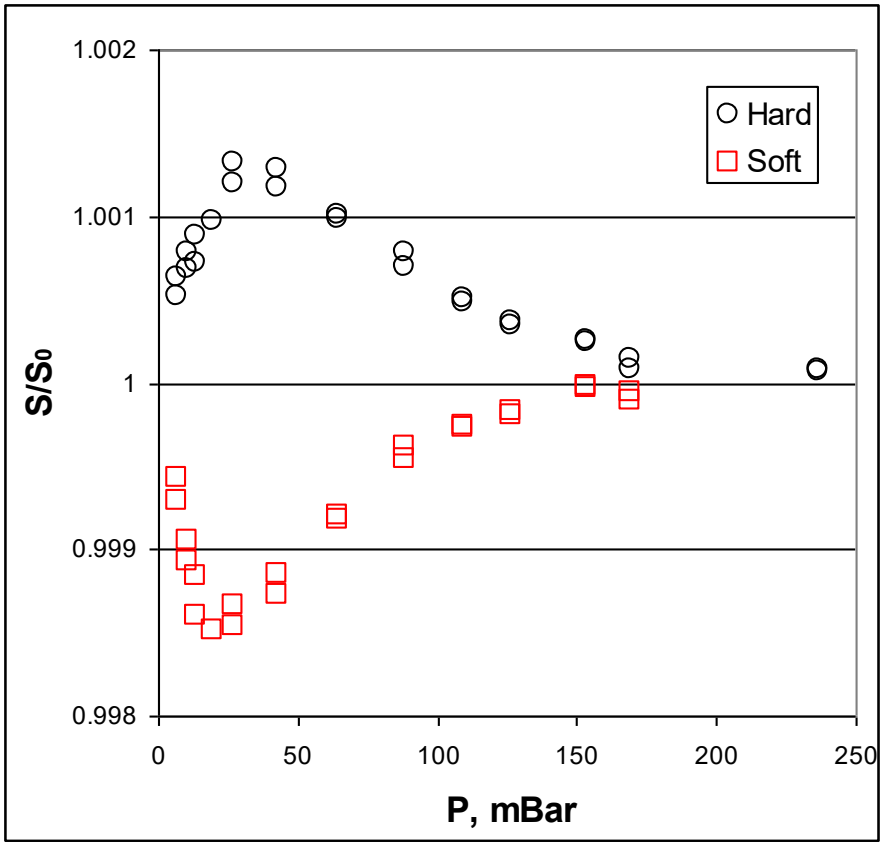
Nevertheless, experiment shows that for the gas mixture under consideration correct model is close to hard one.

15. Conclusions

1. Software to fit high accurate experimental spectral data was developed and its operation was tested and analyzed.
2. Line shape fitting with NEA = 2 10^{-4} can be done using Soft or Hard models with 5 parameters: S (integral intensity), v0 (line center), D (Doppler width), L (Lorentz width), B (narrowing). Usage of other parameters list has to be investigated depending on NEA available.
3. Usage of more fitting parameters is not correct because leads to parameters correlation and parameters physical meaning loosing.
4. Only for correct model results of fitting have physical meaning. Doppler width fitting can be used to check model in use correctness.

Integral intensity

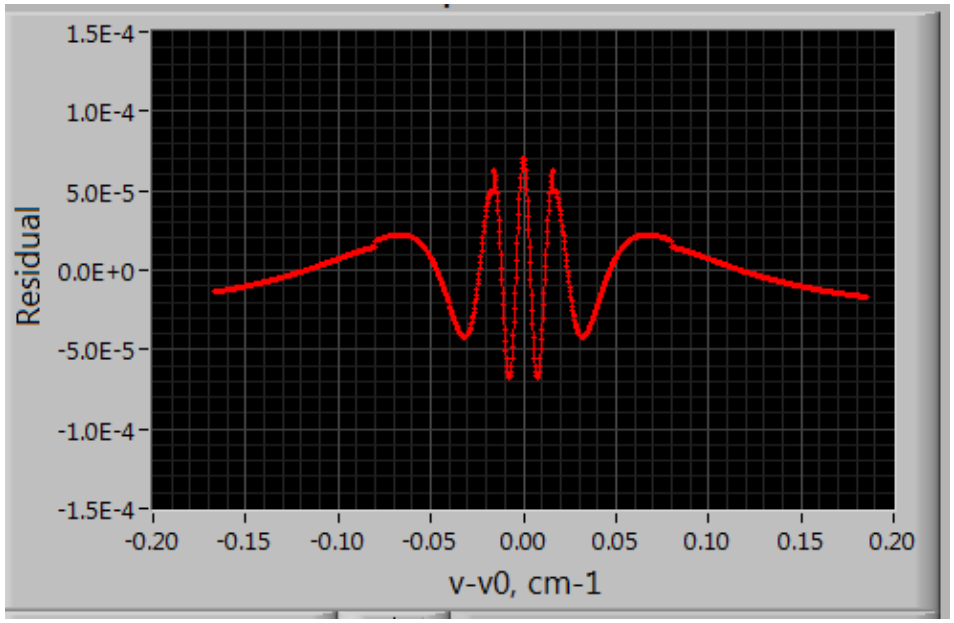
Results of CO_2 line (6953.46708 cm^{-1}) fitting using Hard and Soft models, S_0 is average value of both models.



For isolated line, S/S_0 has to be equal 1. Significant difference at 0.15 % level can be observed. Hence, models - correction.
Both models consider line as convolution of Doppler and Lorentz profiles. If there is correlation between phase and velocity changes during collision, third profile describing this correlation has to be included in the convolution.
CO_2 molecule is good candidate to investigate this problem because it has close cross sections for broadening and narrowing.

This profile has important characteristics: it is negligible both for low and high P: no phase changes and Doppler counter collapse, respectively.
Conclusion: it looks like presence of profile describing correlation between phase and velocity changes during collision was experimentally observed for the first time.

Soft - Hard

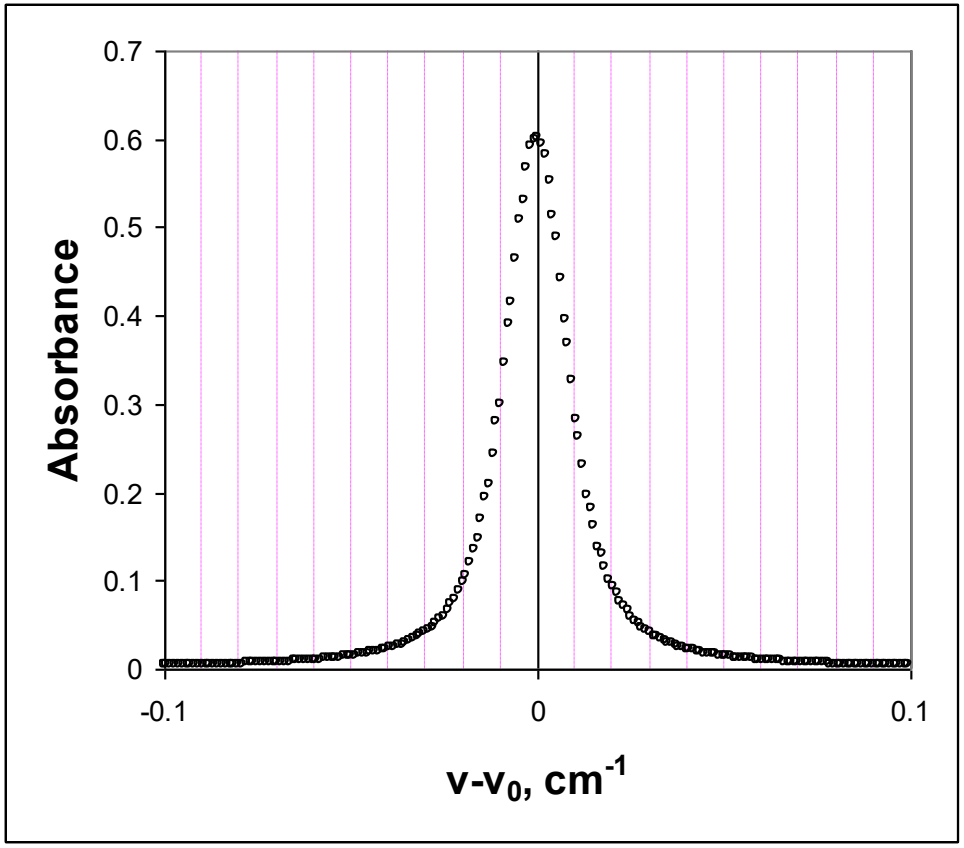


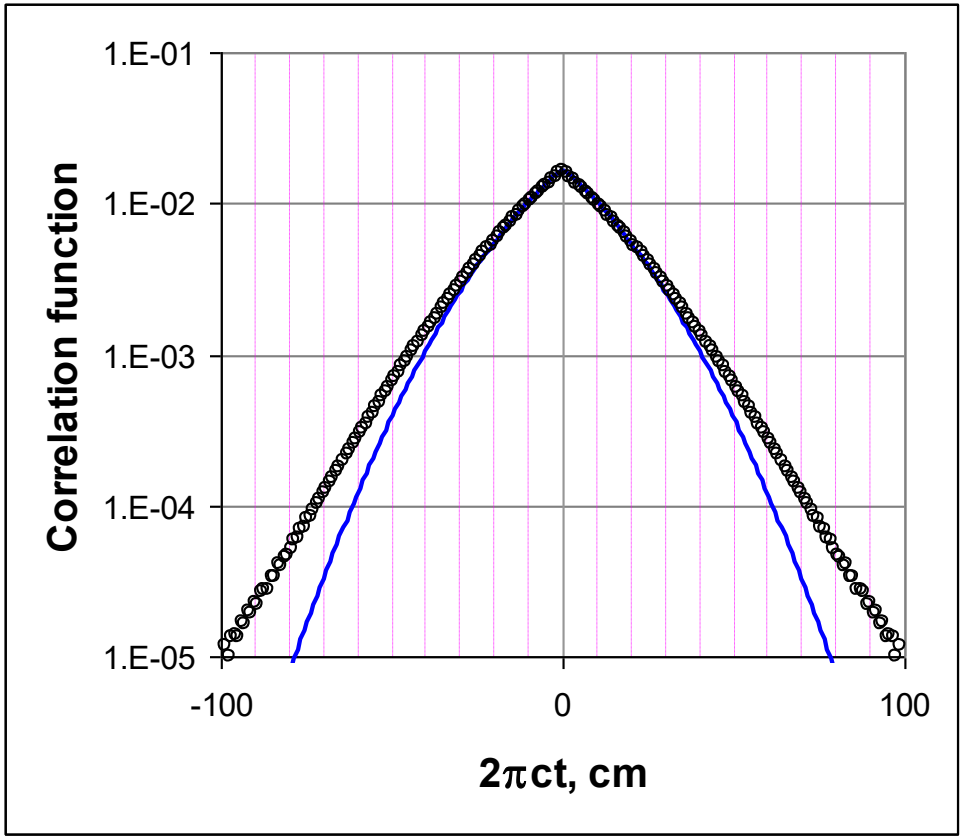
Оценим различие между Soft и Hard.
Для этого экспериментальный спектр был аппроксимирован моделью Hard, которая затем подгонялась моделью Soft. Как и следовало ожидать видны 8 корней.
Величина Residual - 7 10^{-5} в три раза меньше точности эксперимента.

Вывод: при существующей точности эксперимента – 2 10^{-4}, по невязке невозможно различить модели Soft и Hard.

Experimental line shape

In spectroscopy there are two ways to present and analyze experimental results: spectrum (left) and correlation function (right). Spectrum and correlation function are Fourier transformations of each other. In present case CO_2 line (6953.46708 cm^{-1}) is presented for P = 66.3 mBar.





For correlation function obvious difference between experimental line shape and Voigt profile (blue line) can be observed.