Line shape models analysis for high accurate experimental data

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1. Introduction

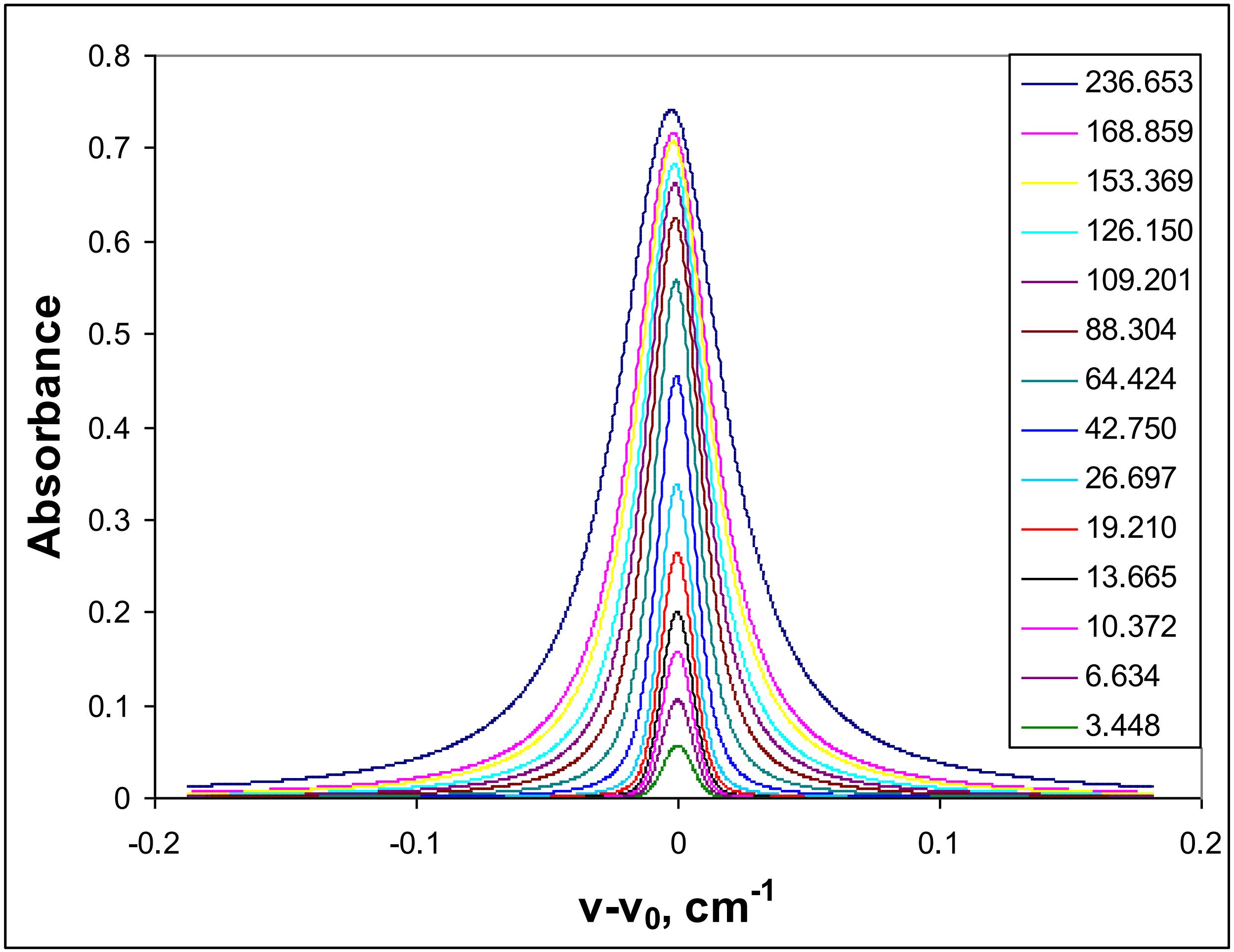
DL spectrometer for high accurate measurements was developed. The spectrometer subsystems were calibrated and error sources were analyzed (see A1). Error budget for line integral intensity measurements.

	Value	Error %
L, cm	183.5	0.022
T, ^{o}C	20 - 25	0.017
P, mBar	100	0.036
CO_2 sample purity, %	99.98	0.020
Subtotal		0.050
PD non-linearity		0.023
$\Delta\nu$, 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 %.

2. Experimental spectra

Isolated CO_2 line (6953.467 cm^{-1}) was selected for present investigation. Analytical cells #2 (L2 = 183.50(4) cm) and #3 (L3 = 1519(1) cm) were filled with pure CO_2 (purity better than 99.98 %) at different pressures. Simultaneously with spectra recording, gas pressure and temperature were measured.



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

Experimental spectra example for one of the series under consideration. Here v_0 is line center position for zero pressure, parameter is pressure [mBar].

3. Line shape

As it was shown in classical paper [1], to obtain spectral line shape in presence of collisions, solution of kinetic equation is necessary. Line shapes for several models of collision integral were obtained.

Doppler profile.

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

Hard: molecule needs one collision for equilibrium velocity distribution.

Hard+Soft: collisions part is Hard and part is Soft.

Phase and velocity are changing in different collisions

No SD: Line shape is convolution of Doppler and Lorentz profiles.

SD: Line shape is not convolution. Asymmetry.

Phase and velocity are changing in the same collisions

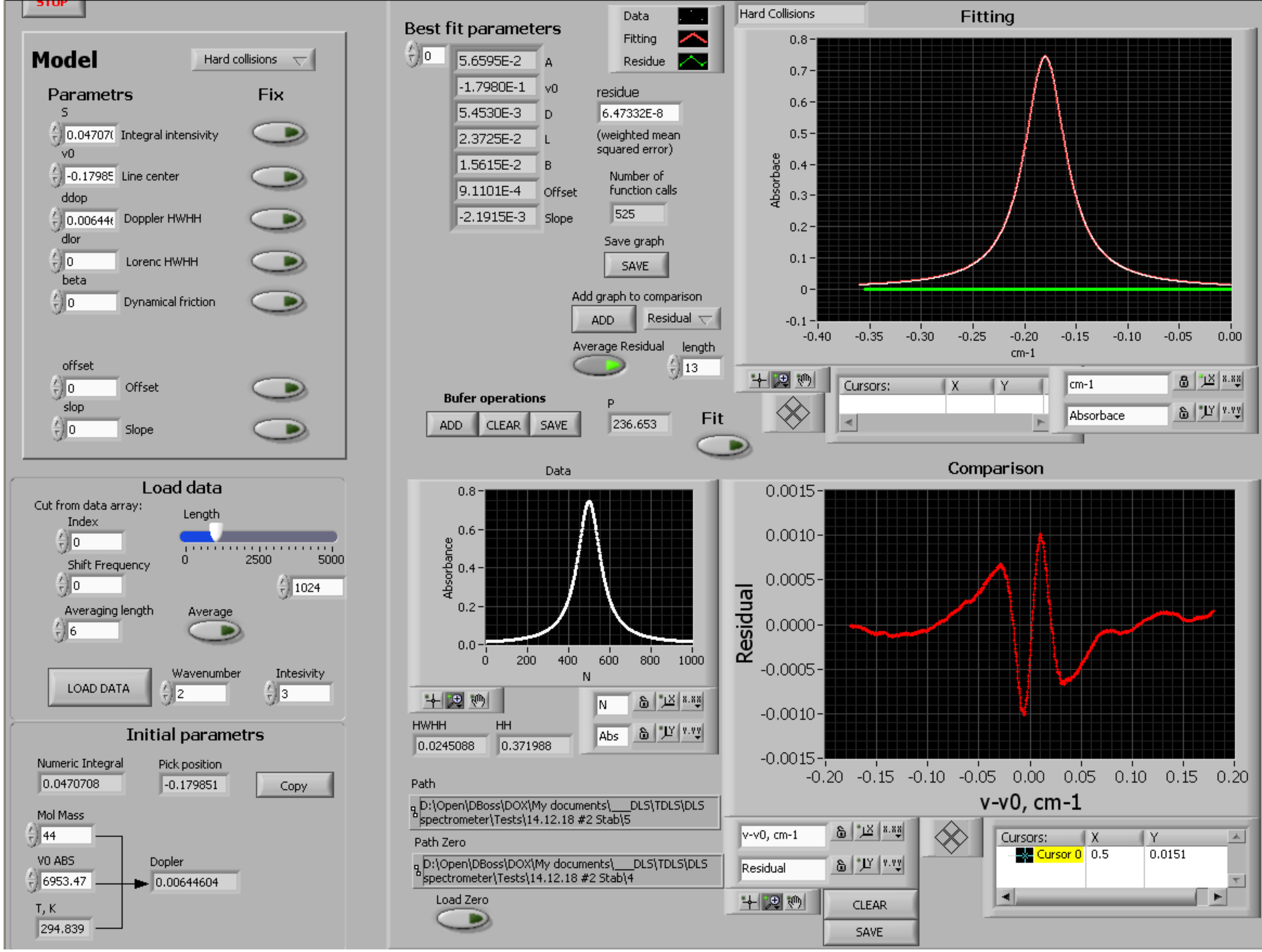
COR: Line shape is not convolution of Doppler and Impact profiles. Asymmetry.

[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).

4. Fitting software

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

Line asymmetry can be observed in residual.



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 [cm^{-1}] – absorbance integral, v0 – line center, D – Doppler width, L – Lorentz width, B – narrowing, offset – baseline. All parameters can be fixed or included in fitting. For present precision no more than 5 parameters can be used (A2).

5. Tests

Parameters obtained by fitting have physical meaning only for correct model. For example, for H_2O:H_2O collision correct model is Soft and for CO_2:SF_6 - Hard.

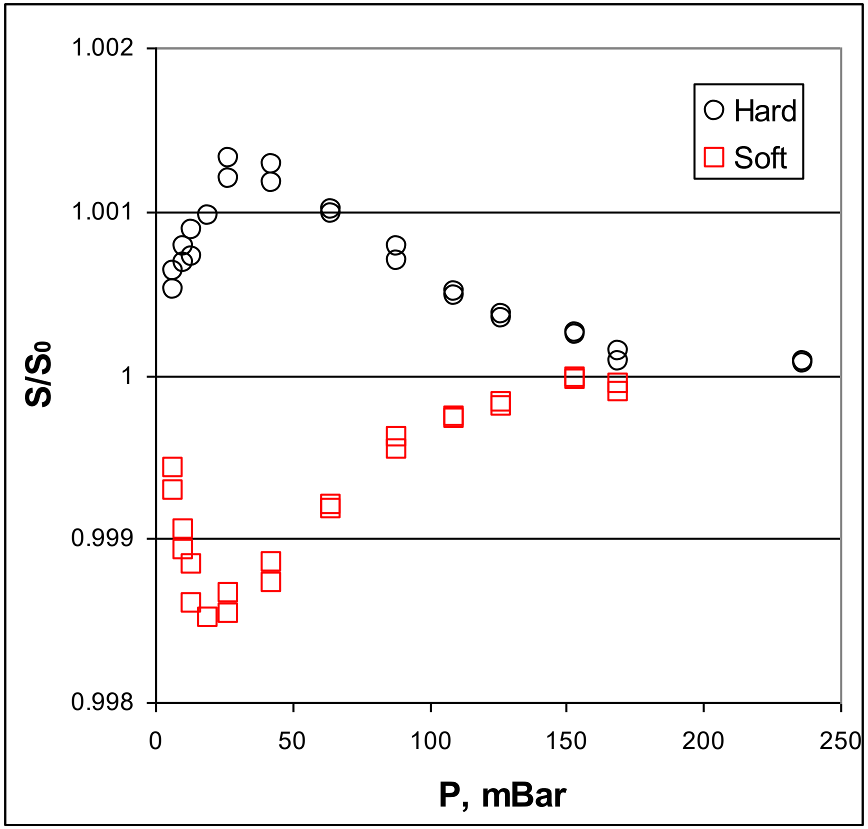
Isolated CO_2 line (6953.467 cm^{-1}) was selected for present tests. CO_2 molecule is very convenient for experiments. For CO_2 practically all model situations considered in [1] can be found (see below).

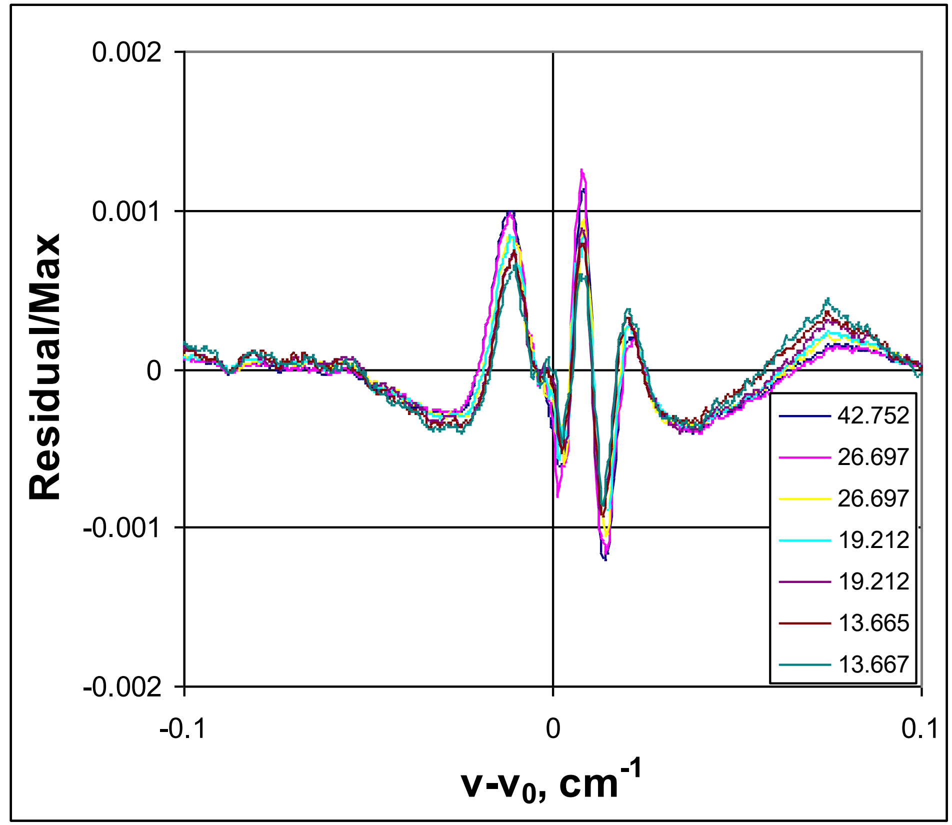
Analyzes of their importance for different experimental situations is subject of present tests:

1. For isolated spectral line integral intensity has to be constant.
2. Doppler width has to be constant.
3. Broadening coefficient has to be constant
4. Narrowing coefficient has to be constant

6. Integral intensity

Results of CO_2 line fitting using Hard and Soft models, S_0 is average value of both models. For isolated line, S/S0 has to be equal 1.





Significant difference at 0.15 % level can be observed. Hence, models - correction.

Residuals for some pressures has similar form (not as on 6) having both odd and even harmonicas.

7. 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.

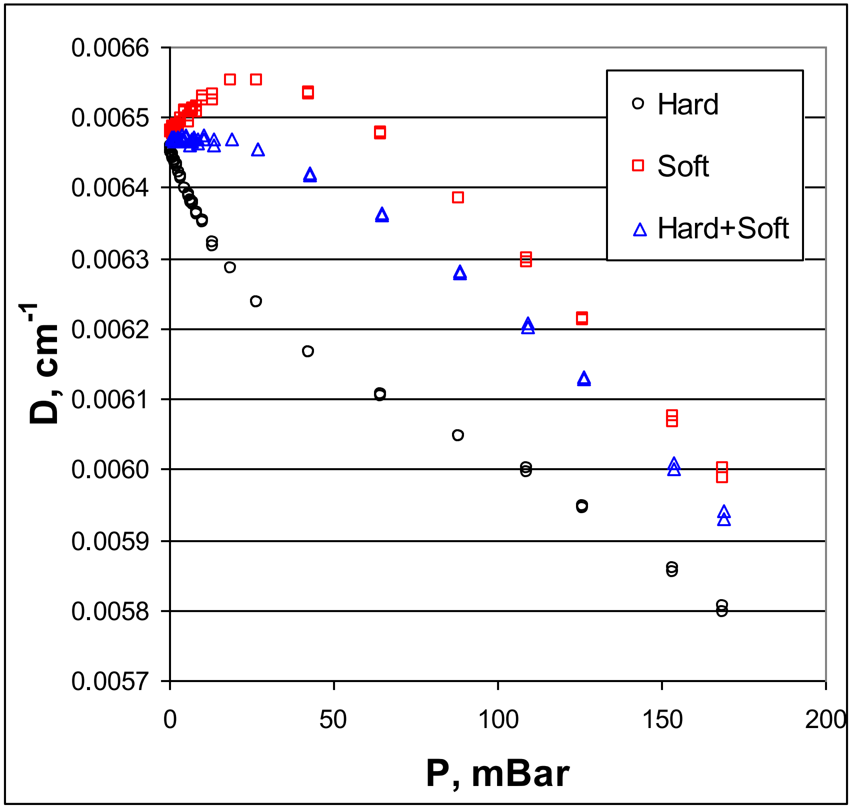
COR: Its influence is negligible both for low (no collisions) and high pressures (for high number of collisions, the process is normal – no correlation). Line shape is not convolution of Doppler and Lorenz profiles. Asymmetry. Residual has both odd and even harmonics. Author has no information that this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

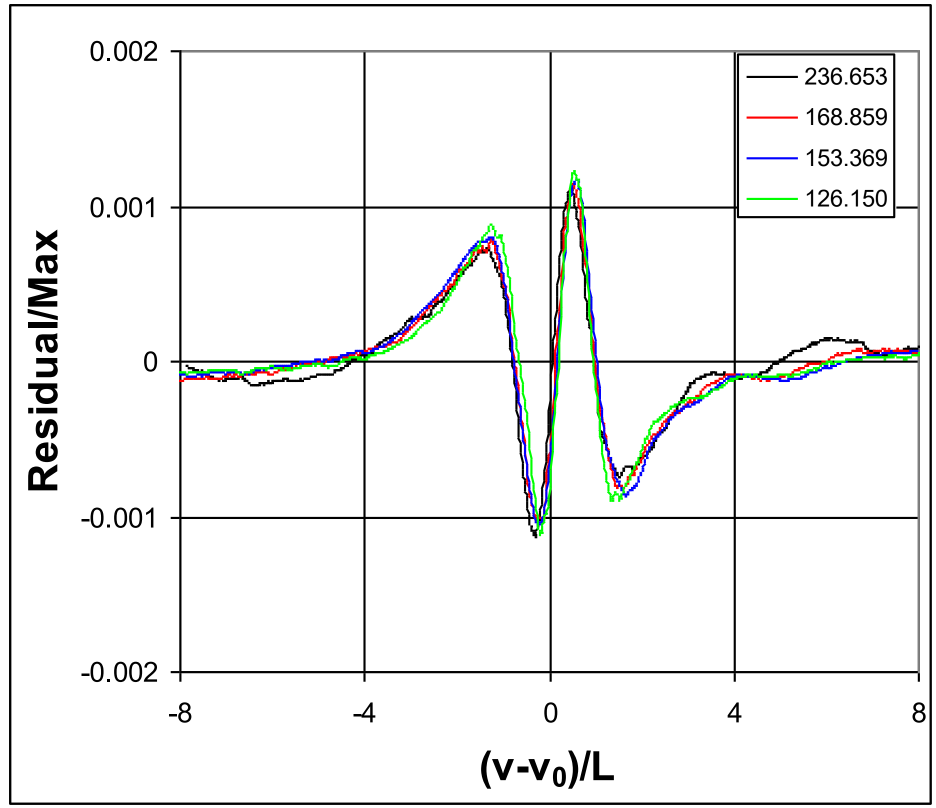
Conclusion: Correlation between phase and velocity changes during collision was experimentally observed for the first time. CO_2 molecule is good candidate for this effect observation, because both broadening and narrowing cross sections have close values.

Conclusion: Line integral intensity with accuracy 0.06 % has to be measured at high pressures using either Soft or Hard.

8. Doppler width - D

Results of CO_2 line fitting using Hard and Soft models, D_0 is calculated Doppler width. **Hard+Soft = Hard$^{0.3}$*Soft$^{0.7}$**.



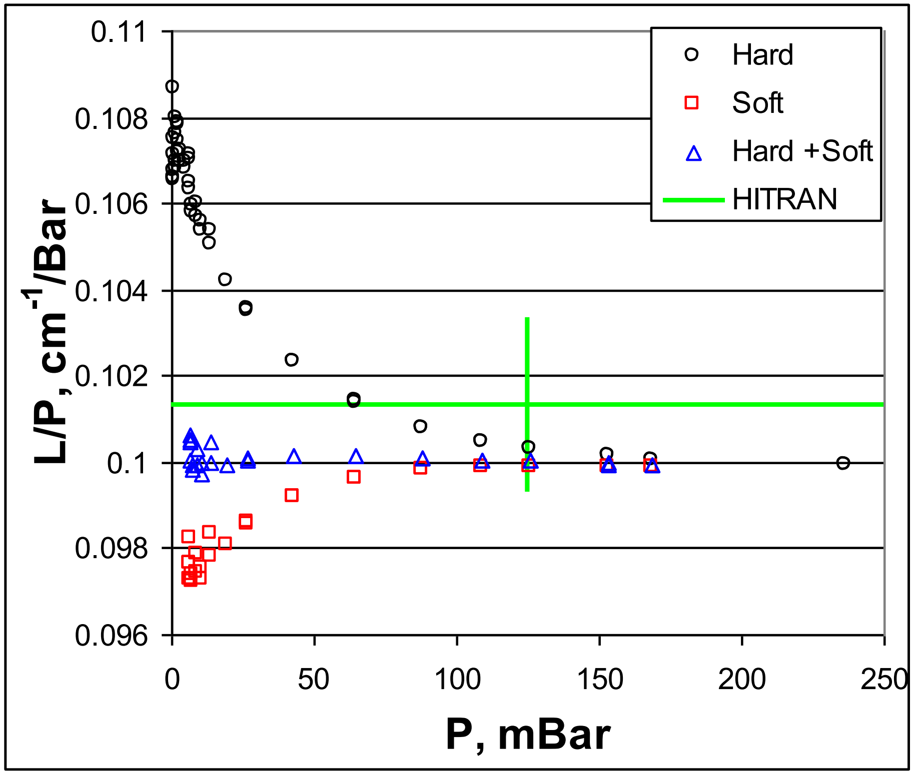


Significant difference can be observed. D is constant below 20 mBar for Soft+Hard.

Residuals for different P have similar form - third harmonic (not as on slide 6). It is asymmetry.

9. Broadening - L

Results of CO_2 line fitting using Hard and Soft models for broadening coefficient γ=L/P. DL line width was measured (72 kHz) and subtracted.



Significant difference (~10%) between models can be observed for small P. Using **<u>Hard+Soft = Hard$^{0.3}$*Soft$^{0.7}$</u>** final values were calculated.

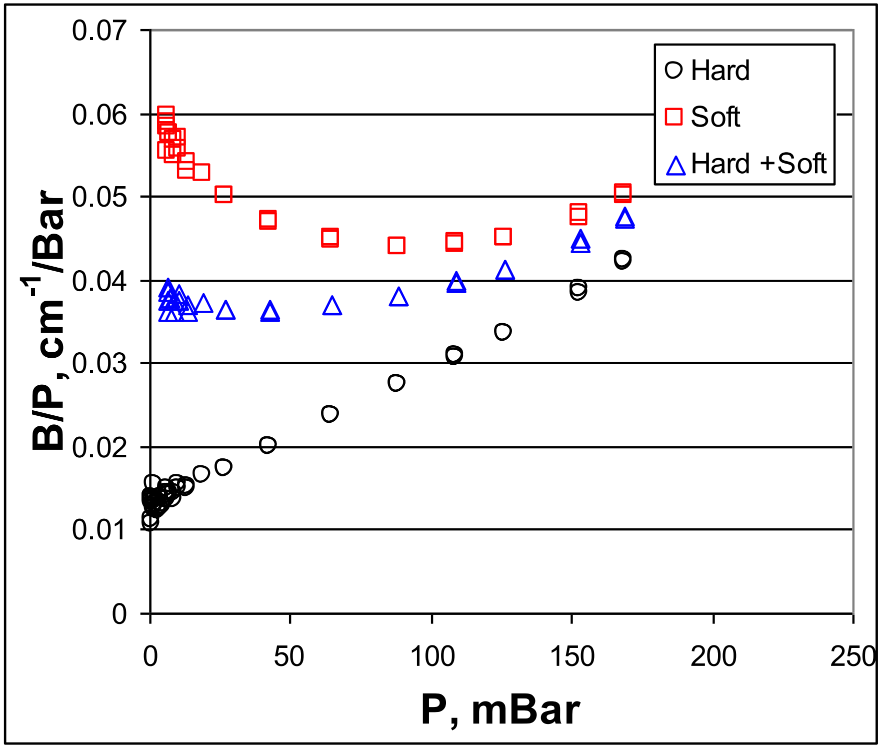
Final values are constant for whole pressure range under investigation.

Green constant – HITRAN (accuracy 1-2 %), green bar – 2 %. TDLS accuracy – symbols height.

Conclusion: To obtain high accurate broadening coefficient (0.08 %), measurements have to be performed above 20 mBar. Soft+Hard model has to be used to obtain final value.

10. Narrowing - B

Results of CO_2 line fitting using Hard and Soft models for narrowing coefficient δ=B/P.



Dramatic difference (6 times) between models can be observed for low pressures.

Using **<u>Hard+Soft = Hard$^{0.3}$*Soft$^{0.7}$</u>** final values were calculated. Final values are constant for pressures below 0 - 50 mBar.

Conclusion: To obtain narrowing coefficient with accuracy 2 %, measurements have to be performed for pressure range 0 – 50 mBar and Hard+Soft model has to be used to obtain final value.

11. Hard+Soft model

All parameters - D, γ, δ (slides 8, 9, 10) differ significantly for fitting with either Soft or Hard.

Using the same model **Hard+Soft = $Hard^{0.3}$*$Soft^{0.7}$** all parameters constant values were obtained for pressures below 50 mBar (slides 8, 9, 10) in agreement with requirements of tests (slide 5).

For higher pressures deviation from constant can be observed for Doppler width (slide 8, left graph) and narrowing coefficient (slide 10).

For pressures above 120 mBar normalized residuals (slide 8, right graph) are similar, demonstrating line asymmetry (third harmonic).

Last two facts are due to Speed Dependence (SD).

12. Speed Dependence - SD

Let us consider ensemble of molecules with speed **u** in gas with temperature **T**. If time of collision << time between collisions – Lorentz with temperature and speed depended parameters.

$$K(\nu,T,u)=\frac{S\Gamma(T,u)}{\pi\left[\left(\nu-\nu_0-\Delta(T,u)\right)^2+\Gamma(T,u)^2\right]}$$

Temperature and speed dependence is determined by only one parameter **n** – temperature exponent (**n_{HITRAN} = 1-n**).

$$\left[\frac{u^2}{\langle u\rangle_T^{\,2}}\frac{T}{T_0}\right]^n$$

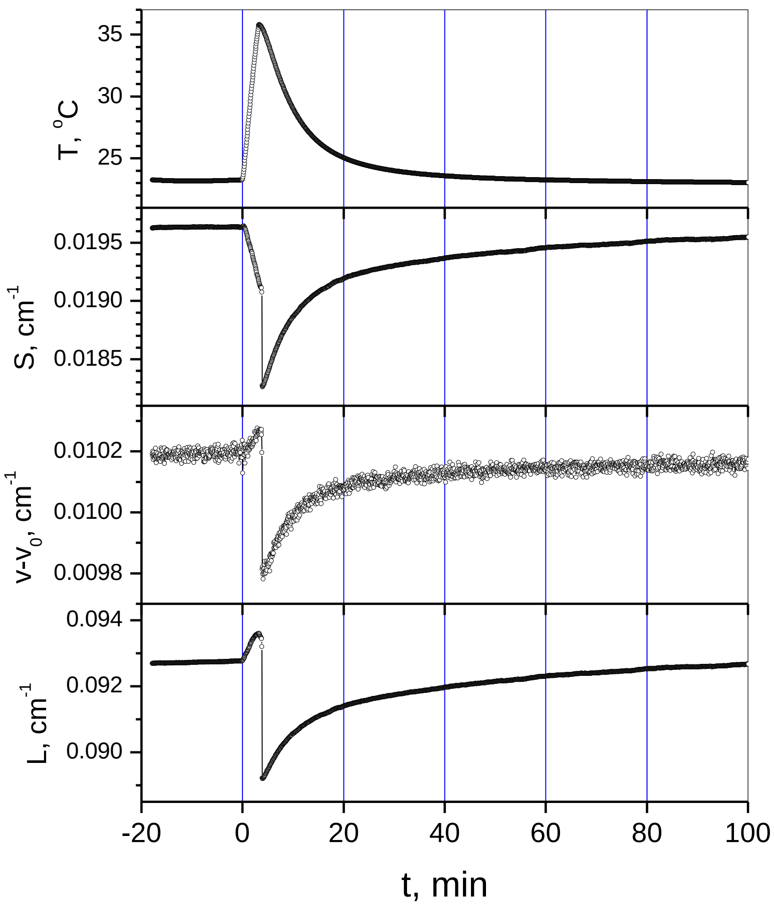
To model speed dependence, Lorentz profiles were averaged over Maxwell distribution of molecules velocity.

$$K_{SD}(\nu)=\int_0^\infty \frac{S\gamma P x^{2n_\gamma}\exp\left[-x^2\right]}{\pi^{1.5}\left[\left(\nu-\nu_0+\delta P x^{2n_\delta}\right)^2+\left[\gamma P x^{2n_\gamma}\right]^2\right]}2x^2dx$$

Here γ, δ, n_γ, n_δ are broadening and shift coefficients and temperature exponents for broadening and shift, respectively. There are no free parameters in this formula, all parameters are known from experiment.

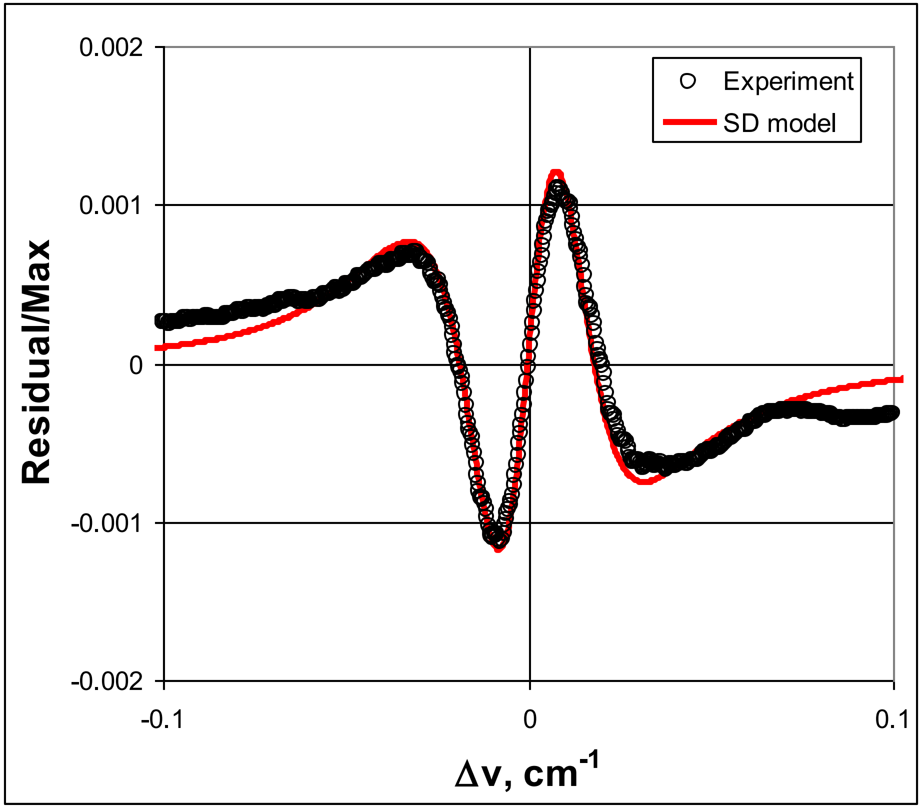
13. Temperature Exponents (TE)

Speed dependence calculation (slide 12) requires TE for broadening and shift. Traditionally it is hard job in broad temperature range. We use other approach - real time TE measurements.



TE measurements of CO_2 analytical line.
The cell and huge volume were filled with CO_2 (T_0, P_0, N_0). The cell was closed.
After t=0 gas in cell was heated (increasing of T and P, $N=N_0$=const).
At t=3.8 min – cell was connected to the volume (T=const, $P \to P_0$, $N_0 \to P_0/P\ N_0$).
After 3.8 min – gas cooling ($P=P_0$=const).
The step (n=-1) is using for TE calibration.
Final TE data:
n_γ=0.226(12) (close to Q-Q = 0.25)
n_δ=0.105(14) (between D-Q = 0.16, and D-D = 0).

14. Experiment vs. SD model



Experiment (black circles) – analytical CO_2 line residual for 236.65 mBar (slide 5). It is asymmetry due to speed dependence.

Using slides 12 and 13 impact profile of analytical line was calculated taking into account speed dependence and TE measured. It was fitted by the same procedure as experimental data. Its residual is presented by red curve. Good agreement can be observed.

Conclusions: Speed dependence fitting is mistake. Impact profile due to speed dependence can be calculated with experimental accuracy using K_{SD} (slide 12) and experimentally determined parameters: γ, δ, n_γ, n_δ. This profile has to be included in fitting instead of Lorenz one.

15. Conclusions

1. Parameters of high accurate experimental spectra fitting were analyzed based on models considered in classical paper [1].
2. Model Soft+Hard = $Hard^{0.3}*Soft^{0.7}$ was proposed. For this model Doppler width, broadening and narrowing coefficients are constant in some pressure range.
3. To obtain spectral line parameters with highest accuracy, different experimental regimes have to be used:
   integral intensity (0.06 %) – P > 170 mBar, either Soft or Hard;
   Doppler width (0.05%) – P < 20 mBar, Soft+Hard model;
   broadening coefficient (0.08 %) – P > 20 mBar, Soft+Hard model;
   narrowing coefficient (2 %) = P < 50 mBar, Soft+Hard model.
4. Correlation between phase and velocity changes during collision was experimentally observed for the first time.
5. Self broadening and shift temperature exponents were measured.
6. Using experimental parameters (γ, δ, n_γ, n_δ) asymmetry was calculated (no fitting) with experimental accuracy for P > 200 mBar.

4. Soft collisions model

Doppler profile in presence of collisions is determined by solution of kinetic equation [1]. Solution of kinetic equation diffusion approximation is **Soft** collisions line shape model [1]:

$$K_{Soft}(\omega) = \frac{1}{\pi}\int_0^\infty \exp\left[i\omega t - \frac{(\mathrm{kV_0})^2}{2}\left(\frac{|\mathrm{t}|}{\beta P} + \frac{1}{(\beta P)^2}\left[\exp(-\beta P|\mathrm{t}|) - 1\right]\right)\right] dt$$

Soft: molecule needs infinite number of collisions to achieve equilibrium velocity distribution.

Galatry obtained the same line shape for Doppler profile of heavy molecule in buffer gas of very light molecules [2]. Soft model is more general in comparison with Galatry model.

For example, Soft model is applicable for collisions of dipole molecules.

[2] L.Galatry, Simultaneous Effect of Doppler and Foreign Gas Broadening on Spectral Lines, Phys.Rev., 122, 1218 (1961)

5. Hard collisions model

Doppler profile in presence of collisions is determined by solution of kinetic equation [1].

If molecule needs one collision to achieve equilibrium velocity distribution, **Hard** collisions line shape model was obtained [1]:

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