Doppler profile investigation

DLS LAB

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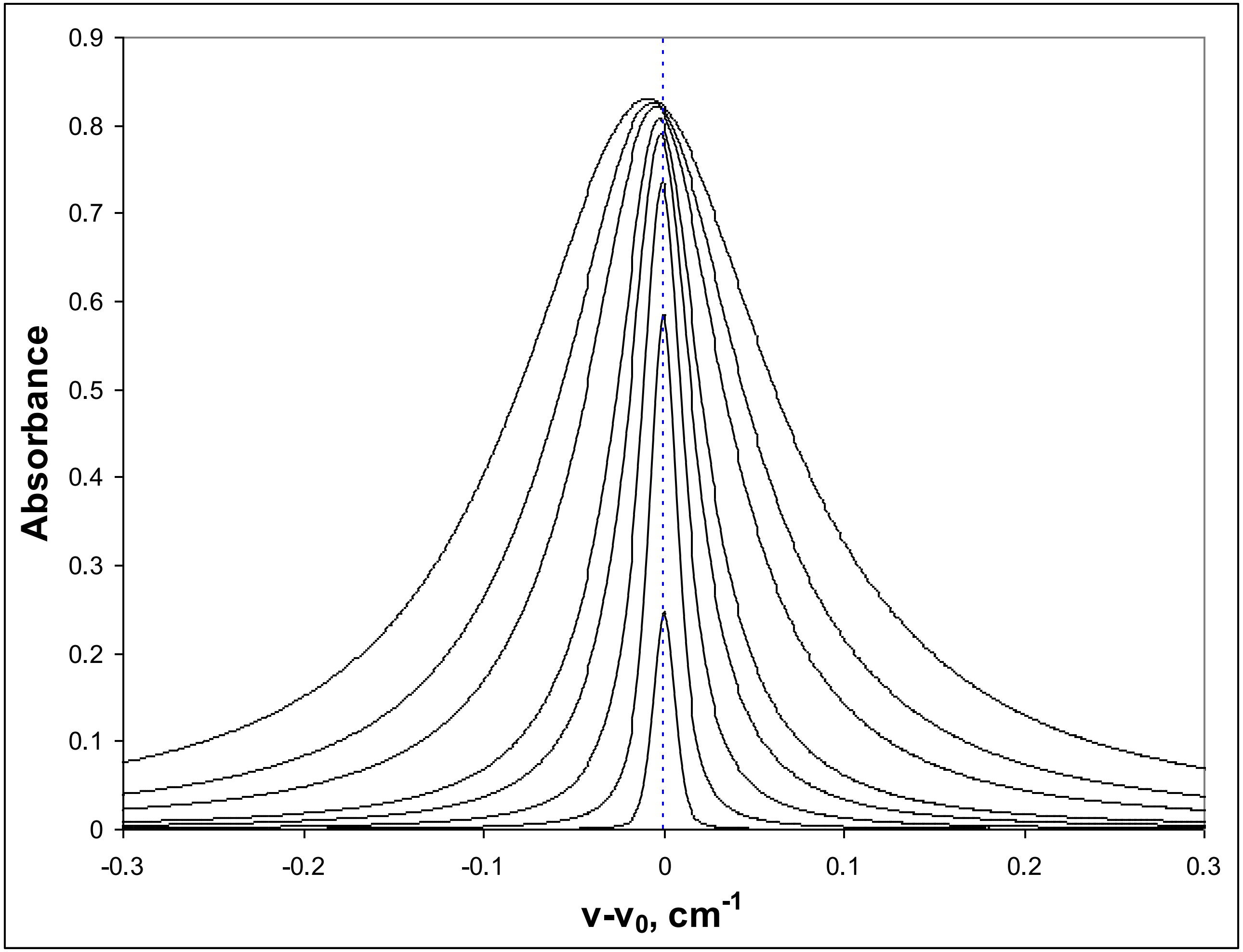
Introduction

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 presently achieved (see A2). Now investigation of new physical effects variety is possible. Present paper deals with investigation of spectral line Doppler profile.
No collisions: Doppler profile is determined by molecules Maxwell distribution and its width can be calculated - w_D. Collisions presence leads to Dicke narrowing. There are two line shape models widely used to take this effect into account: Galatry and Rautian profiles.
However, at the moment there is no answer what Doppler profile model is correct and what means information obtained when these profiles are using for fitting.
In present paper we'll try to give some answers.

Experiment



Spectral line shapes in this experiment were recorded for different pressures. In present case pure CO_2 was used. Spectra of its isolated line (v_0 = 6953.46708 cm^{-1} [HITRAN 2008]) were obtained for pressures 16 – 900 mBar.

Line shape is convolution of Lorentz and Doppler profiles.

Observed pressure broadening and shift are determined by Lorenz profile. Doppler profile is subject of present paper.

Doppler profile

No collisions: Doppler profile is determined by Maxwell distribution of molecules velocity and its width w_D can be calculated.
In [1] Doppler profile line shape in presence of collisions was analyzed.
It was shown that to determine Doppler profile, solution of kinetic equation is necessary. 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. Question: how number of collisions - N required to achieve equilibrium velocity distribution will influence results obtained?

[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:

$$C_{soft}(t) = \exp\left[-\frac{(\mathrm{kV}_0)^2}{2} \left(\frac{|\mathrm{t}|}{\beta P} + \frac{1}{(\beta P)^2} \left[\exp\left(-\beta P |\mathrm{t}| \right) - 1 \right] \right) \right]$$

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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.

[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).

Hard collisions model

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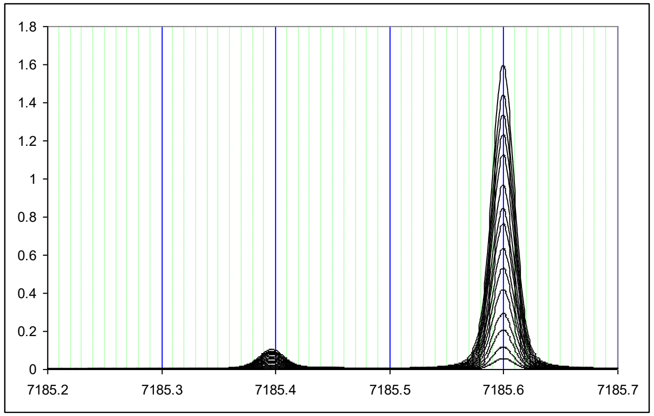
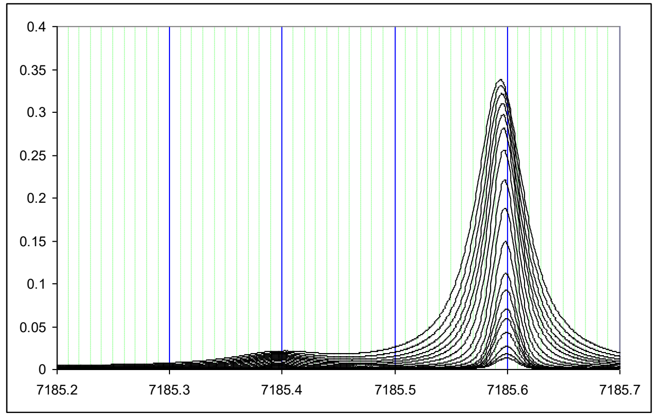
$$K_{hard} = \mathrm{Re}\,\frac{\dfrac{1}{\pi}\displaystyle\int \frac{W(\vec{V})d\vec{V}}{\beta P + i\left(\omega - \vec{k}_0\vec{V}\right)}}{1 - \beta P \displaystyle\int \frac{W(\vec{V})d\vec{V}}{\beta P + i\left(\omega - \vec{k}_0\vec{V}\right)}}$$

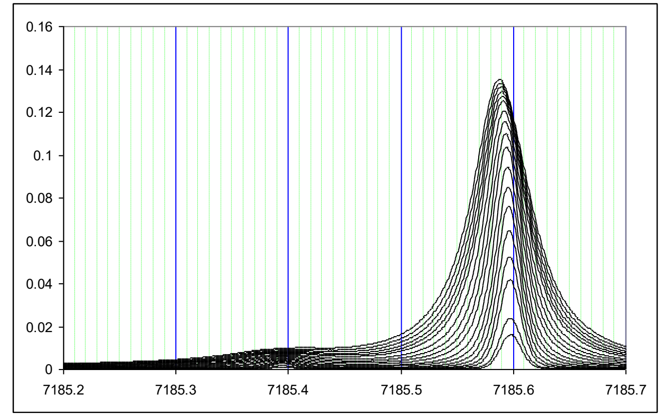
H_2O spectra for different gas mixtures



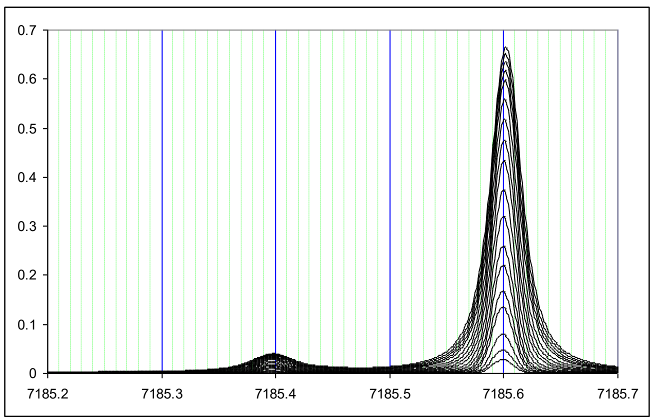
$H_2O:H_2O$



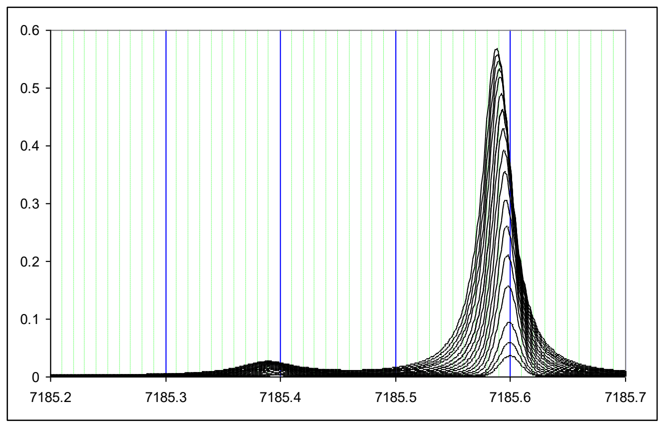
$H_2O:N_2$



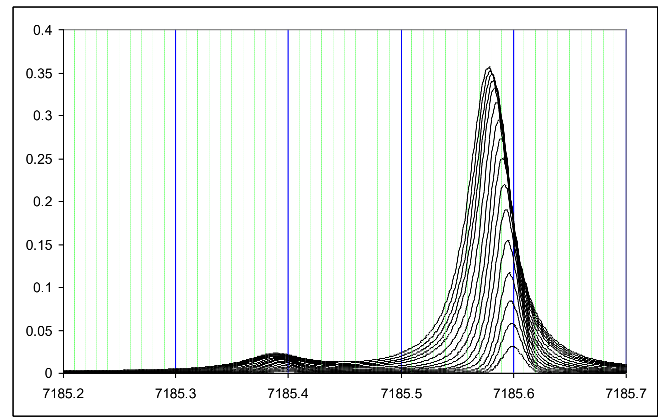
H_2O:air



H_2O:He



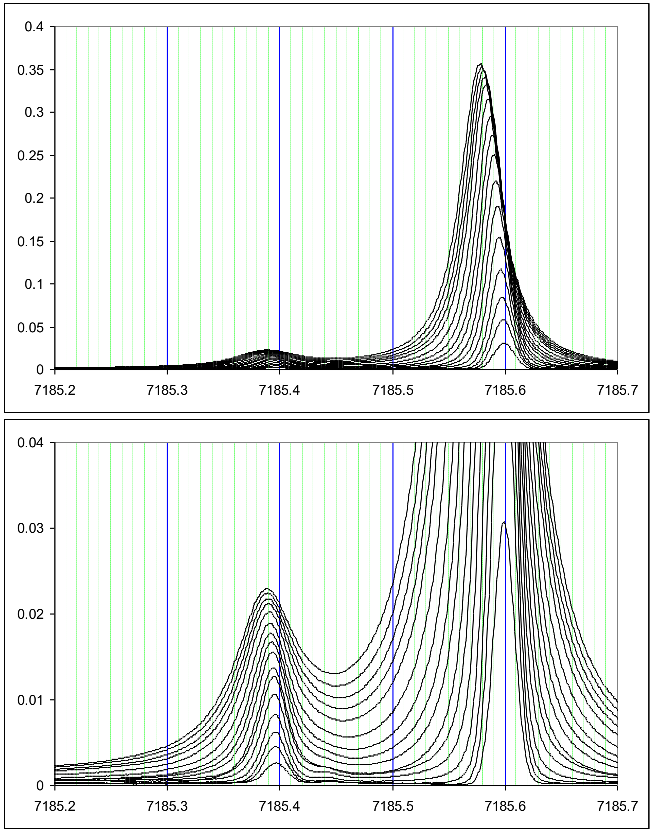
H_2O:Ar



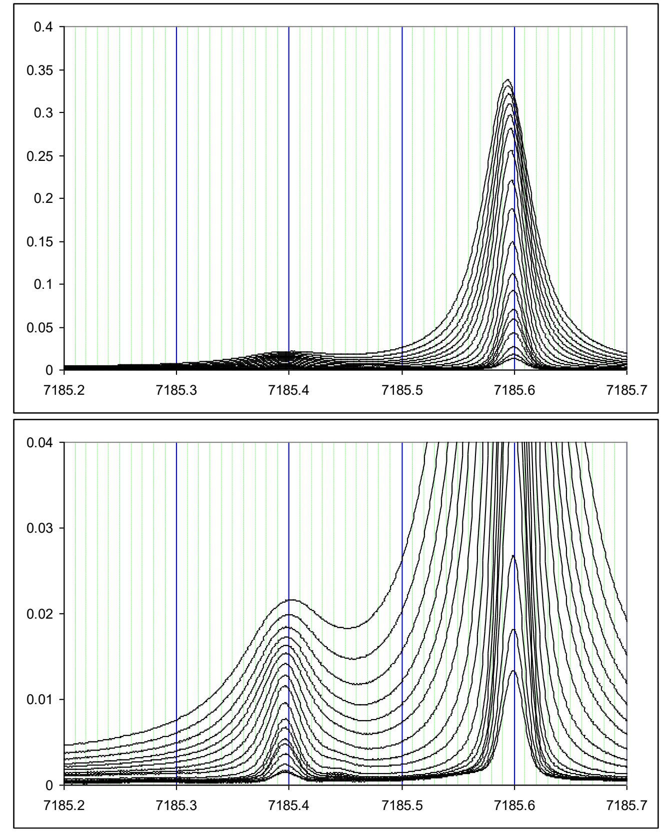
H_2O:Xe

Behavior of the same water lines (broadening and shift) is different for different partner of collision.

Lines mixing



Observed line shape depends on several physical processes. One of them is lines mixing - possible for water doublet under considered. In this case both soft and hard models are not valid.

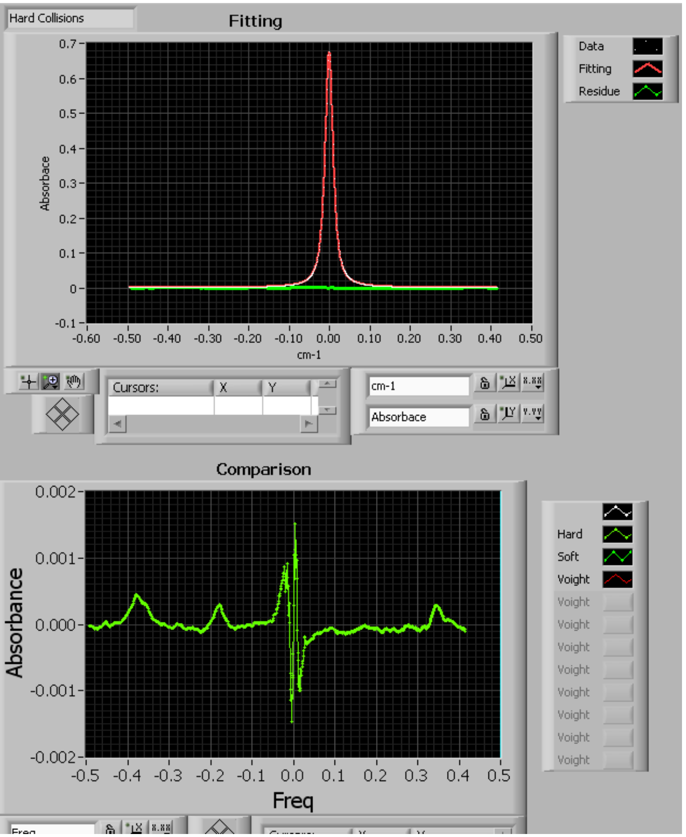


H_2O:Xe – no lines mixing. Both lines are shifting parallel.

H_2O:N_2 – presence of lines mixing. Two lines have opposite shits in direction to their center of gravity.

To test collision models both spectral lines and collision partner have to be selected and analyzed.

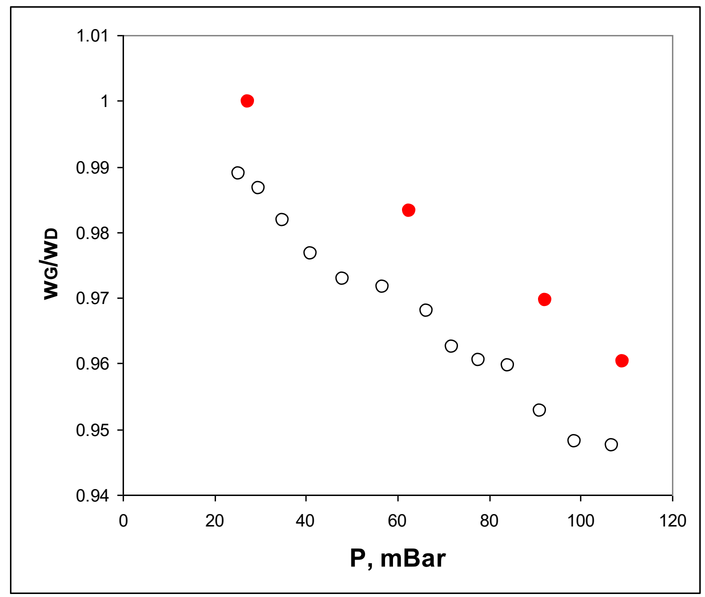
Fitting



Experimental data obtained were fitted using software developed (see B1). It used following fitting parameters of line shape.

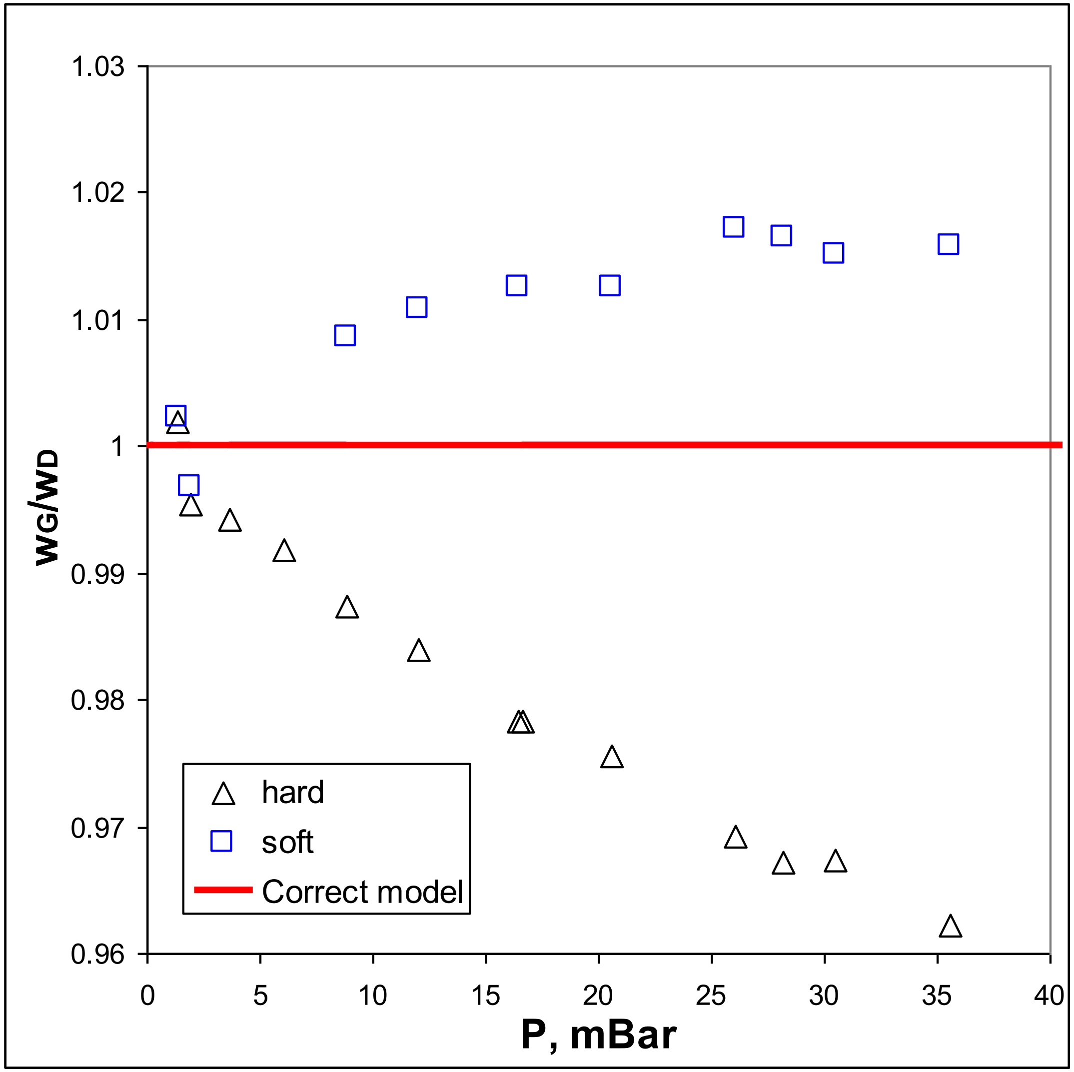
Value	Parameter	Meaning
4.3772E-2	S	Integral intensity
-4.0341E-1	v0	Frequency
5.8159E-3	WG	Gauss width
1.7170E-2	WL	Lorentz width
6.1668E-3	beta	Narrowing parameter
4.8059E-4	Offset	Baseline
0.0065019	wD	Can be calculated

$$w_D = \nu_0 \sqrt{\ln(2)\frac{2kT}{Mc^2}}$$



Traditionally $w_G = w_D$ is fixed. ***<u>It is not correct</u>***. Fitting results for CO_2 line. Gauss width is not constant (open black circles). Presence of excitation current noise results in additional broadening (solid red circles).

Correct model selection



Pressure dependence of fitting parameter - w_G/w_D for CO_2 line mentioned above.

Both soft (squares) and hard (triangles) models are not correct in present case. This result can be expected for CO_2 molecules collision.

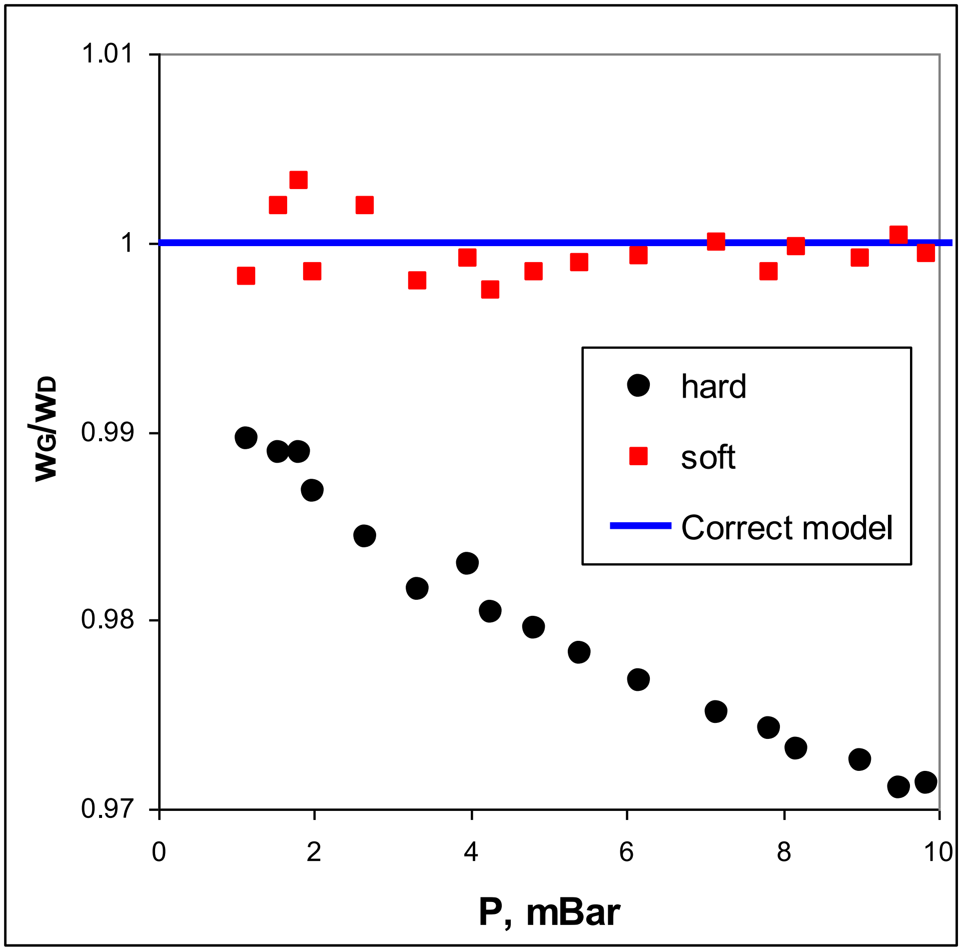
For correct model w_G/w_D has to be equal to 1 (red constant).

Conclusion: above mentioned dependence is measure of Doppler profile model correctness.

To check this approach different collision partners have to be used.

Soft collision model

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

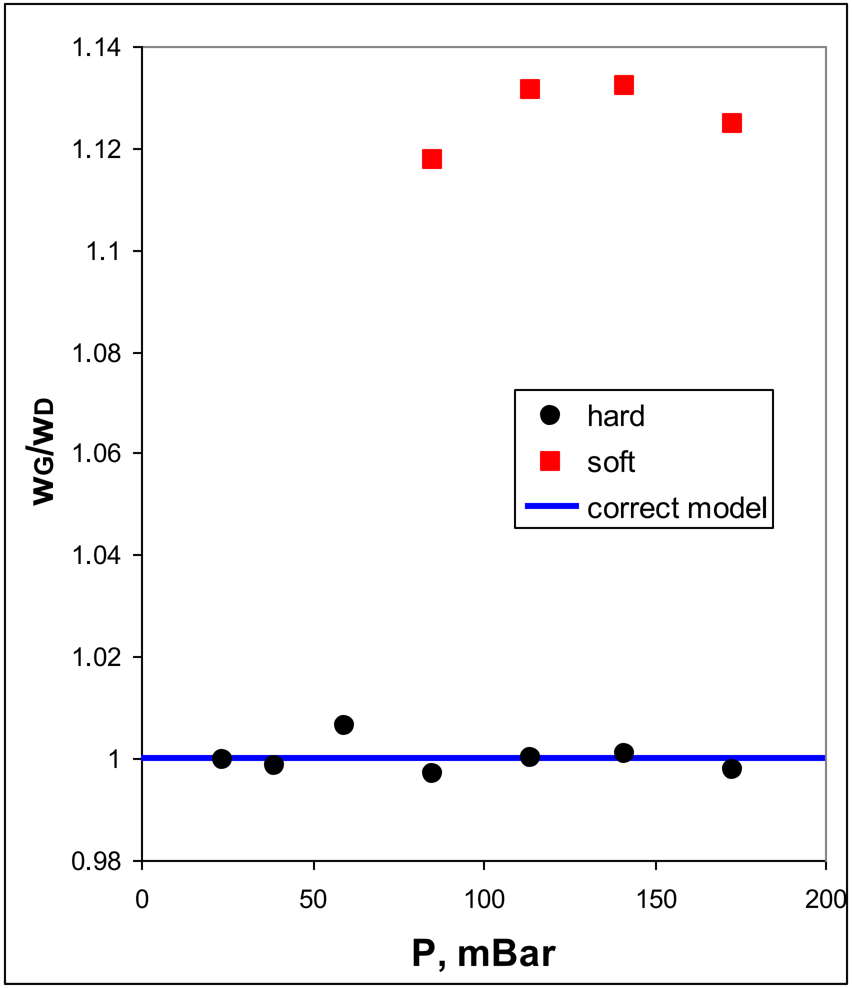


Hence, for dipole molecules collisions, Doppler profile is described by soft model.

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

Hard collisions model

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



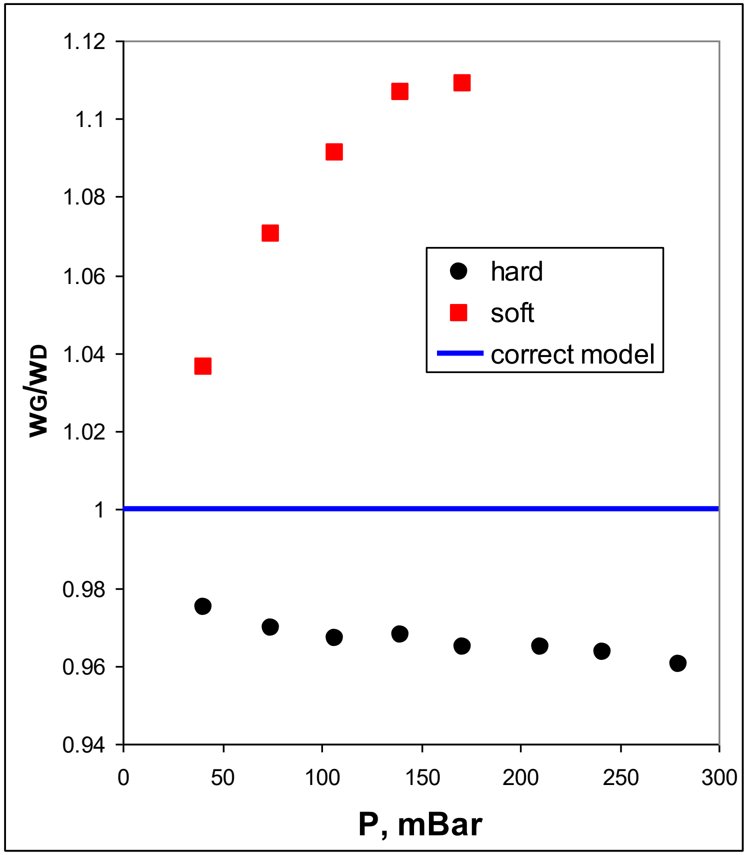
Investigation of water line in H_2O : Xe gas mixture.

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.

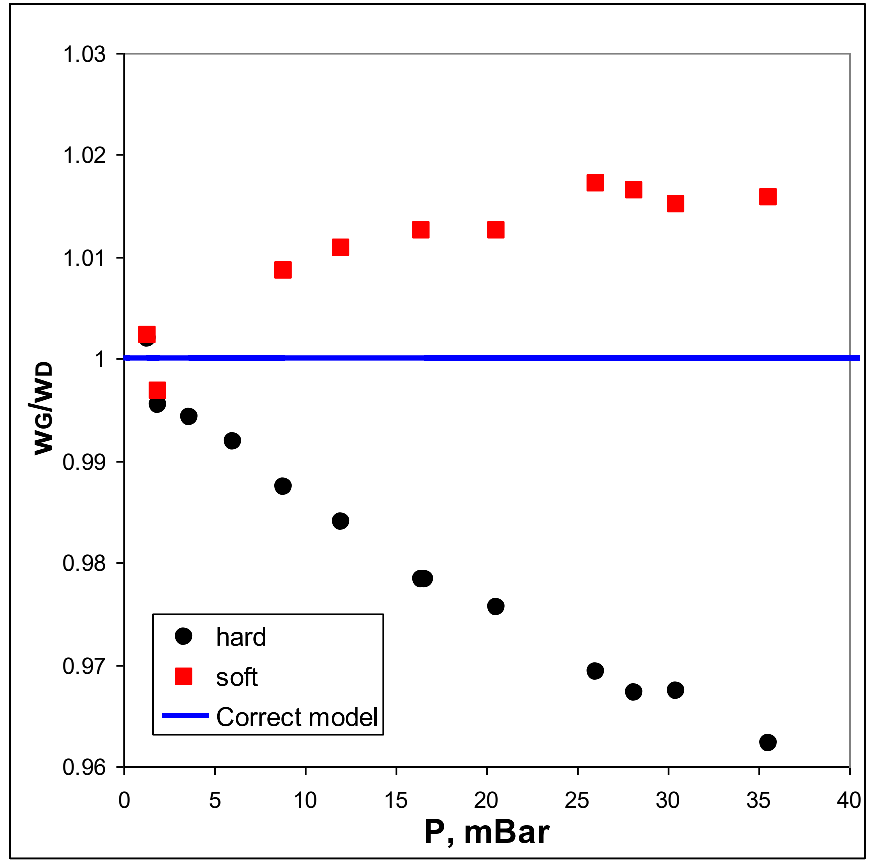
Nevertheless, experiment shows that for the gas mixture under consideration correct model is close to hard one.

Intermediate situation

For majority of cases, intermediate situation takes place – neither soft nor hard models are valid.

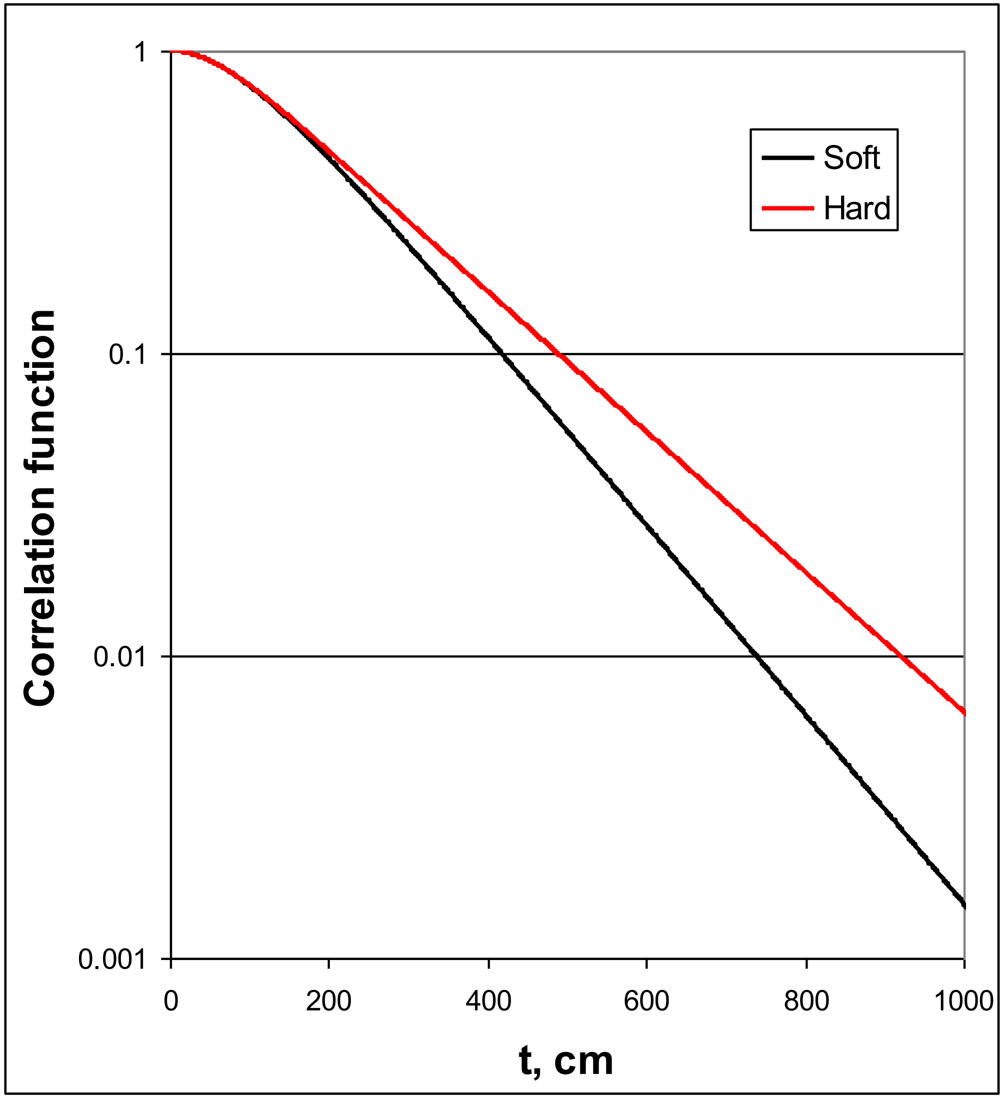


Investigation of water line in H_2O : Ar gas mixture.



Investigation of pure CO_2.

Soft and hard models of Doppler profile



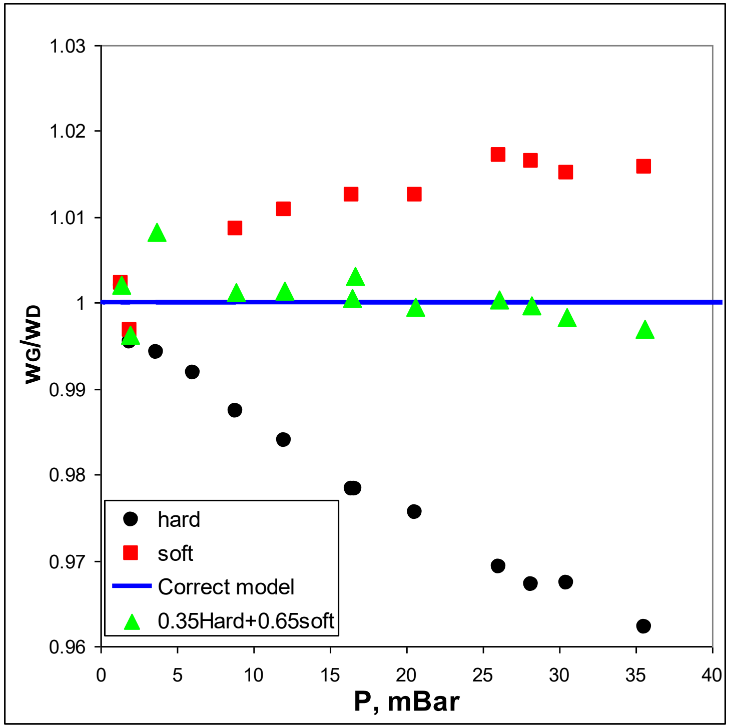
Modeling of soft and hard correlation functions for following parameters: $HWHH_D$=0.01, $HWHH_L$=0, B=0.01.

For central part (Doppler profile wings) both models give the same result. For large t (Doppler profile center) significant difference can be observed. Reality is between these two limit cases.

As first iteration, soft and hard linear superposition can be considered as model for intermediate cases.

Model = α soft + (1- α) hard

Number of collisions

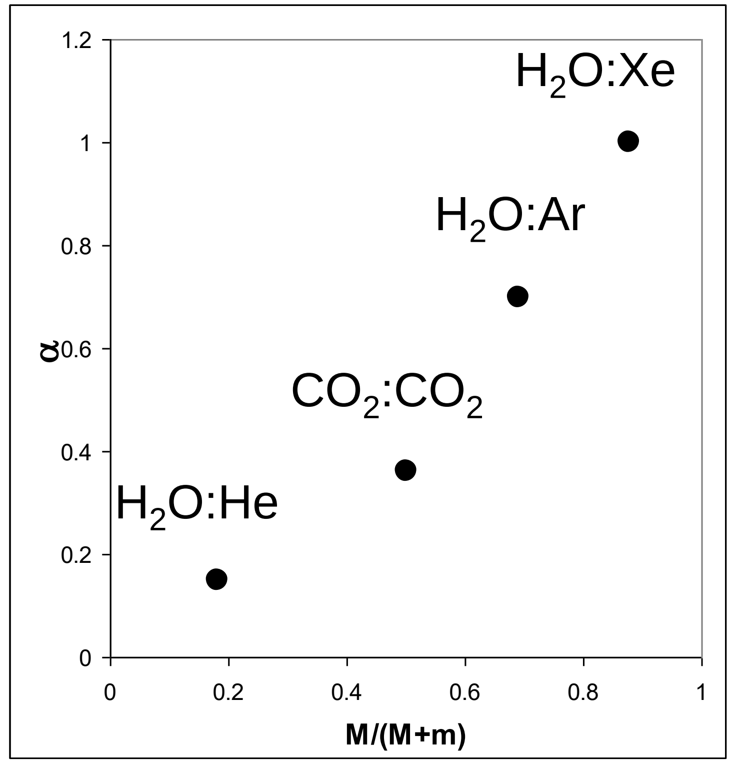


Soft and hard linear superposition can be considered as model for intermediate cases.

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

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

The same α value leads to correct broadening and narrowing dependences.



α is measure of collisions number required to achieve equilibrium velocity distribution: 0 – infinite collisions number (soft); 1 – one collision (hard). α dependence for several gas mixtures. Here m and M are masses of molecule under investigation and buffer molecule, respectively.

Conclusions

- High accurate spectra of several gas mixtures were recorded.
- Doppler profile models: soft and hard were considered.
- It was demonstrated that for dipole – dipole interaction (pure water vapor) soft model is correct.
- It was demonstrated that for H_2O : Xe gas mixture hard model is correct.
- For intermediate cases soft and hard models linear superposition was proposed.
- It was demonstrated that parameters of this linear superposition are measure of collisions number required to achieve equilibrium distribution of molecules velocity.