Spectral line asymmetry

DLS LAB

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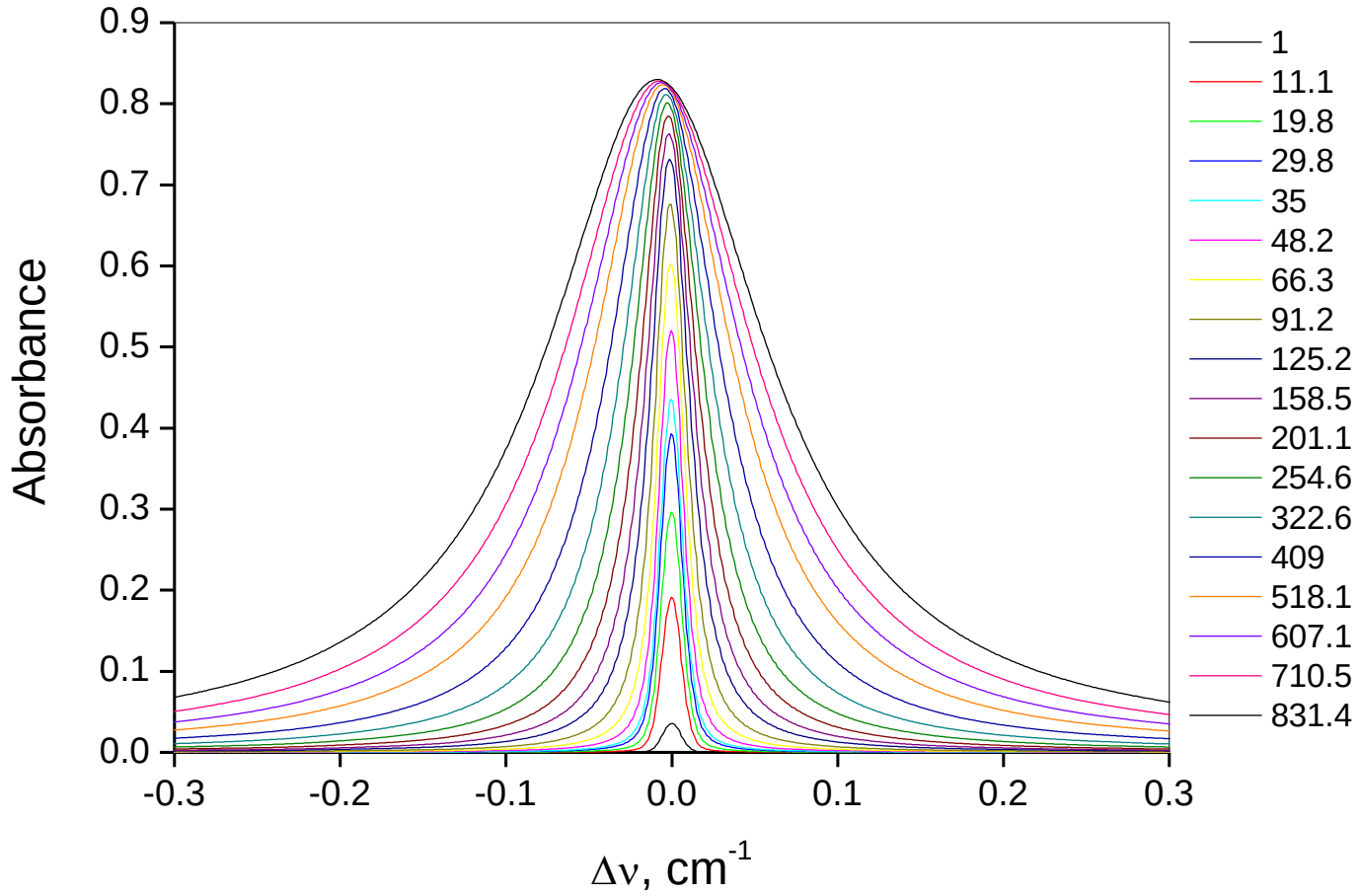
Introduction

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 recently achieved in TDLS (A2). High accurate spectra of several gas mixtures were obtained for different pressures (C2, C3). Spectral line shapes obtained were fitted using procedure developed (B1).
For all cases, asymmetry of analyzed spectral line was observed. The subject of present paper is attempt to understand physical origins of this asymmetry and its relation with properties of diode laser and molecule under investigation.

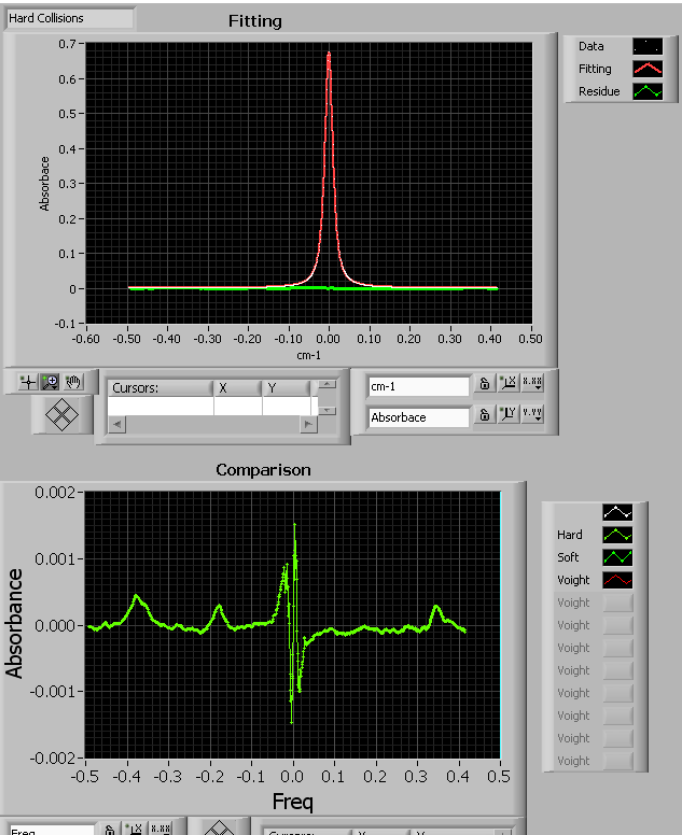
Experiment

High accurate spectra of several gas mixtures were obtained for different pressures (C2, C3).



Shapes of analytical CO_2 line for different pressures (mBar). Pressure broadening and shift can be observed.

Fitting

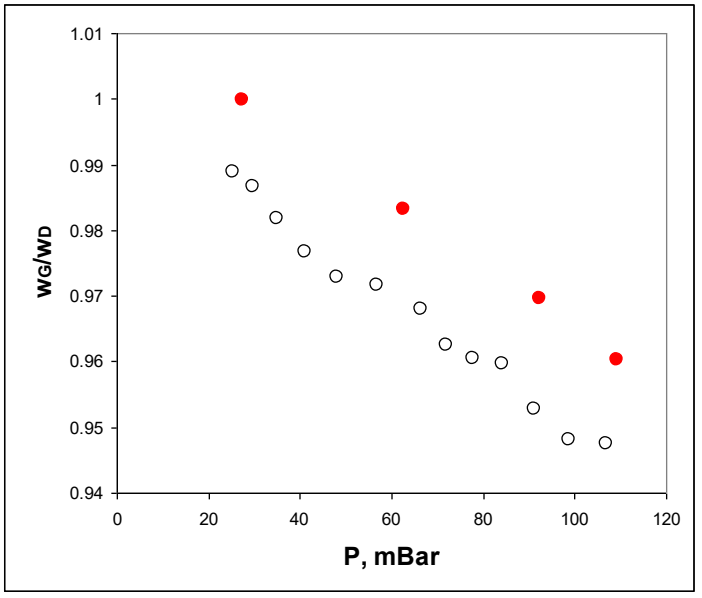


Experimental data were fitted using software developed (see B1). Fitting used following parameters set of line shape.

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

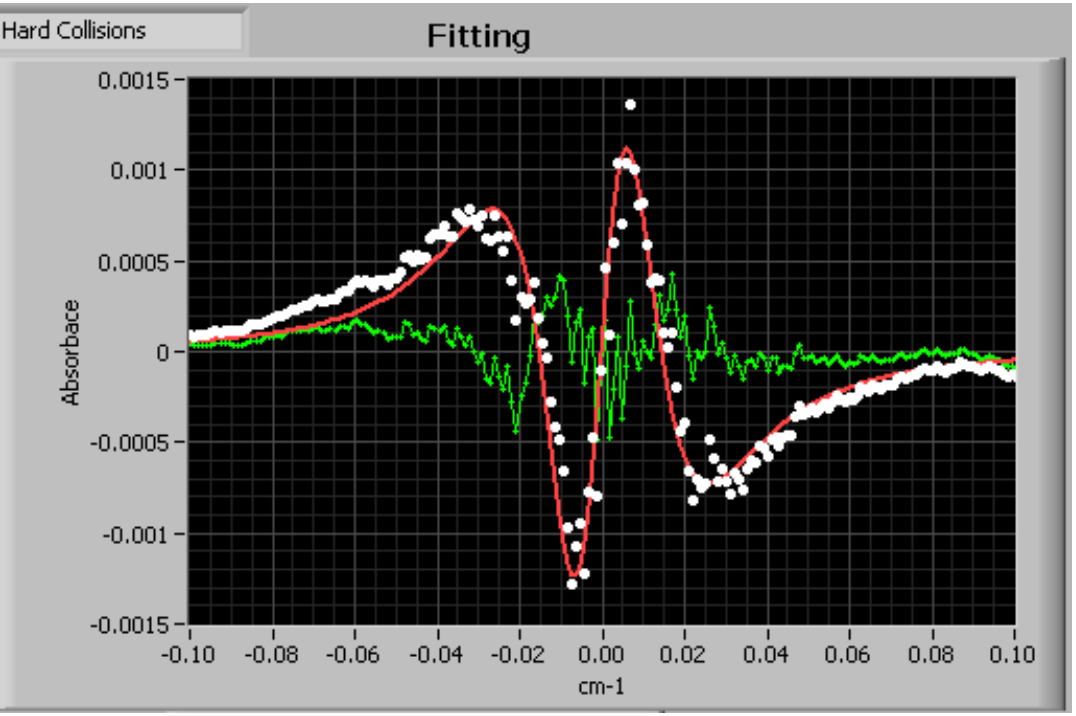
$$w_D = \nu_0 \sqrt{\ln(2)\frac{2kT}{Mc^2}}$$

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



Line shape asymmetry

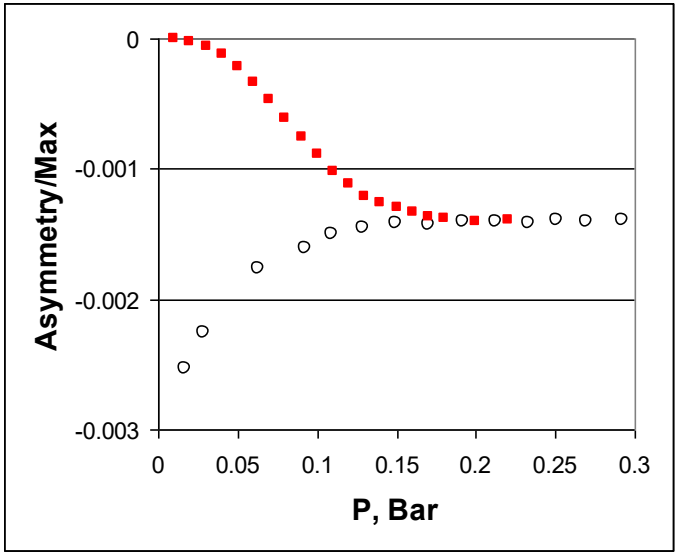
For all cases, asymmetry of analyzed spectral line was observed. White circles – CO_2 line residual for 171.4 mBar normalized to line maximum demonstrating spectral line asymmetry (3 roots).



To measure asymmetry, empirical model function was developed. Asymmetry model function is determined by derivatives of line under consideration shape. Using this function asymmetry can be fitted (red curve). This approach was tested for all pressures in use and gave ability to measure asymmetry value.

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

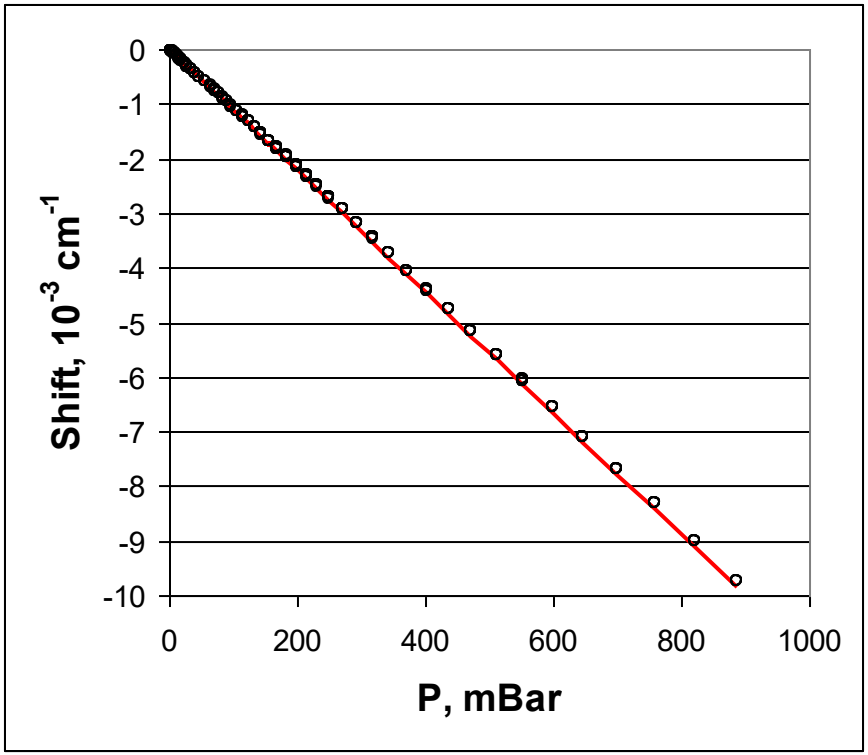
Asymmetry mechanisms



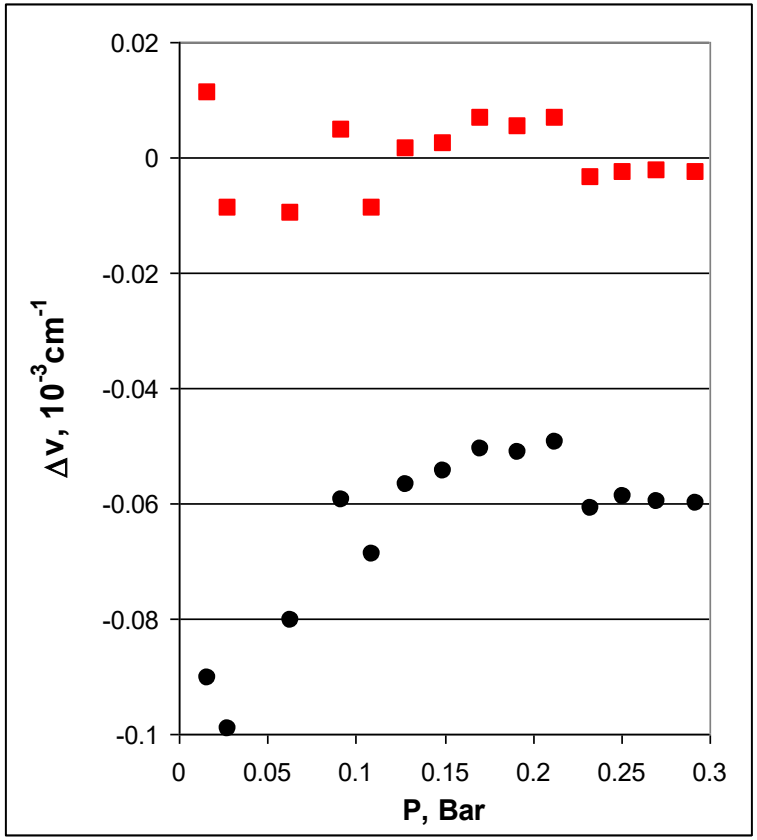
Asymmetry pressure dependence (black open circles) of CO_2 line.
There are 3 mechanisms of line asymmetry: correlation of DL frequency and intensity noises (A2), Lorentz profile asymmetry, and asymmetry due to lines mixing. All three mechanisms were observed experimentally.

For interacting lines overlapping, asymmetry is due to line mixing. In present case isolated line was investigated.
Asymmetry of Lorentz profile (red solid squares) is negligible for low pressures and achieve constant value for pressure when Lorentz width is above Doppler one. Asymmetry due to DL frequency and intensity noises correlation dominates at low pressures (difference between two dependences) and decreases with pressure line broadening.
Asymmetry pressure dependence has to be taken into account. For pressures above 0.15 Bar asymmetry of Lorentz profile dominates.

Asymmetry and pressure shift

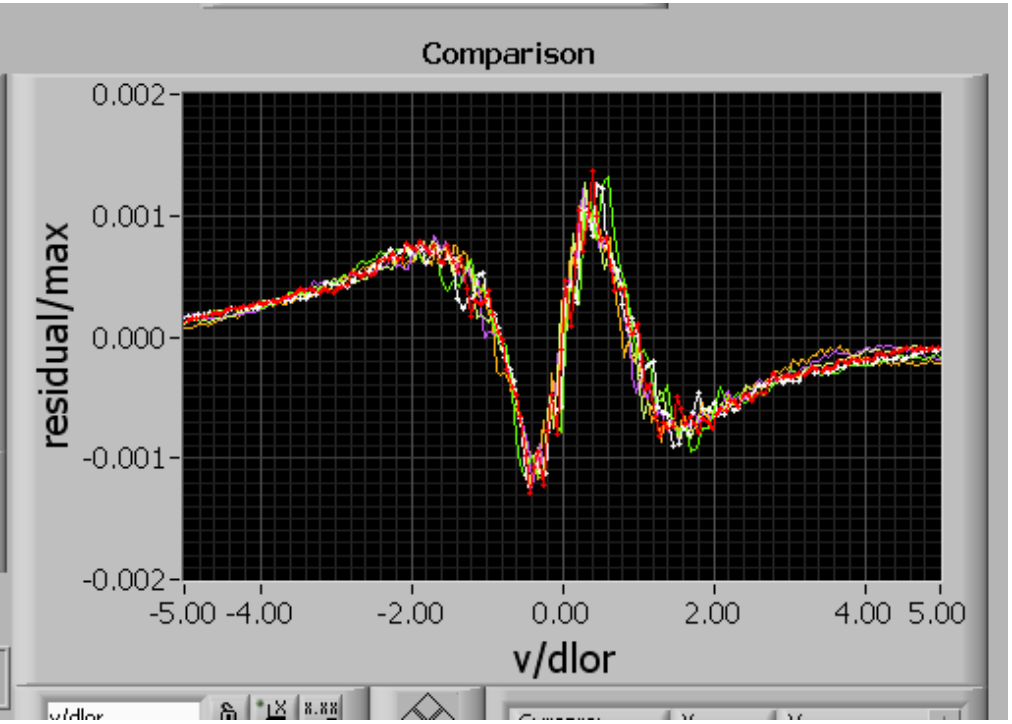


Left – pressure shift of CO_2 line.
Below - pressure shift after deduction of linear dependence δ = -0.0110 cm^{-1}/Bar.
Line asymmetry presence leads to the line position shift from real value (black circles).
Red squares – asymmetry was taken into account.



Accuracy of line frequency determination is 10^{-4} and 10^{-5} cm^{-1}, without and with taking into account asymmetry, respectively.
For pressure shift, accuracy is 3 10^{-4} (3 %) and 3 10^{-5} (0.3 %) cm^{-1}/Bar without and with taking into account asymmetry, respectively.

Lorentz line shape asymmetry



Residuals of CO_2 line for pressures 150 – 300 mBar in normalized coordinates. These pressure range corresponds to ratio of Lorentz to Doppler widths 1.7 – 3.8.
For high pressures line asymmetry in normalized coordinates does not depend on pressure. It is prove that line asymmetry in pressure range under consideration is due to asymmetry of Lorentz profile.

Conclusions:

1. ***For high pressures observed spectral line asymmetry is due to asymmetry of Lorentz profile.***
2. ***If line shape is known, its asymmetry can be calculated straightforward using asymmetry model function***
3. ***It is not true for low pressures where DL asymmetry dominates.***

Potential of interaction

Let us consider this in more details. Potential of interaction between colliding molecules is $V_k r^{-k}$ (r is distance between molecules, k determines interaction type; k = 3, 4, 5, 6 corresponds to dipole – dipole, dipole – quadrupole, quadrupole – quadrupole, and Van der Waals potentials). For linear trajectory, time dependence interaction :

$$V(t) = \frac{V_k}{\left[\rho^2 + (ut)^2\right]^{\frac{k}{2}}}$$

ρ - impact parameter, u – colliding particles velocity. Matrix element - M of colliding molecules interaction:

$$M(\rho,u) = \int_{-\infty}^{\infty} \frac{V_k}{\left[\rho^2 + (ut)^2\right]^{\frac{k}{2}}} dt = \frac{const}{\rho^{k-1}u} = \left(\frac{\rho_0}{\rho}\right)^{k-1}; \qquad \rho_0 = \frac{const}{u^{\frac{1}{k-1}}}$$

ρ_0 - Weisskopf radius, $M(\rho_0) = 1$.

Lorentz profile

Let us consider colliding molecules ensemble with relative velocity – u. For impact approximation (negligible collision time) line shape will have Lorentz profile.

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

$$\Gamma(u) = Nu\,\sigma'(u)$$

$$\Delta(u) = Nu\,\sigma''(u)$$

Next step is quasi classical approximation (interaction potential is small with respect to kinetic energy). In this case cross sections can be calculated using interaction matrix elements.

$$\sigma'(u) = 2\pi\int_0^\infty \left\{1 - \cos\left[M(\rho,u)\right]\right\}\rho d\rho$$

$$\sigma''(u) = 2\pi\int_0^\infty \sin\left[M(\rho,u)\right]\rho d\rho$$

Finally Anderson model was used to calculate these cross sections.

Temperature and velocity dependence of Lorenz profile parameters

Let us consider colliding molecules ensemble with relative velocity – u. For impact approximation (negligible collision time) line shape will have Lorentz profile.

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

Lorentz line asymmetry usually is associated with line parameters velocity dependence.

Using above mentioned approximations temperature and velocity dependences of Lorentz profile parameters can be estimated. If temperature exponent was measured, velocity dependence can be obtained.

$$\Gamma(u) = \gamma_0 P_0 \left(\sqrt{\frac{T}{T_0}} \frac{u}{\langle u \rangle} \right)^{\frac{k-3}{k-1}}$$

$$\Delta(u) = \delta_0 P_0 \left(\sqrt{\frac{T}{T_0}} \frac{u}{\langle u \rangle} \right)^{\frac{k-3}{k-1}}$$

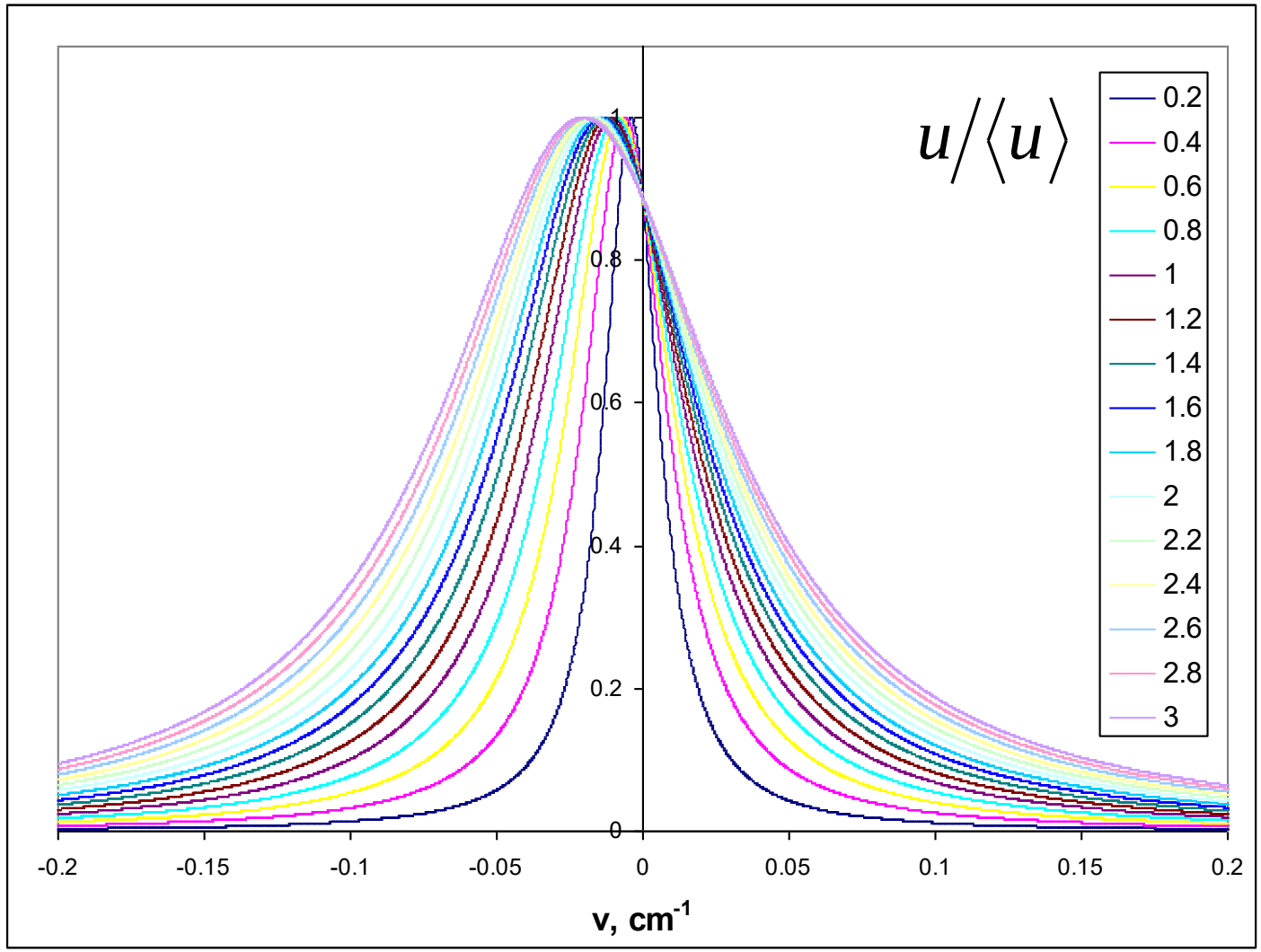
Velocity dependence

Molecular ensemble with velocity – u will have Lorentz profile with parameters depending on velocity (see above).

Velocity dependence leads to the profile broadening and shift with increase of velocity.

Modeling for Van der Waals potential:

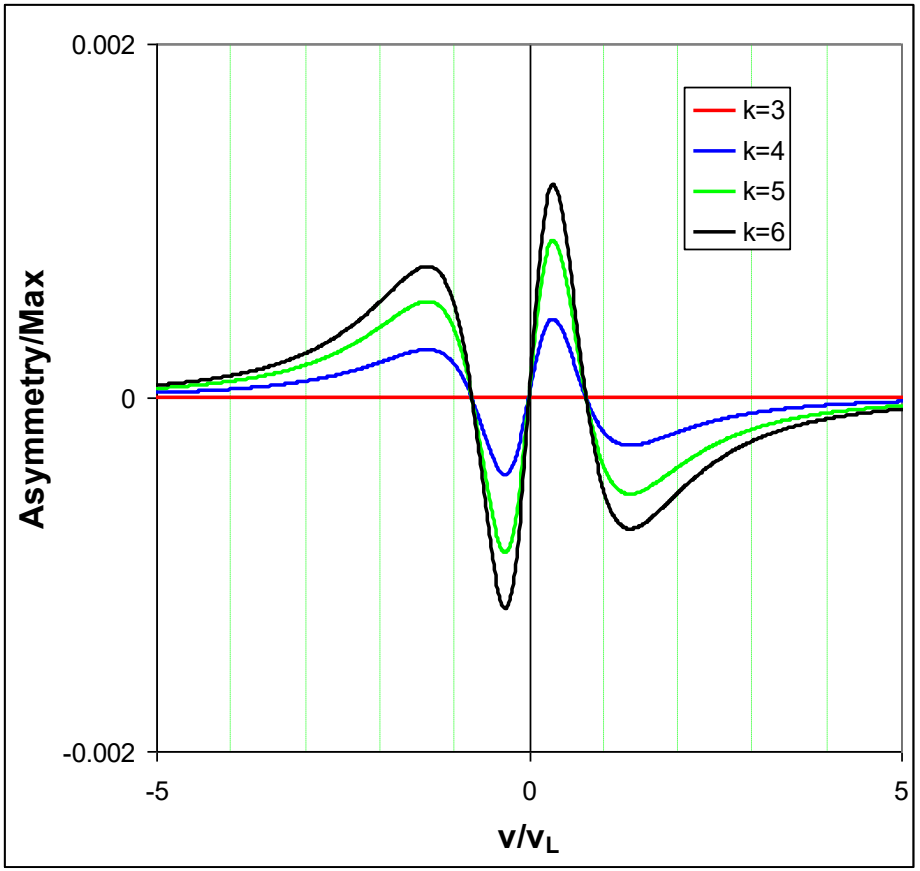
k = 6, $\Delta/\Gamma = 0.36$ (Sobel'man).



Lorentz profile asymmetry modeling

Final line shape can be obtained after averaging over molecules velocity distribution (Maxwell). γ and δ are determined by broadening and shift coeffitients.

$$K(\nu) = \int_0^{\infty} \frac{S\gamma P x^{\frac{k-3}{k-1}} \exp\left[-x^2\right]}{\pi\left[\left(\nu - \nu_0 + \delta P x^{\frac{k-3}{k-1}}\right)^2 + \left[\gamma P x^{\frac{k-3}{k-1}}\right]^2\right]} 2x dx$$

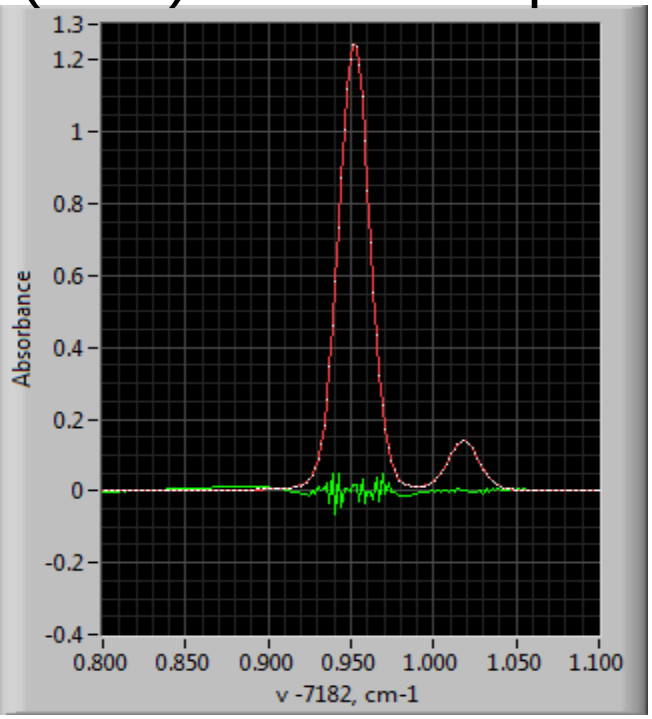


Final line shapes were calculated for different types of molecules interaction. These shapes were fitted. Figure presents results of asymmetry modeling.

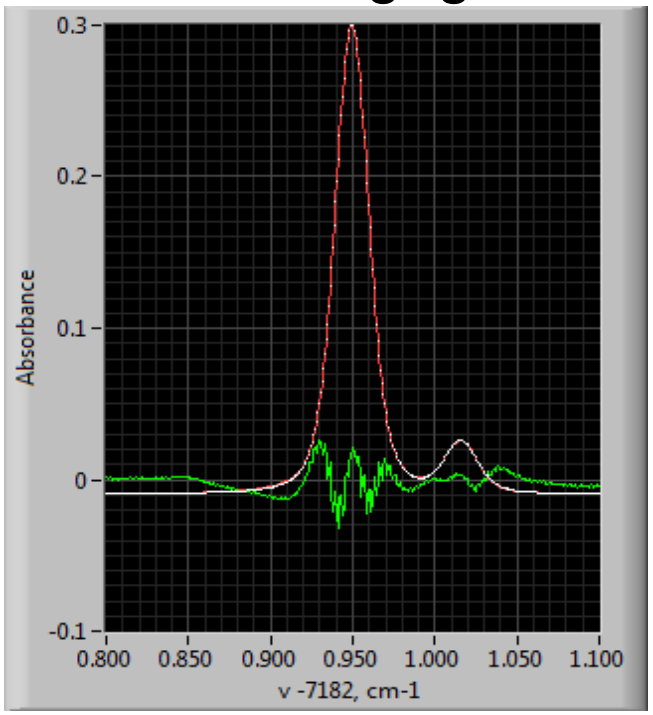
Asymmetry is absent for k = 3 (dipole – dipole potential) and increases with k increase.

Type of interaction potential

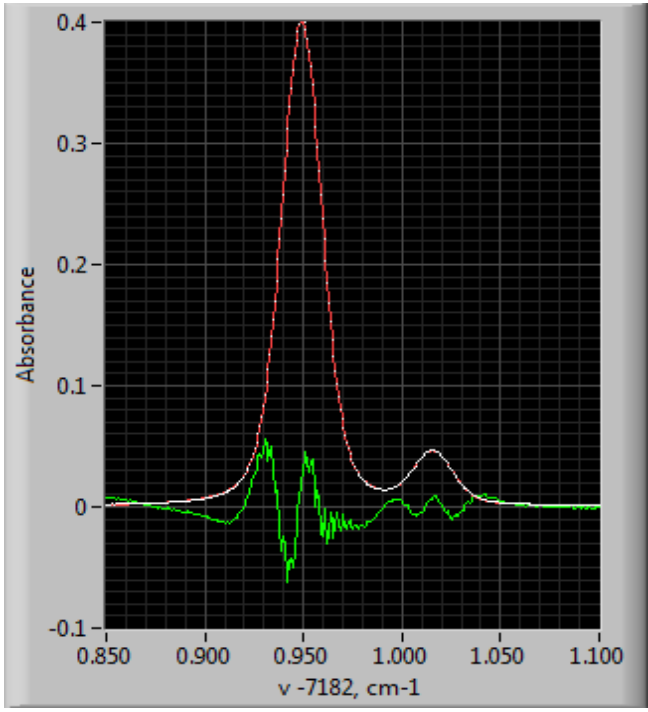
To test above mentioned modeling, the same water line was fitted (hard). White – experiment, red – fitting, green – residual * 20.



H_2O:H_2O (k = 3)
Dipole – Dipole,
asymmetry is absent.



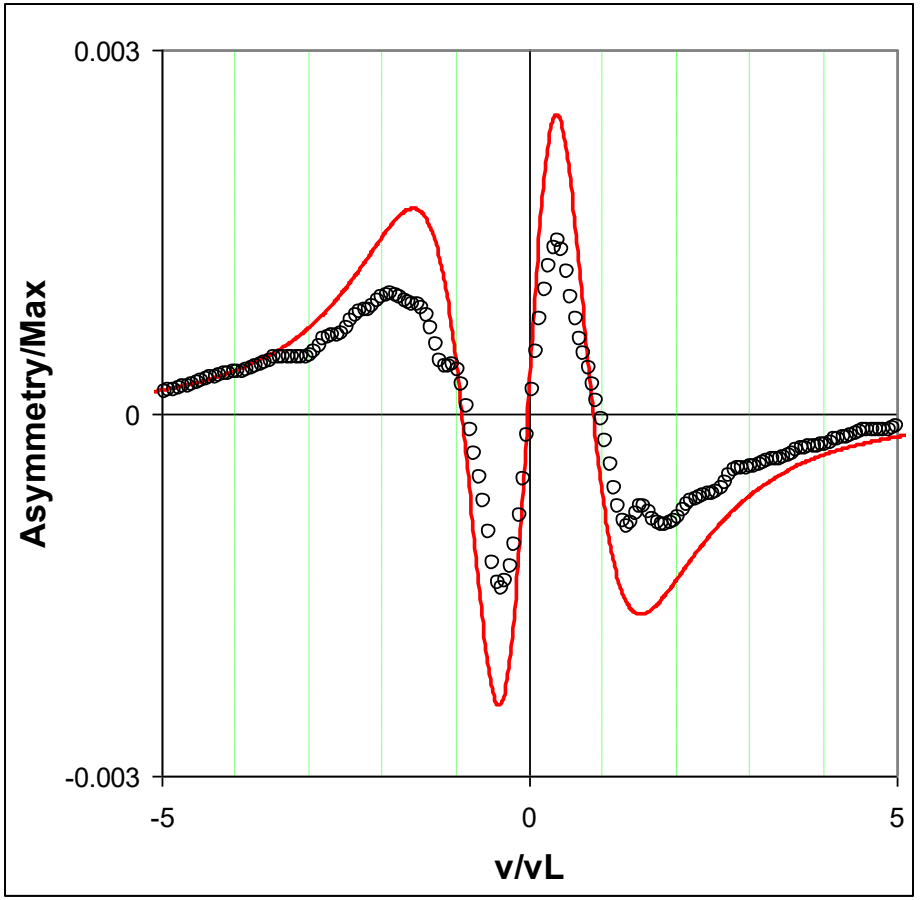
H_2O:N_2 (k = 4)
Dipole – Quadrupole,
asymmetry is present.



H_2O:Xe (k = 6)
Van der Waals,
strong asymmetry.

Asymmetry results obtained are in agreement with modeling performed above.

Experiment and modeling



Experiment (black circles) – asymmetry of CO_2 line (CO_2:CO_2). Red curve – modeling for quadrupole – quadrupole (k = 5). No free parameter because both broadening and shift parameters were obtained from experiment.

Experimental asymmetry shape is described by the model very well. Although amplitude of experiment and model differ, agreement is good taking into account following:

absence of free parameters, fairly rough models in use: Anderson model, Maxwell (no Dicke), etc.

Conclusions

- High accurate line shapes of several molecules in different gas mixtures were recorded.
- Data obtained were fitted using fitting procedure developed.
- Line asymmetry was observed. Three mechanisms of asymmetry were identified: line mixing, DL frequency and intensity noises correlation, and asymmetry of Lorentz profile. All three mechanisms were observed experimentally.
- Experimental parameters to investigate Lorentz profile asymmetry were determined.
- Measured Lorentz profile asymmetry is due to velocity dependence of line broadening and shift parameters.
- Model developed is in agreement with significant asymmetry difference for different types of molecules interaction potentials, asymmetry shape, and asymmetry amplitude.