

Accuracy in TDLS.

TDLS as gas mixtures primary standard

DLS
LAB

A. Nadezhdinskii

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

Leonid Konopelko

*D.I. Mendeleev Institute for Metrology
Moskovsky pr. 19, St. Petersburg 190005, Russia*

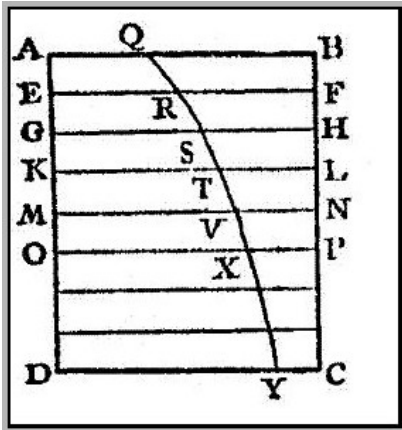
Introduction

Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). Several TDLS applications require measurement accuracy at level 0.1 – 0.01 %. This accuracy is necessary for: UF₆ enrichment, isotope ratio (¹³C/¹²C, ¹⁸O/¹⁶O, D/H, ...), green house gases concentration (global climate changing), gas mixture standards development, screening medical diagnostics, etc.

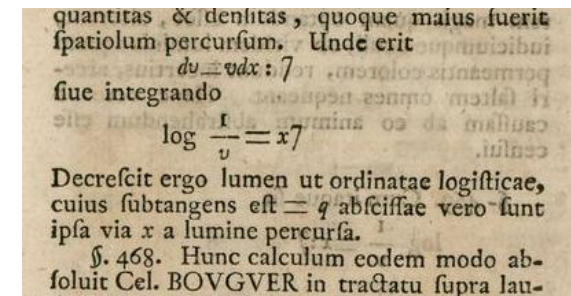
In present paper fundamental limits due to physical laws in use approximations as well, as DL radiation properties will be considered with respect to high accurate measurements.

Historical background

TDLS is based on exponential dependence of radiation transmitted through media under investigation as function of its optical length – absorption law.



It was discovered by Pierre Bouguer in “Essai d'Optique sur la Gradation de la Lumiere” (Claude Jombert, Paris, 1729). He considered absorbing media as slices having similar absorbance and found exponential (logarithmic) dependence.



I. Lambert “Photometry” (1760). 583 pages considering different aspects of photometry (**look at it, I was excited**). Between them one page where he used differential equation (available at this time) for Bouguer law. Now inhomogeneous absorbing media can be considered.

A. Beer (1852) extended the exponential absorption law for solutions. It is the linear relationship between absorbance and concentration of an absorber.

Beer law is not valid in TDLS. Examples: molecular absorbance at low pressures, water vapor absorbance in atmosphere.

Bouguer law for gases

Bouguer law for gases (small absorption) can be obtained from both Maxwell equations or energy consumption law for electromagnetic field:

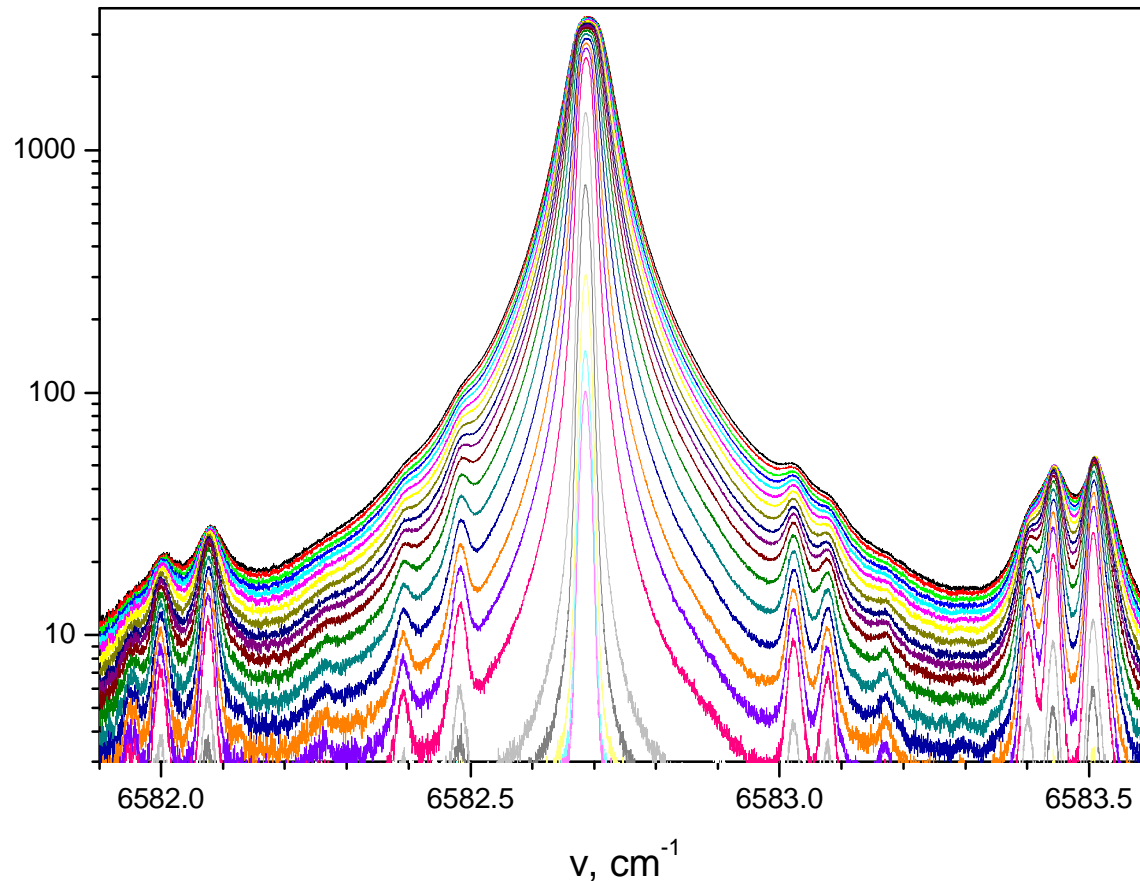
$$\sqrt{1 + 4pcN(x)} \frac{\partial W_x(n)}{\partial x} = -s(n)N(x)W_x(n)$$

χ and σ are molecular polarizability and absorption cross-section, respectively; N – molecules number density. Square root in this equation describes influence of rest gas polarization on DL radiation absorption by particular molecule (refractive index). For $N = \text{const}$ exponential absorption law can be obtained:

$$W_L(n) = W_0(n) \exp\left[-\frac{s(n)NL}{\sqrt{1 + 4pcN}}\right]$$

Absorbance in TDLS is determined by molecule number density - N , absorption cross-section - s , and optical length - L . Usually influence of rest gas (denominator) is ignored. For high accuracy it has to be taken into account and leads to non-linear absorbance pressure dependence. For methane correction is 0.05 % for 1 Bar.

Spectral line shape



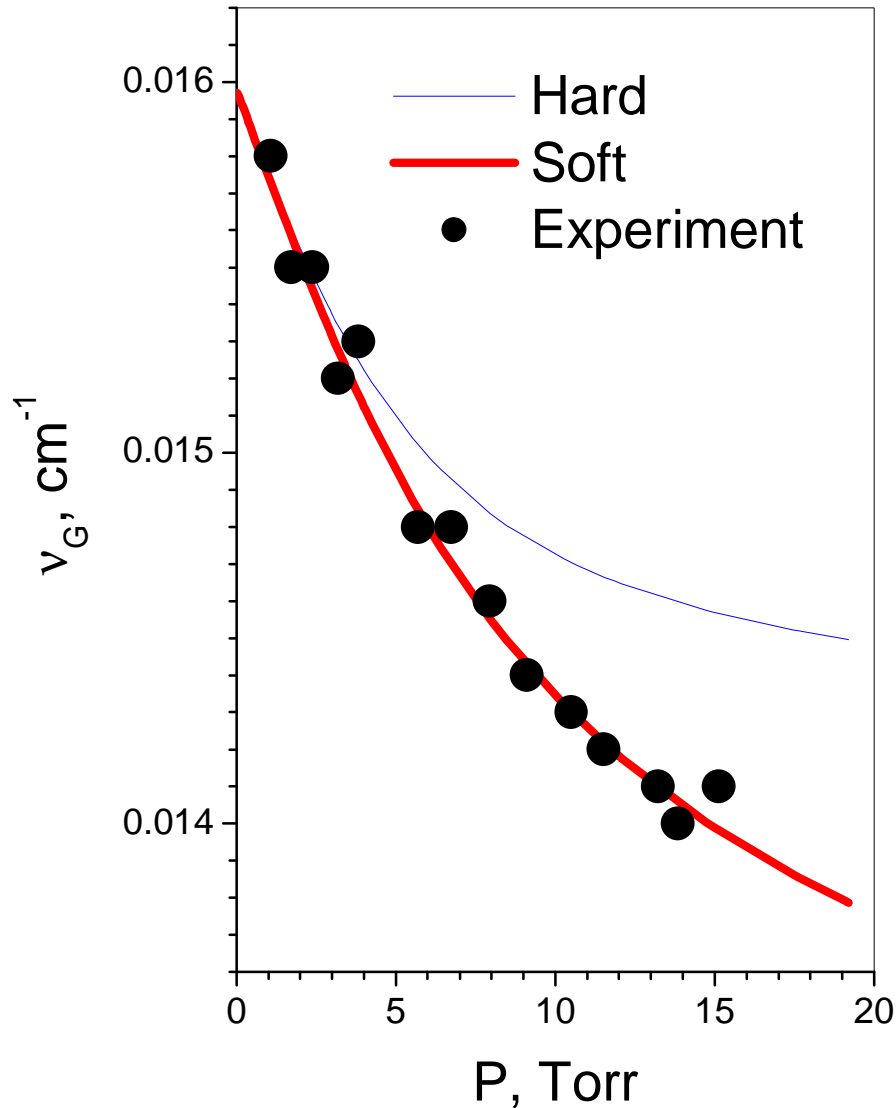
Absorbance spectrum fragment of molecule under investigation for different pressures.

Vicinity of R(11) $\nu_1 + \nu_3$ line of C_2H_2 .

Recorded absorbance spectra are fitting using different line shape models to determine gas-mixture under investigation parameters.

- There are several challenges for accuracy of these measurements:**
- 1. Weak lines of hot bands, isotopomers, and atmosphere molecules presence.**
 - 2. Line shape model using in fitting.**
 - 3. Spectral lines mixing effect.**

Spectral line fitting



As line shape model we are using Voigt profile with 4 parameters: line center – ν_0 , line intensity – S , Gaussian and Lorentzian widths – ν_G and ν_L , respectively.

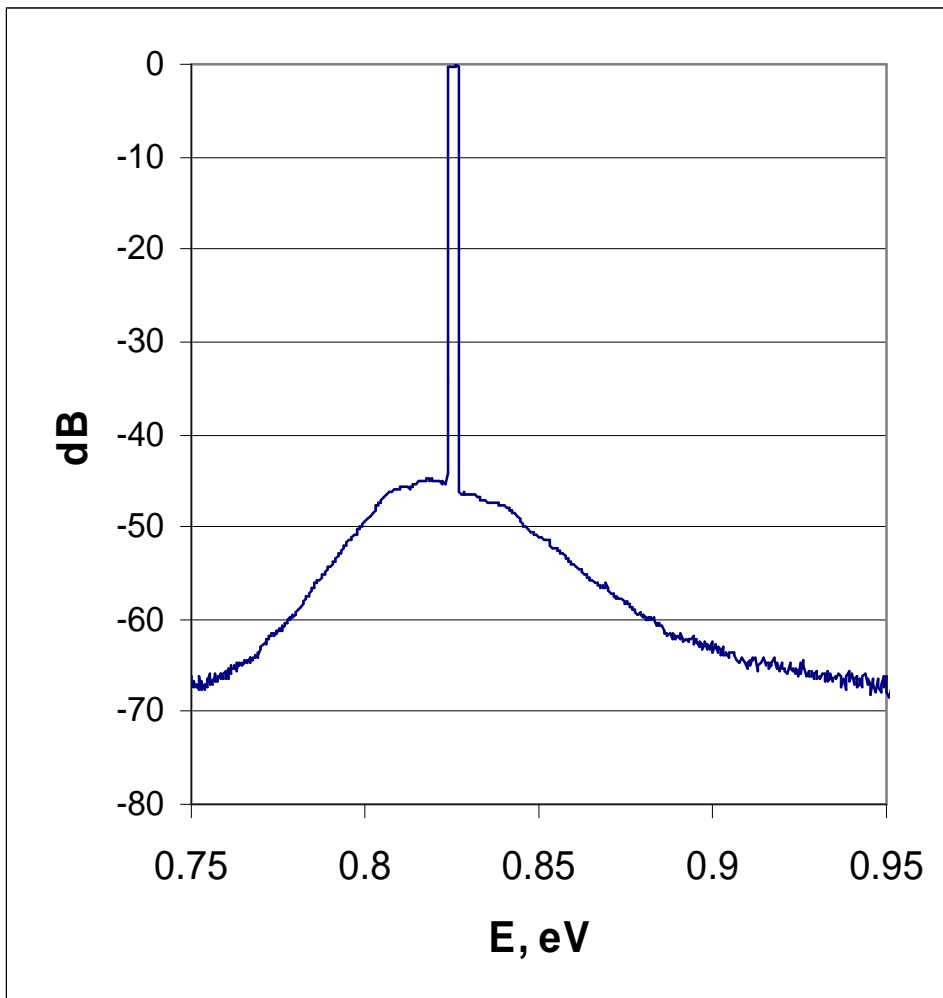
Dike narrowing of 5_{42} - 4_{41} water vapor line near 5475 cm^{-1} . Solid curves – results of fitting for two opposite line shape models: soft and hard collisions (Residual below 10^{-4}).

Solid circles – experiment. In present case soft collision model is correct as result of dipole-dipole interaction between water molecules participating in collision.

More common is something between soft and hard models. It leads to non-linear pressure dependence of parameters obtained by fitting.

Spontaneous emission

Bouguer law is valid for plane-parallel beam of monochromatic radiation. DL radiation is not monochromatic. Together with coherent component it contains broad spontaneous emission one.



Some light will be recorded even for saturated spectral line – optical zero”.

$$W_L(n) = \Delta W + W_0(n) \exp[-s(n)NL]$$

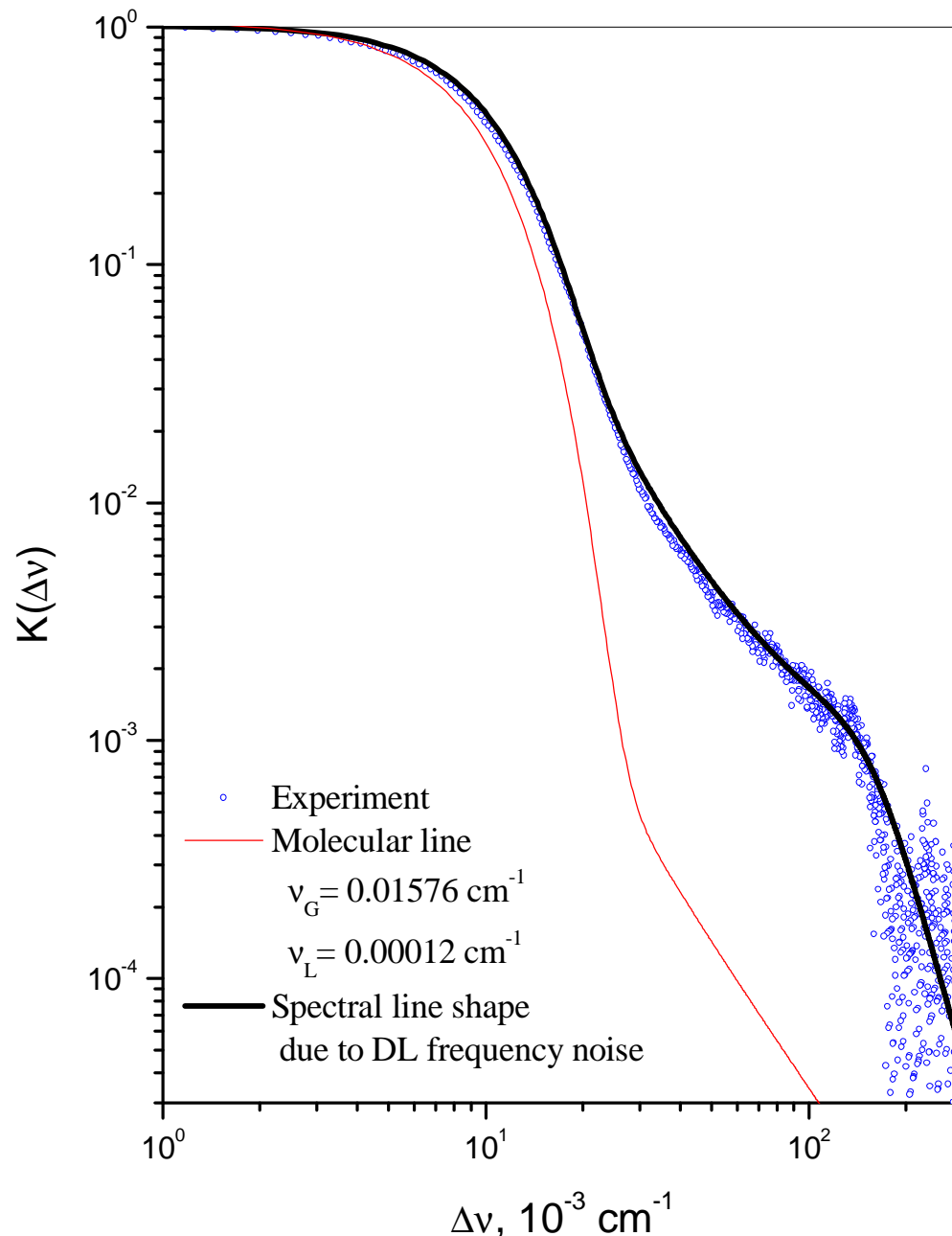
Related error can be of the order of 1 - 10 %.

It is unacceptable for accurate measurements under consideration.

Solution: remove spontaneous emission by spectral filter (for example, monochromator) using.

Spectral line shape in TDLS

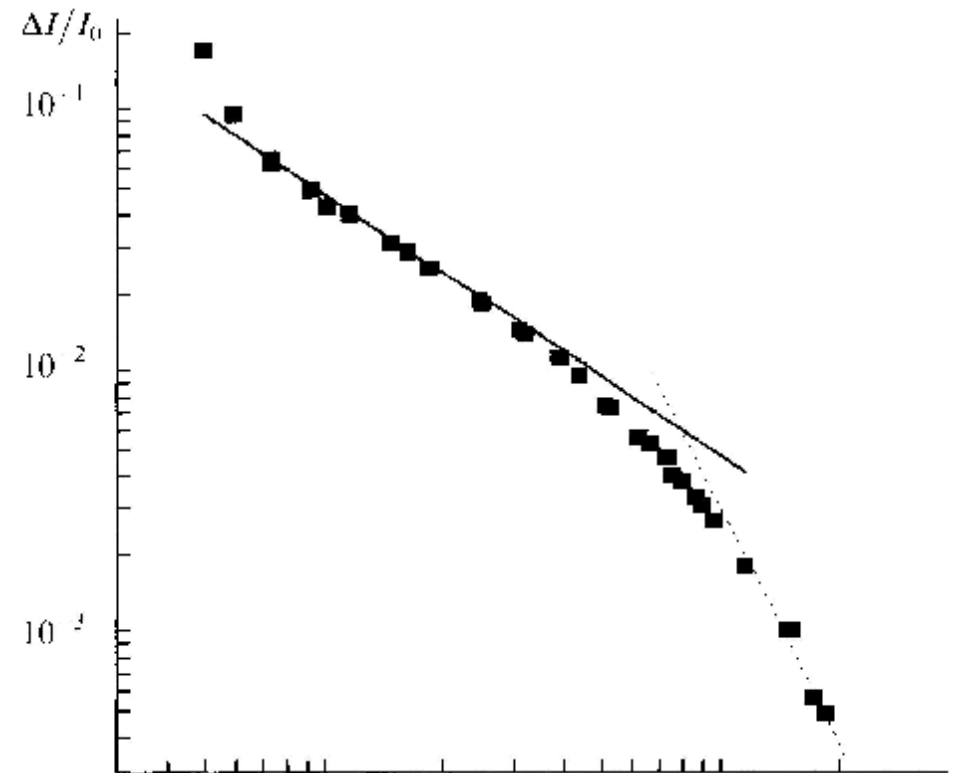
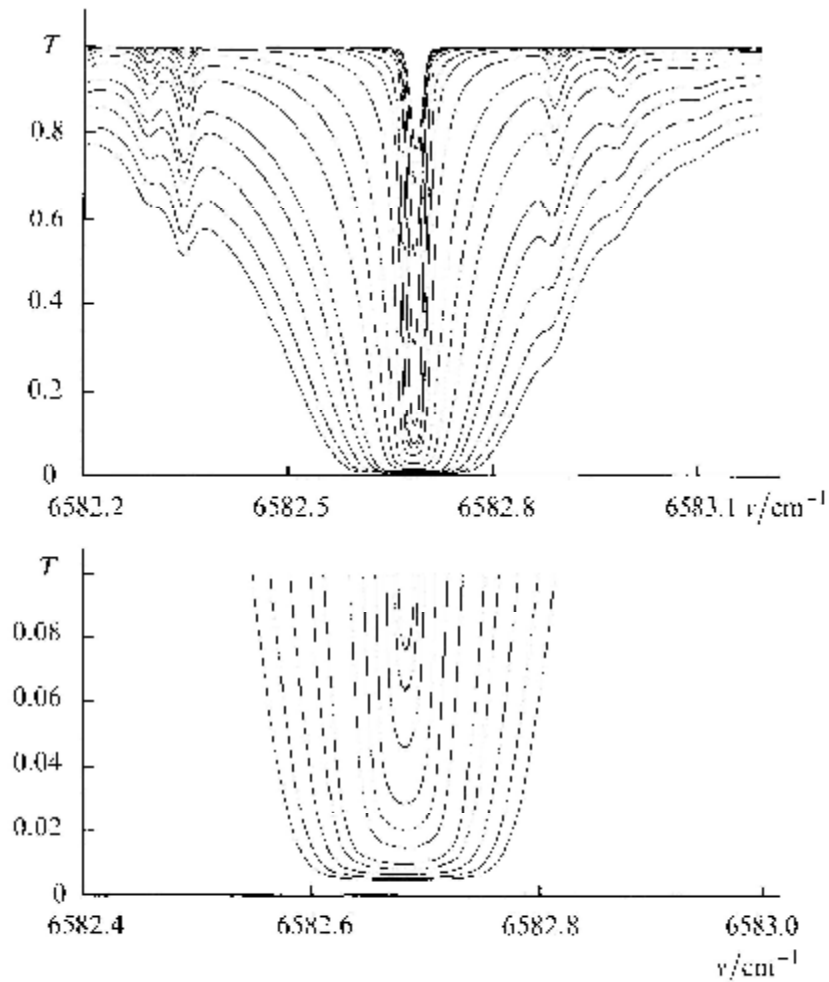
C₂H₂ spectral line shape due to known parameters of experiment and molecule under investigation (red line) and as it was recorded by TDLS.



Recorded line shape in TDLS is result of convolution of sample transmittance and DL emission spectra.

“Optical zero”

Spontaneous emission was removed by monochromator



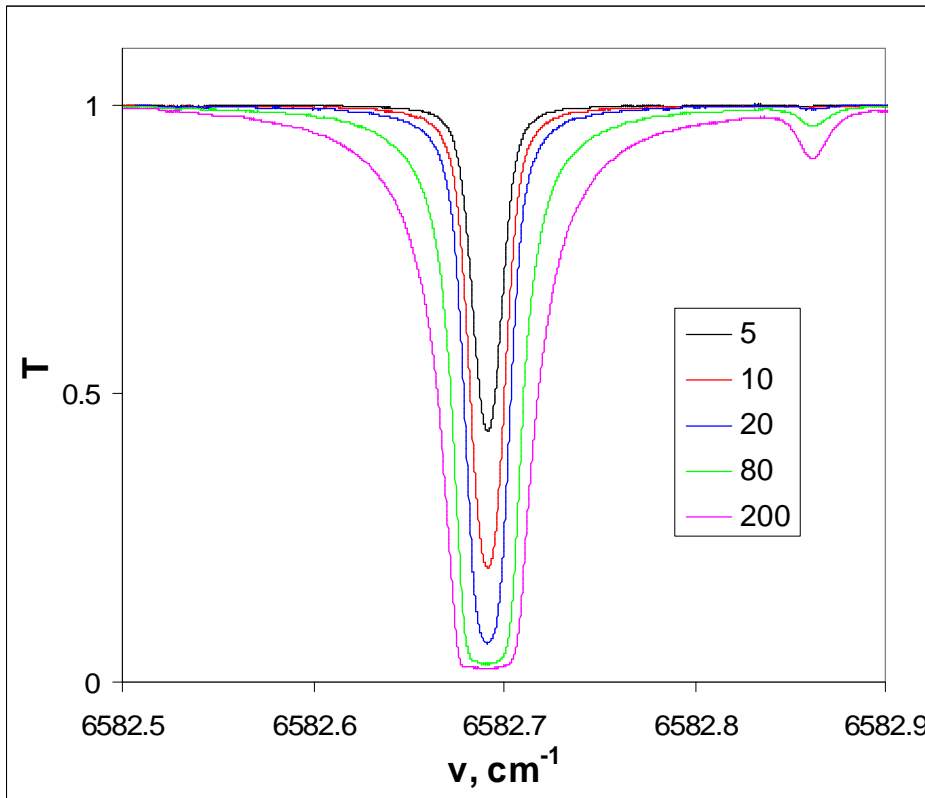
Acetylene transmission spectra in 200 cm cell and pressures between 0.02 and 92 Torr. Presence of “optical zero” and its pressure dependence can be observed.

“Optical zero” pressure dependence demonstrates correlation with DL emission spectrum parameters.

DL emission spectrum

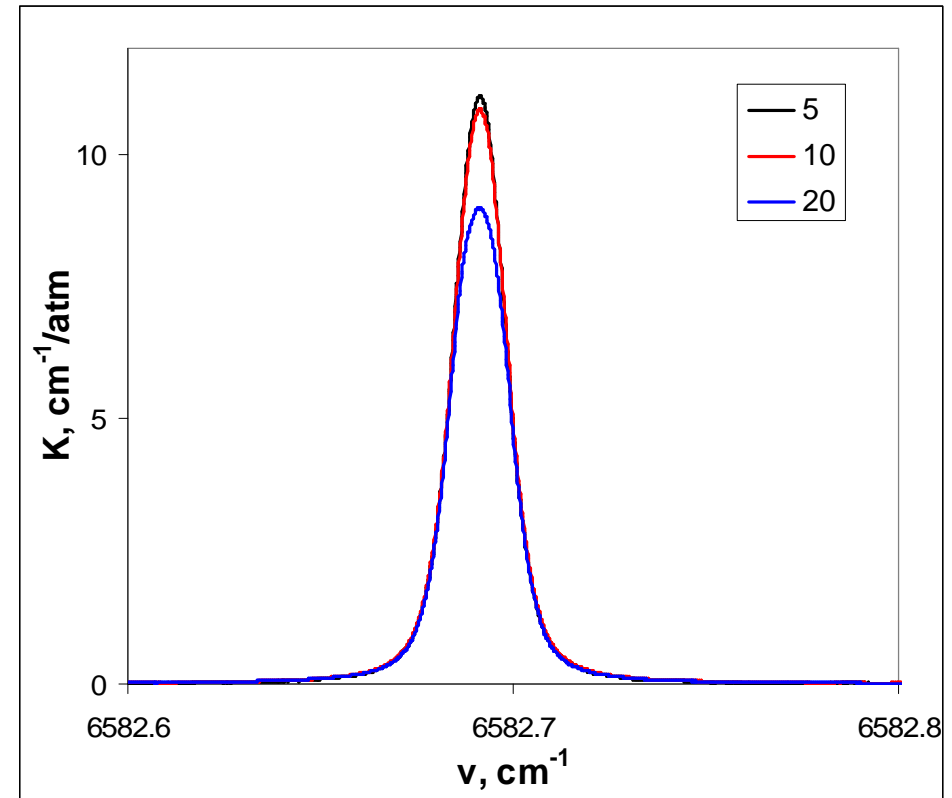
Spontaneous emission was removed by monochromator

Same sample of pure C_2H_2 was investigated using 5 connected cells with different $L = 5, 10, 20, 80, 200$ cm.



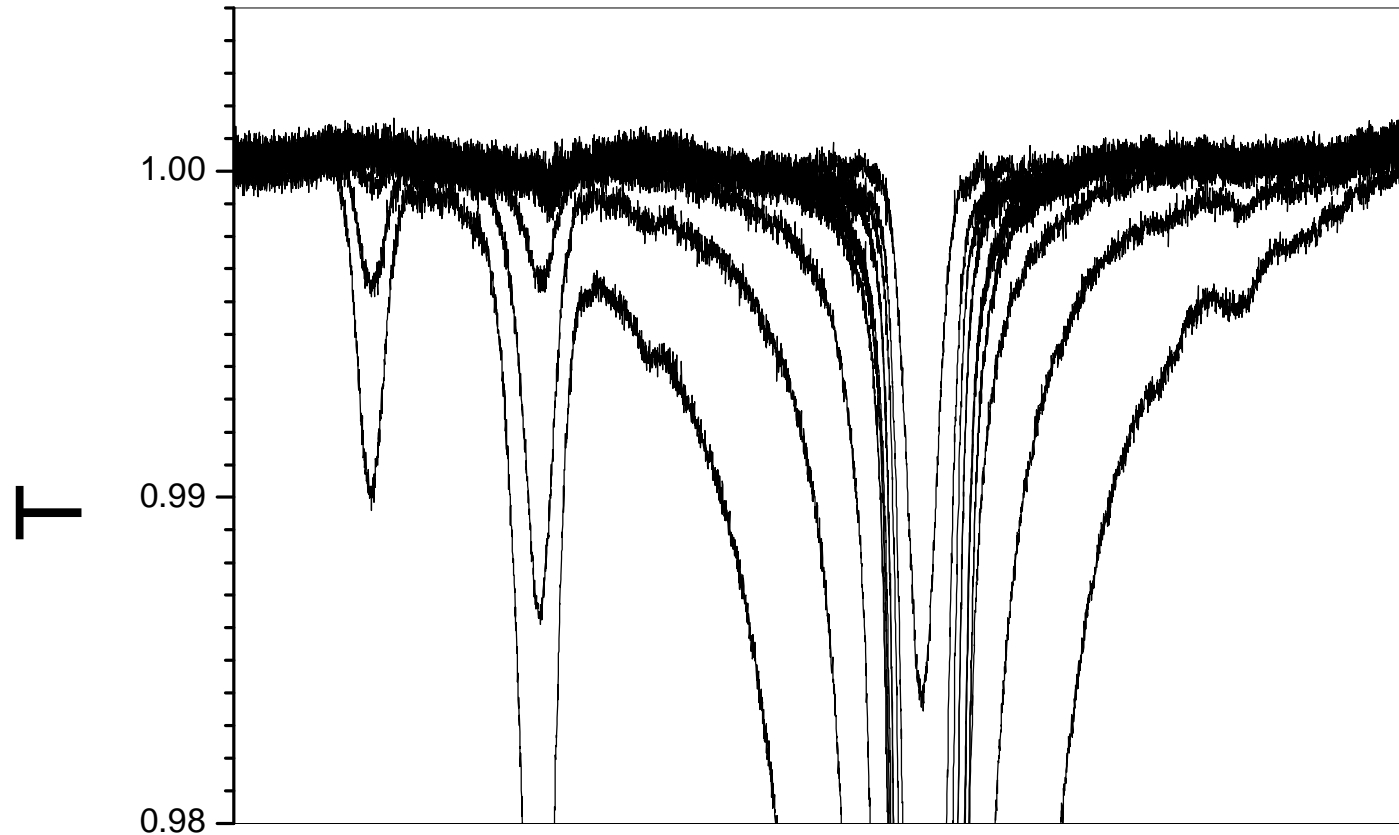
Acetylene transmission spectra in cells with different L for $P = 11.4$ Torr.

To remove DL emission spectrum influence line absorbance has to be as small as possible.



Absorption coefficient obtained for the same sample using different cell length.

Baseline



Transmittance spectra for different pressures of molecule under investigation.

Baseline presence at 10^{-3} level can be observed leading to error of spectral line parameters determination.

To reduce baseline influence large line absorbance has to be used in contradiction with previous requirement.

Gas sample and TDLS

Requirements for gas sample:

Purity – better 10^{-4} , dry vacuum;

Gas pressure accuracy better 0.01 %;

Gas temperature accuracy better 0.03 K;

Known isotope ratio. For examples, samples from different sources have different $^{13}\text{C}/^{12}\text{C}$ ratios:

Inorganic	-0 ‰
Atmosphere	-7 ‰
Biogenic	-60(5) ‰
Fossil	-40(8) ‰
Biomass burning	-24(3) ‰

DL radiation interaction with molecules will change molecular levels population. Requirement for DL intensity: less 1 mW/cm².

Non-ideal molecule

In TDLS molecules number density – N is measured. To determine its gas pressure – P is measured. At this point non-ideal molecular gas behavior has to be taken into account.

$$\frac{P}{kNT} = 1 + BN + CN^2 + \dots$$

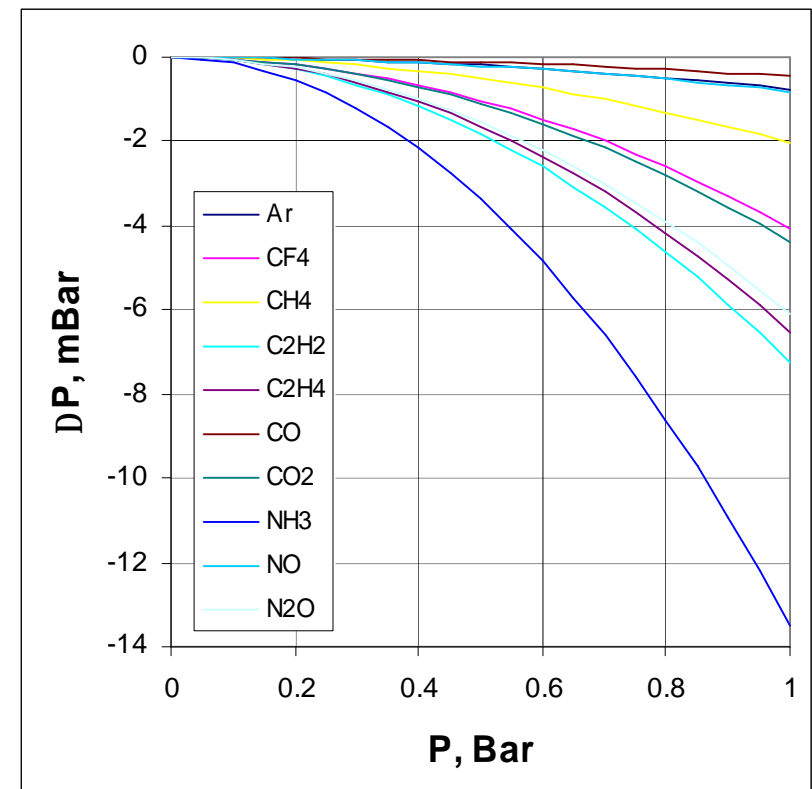
Non-ideal molecular gas behavior:

1 – ideal gas (no interaction between molecules);

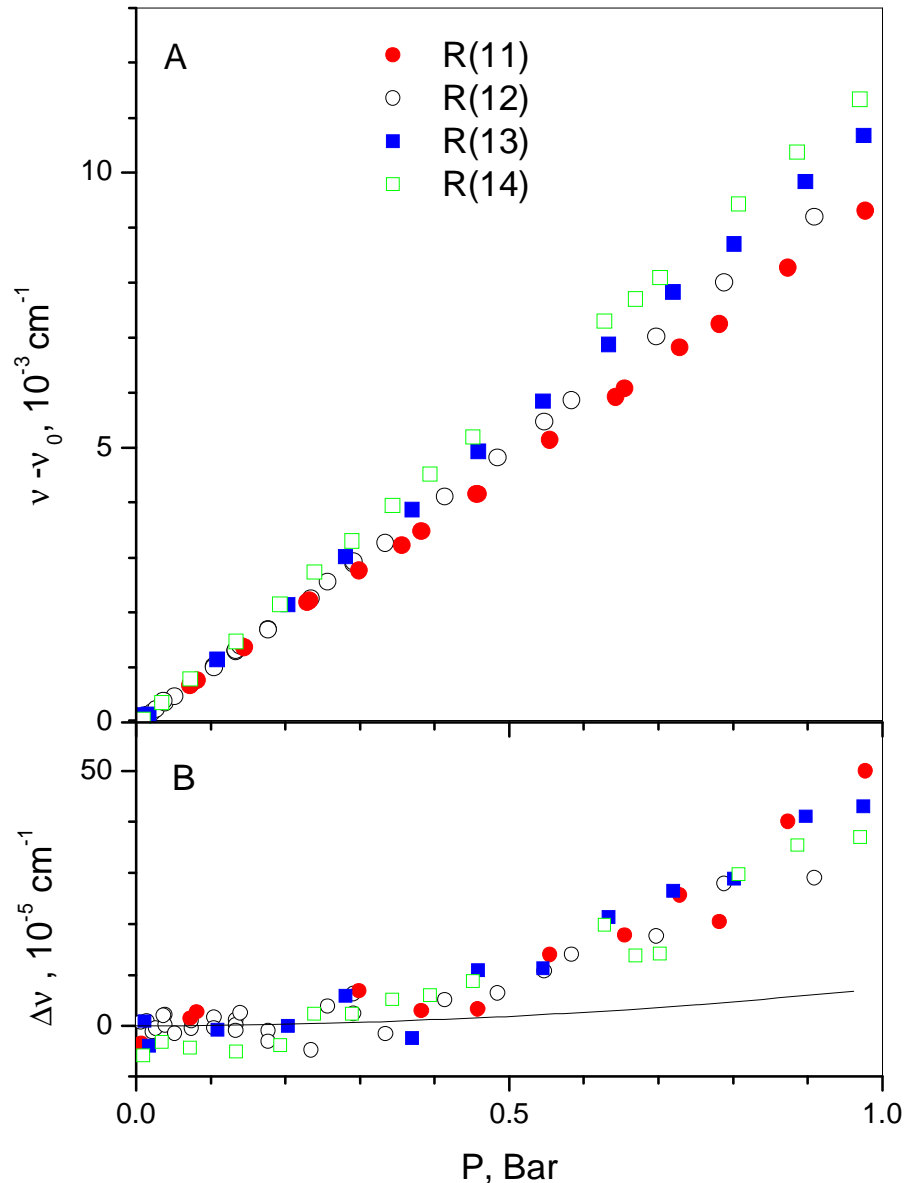
B – second virial coefficient due to two molecules interaction;

C – third virial coefficient due to three molecules interaction; ...

Pressure correction due to non-ideal gas behavior for several molecules at room temperature. Pressure correction for 1 Bar is of the order 0.1 - 1 % for different molecules.



Three molecules interaction



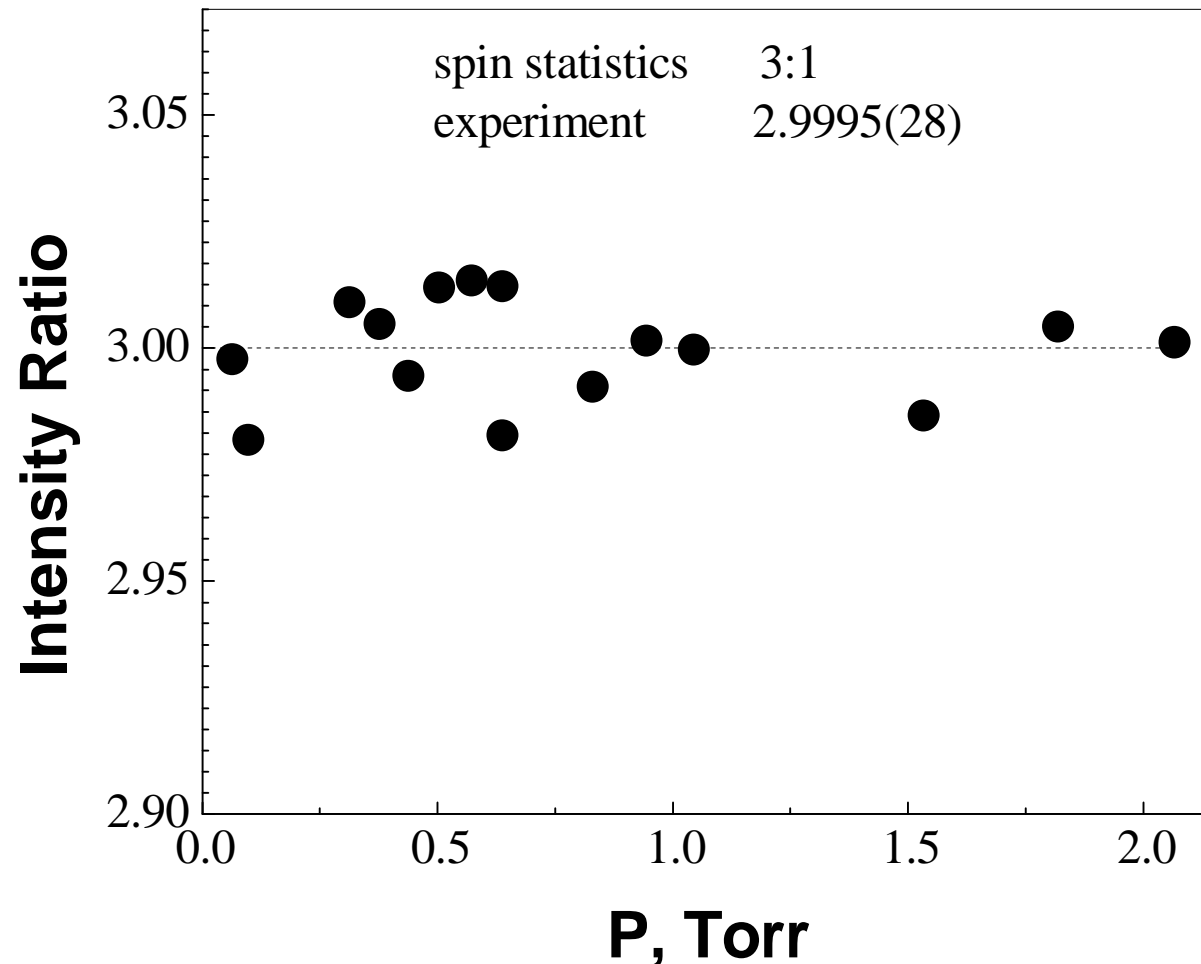
C_2H_2 lines self shift pressure dependence (A) and its non-linear behavior (B). Solid line corresponds to non-ideal molecular gas behavior due to second virial coefficient.

Line intensity non-linear pressure dependence is due to second virial coefficient due to two molecules interaction.

Line broadening and shift are determined by two molecules collisions.

Origin of their non-linear behavior with pressure is due to three molecules collision.

Line intensity with accuracy 10^{-3}



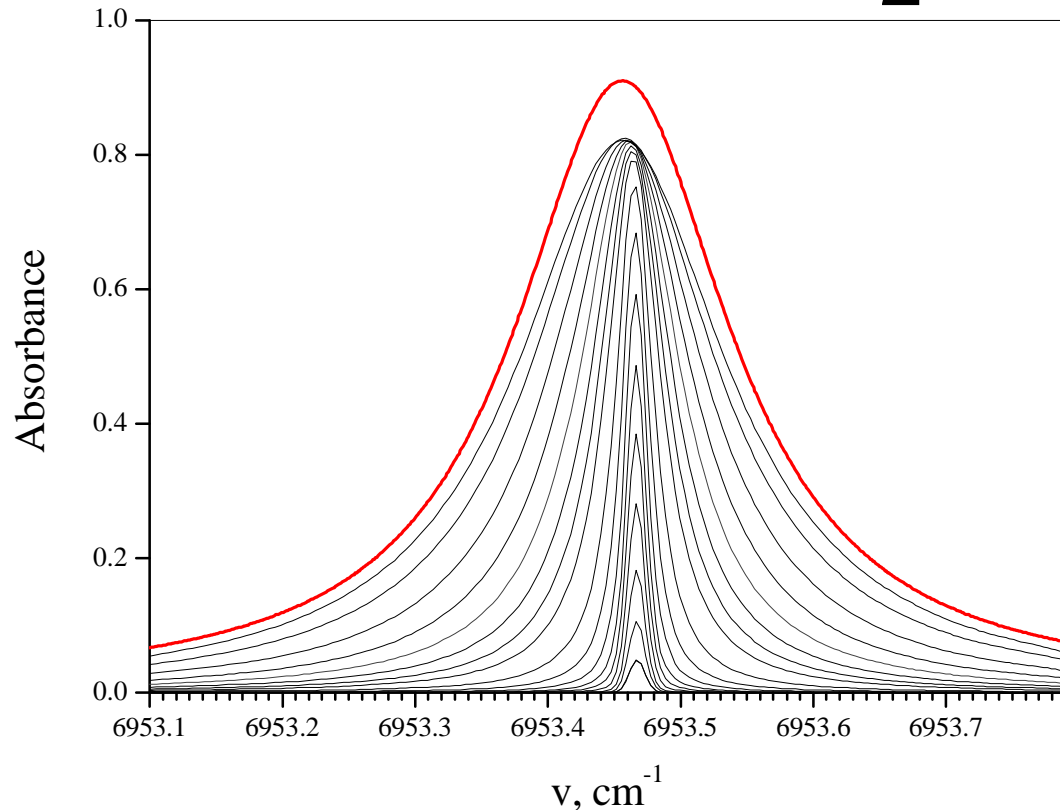
Intensity ratio of water vapor doublet with closely spaced orto-para lines as function of water pressure - P.

Such lines can be considered as standard for molecular lines intensity measurements. Due to spin statistics their ratio in equilibrium has to be 3:1.

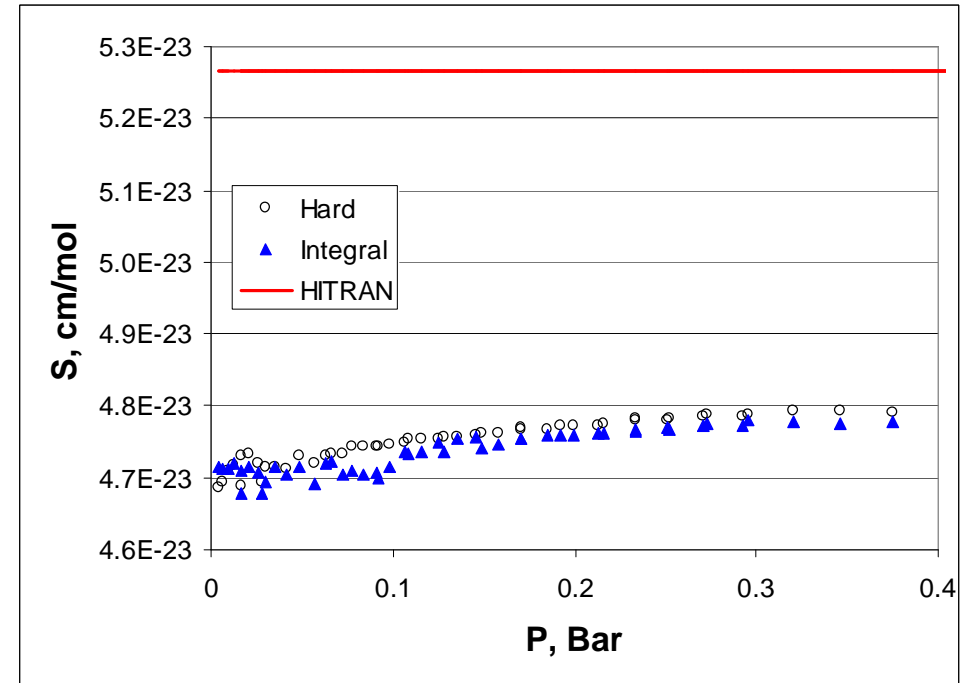
When all error mechanisms mentioned above were identified, investigated, and suppressed required accuracy can be achieved.

Presented picture demonstrates possibility of accuracy 10^{-3} achievement for spectral line intensity measurements.

0.2 % CO₂ measurement



Black - CO₂ line shapes (different P, L=2 m)
Red - HITRAN (P = 0.987 Bar, L = 2 m)



Pressure dependence of line intensity.
Black – Hard collision model fitting
Blue – direct line shape integration
Red – HITRAN

0.2 % accuracy of line intensity measurement was demonstrated.
HITRAN (1-2 % declared accuracy) has error 10 % and needs correction.

Conclusion

Several error mechanisms of accurate measurements in TDLS were considered:

- Bouguer law correction due to rest gas influence on DL radiation interaction with molecule under investigation.
- Weak lines of hot bands, isotopomers, and atmosphere molecules presence.
- Line shape model using in fitting.
- Spectral lines mixing effect.
- Presence of spontaneous emission.
- DL emission spectrum.
- Baseline.
- Molecular gas non-ideal behavior.

When all error mechanisms mentioned above were identified, investigated, and suppressed, required accuracy can be achieved.

Possibility to achieve 10^{-3} accuracy for spectral line intensity measurements in TDLS was demonstrated.
Based on achieved accuracy and analysis performed, TDLS can be considered as high accurate primary standard for gas mixtures.