

# TDLS accuracy analysis



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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 of 0.1 % or even better.

1. High measurement accuracy provides possibility to discover and investigate new physical phenomena.
2. High accurate determination of molecules spectral line parameters provides possibility of high accurate molecular absorbance modelling.
3. Some TDLS analytical applications ( $\text{UF}_6$  enrichment, gas mixture standards, green house molecules measurement, etc.) require accuracy at 0.1 – 0.01 % level.

At this accuracy level several fundamental physical laws as well as error mechanisms have to be considered – subject of the present paper.

# Absorption law

TDLS is based on absorption law. There are several names related to this 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). Between them there is one page where he used differential equation for Bouguer law. Now inhomogeneous absorbing media can be considered. A.Beer (1852) extended the exponential absorption law for solutions: linear relationship between absorbance and concentration of an absorber. **For molecular spectroscopy Beer law is not valid.** For present accuracy level, correct absorption law has to be used based on Maxwell equations solution. Correct absorption law for homogeneous absorbing media:

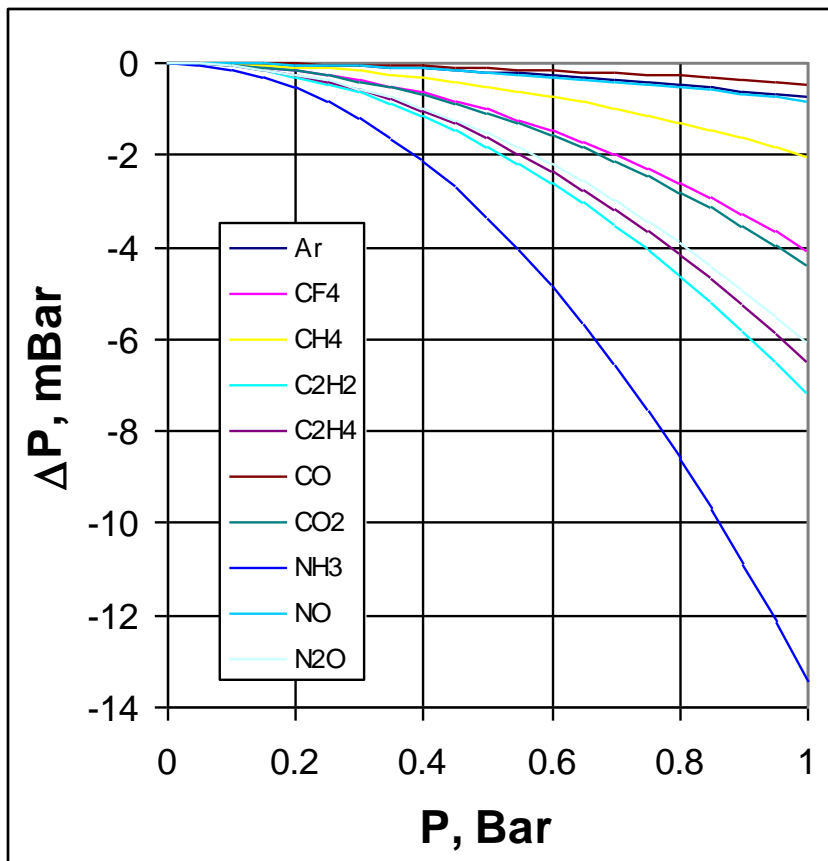
$$W_L(\nu) = W_0(\nu) \exp \left[ - \frac{\sigma(\nu)NL}{\sqrt{1 + 4\pi\chi N}} \right]$$

Absorbance is determined by molecules number density – N, optical length – L, and absorption cross section  $\sigma(\nu)$ . Denominator describes rest gas polarization influence on DL radiation absorption by particular molecule ( $\chi$  is molecular polarizability). The dependence is not linear. Correction for methane is 0.05 % for 1 Bar.

# Real gas

Due to absorption law, absorbance is proportional to molecules number density  $N$  (see above). Pressure  $P$  is measuring in experiment.

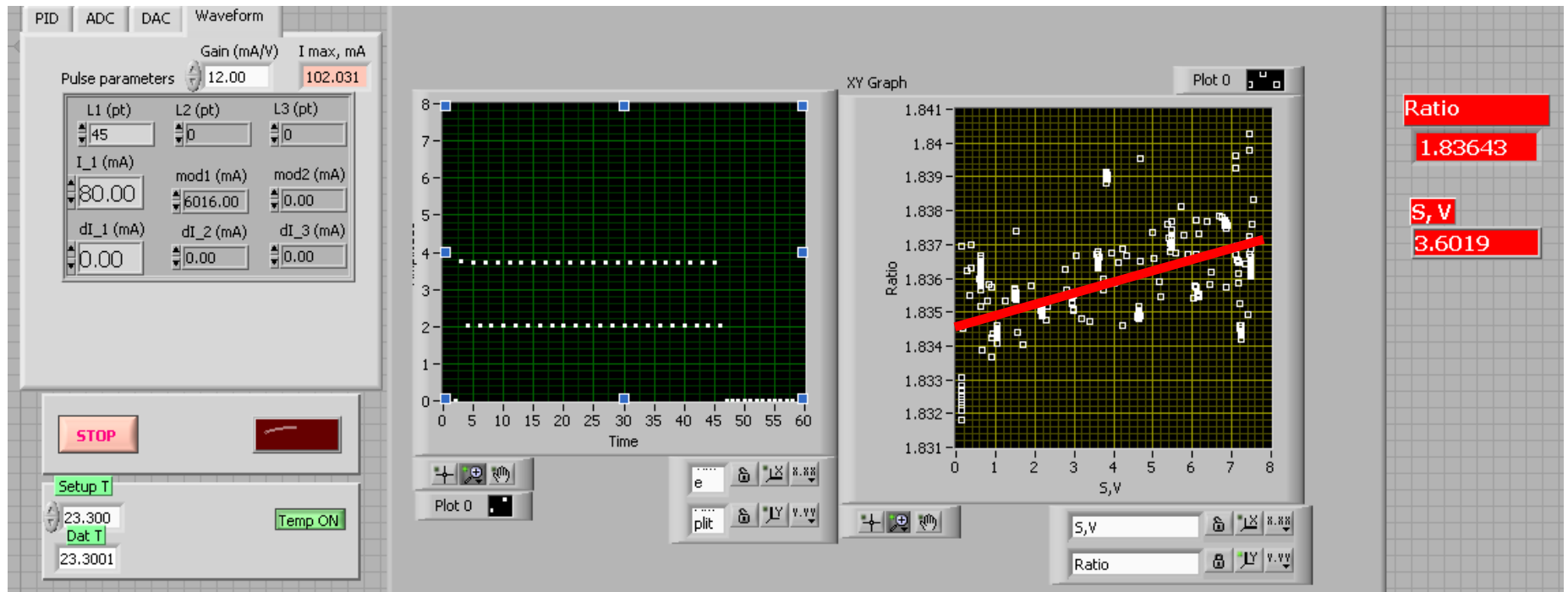
Real gas law ( $B$  – second virial coefficient)  $P = RTN[1 + BN + \dots]$



For real gas, pressure has not linear dependence on molecules number density as for ideal gas. For different molecules correction is of the order of 0.1 – 1 % for 1 Bar. This correction has to be taken into account for high accurate measurements in TDLS.

# PD + preamplifier

To record correct absorbance PD + preamplifier response has to be linear.



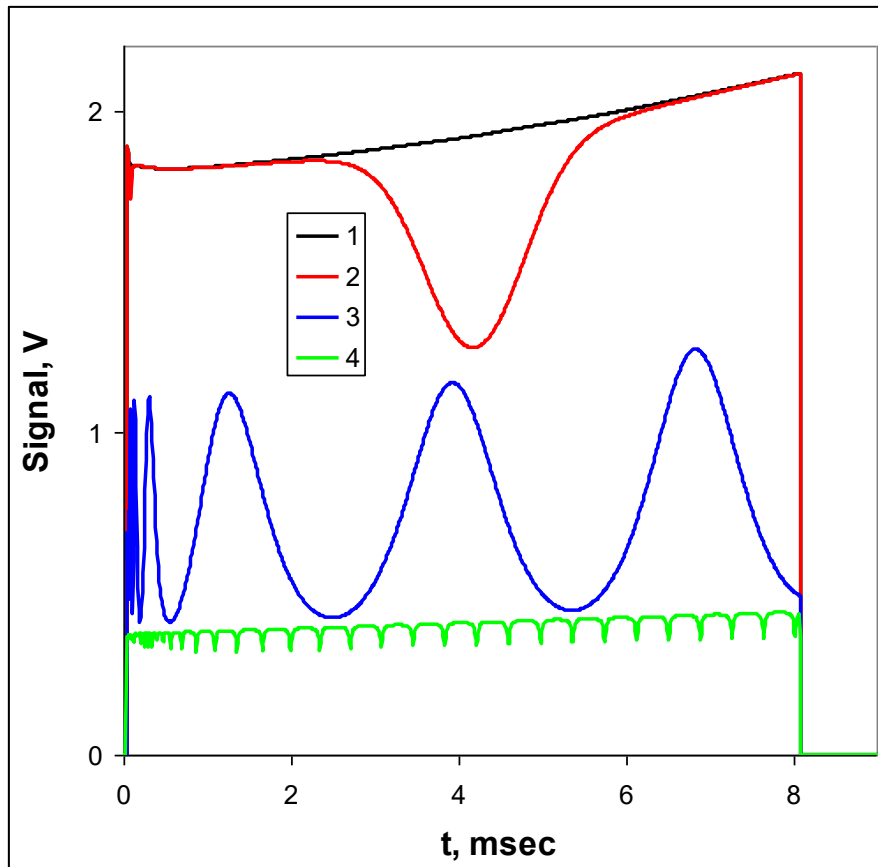
Interface of PD + preamplifier linearity investigation.

Linearity investigation of one of PD + preamplifier in use ( $R = 5.1 \text{ k}\Omega$ ). Observed nonlinearity is 0.15 % for photocurrent 1.6 mA.

To reduce PD + preamplifier nonlinearity smaller photocurrent has to be used.

# Present TDLS operation mode

Next player in the game is Diode Laser. TDLS accuracy is determined by several DL properties: accurate measurement of DL frequency tuning, presence of DL spontaneous emission, DL intensity and frequency quantum noises, DL Spectrum..



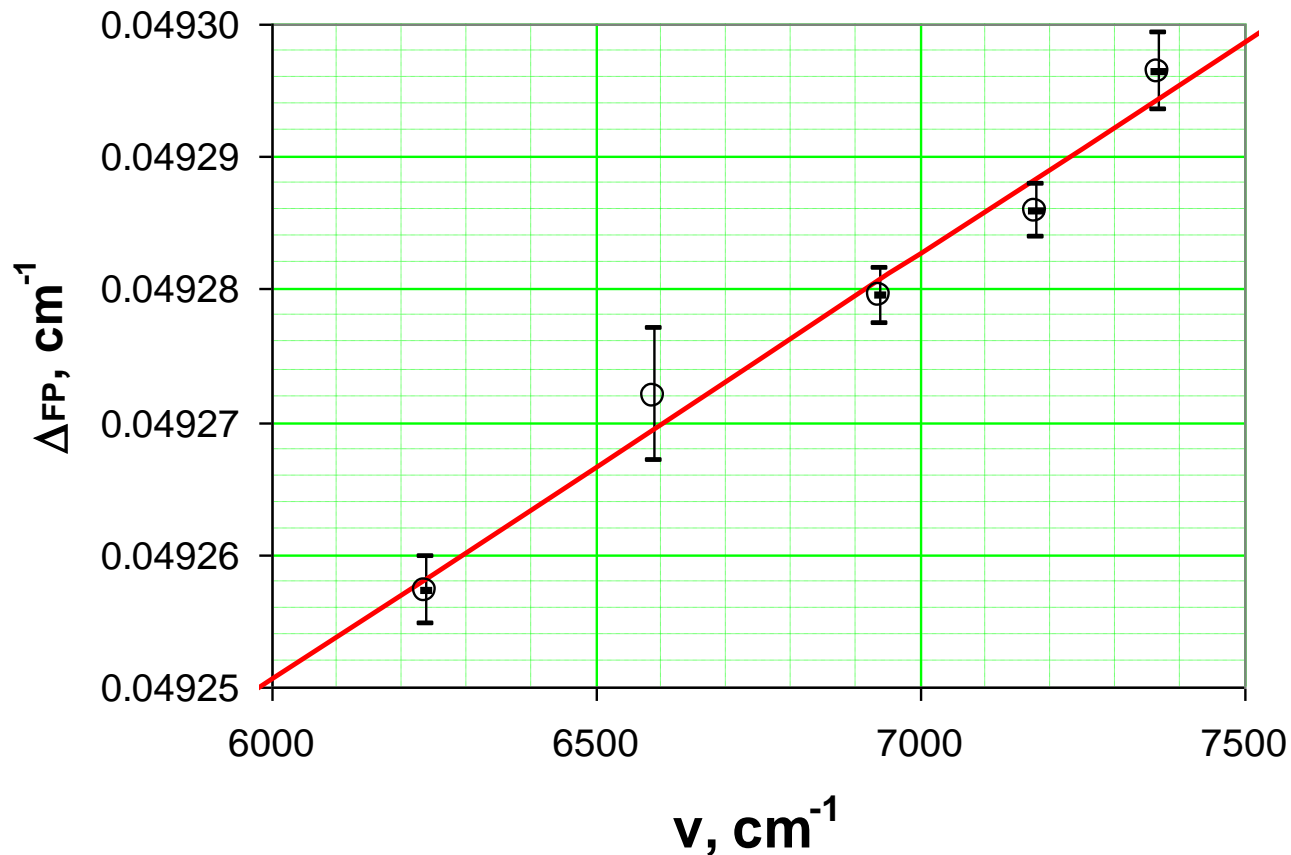
DL was excited by periodic trapezoidal excitation current pulses. At the moment 4 signals are recorded.

1, 2 – signals without and with molecular absorption. These signals are using to obtain absorbance.

3, 4 – Transmission spectra of FP etalon and fiber interferometer. These signals are using for DL frequency tuning calibration.

Recording and processing of all signals have to be done with highest possible accuracy.

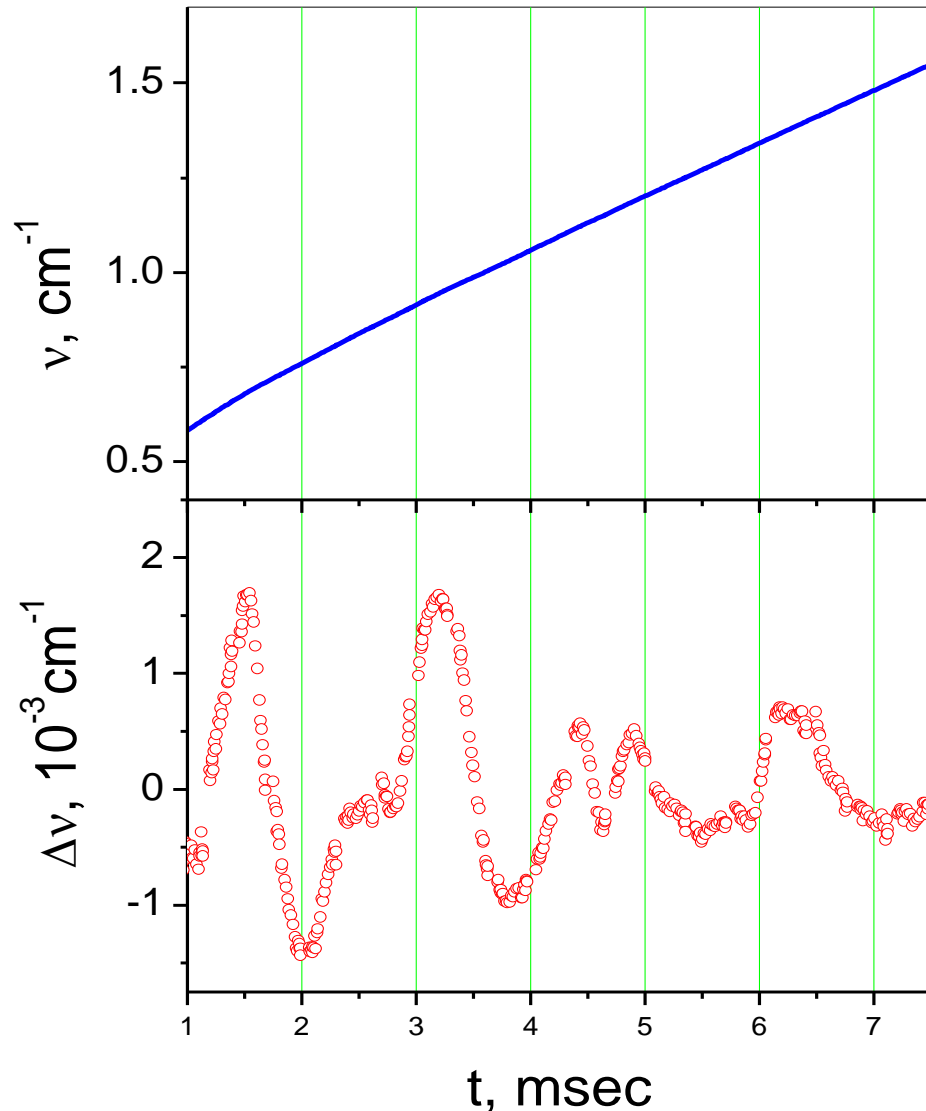
# DL frequency scale calibration



To calibrate DL frequency tuning, FP etalons are using. Spectral dependence of free spectral range of one FP etalon (fused silica) in use.

**Conclusion: for high accurate measurements each FP etalon, using to determine DL frequency tuning, has to be calibrated and spectral dependence of its free spectral range has to be taken into account.**

# DL frequency tuning fine structure



DL frequency tuning due to trapezoidal excitation current pulse. This tuning can be described by:

$$\nu = A \ln(t) + Bt$$

$t$  – time moment when current was switched on.

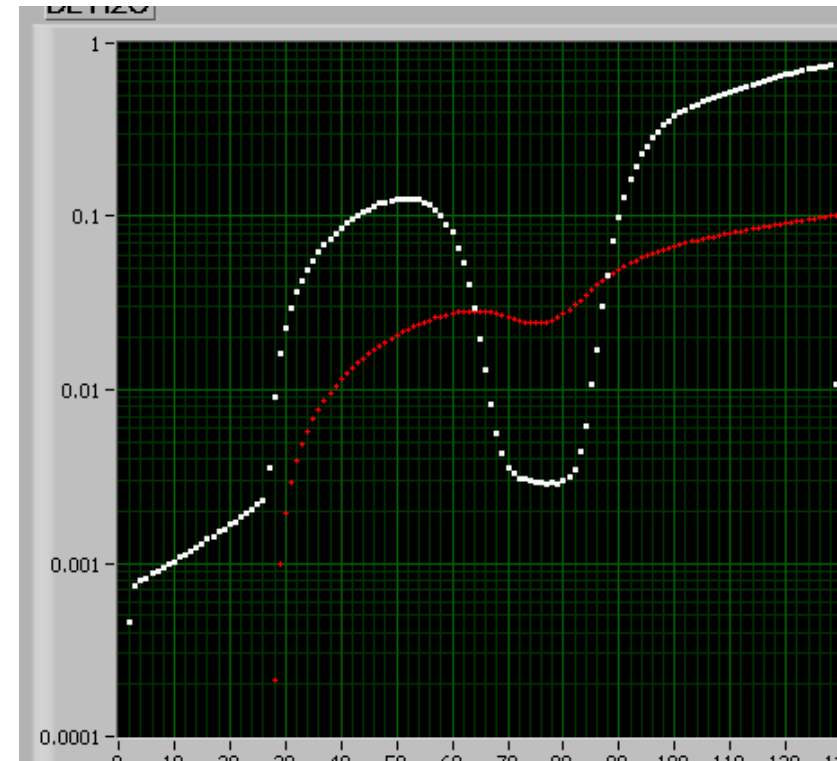
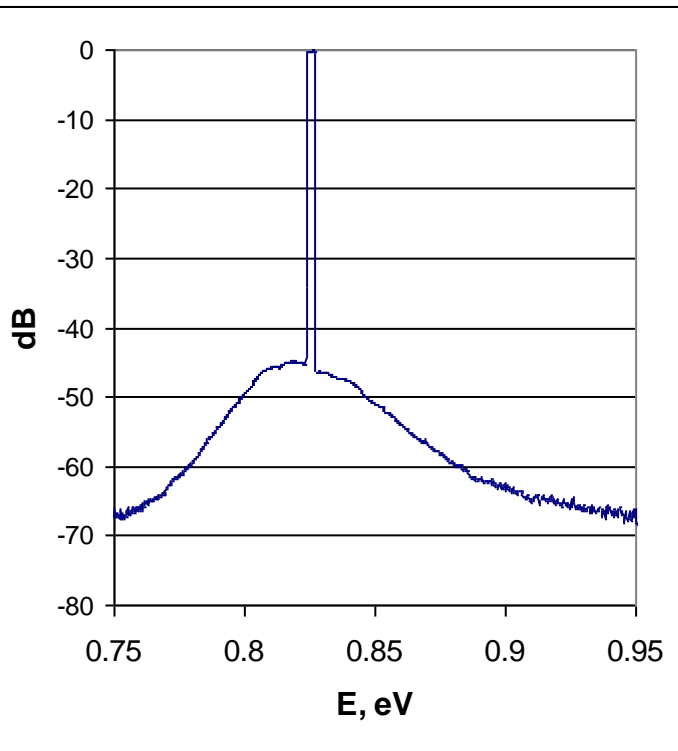
Tuning was measured using fiber interferometer ( $0.006495 \text{ cm}^{-1}$ ). Difference between experiment and model considered above has fine structure. Fine structure amplitude is significant ( $\sim 10\%$  of Doppler width), and distance between peculiarities is of the order of  $0.05 \text{ cm}^{-1}$ .

**Conclusion: high accurate measurements need careful frequency tuning calibration.**



# DL – spontaneous emission

DL spectrum consists of two components (left): coherent and broad one (spontaneous emission). Spontaneous emission presence leads to “Optical Zero” problem – presence of transmitted light even for saturated lines (right).



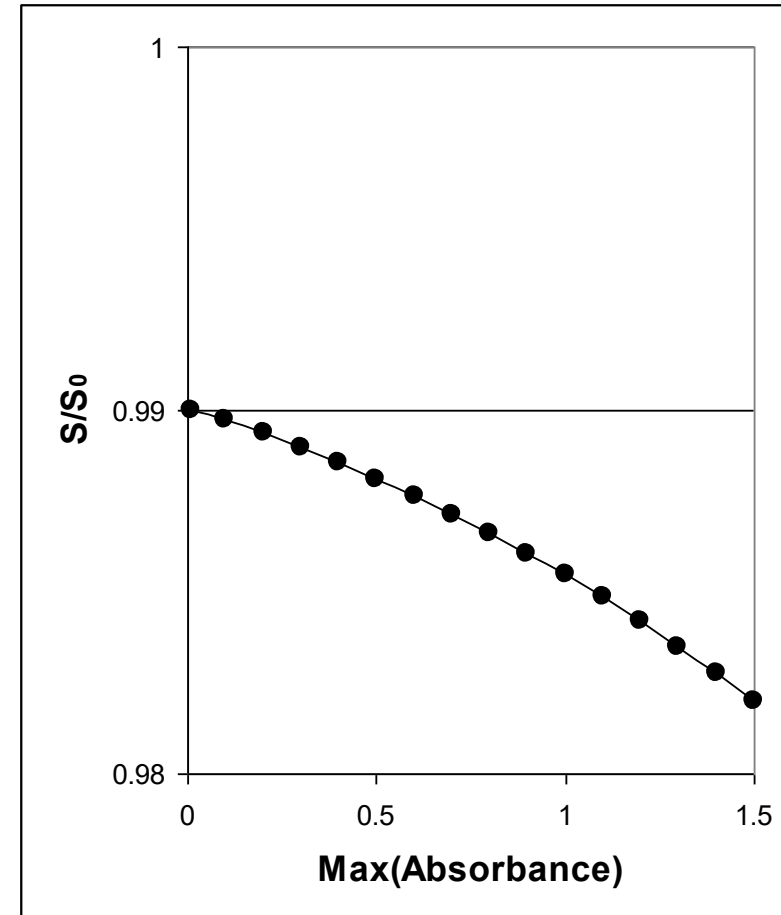
For present DLs “Optical Zero” is of the order of 0.1 - 1 %.

# “Optical Zero” modeling

Direct modeling for “Optical Zero” = 0.01.  
Relative error of S - line integral intensity  
as function of absorbance in line center.

**Relative error of S - line integral  
intensity is 1 - 2 of “Optical Zero” value.  
For data presented in previous slide it  
is 0.3 – 0.6 %.**

**Influence of DL spontaneous emission  
can be significantly reduced by using  
narrow spectral filter (monochromator).**



# Quantum noises of DL emission

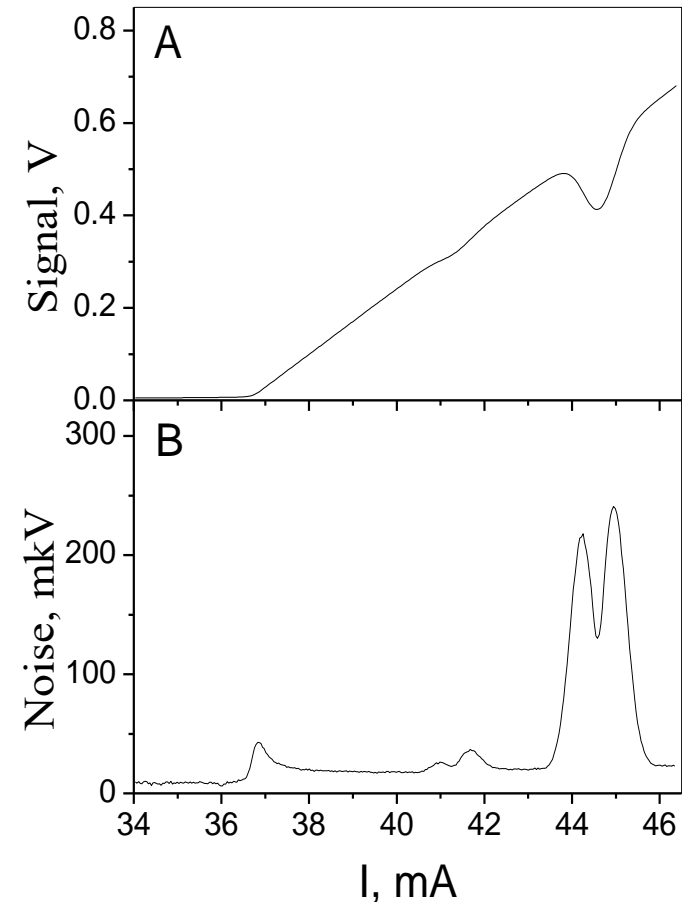
Presence of quantum noise leads to frequency and intensity noises of DL emission.

$$\langle K(\nu, t) \rangle = K(\nu) + \left\{ \frac{1}{2} \left( \frac{\partial K(\nu)}{\partial \nu} \right)^2 \langle \Delta \nu(t)^2 \rangle - \frac{\partial K(\nu)}{S_0 \partial \nu} \langle \Delta S(t) \Delta \nu(t) \rangle \right\}$$

Signal with lines of low pressure water vapor (A) and its noise (B) as function of excitation current near threshold.

DL frequency quantum noise leads to additional line broadening.

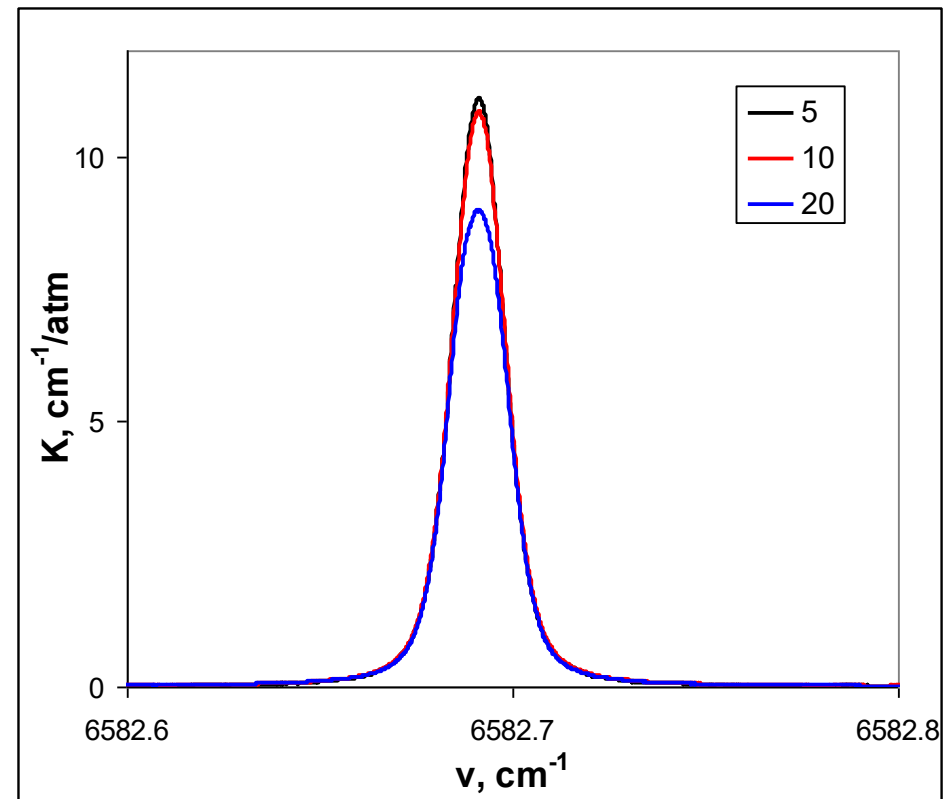
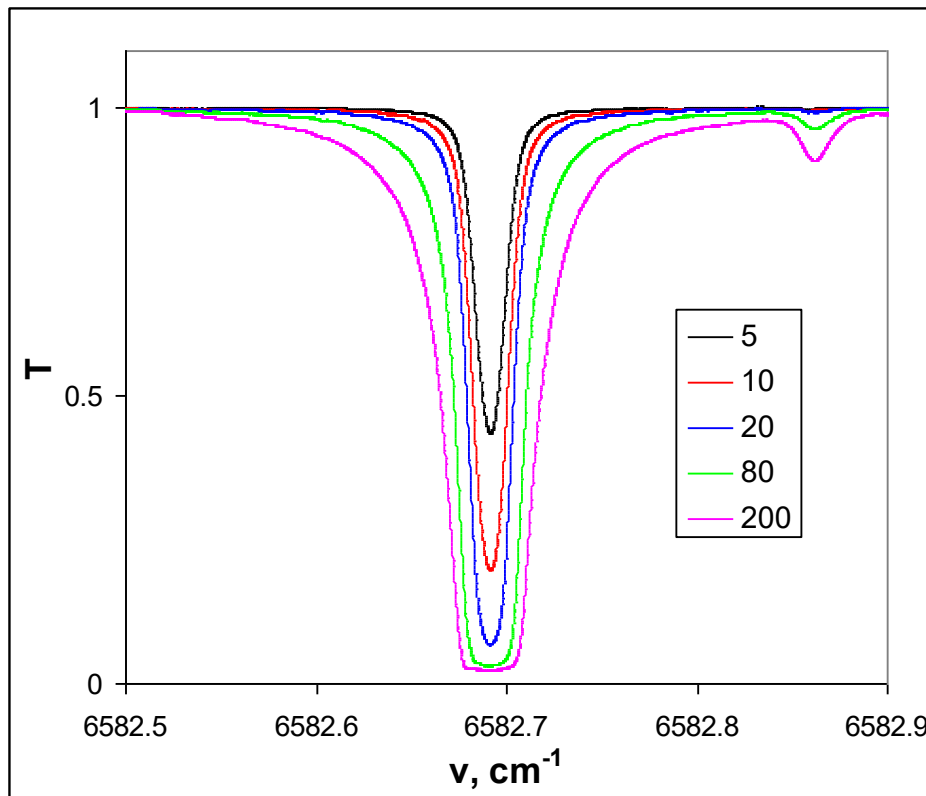
Intensity and frequency noises correlation results in line asymmetry.



# DL spectrum

Spontaneous emission was removed by monochromator.

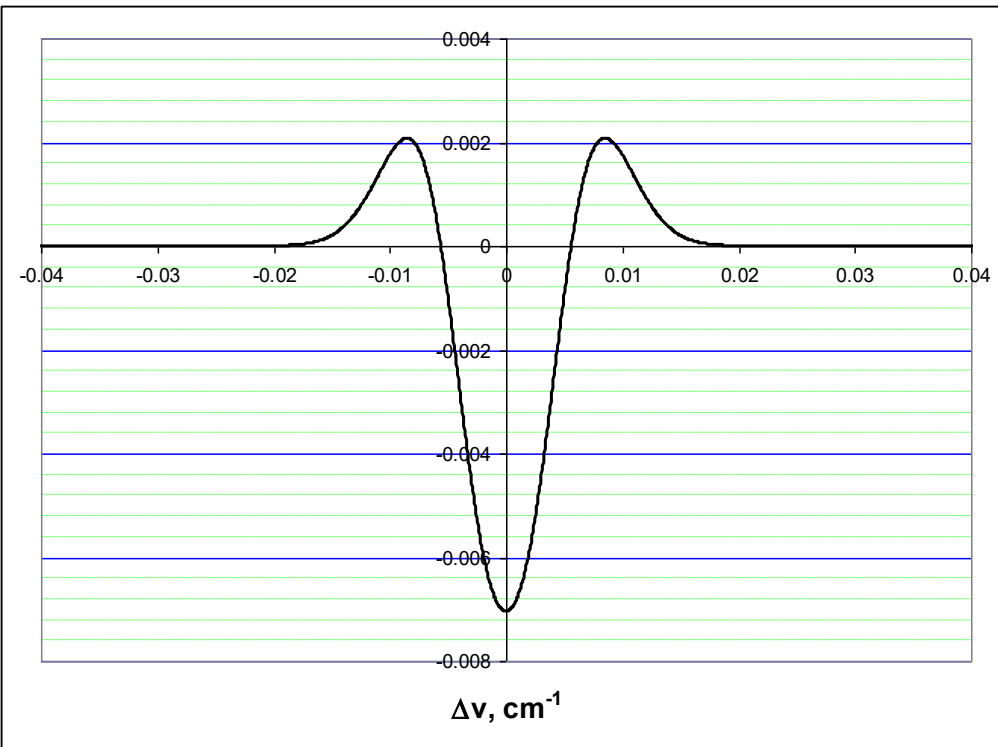
Recorded signal in TDLS is convolution of transmission and DL spectra. For absorbance the procedure is non linear resulting in line shape distortion.



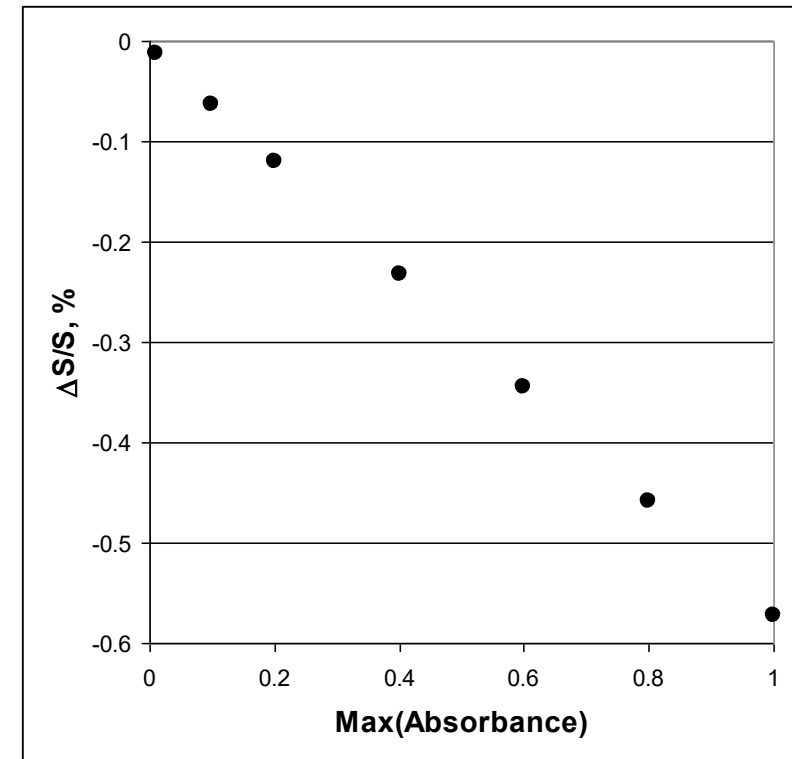
Connected gas cells with difference lengths (L = 5, 10, 20, 80, 200 cm) were filled with the same sample of pure C<sub>2</sub>H<sub>2</sub> (P = 15.20 mBar). Spectra of transmission (left) and absorption coefficient (right) obtained. Significant "Optical Zero" and line shape distortion can be observed.

# DL spectrum – modeling

Direct modeling for Doppler line. Transmission spectrum was convoluted with DL spectrum ( $WHH_{DL} = 4.92$  MHz). Absorbance was calculated and fitted by hard model.



Residual for line having maximum absorbance = 1.

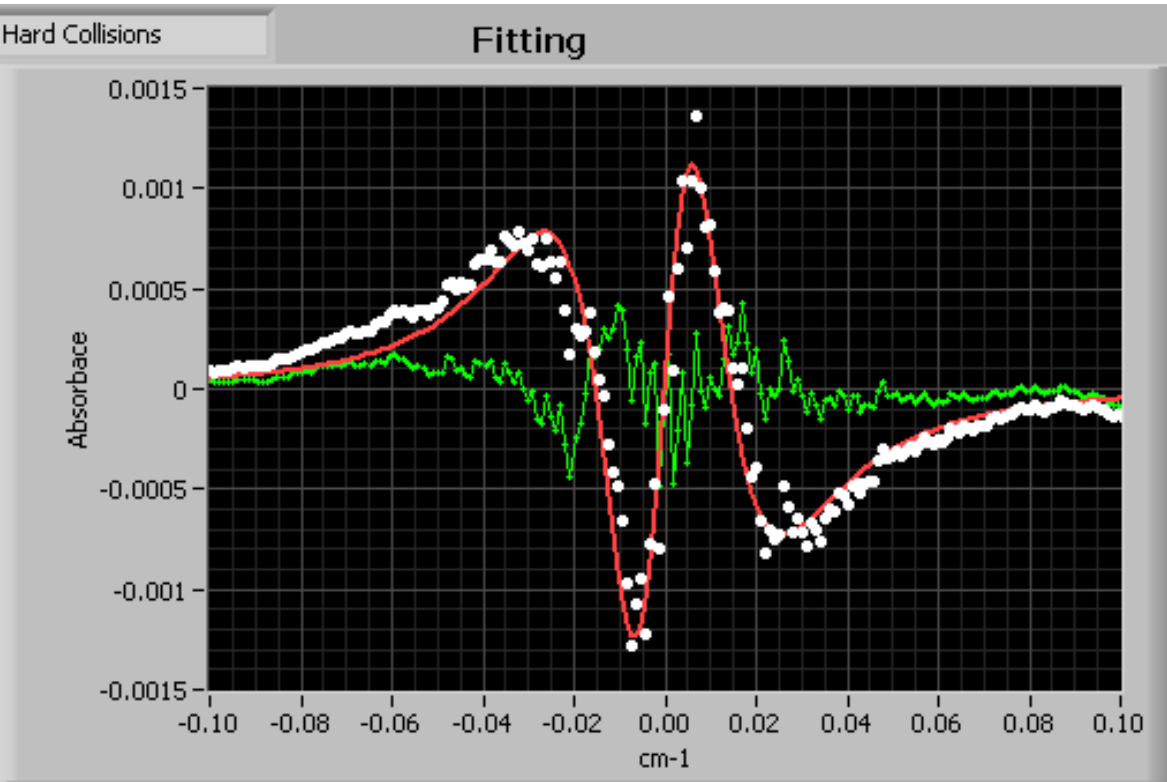


Relative error of S – line integral intensity as function of absorbance in line center.

**To achieve accuracy below 0.1 %, absorbance in line center has to be smaller than 0.1.**

# Fitting

Experimental data were fitted using software described in B1.



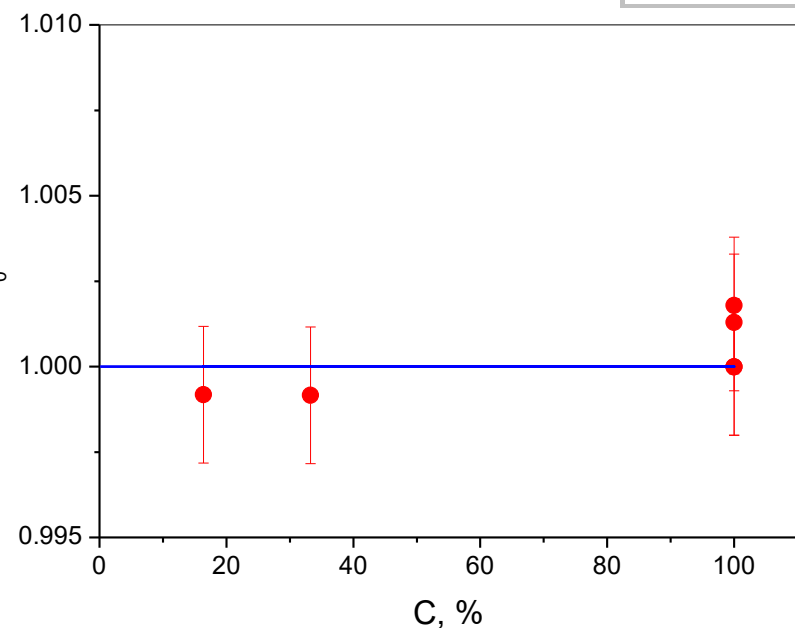
White circles – CO<sub>2</sub> line residual for 171.4 mBar normalized to line maximum demonstrating spectral line asymmetry. To measure asymmetry, empirical model function was developed. Using this function asymmetry can be fitted (red curve). For details see B2.

Final residual (green) is at level of 0.04 % of line maximum. It is measure of present experiment precision.

# Accuracy estimation

Results presented above were used to estimate accuracy of measurements – 0.13 %.

	Value	Error	Error %
L, cm	99.95	0.05	0.05
T, °C	20 - 25	0.1	0.03
P, mBar	0 - 100	0.07	0.07
CO <sub>2</sub> sample purity, %	99.98	0.02	0.02
PD non-linearity			0.02
$\nu$ , 10 <sup>-3</sup> cm <sup>-1</sup>		0.03	0.04
Optical zero			0.04
Baseline			0.01
DL Spectrum, MHz	2.5		0.07
<b>Total</b>			<b>0.13</b>



To test this estimation, several calibrated CO<sub>2</sub>:N<sub>2</sub> gas mixtures were prepared and measured. Result: accuracy std obtained is 0.11 %. It is in agreement with accuracy estimation presented above.

# Conclusion

- For high accurate TDLS measurements several physical mechanisms have to be analyzed and calibrated
- Correct absorption law and real gas equation
- PD + preamplifier linearity
- DL emission properties
- Based on calibrations, modeling, and analysis performed, estimation of TDLS accuracy is 0.13 %
- This estimation is in agreement with experiment of calibrated gas mixtures measurement – 0.11 %