DL SPECTROMETER FOR HIGH ACCURATE MEASUREMENTS

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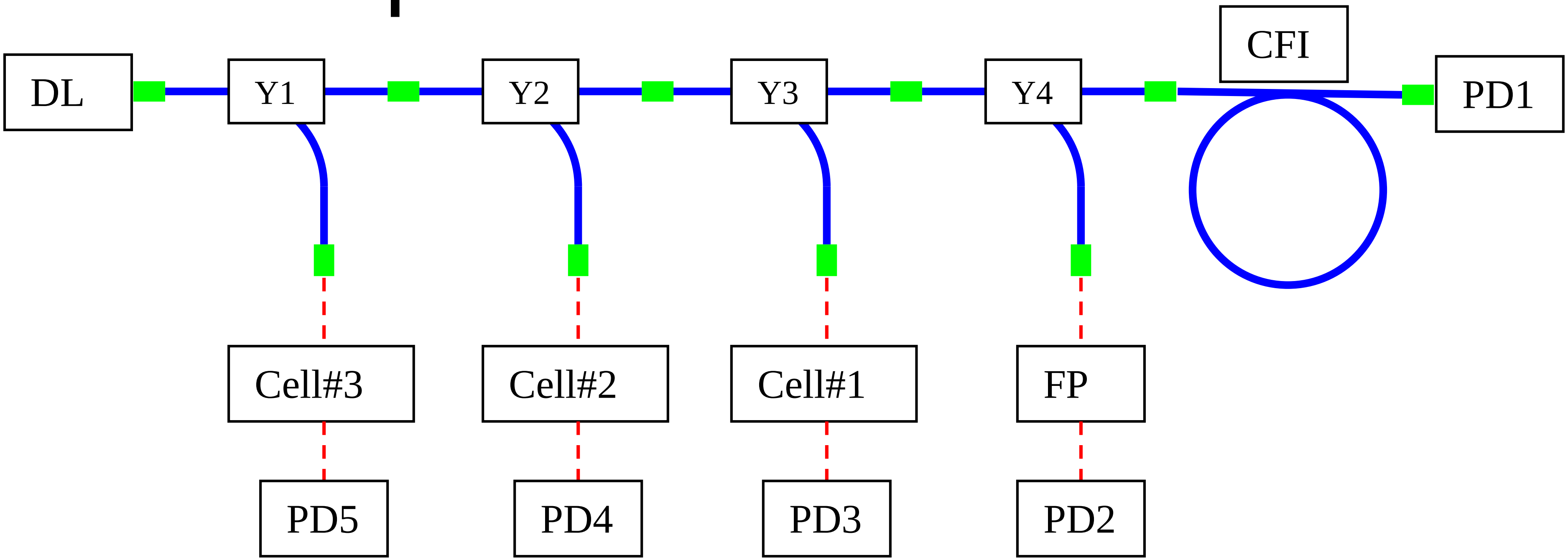
1. Abstract

Diode Laser (DL) spectrometer for high accurate measurements was developed. DL radiation using fiber optics was split in 5 beams. These beams pass five optical channels and are recorded by five Photodiodes (InGaAs). Optical channels contain: calibrated FP etalon, circle fiber interferometer, reference cell (L = 183.42(8) cm), analytical cell (L = 183.50(4) cm), and multipass cell (L = 1519(1) cm). The spectrometer reconfiguration for different experimental tasks is doing by the spectrometer operation program (no changes in optics). This provides very stable and reproducible signals of the spectrometer operation.
To pump cells we are using Turbo pumping station HiCube 80 Eco (10^{-7} mBar). To measure gas pressure, 3 pressure sensors are used: EDWARDS WRG (Wide range Gauge) (10^{-9} мБар – 1000 мБар), EDWARDS ASG (Active Strain Gauge) (0 – 1000 mBar), and Setra model 764 (0 – 1000 Torr). To measure cells temperature 3 thermo resistors are using for each cell located in the middle and both side of the cells.
Pressure and temperature sensors were calibrated with respect to state etalons of 1 category at ROSTEST.
Diode laser frequency tuning, PD and preamplifier nonlinearity, DL spectrum influences were investigated and analyzed.
For present spectrometer spectral line integral intensity can be measured with accuracy 0.06 %.

2. DL spectrometer block scheme



DL with fiber output is in use. Blue– fibers, green – APC connectors. Four fiber Y splitters are using to direct DL radiation to five channels of the spectrometer. Channels signals are recorded by five PDs. Fiber X splitter is using to form CFI (Circle Fiber Interferometer). Several elements are installed in spectrometer channels: CFI, FP – calibrated Fabry-Perot etalon, and three gas cells. The spectrometer reconfiguration is doing by software. Hence, recorded signals are stable and reproducible.

3. Gas cells

Three gas cells are installed in the spectrometer channels.

Cell #1 (L1 = 183.42(5) cm) – reference cell filled with known gas. Its signal is using to stabilize DL frequency tuning cycles.

Cell #2 (L2 = 183.50(4) cm) – analytical cell.

Cell #3 (L3 = 1519(1) cm) – multi pass cell.

The cells lengths either were measured or determined during calibration tests.

Gas temperature in last two cells was measured by three thermo-resistors installed in the middle and both ends of the cells.

Thermo-resistors were calibrated. Temperature gradient across cells was less then 0.05 ^{o}C.

4. Temperature sensors calibration

Результаты калибровки:

1. Условия калибровки:

температура:	21,5 °C
влажность и атмосферное давление	55%, 750 мм рт.ст.

2. Калибровка проведена по методике: ГОСТ 8.279-78.

3. Применяемые эталоны: 3.1.ZMA.0018.2013, свидетельство № 45-442-0018-2013, действительно до 25.01.2015 г; 3.1.ZMA.0165.2013, свидетельство № 260-442-0165-2014, действительно до 03.03.2015 г.

Температура эталонного термометра, °C	Показания калибруемого термометра, °C
10,020	10,04
15,074	15,09
20,028	19,99
22,056	22,02
24,076	24,10
26,048	26,10
28,070	28,16
30,043	30,15
35,051	35,09
40,060	40,00

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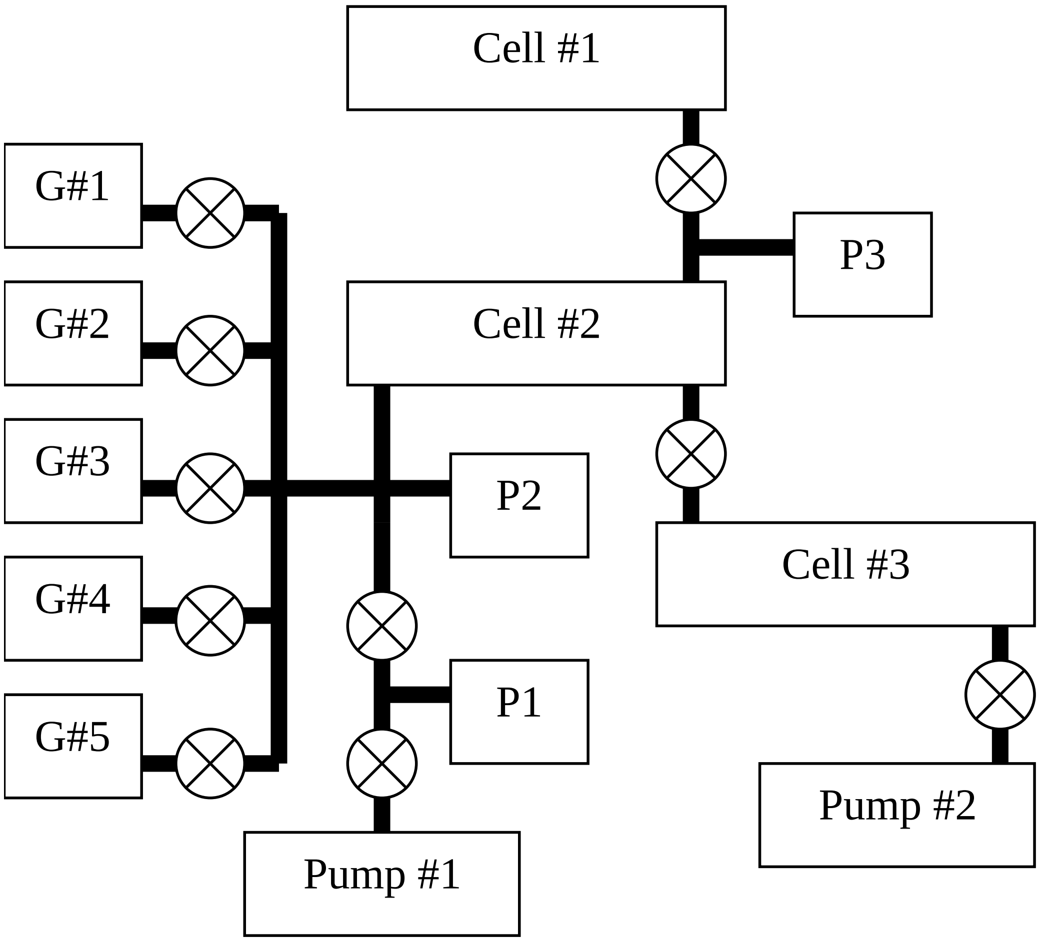
It is based on calibration in ROSTEST using GOST 8.278-78 and state temperature etalon of first category in temperature range -196 до 420°C.

Final accuracy of gas temperature measurements in the cells is 0.05 ^{o}C.

5. The spectrometer Vacuum-Gas system



To deal with gas mixtures under investigation vacuum-gas system was developed.
Pump #1 (PFEIFFER HiCube 80 Eco) can pump the system up to 10^{-7} mBar.
Pump #2 (10^{-2} – 1000 mBar) controls pressure of gas mixture under investigation.
There are five bottle (G) with pure gases and gas mixture samples.
To measure pressure, 3 sensors are using: P1 - EDWARDS WRG (10^{-9} – 1000 мБар), P2 - Setra 764 (0 – 1000 Торр), P3 - EDWARDS ASG (0 – 1000 mBar).

P1 is using to control high vacuum level achievement. P2 and P3 are using for accurate measurement of gas pressure. They were calibrated.

РЕЗУЛЬТАТЫ КАЛИБРОВКИ:

Показания эталона,		Показания калибруемого СИ, мм рт.ст. (torr)	
гПа	мм рт.ст.	при повышении давления	при понижении давления
20	15	16,7	16,7
40	30	32,0	32,2
60	45	47,1	47,0
80	60	62,4	62,5
100	75	77,4	62,5
200	150	152,5	152,6
300	225	228,1	228,3
400	300	303,4	303,2
500	375	378,5	378,5
600	450	454,2	454,4
700	525	529,5	529,4
800	600	604,9	604,8
900	675	680,2	680,4
1000	750	755,5	755,5

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6. Pressure sensors calibration

It is based on calibration in “ROSTEST” using state etalon of first category for pressures up to 700 mBar.

Calibration was performed both for pressure increasing and decreasing (hysteresis < 0.04 mBar). Final accuracy of pressure measurements is 0.02 %.

7. Control of gas sample purity

For high accurate measurements, gas samples of high purity are required. Sometimes purification of gas under investigation is necessary. Moreover, additional impurities (mainly air and water vapor) can appear during cells filling. Hence, control of gas sample under investigation is needed. It is not simple task.

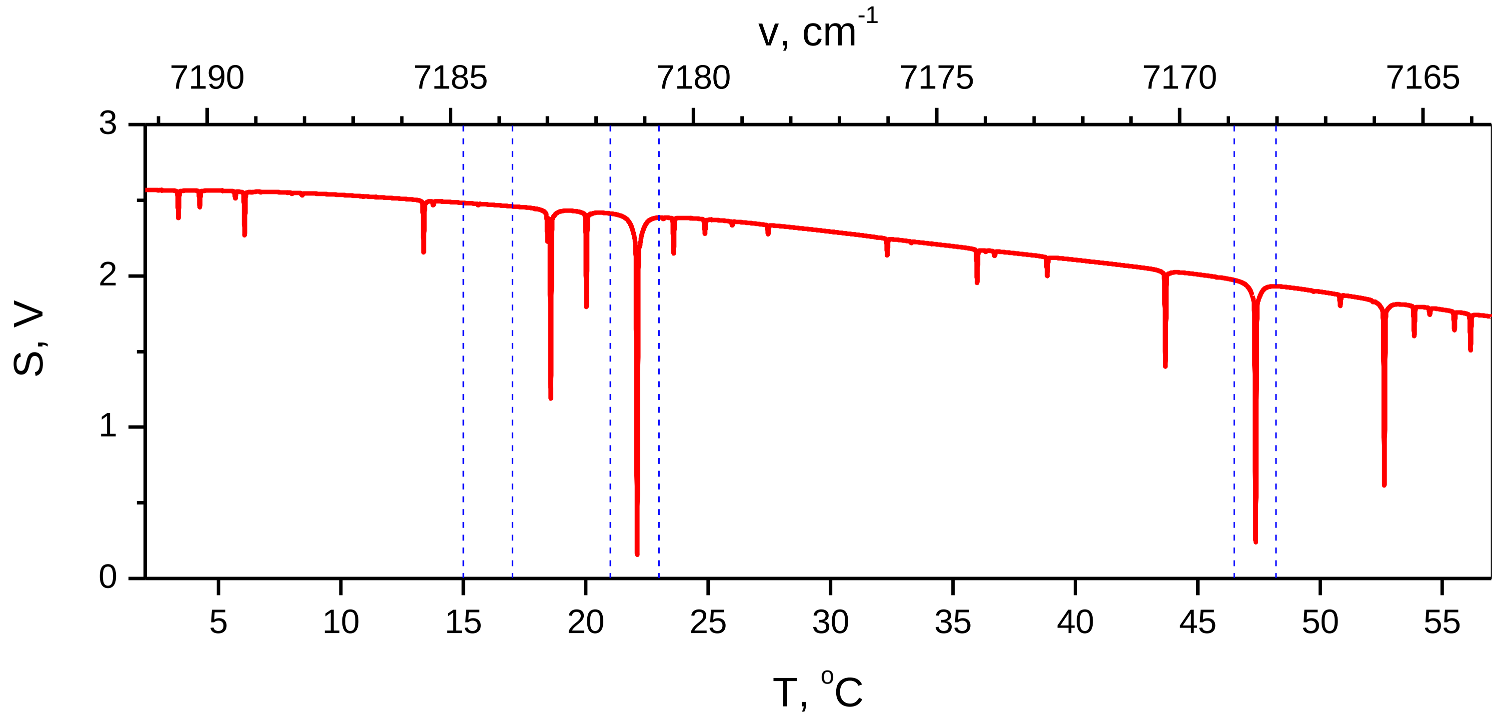
CO_2 was selected for tests of spectrometer. Boiling temperatures of CO_2, water vapor (Heavy Fraction - HF) and air (Light Fraction - LF) differ significantly and cryogenic technique can be used both for purification and filling procedures. After 7-10 iterations of gas sample freezing at LN2 temperature and its evaporation, required purity can be achieved.

The gas sample under investigation purity control is performing during experiment. LF (air) – rest pressure after the gas sample freezing at LN2 temperature. HF (H_2O) – H_2O absorption in analytical cell measured by DL.

Final gas sample purity is better than 99.98 %.

8. DL calibration

Set of spectrometer diode lasers was calibrated using temperature tuning.

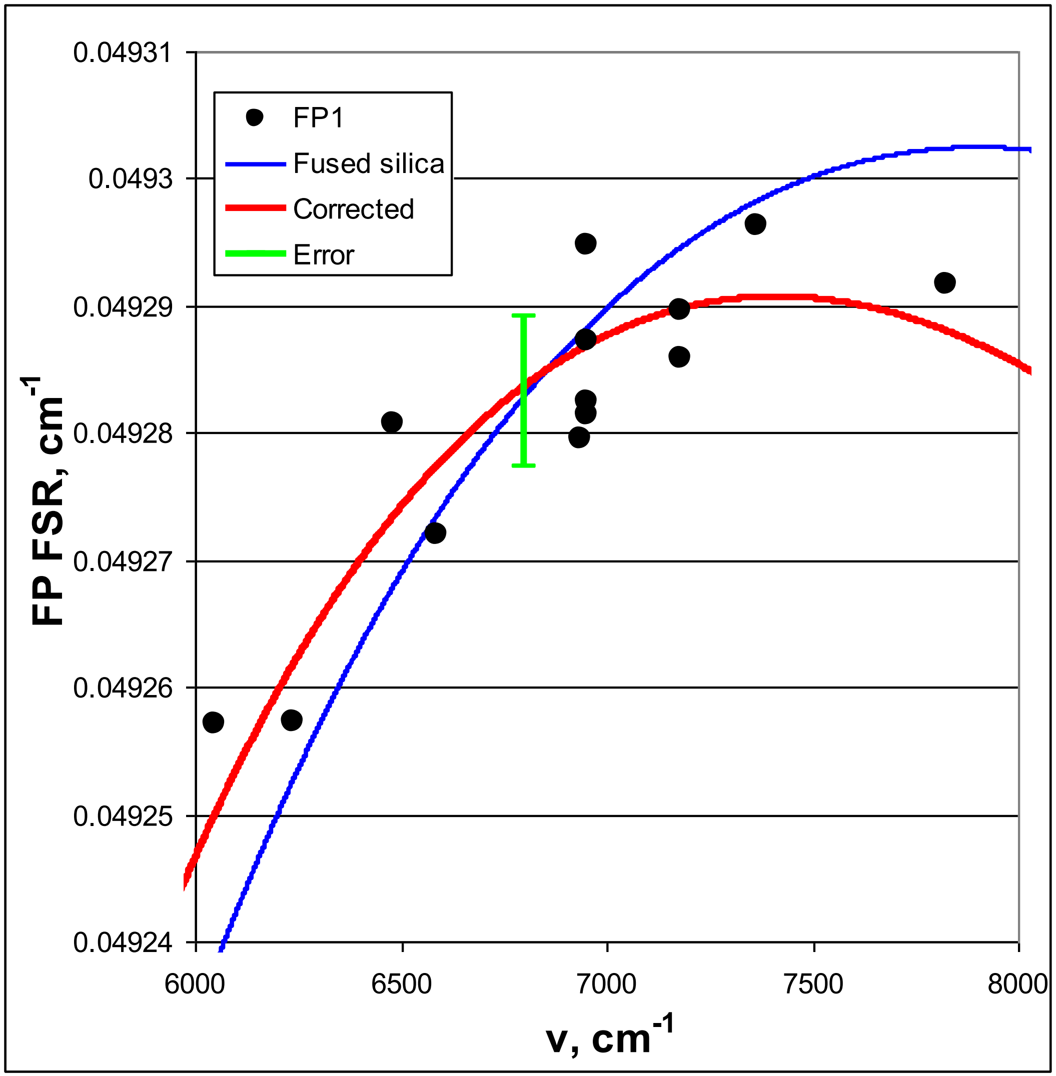


Example of DL calibration with water vapor absorption. After identification of observed lines, analytical spectral ranges can be determined as well as DL temperature to operate in these ranges.

In present case three spectral ranges (dashed vertical blue lines) were selected to investigate H_2O with this DL for different applications.

9. FP calibration

Using the DLs set available, molecular and FP spectra in different spectral ranges were recorded using DL temperature tuning (slide 8).



Observed spectral lines were identified using HITRAN and FP etalon Free Spectral Range (FSR) was determined (solid black circles).

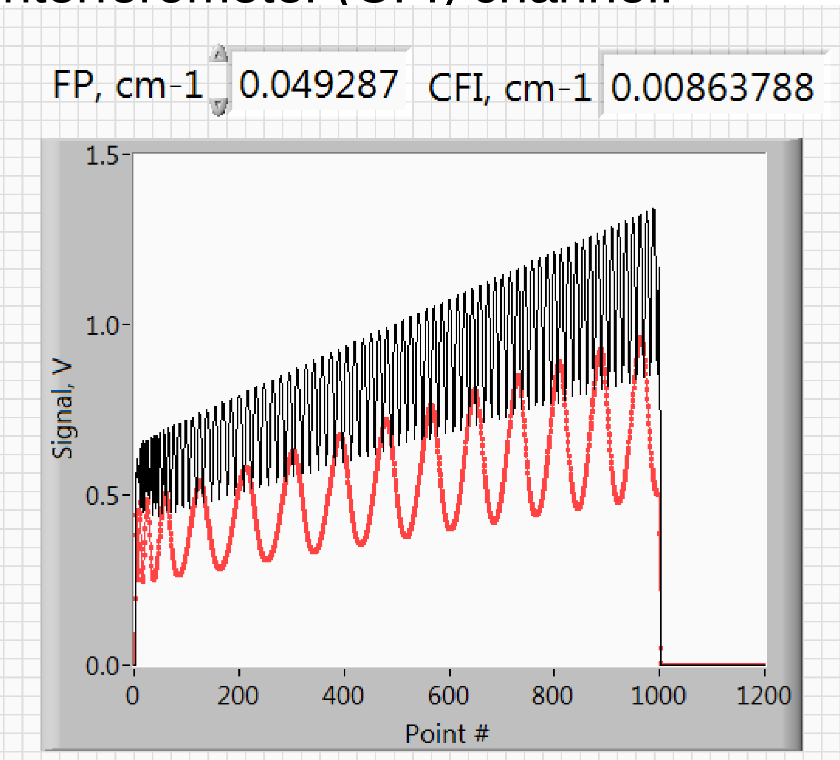
For high accurate measurements spectral dependence of FP FSR has to be taken into account.

Accuracy of FP FSR determination and DL frequency tuning is 0.012 %.

For details see B1.

10. CFI calibration

FP etalon FSR (≈ 0.05 cm^{-1}) is too large for some applications (Doppler and DL widths measurements, etc.). To fix this problem the spectrometer has Circle Fiber Interferometer (CFI) channel.

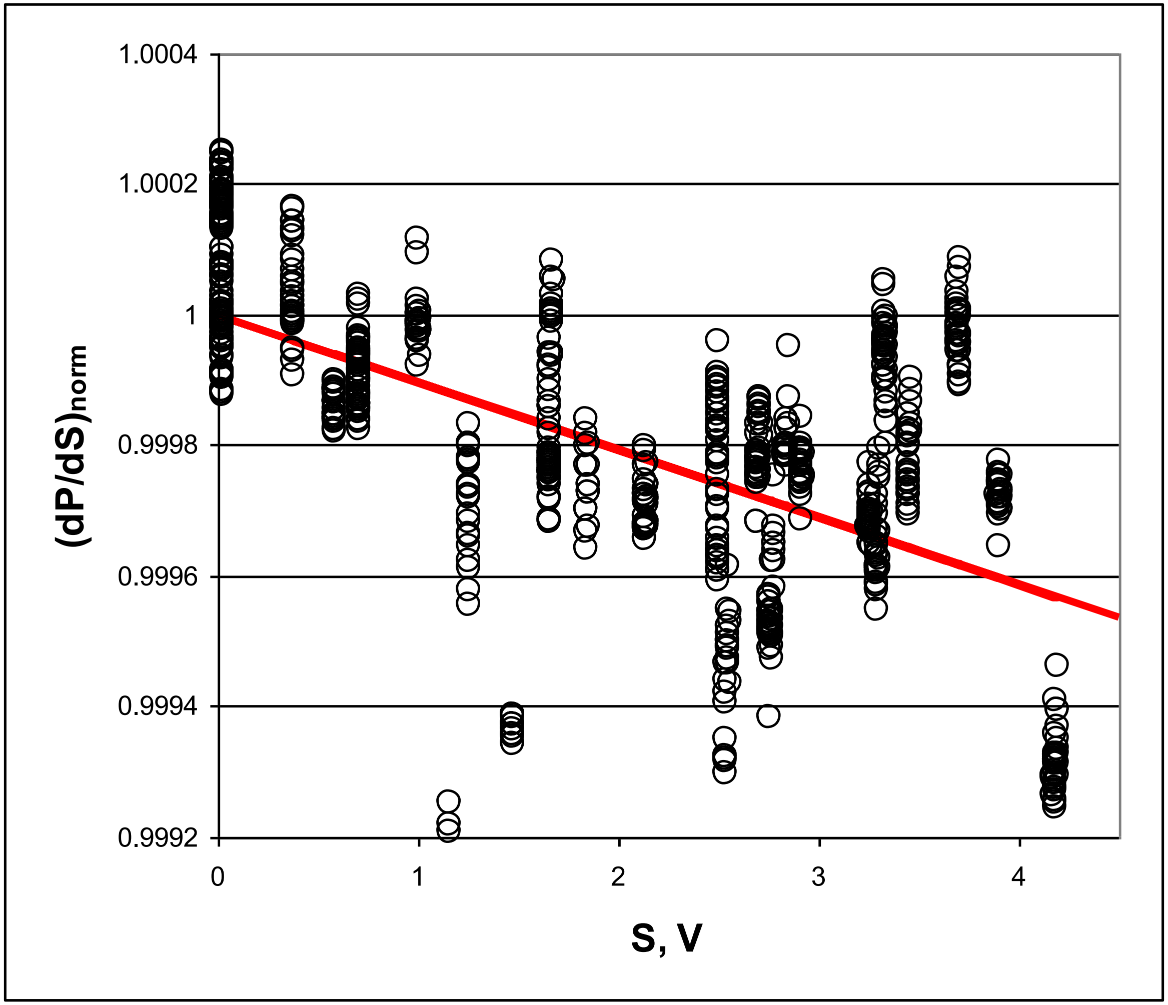


X fiber splitter was used for CFI. To form CFI, two splitter fibers were connected though 10 dB attenuator. CFI FSR (~ 0.00864 cm^{-1}) is in agreement with high resolution spectroscopy requirements.
CFI disadvantage: there are two CFI modes corresponding to two light polarizations. The modes FSR difference is 0.03 % (too much). Due to long term polarization instability, CFI needs calibration for each experiment.

CFI calibration interface. Signals from both FP (red) and CFI (black) channels are recorded simultaneously. For particular DL FP FSR can be calculated (slide 10). Calibration software developed automatically determines CFI FSR.

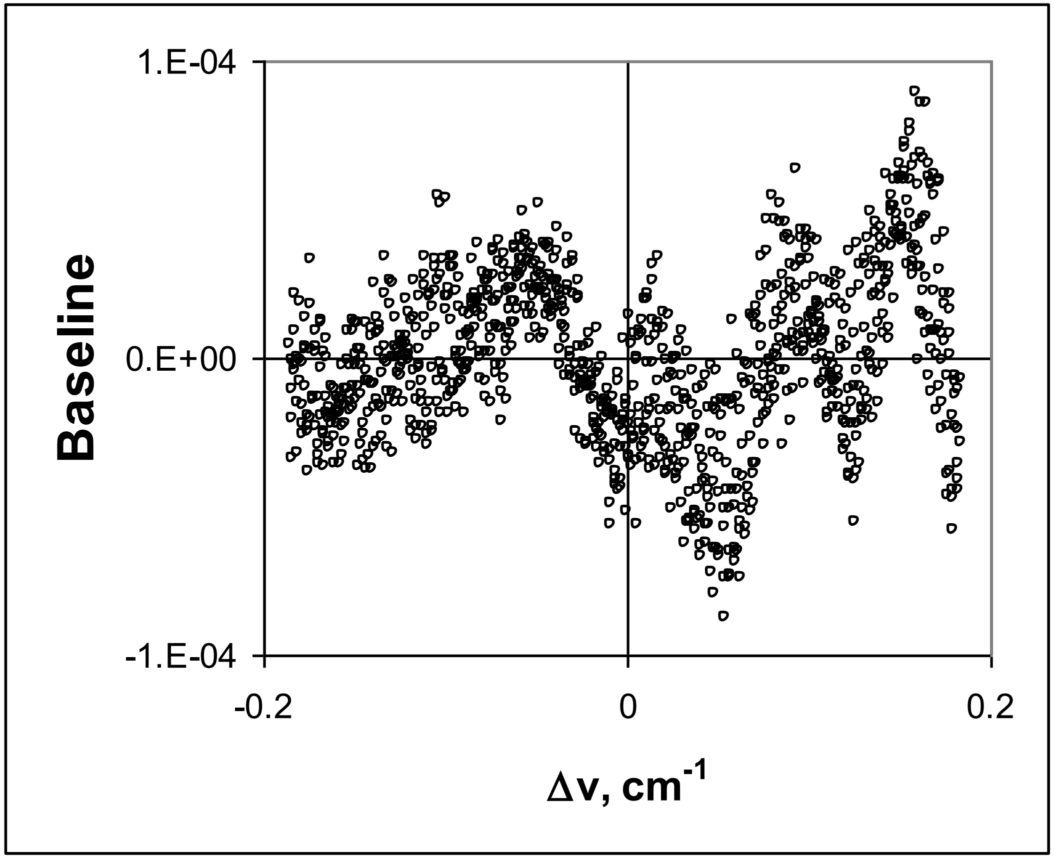
11. PD and preamplifier calibration

PD and preamplifier nonlinearity lead to recorded signal and spectra obtained disturbances.



Nonlinearity of all PD and preamplifiers of the spectrometer was calibrated. Example of nonlinearity calibration of analytical cannel PD#4 - 0.023 % (red line).

12. Baseline and DL spectrum

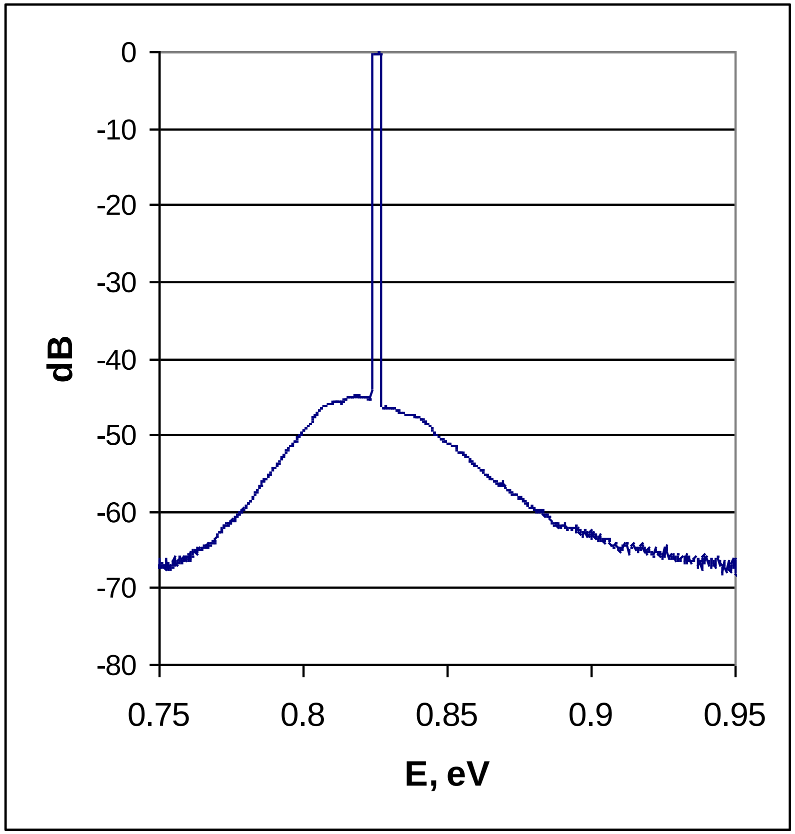


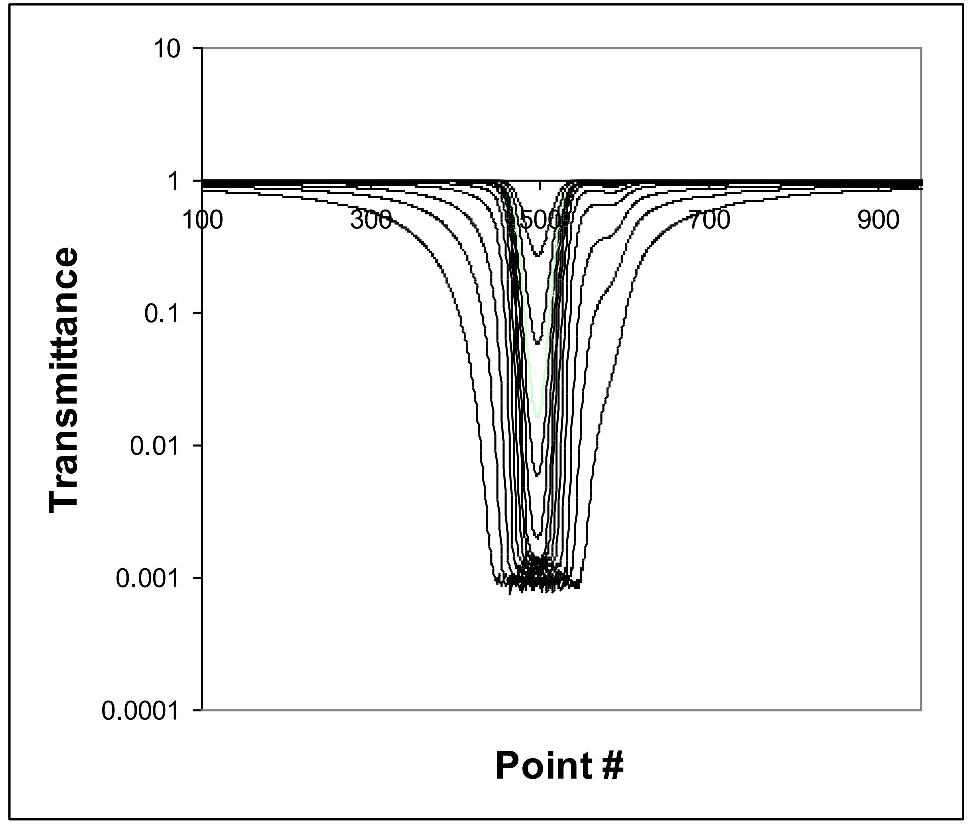
Due to present spectrometer configuration, recorded signals have long term reproducibility. Baseline is difference of empty cell absorbance for signals recorded during time of experiment (20 min).

Baseline std = 2.8 10^{-5}.

Recorded signal is convolution of real signal with DL spectrum. DL spectrum width was measured. Its influence on recorded signal was analyzed. For DL spectrum width 5 MHz error in final spectrum was found 0.014 %.

13. Optical zero

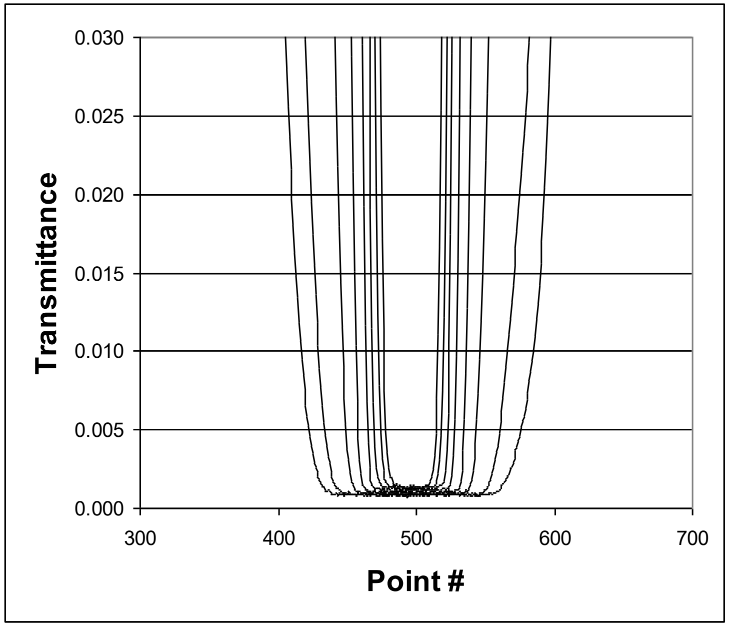




DL spectrum contains coherent and broad (spontaneous emission) components. Even for saturated narrow spectral line, part of DL radiation will be recorded by PD.

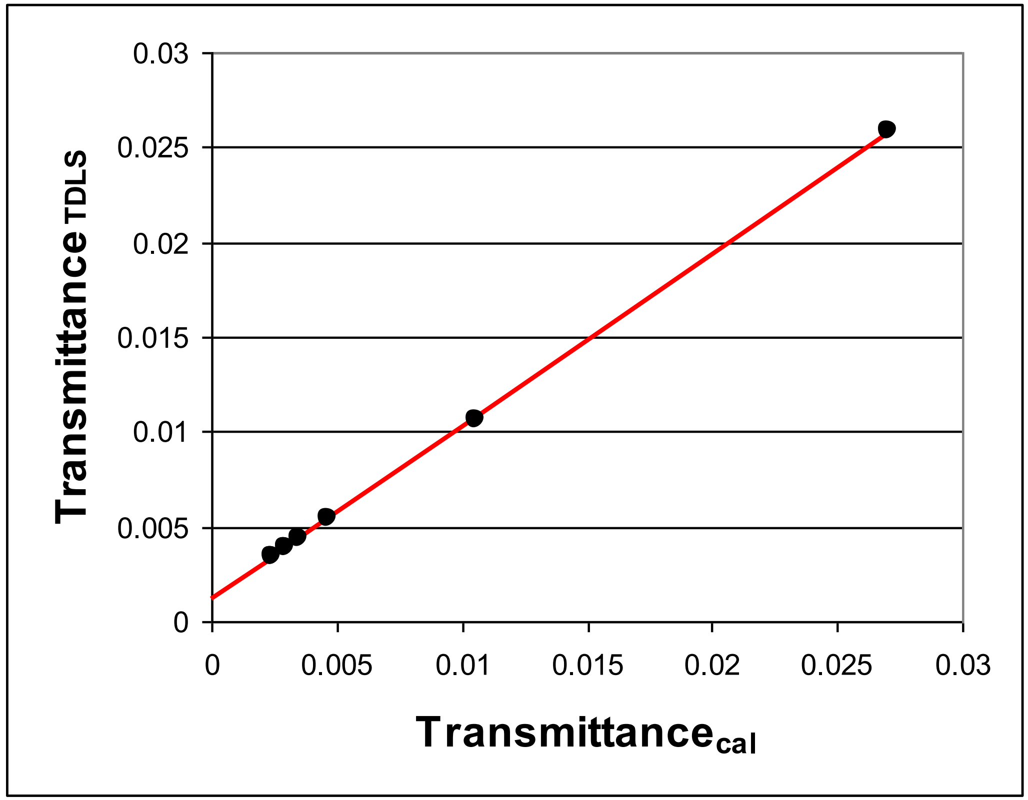
Transmission spectra of strong H_2O line for cell #3. Optical zero due to DL spontaneous emission at level 10^{-3} can be observed.

14. Optical zero calibration



Fragment of spectra presented on previous slide. Optical zero can be easily observed subject of its calibration.

To calibrate optical zero, molecular spectra were obtained for different gas pressures. Minimum transmittances were determined (vertical scale). Using known pressures and line parameters, minimum transmittances were calculated (horizontal scale). Linear fitting shows that for present DL optical zero is 1.13 10^{-3}. After its compensation error is 4.4 10^{-5}.



15. Conclusions

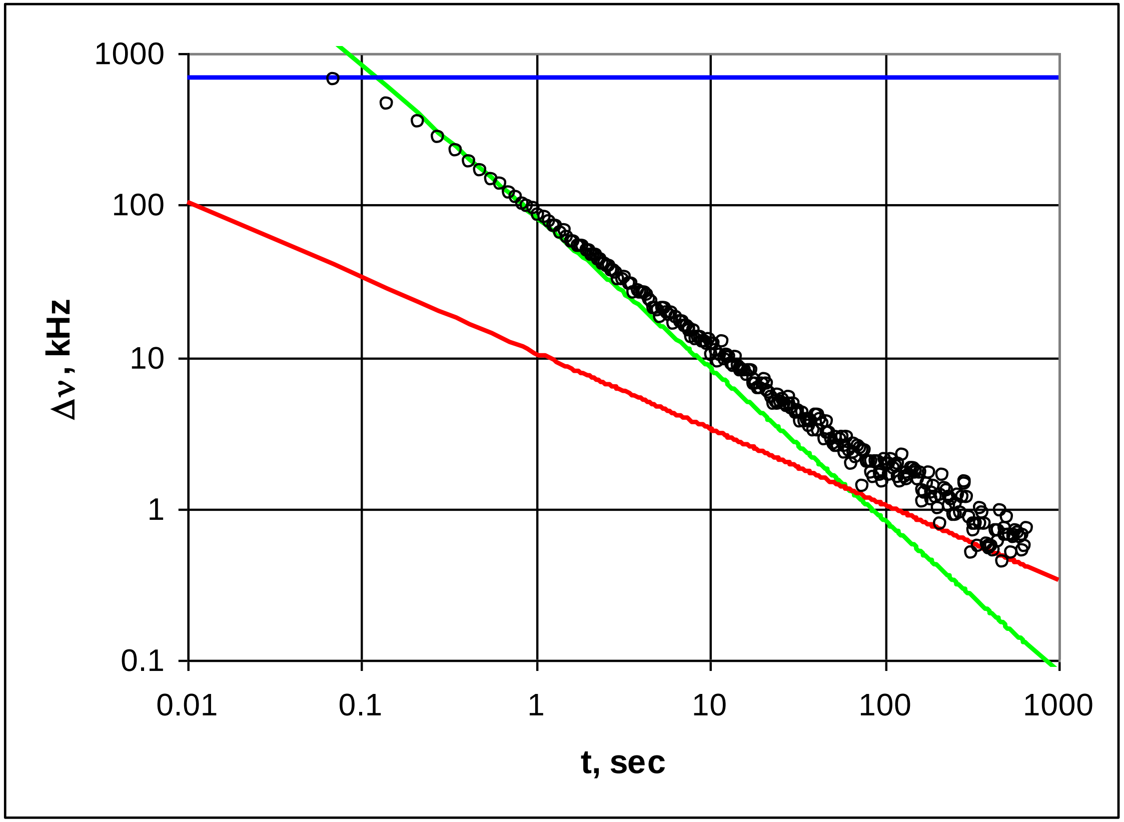
DL spectrometer for high accurate measurements was developed. The spectrometer subsystems were calibrated and error sources were analyzed. Error budget for line intensity measurements.

	Value	Error %
L, cm	183.5	0.022
DT, oC	20 - 25	0.017
P, mBar	100	0.036
CO2 sample purity, %	99.98	0.020
Subtotal		0.050
PD non-linearity		0.023
Dv, 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 %.

DL frequency tuning cycles stabilization

График Аллана нестабильности частоты ДЛ при стабилизации циклов сканирования (черные кружки) и основные механизмы, определяющие работу системы.

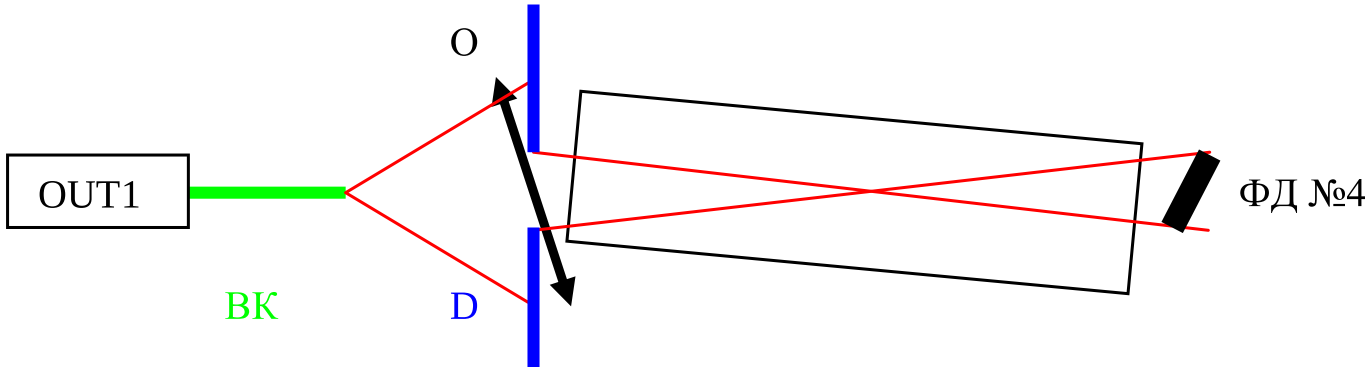


Синяя линия – Фликкерный шум частоты ДЛ.
Зеленая линия – подавление шума за счет стабилизации циклов сканирования.
Красная линия – квантовые шумы частоты ДЛ.
Продемонстрирована стабилизация частоты ДЛ на уровне 1 кГц, которая определяется квантовыми шумами ДЛ.

Для времени усреднения 1 сек воспроизводимость частотной шкалы ДЛ составляет 5 10^{-6} $см^{-1}$. Очень хорошо для высокоточной ДЛС.

Аналитический канал

Приходится делать выбор между точностью измерения длины (параллельный пучок, окна кюветы перпендикулярны) и подавлением интерференции.
Оптическая блок-схема аналитического канала с кюветой №2.



Выход OUT1 ВО модуля с помощью волоконного кабеля ВК подается на вход аналитического канала. Это излучение с помощью объектива O фокусируется между объективом и ФД №4. Между ними установлена кювета №2. Для подавления интерференции отражений на поверхностях, все элементы установлены под значительными углами к направлению распространения излучения (~20^{o} для объектива и ФД). Для подавления оболочечных мод волокна используется диафрагма объектива (D) диаметром 2.8 мм.
В этой схеме, длина аналитической кюветы №2 составляет L2 = 183.50(4) см, что достаточно для высокоточной ДЛС. Подобные меры предосторожности приняты и для аналитического канала с многоходовой кюветой №3.

Conclusions

1. Software to fit high accurate experimental spectral data was developed and its operation was tested and analyzed.
2. Line shape fitting with NEA = 2 10^{-4} can be done using Soft or Hard models with 6 parameters: S (integral intensity), v0 (line center), D (Doppler width), L (Lorentz width), B (narrowing), SA (asymmetry). Usage of other parameters list has to be investigated depending on NEA available.
3. Usage of more fitting parameters is not correct because leads to parameters correlation and loosing of parameters physical meaning.
4. Only for correct model results of fitting have physical meaning. Doppler width fitting can show model in use correctness.
5. It looks like presence of profile describing correlation between phase and velocity changes during collision was experimentally observed for the first time.