Measurement of formaldehyde concentration in air by 1.78 μ VCSEL

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- **Formaldehyde is an reactive intermediate product in troposphere hydrocarbon oxidation initiated by the OH radical. The H_2CO concentration in the atmosphere is in the 1 to 10 ppb range [1–4].**
- **Goal of present paper was to investigate possibility to develop instrument to measure trace formaldehyde concentration using near IR range (1.78μ). Specific feature of the instrument under investigation was absence of H_2CO reference cell to stabilize VCSEL frequency tuning [5].**
- **There is only one source of H_2CO spectra in near IR [6] known for authors. Most pronounced formaldehyde absorption features are located are in 5500 – 5700 cm^{-1} spectral range. Using instrument developed formaldehyde absorption spectra were obtained in range 5578 – 5605 cm^{-1}. Optimal spectral range was determined [see 7] to have no interference with atmosphere water, methane, and CO_2.**
- **Minimum detectable concentration of H_2CO was found to be 1.3 ppb for 10 sec averaging time. Averaging time increasing demonstrated white noise behavior up to 100 sec. However, long averaging times are not acceptable for real applications.**

References

[1] J.A. Logan, M.J. Prather, S.C. Wofsy, M.B. McElroy: J. Geophys. Res. 86, 7210 (1981)

[2] X. Zhou, K. Mopper: J. Geophys. Res. 98, 2385 (1993)

[3] A. Fried, S. McKeen, S. Sewell, J. Harder, B. Henry, P. Goldan, W. Kuster, E. Williams, K. Baumann, R. Shetter, C. Cantrell: J. Geophys. Res. 102, 6283 (1997)

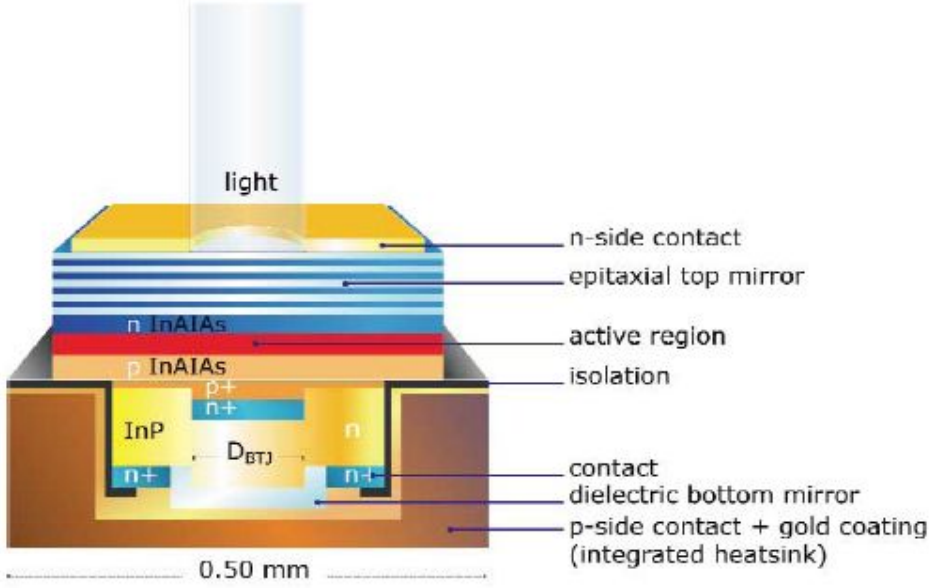
[4] T.E. Graedel: Chemical Compounds in the Atmosphere, Chapt. 4, (Academic Press, New York 1978), pp. 158-161

[5] Yu.Kosichkin, A.Kuznetsov, A.Nadezhdinskii, A.Perov, E.Stepanov, Sov.J.Quantum Electronics, 12, 518 (1982);

[6] http://vpl.ipac.ca ltech.edu/spectra/H_2CO

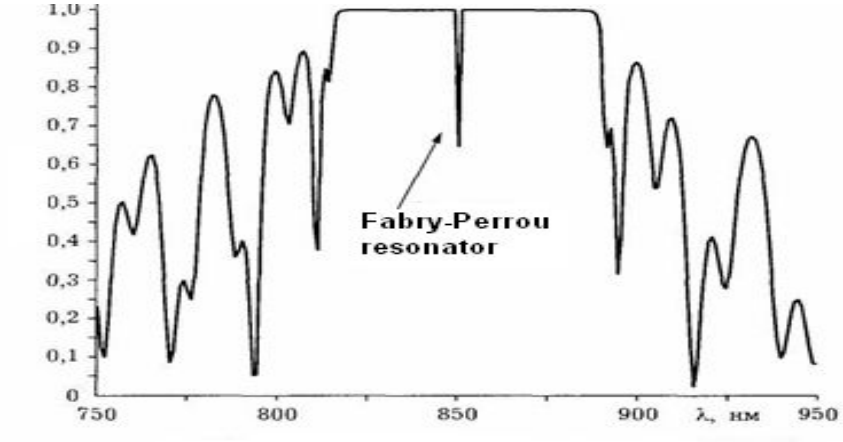
[7] L.S. Rothman, et.al., Journal of Quantitative Spectroscopy and Radiative Transfer, vol. 96, pp. 139-204 (2005)

VCSEL structure

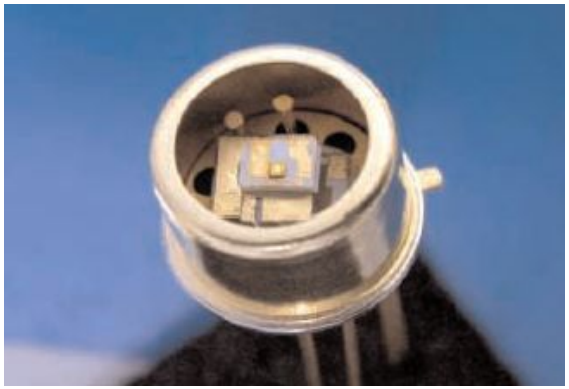


- N – number of dielectric mirrors layers (25-35)
- Size of active zone ~1μ
- Single pass gain – 1%
- R (coefficient of reflection) ≥ 0.995
- Laser light aperture - 5 - 10μ
- Divergency 10-20º
- Mode TEM (oor)

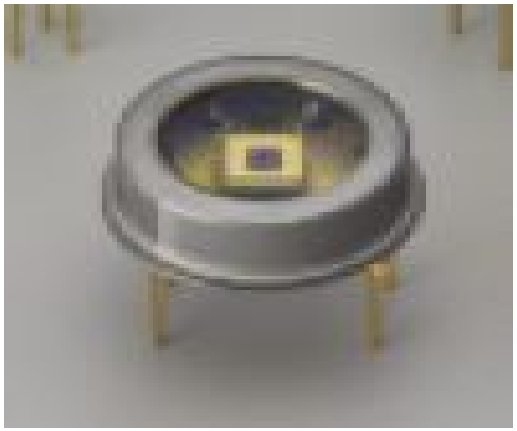
Reflection spectrum



VCSEL 1.78 μ «VERTILAS»
(info@vertilas.com)

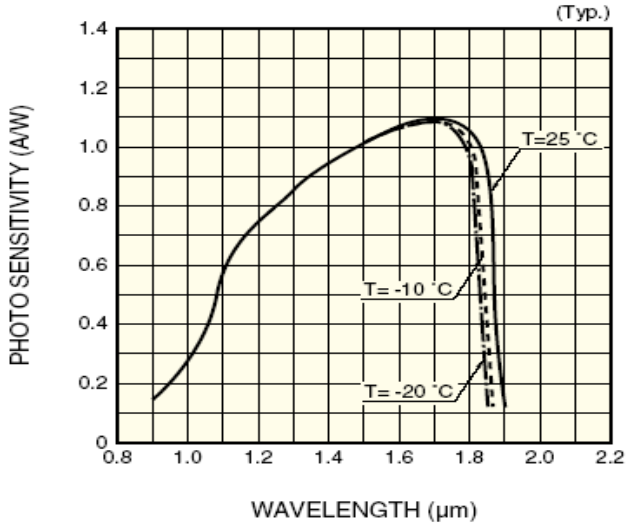


InGaAs photodiode
"HAMAMATSU"



View of laser module with collimator

■ Spectral response

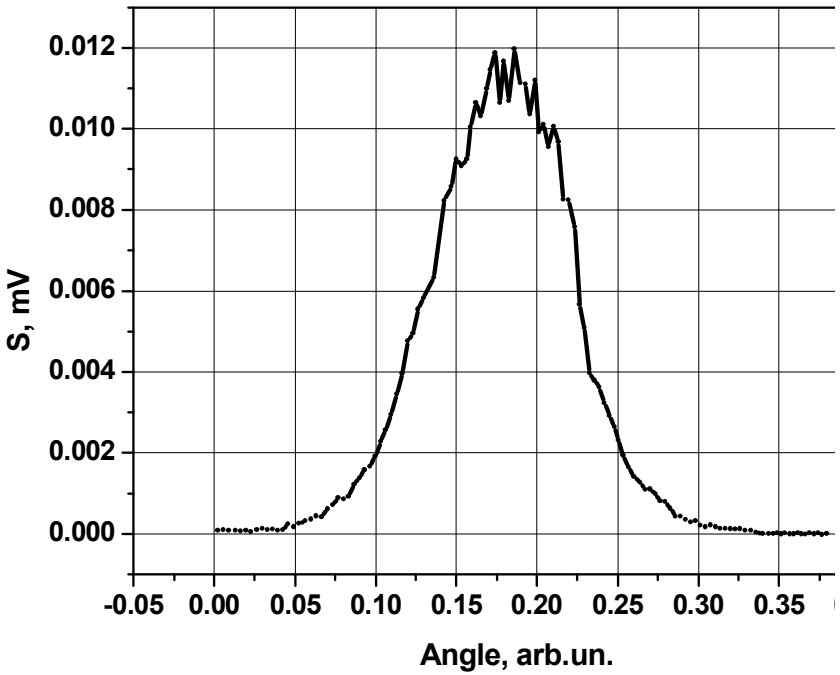


Electrical / Optical Characteristics at T_0 = 25°C

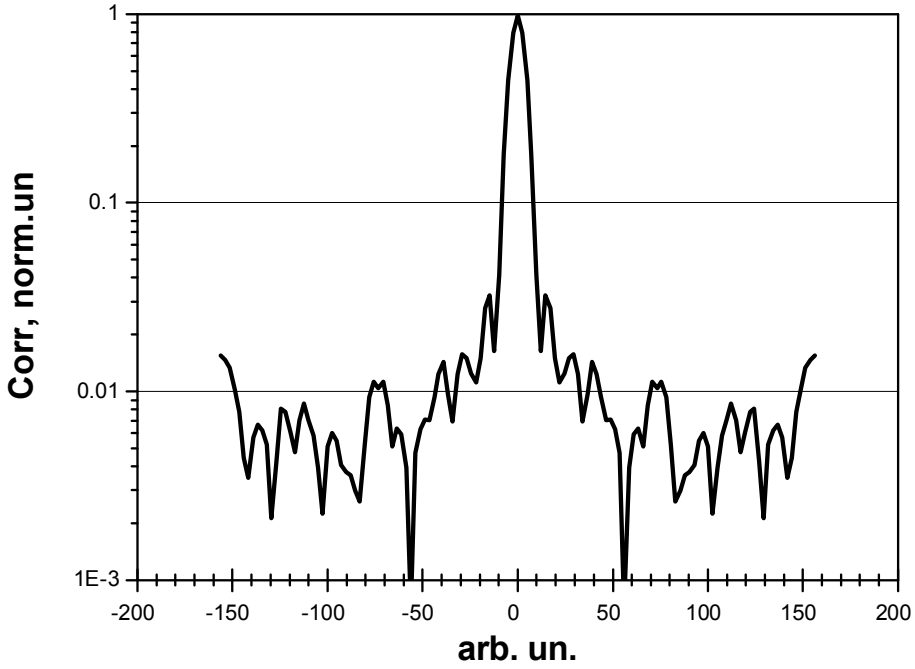
Parameter	Condition	Symbol	Units	Ratings		
	T_0=25°C[4]			Min	Typ	Max
Target Wavelength	T_0	λ_0	nm	1400		2050
Current at Target Wavelength [2]	λ_0, T_0	$I\lambda_0$		Iop_{min}		Iop_{max}
Wavelength Precision at Iop_{min} [3]	T_0	$\Delta\lambda_0$	nm	-1.5	-1.0	
Wavelength Precision at Iop_{max} [3]	T_0	$\Delta\lambda_0$	nm		+1.0	+1.5
Maximum Optical Power						
Between 1500 – 1600nm	T_0	P_{max}	mW	0.5	0.7	1.3
Between 1601 – 1800nm	T_0	P_{max}	mW	0.3	0.6	1.1
Between 1801 – 2050nm	T_0	P_{max}	mW	0.2	0.4	0.8
Threshold Current	T_0	I_{th}	mA	0.4	0.9	2.0
Operating Voltage at P_{max}	T_0	V_{max}	V			2.0
Absolute Maximum Current [1]	T_0	I_{max}	mA			15
Maximum Operating Current to reach λ_0 [2]	T_0	Iop_{max}			I at 90% of P_{max}	
Minimum Operating Current to reach λ_0 [2]	T_0	Iop_{min}			I at 10% of P_{max}	
Current tuning coefficient	T_0	$\Delta\lambda/\Delta I$	nm/mA	0.6	0.7	0.8
Maximum current tuning range	T_0, Iop_{min} <I<Iop_{max}	$\Delta\lambda$	nm	1.5	3	4
Temperature tuning coefficient	λ_0	$\Delta\lambda/\Delta T$	nm/°C	0.08	0.11	0.15
Side Mode Suppression Ratio at target wavelength	Including transverse and polarization modes at λ_0	SMSR	dB	25	30	
Spectral Line Width	T_0, Iop_{min}<I<Iop_{max}	Δf	MHz		30	
Beam Divergence	Full Width at Half Maximum	FWHM	degree	12	20	30

Note 1: the absolute maximum current is precisely given on the laser diode data-sheet after characterization
Note 2: by sweeping the current between these limits, it is guaranteed that the target wavelength λ_0+/-$\Delta\lambda_0$ will be reached at T_0=25°C
Note 3: the wavelength can be adjusted by slightly varying the temperature to reach the target wavelength
Note 4: T_0 is controlled by the TEC and measured with the thermistor

VCSEL far and near field measurements

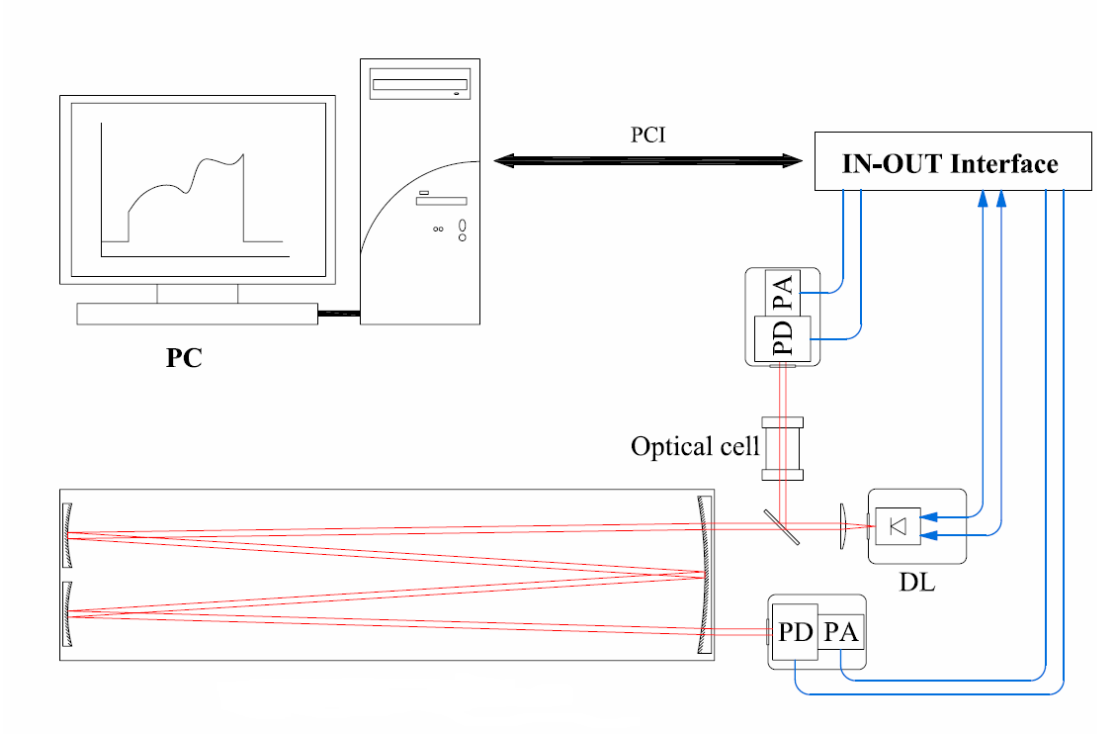


Fine structure of VCSEL far field



Correlation function of near field

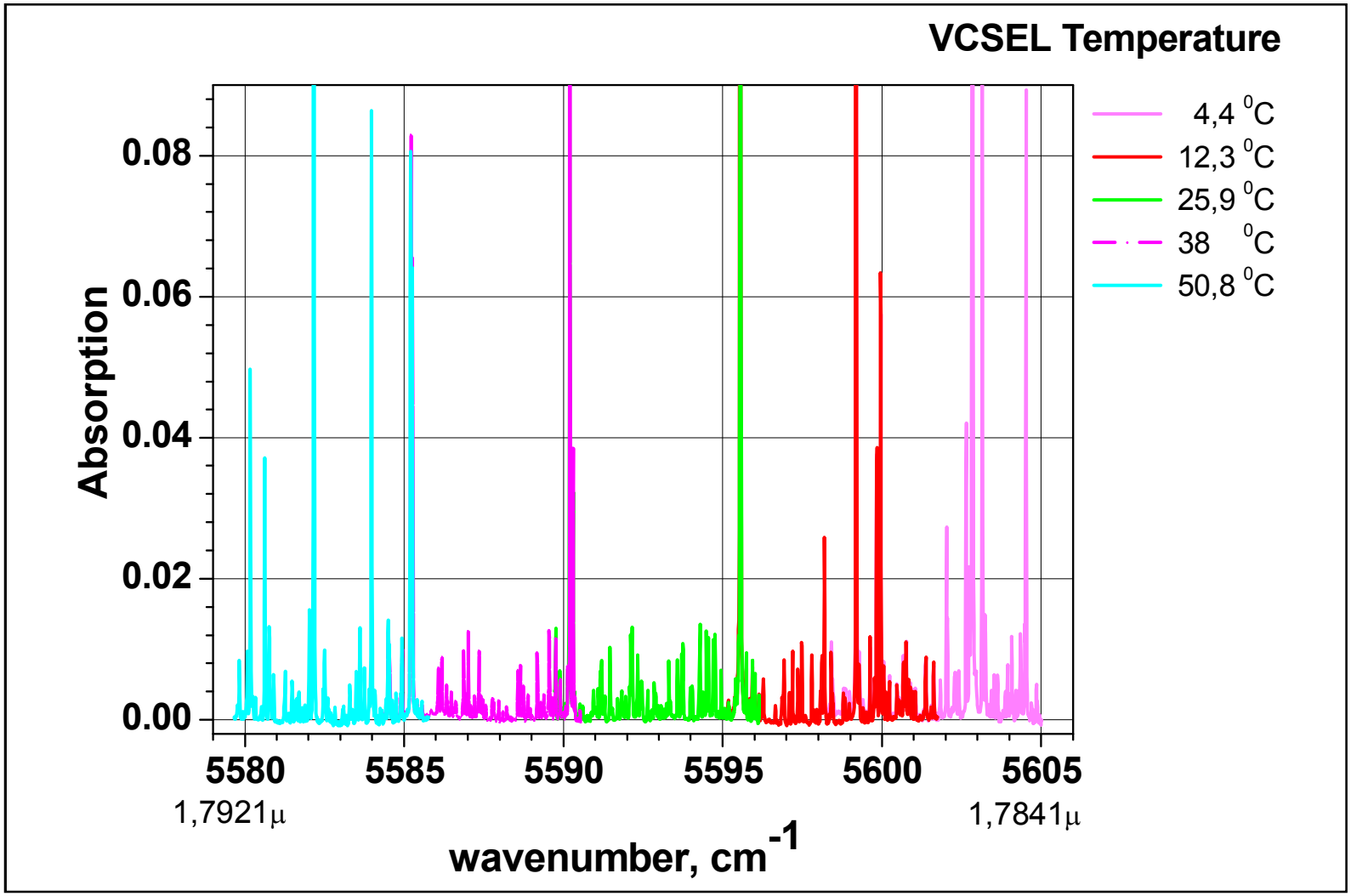
Block-scheme and view of the instrument



"Chernin" multi-pass cell. L= 39m

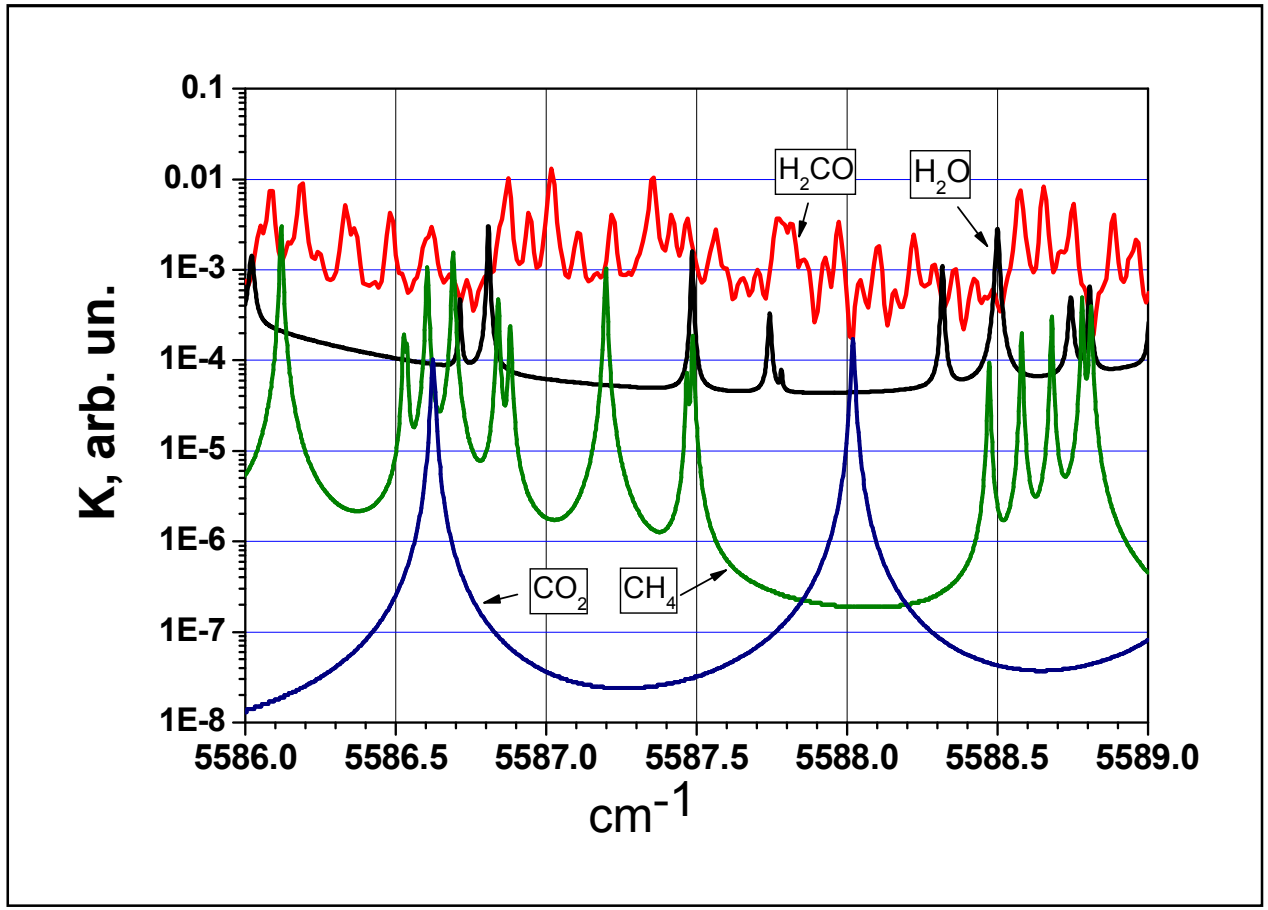
Source of H_2CO: 40% water solution

H_2CO spectrum



Spectrum was recorded by VCSEL in spectral range 1.784 -1.792 m

Analytical spectral range



H_2CO P= 10 mTorr

H_2O P= 10 Torr «HITRAN»

CH_4 C = 1.5 ppm «HITRAN»

CO_2 C = 0.03 % «HITRAN»

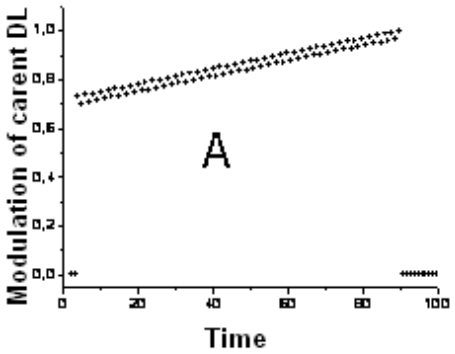
P_{total} = 25 Torr,

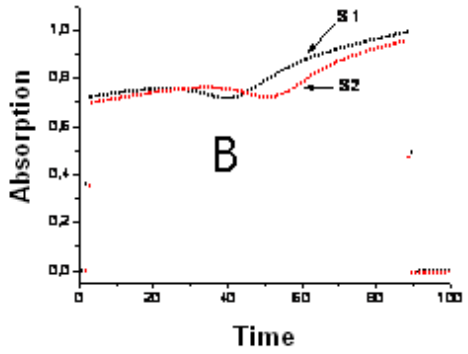
L = 39 m.

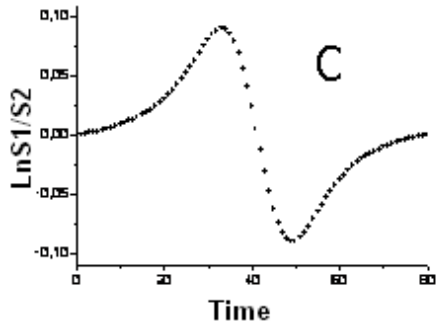
Analytical spectral range for H_2CO registration : 5586.7 – 5587.3 $см^{-1}$

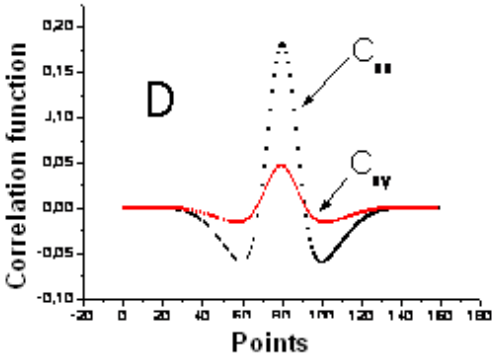
There are few interfering lines of gases: CO_2, CH_4, H_2O

Operation regime









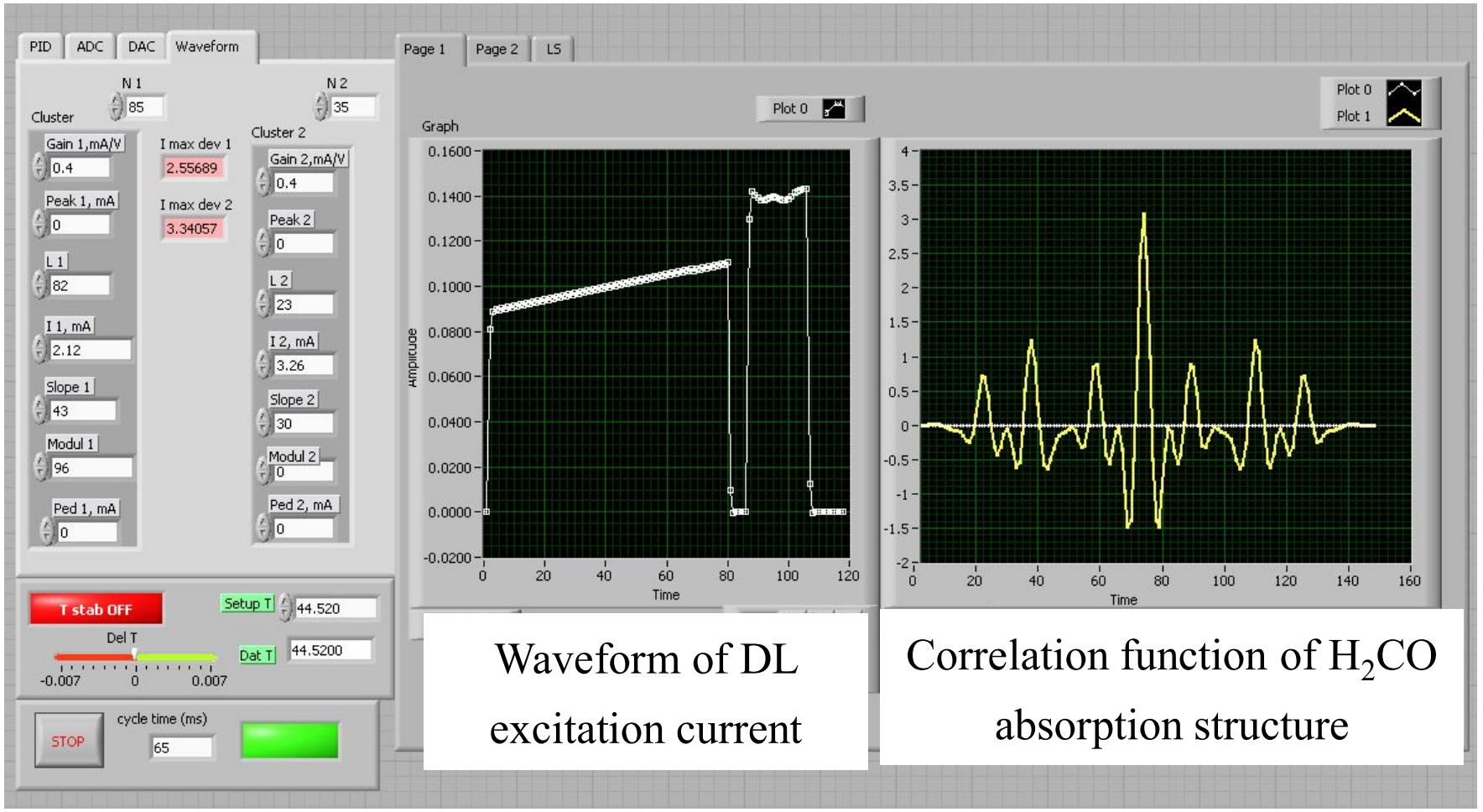
Measurement procedure of trace molecule concentration

$$C = \frac{\alpha \cdot P_R \cdot L_R}{P_A \cdot L_A} \cdot 10^9, [ppb]$$

$$C_{xy} = \alpha^* C_{xx}$$

View of program interface

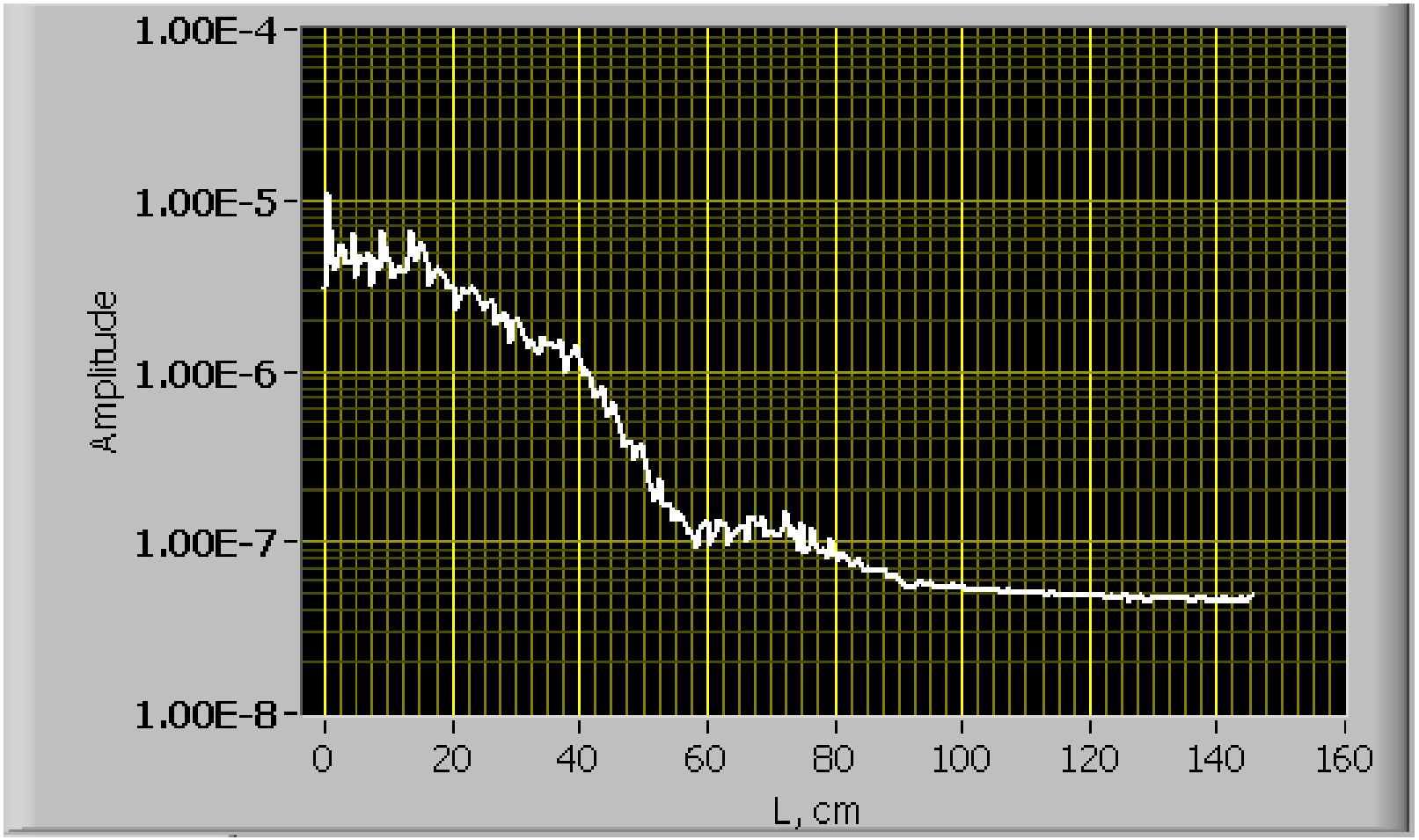
Two pulse waveform of excitation current (left):
First pulse is used to detect H_2CO, second one – to stabilize DL frequency tuning cycles using water lines



Waveform of DL excitation current

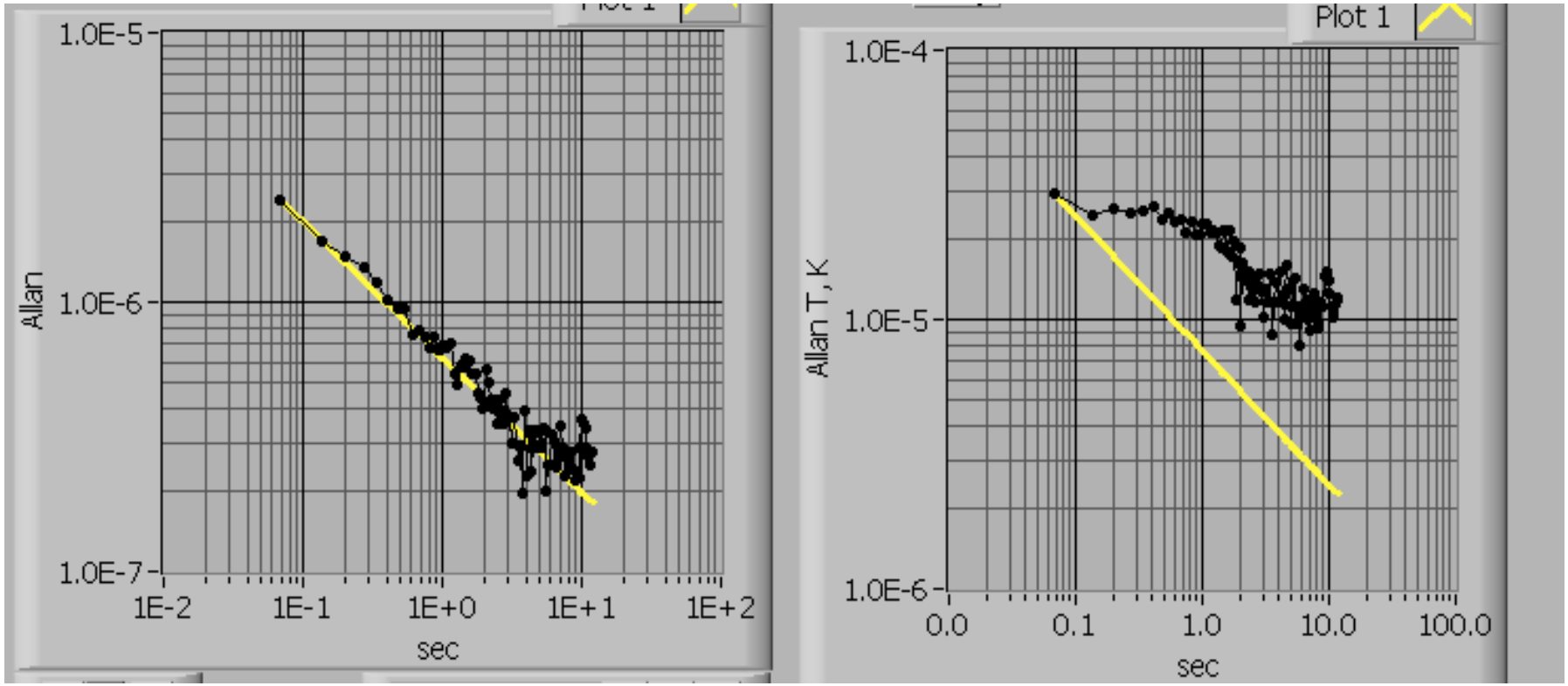
Correlation function of H_2CO absorption structure

Signal Fourier spectrum



Absence of cross-talking and interference fringes

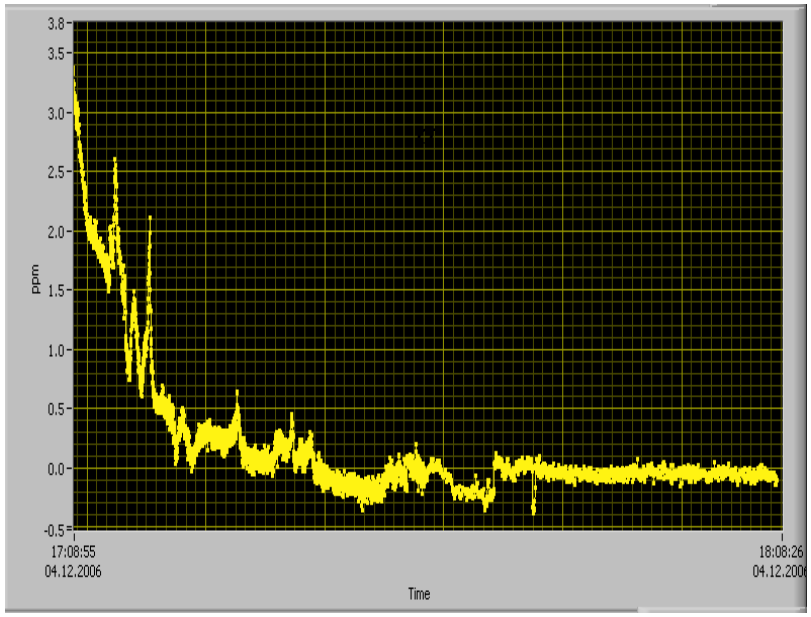
Allan plots



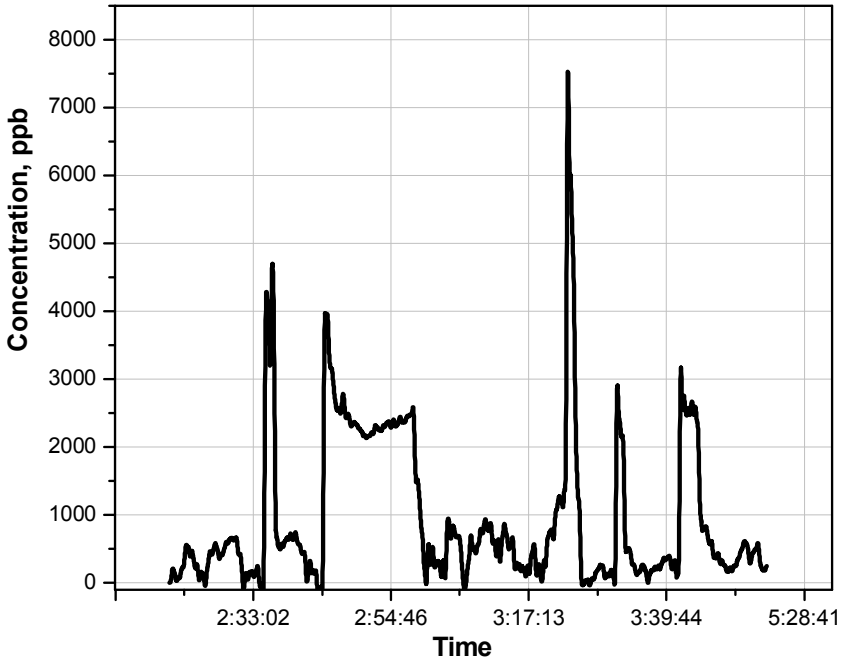
Minimum detectable absorption (left) and temperature stability (right)

Minimum detectable absorption 2.5 10^{-7} was achieved, corresponding to 1.3 ppb for 10 sec averaging time

Formaldehyde monitoring in atmosphere



Calibration curve for H_2CO concentration measurements



Long-term H_2CO measurements : Several H_2CO sources were detected when spatial distribution of formaldehyde concentration was measured

Conclusion

1. VCSEL diode laser characteristics in 1.78 μ spectral region were investigated.
2. Formaldehyde absorption spectrum in 5579 – 5605 cm^{-1} was measured.
3. Analytical spectral range was chosen to minimize interference with H_2O, CO_2, and CH_4 lines.
4. New device was developed for outdoor H_2CO vapors detection.
5. Different noise sources were investigated and methods were developed to suppress them.
6. Minimum detectable absorption 2.5 10^{-7} corresponding to 1.3 ppb was achieved for 10 sec averaging time