ETHANOL VAPOR DETECTION LIMITED BY DIODE LASER FREQUENCY QUANTUM NOISE.

S.Malyugin, T.Moskalev, A.Nadezhdinskii, D.Namestnikov, Ya.Ponurovskii, Yu.Shapovalov, D.Stavrovskii, I.Vyazov, V.Zaslavskii

NSC of A.M.Prokhorov General Physics Institute
Vavilov str. 38, 119991 Moscow, Russia
NAD@nsc.gpi.ru

R.Upendra, Jae Jo

Brookhaven National Laboratory, Upton NY 11973, USA

Aim of present paper was trace ethanol vapor detection inside moving car. To start the work, following problems have to be solved (see separate posters)

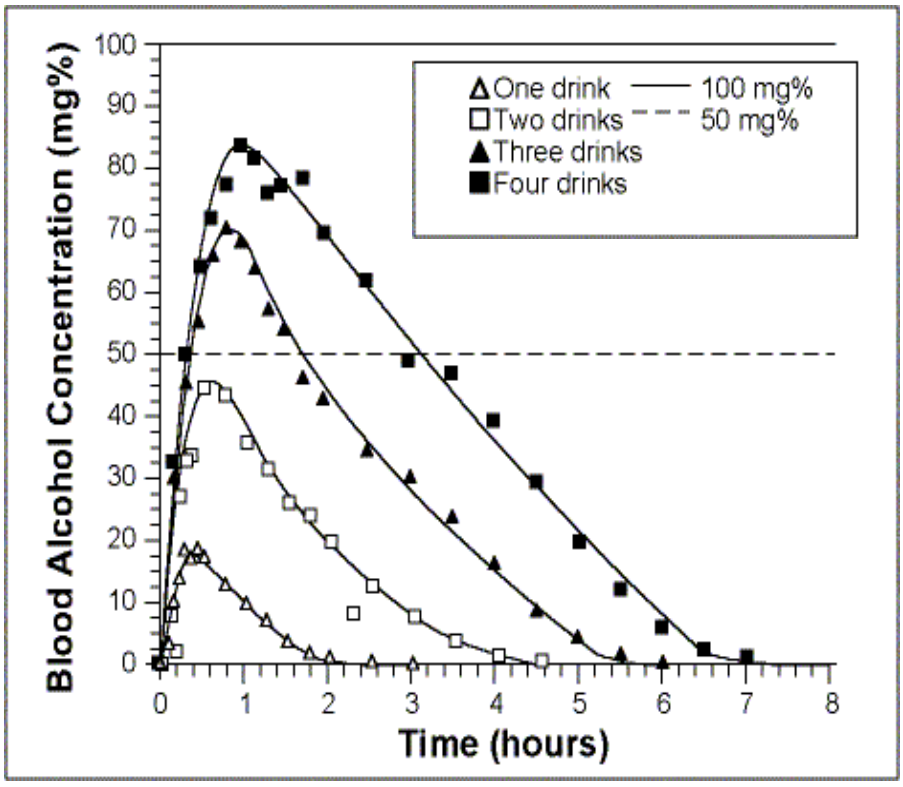
1. Optimization of photo-detector system.
2. No cross-talking in detector system and DL excitation current.
3. Temperature stabilization at 3 10^{-5} K level.
4. Diode laser quantum noise limited operation.
5. No interference above 10^{-6}.
6. Flicker noise reduction.
7. No mode competition noise.

To achieve above mentioned aim we had to solve several additional new fundamentals goals being important for many TDLS applications:

1. Trace absorption measurement of broad spectra having no resolved structure.
2. Selectivity: ethanol spectrum is overlapped with very intensive water vapor absorption.
3. Trace molecule measurement with msec time resolution.
4. Sensitivity: diode laser frequency quantum noise limited.

Alcohol Metabolism

Usually for testing person suspected to be drunk the measurement of Blood Alcohol Concentration (BAC) are used. Legal limit of BAC for vehicle drivers varies from 0.4 to 1.0 $^{0}/_{00}$ in different countries.

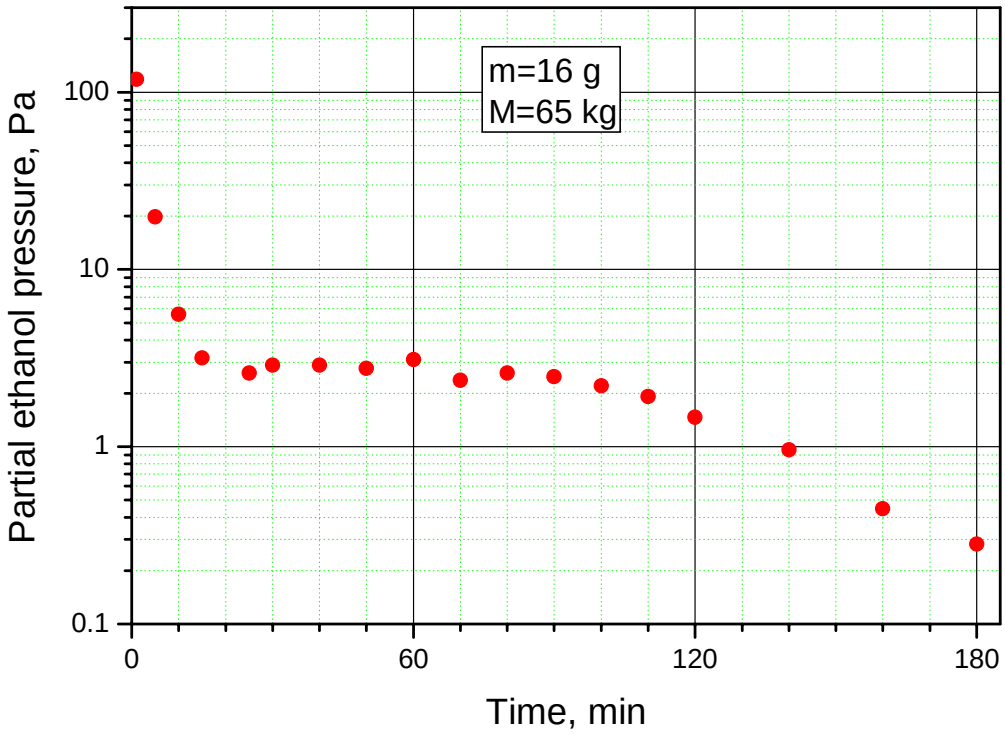


BAC after the rapid consumption of different amounts of alcohol by eight adult fasting male subjects. (Adapted from Wilkinson et al., Journal of Pharmacokinetics and Biopharmaceutics 5(3):207-224, 1977.) (Institute on Alcohol Abuse and Alcoholism "Alcohol Metabolism" No.35 PH 371 January 1997)

The Figure demonstrates that legal level of intoxication for most states will be achieved after 2-5 drinks (one drink is 20 ml of pure ethanol).

Breath Alcohol Concentration (BrAC).

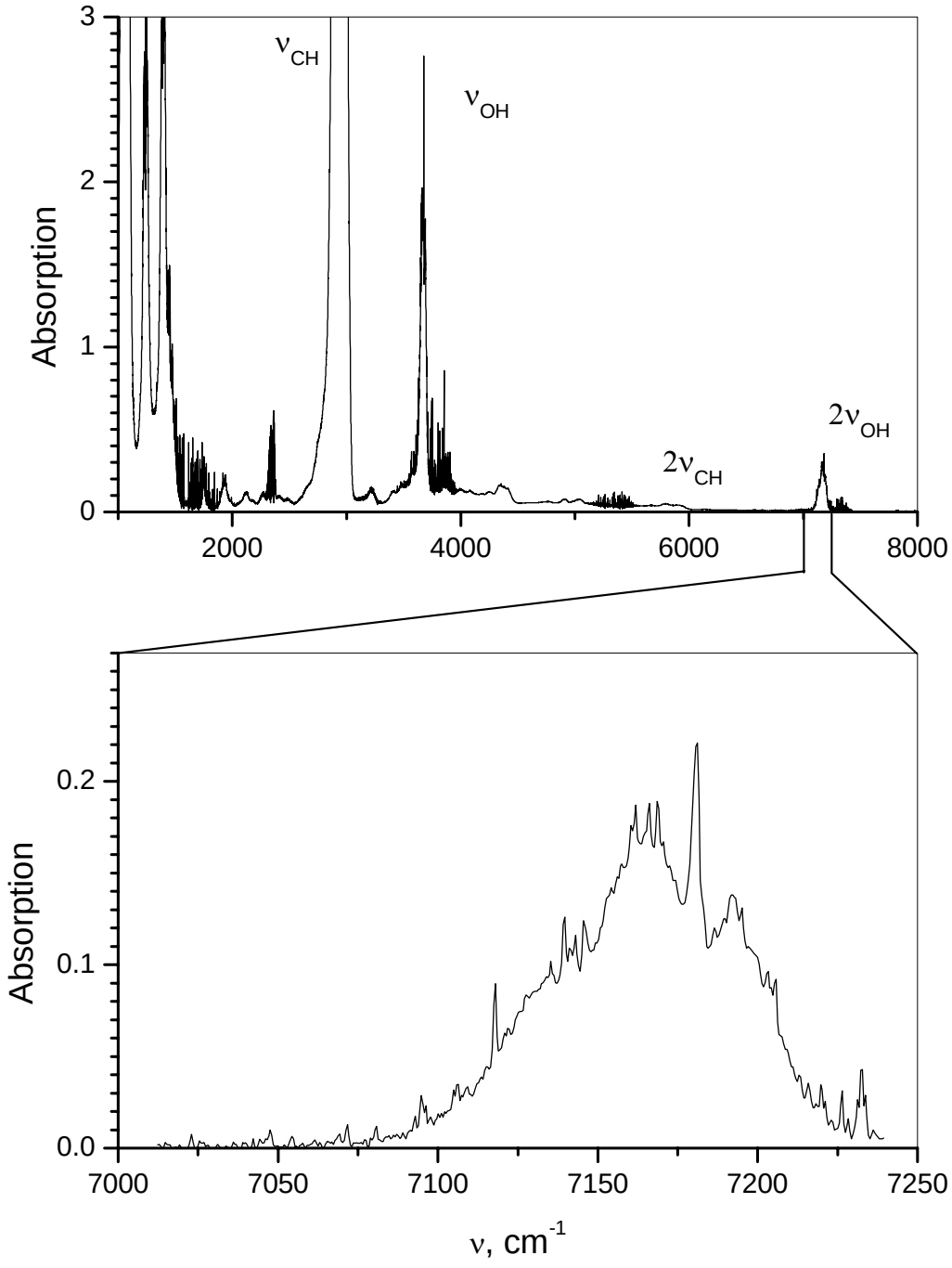
There is direct relationship between BAC and alcohol vapor concentration in human breath - Breath Alcohol Concentration (BrAC). It is determined by thermodynamics of solutions [1]. We've obtained similar results both as theoretical estimations and during experimental measurements for calibrated ethanol solutions in water. BrAC value 16 Pa corresponding to BAC 0.8 $^{0}/_{00}$ will be used as unit in future measurements of alcohol concentration, because this legal limit is fixed in most states of USA. We will use abbreviation LL (Legal Level) for this unit.



Ethanol content in human breath vs. time delay after one drink obtained using FTS «Bruker 66-v» equipped with multipass cell with 5 m optical pass length.

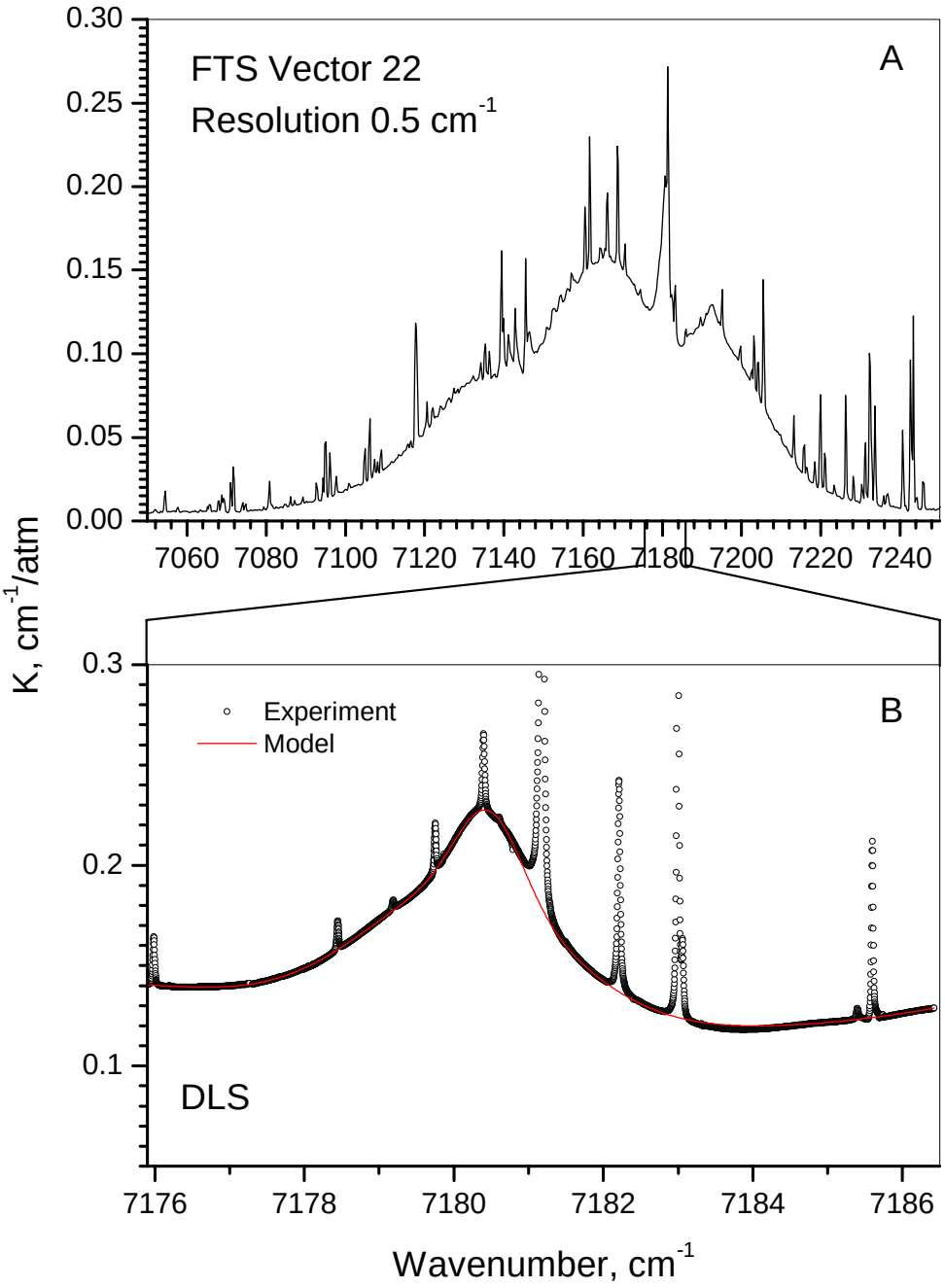
1. R.Thompson, "The Thermodynamics of Drunk Driving", J.Chem.Education **74**, #5, 532 (1997)

Ethanol vapor spectrum



Ethanol vapor absorption spectrum.

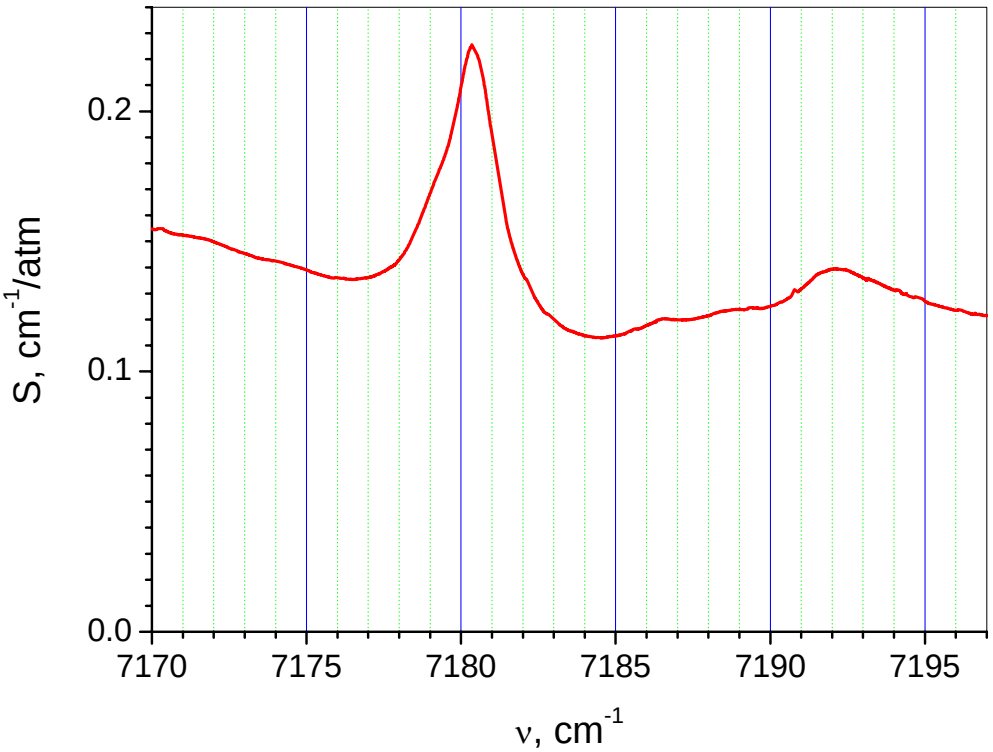
Ethanol vapor spectrum in NIR



A - Ethanol OH overtone in near IR spectral range.
B – Ethanol experimental and model spectra.

Ethanol vapor spectrum structure

Ethanol is broad band absorber as it was introduced in [2]. Ethanol spectrum has not resolved structure because of spectral lines overlapping even at low pressures. Spectra of this type could be considered as challenge for TDLS. Up to authors knowledge first successful trace broad band absorber detection was demonstrated in [3, 4]. Successful solution of this problem opens new areas of TDLS applications in complex molecules detection as well as impurity's concentration measurement in solids and liquids [5].

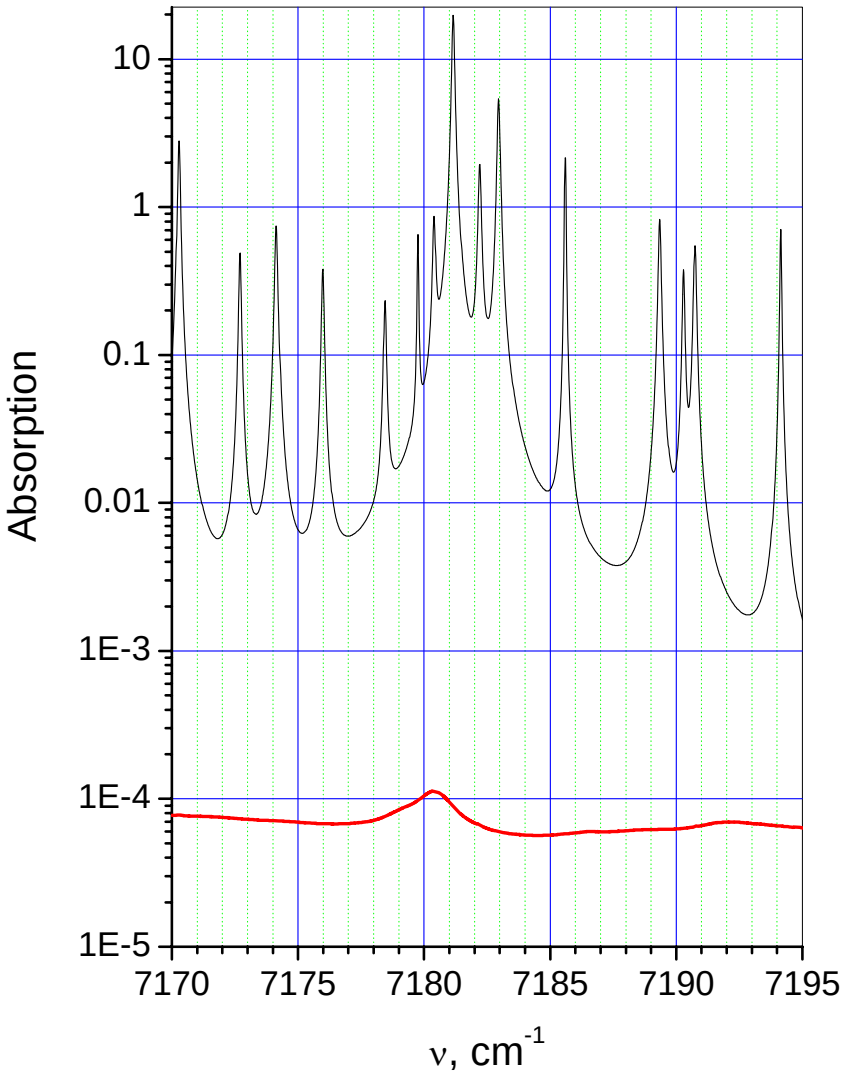


Ethanol vapor spectrum as measured by DFB DL near 1.39 μ

2. K.L. McNesby, R.T. Wainer et al.: Appl.Opt. **39**, 5006 (2000).
3. A. Nadezhdinskii, A. Berezin et al.: Spectrochim. Acta Part A **55,** 2049 (1999)
4. A.I. Nadezhdinskii, A.G. Berezin, O.V. Ershov: Appl. Phys. B **75,** 203 (2002)
5. A.W.Mantz, privet communication

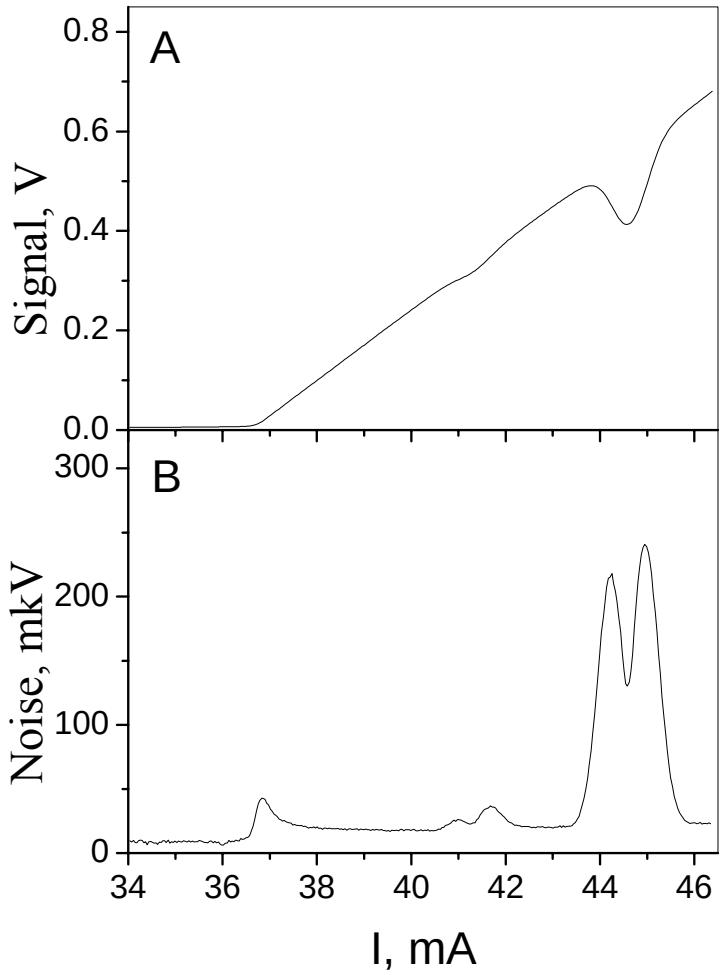
Detection selectivity

Second problem is related to TDLS selectivity. In present work, trace ethanol absorption as small as 10^{-5} has to be measured in presence of water vapor having 4 orders of magnitude more intensive absorption in spectral range under consideration. This problem was also solved.



Ethanol absorption spectrum corresponding 50 Pa*cm (red).
Water vapor spectrum for 50 % humidity and L = 8 m (black)

Diode Laser Quantum Noise Limited Sensitivity.

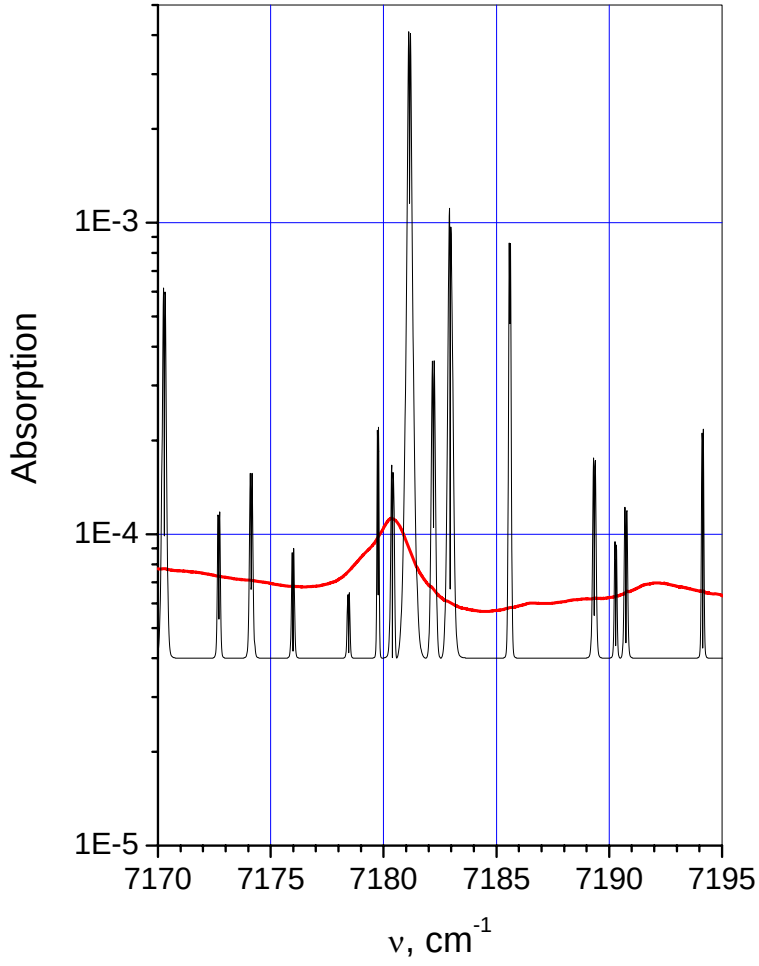


Signal with water vapor (low pressure) absorption lines (A) and its noise (B) as function of excitation current value – **I**.

There is noise peak near threshold (typical to phase transitions). Intensity noise is constants. Additional noise on slopes of spectral line due to DL frequency quantum noise can be observed.

Sensitivity limited by DL frequency quantum noise

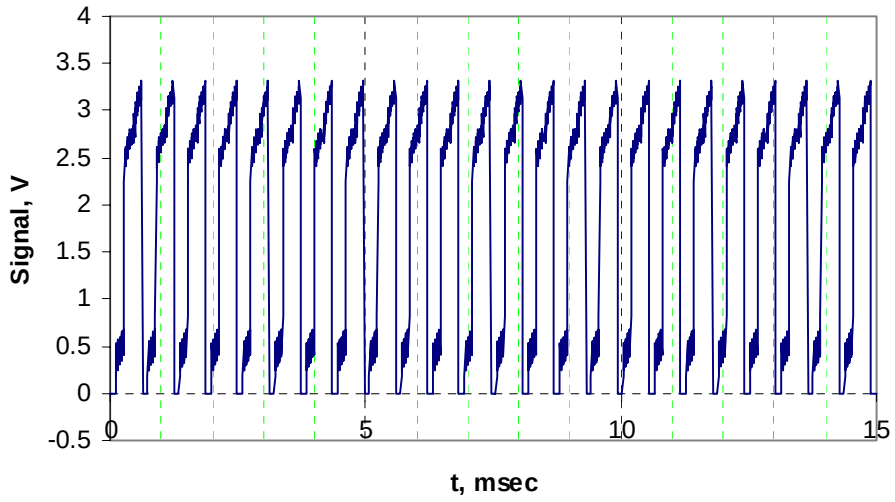
Necessary detection sensitivity needs achievement of absorption sensitivity fundamental limit. In present work absorption sensitivity limited by diode laser frequency quantum noise was demonstrated.



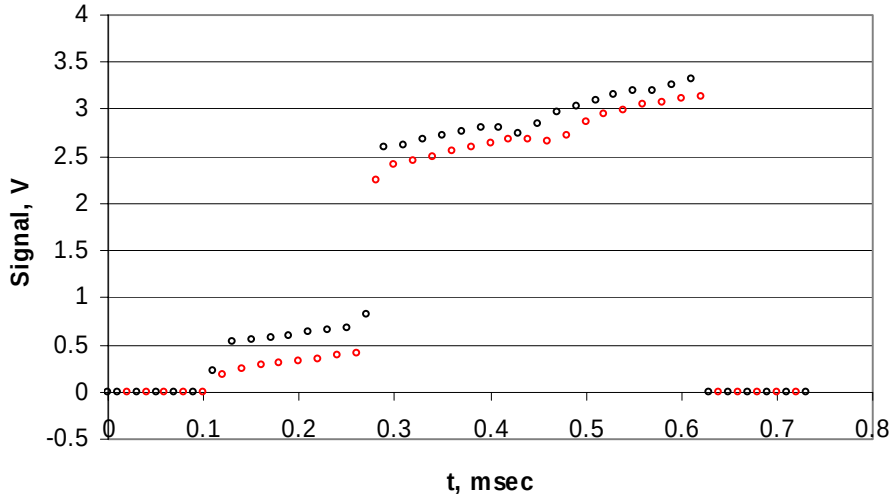
Ethanol absorption spectrum corresponding 50 Pa*cm (red). DL in use quantum noise equivalent absorption - for 50 % humidity and L = 8 m (black)

Instrument operation mode

Real time molecule detection is important for many TDLS applications. In present work trace molecule detection with time resolution better than 1 msec was demonstrated.



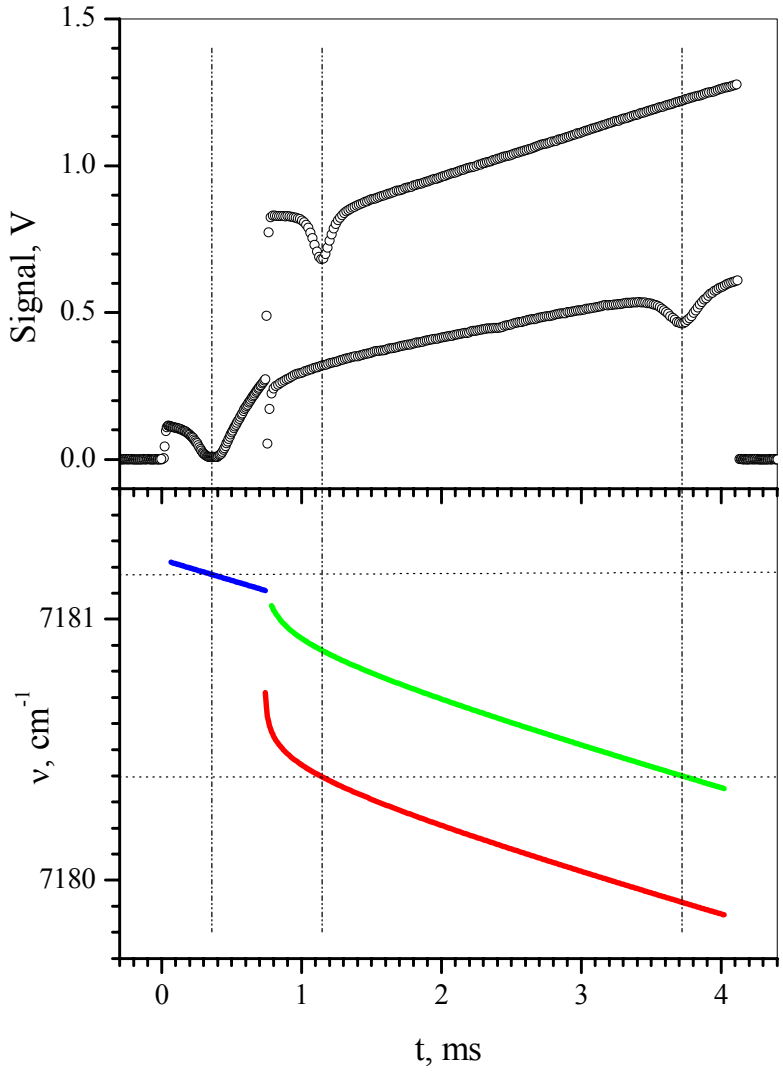
Pulse series of operation mode in use.



Signal pulse waveform.
Trace molecule concentration was determined for each pulse.
Water vapor absorption line was used for DL frequency cycles stabilization (see separate poster).

Instrument operation mode

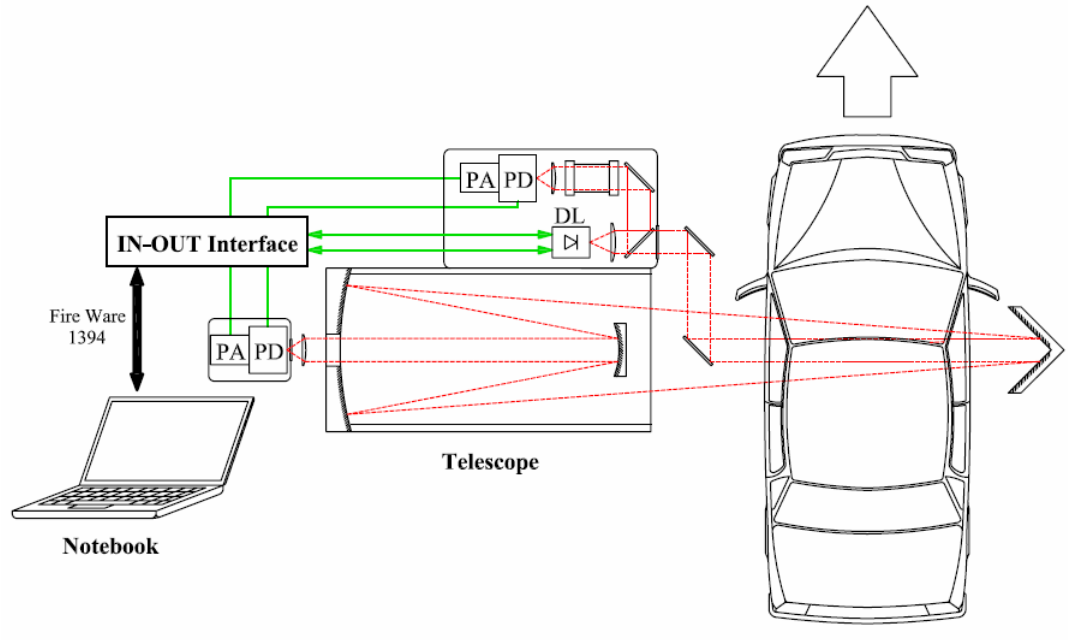
Generation #3 of TDLS operation mode (see separate poster) was used in this case to detect trace ethanol concentration.



Example of recorded signal (top) and DL frequency tuning (bottom) for one of the operation modes in use.

It looks like two frequencies DL operation with tuning.

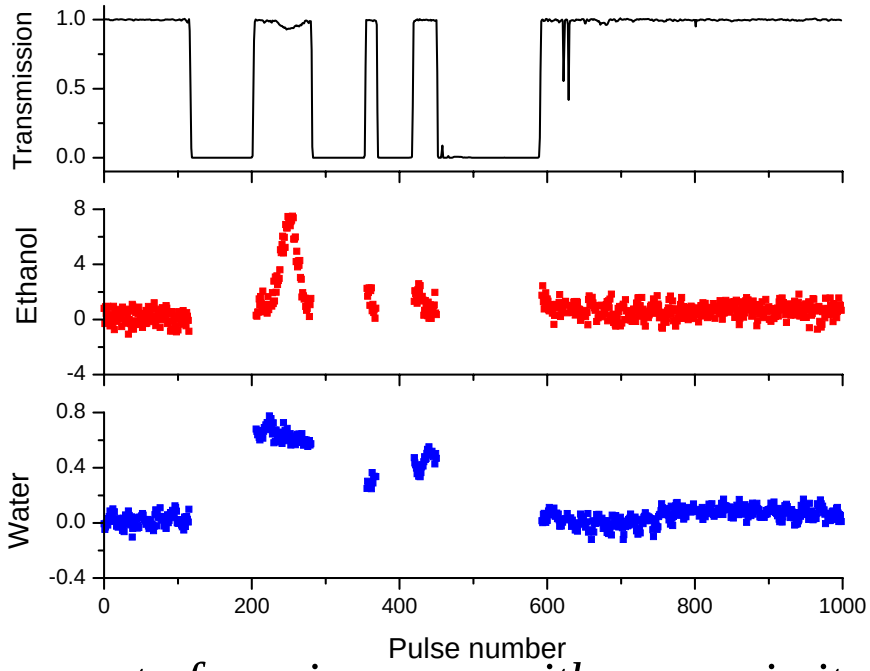
TEST EXPERIMENT



Experiment block-scheme

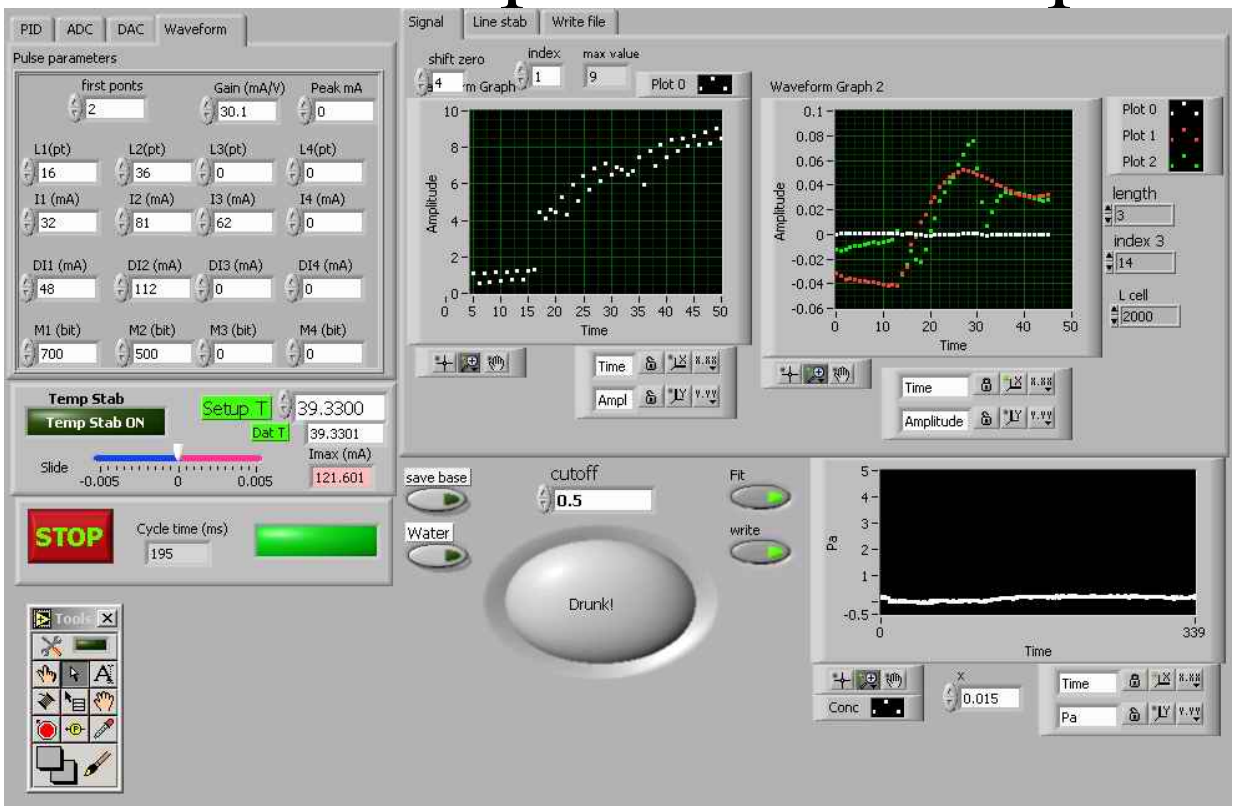
Test experiment view

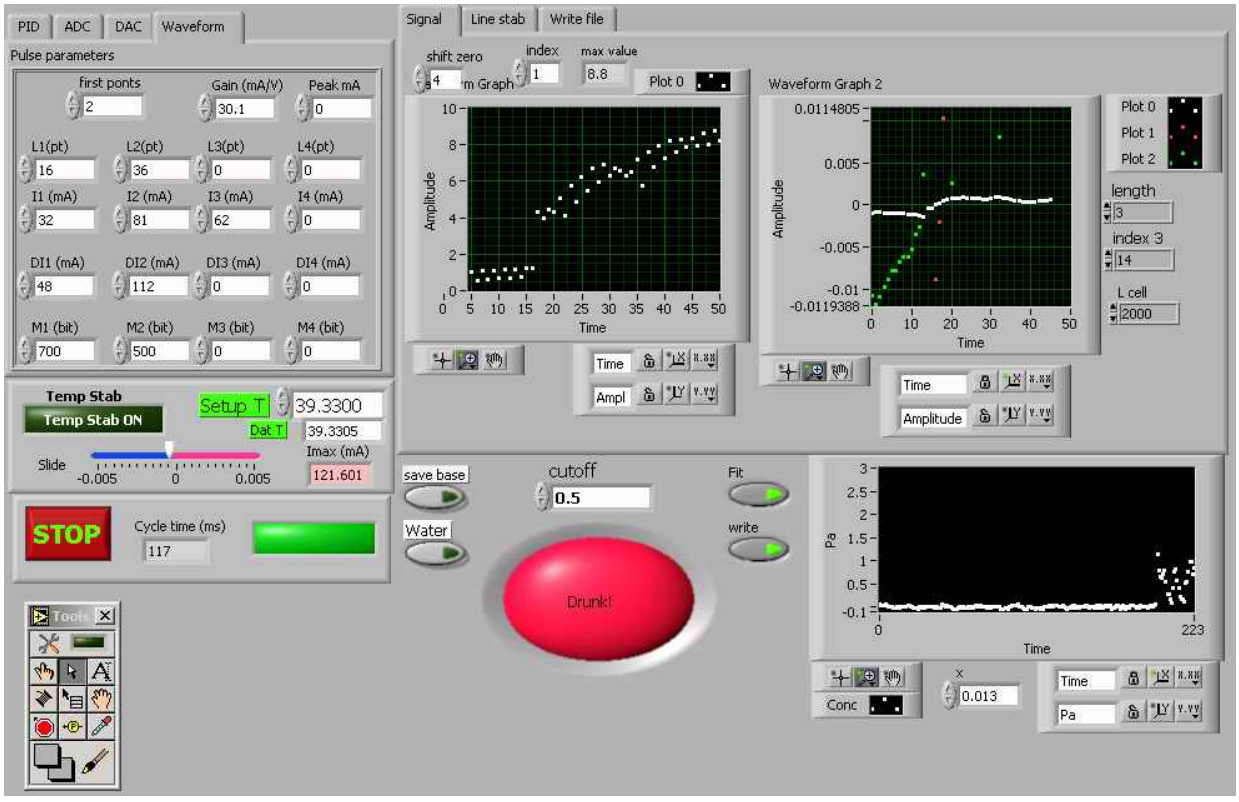
Trace Ethanol Vapor Detection inside moving car



Recording of the event of passing a car with person imitating drunken breath at front seat. Upper graph – transmittance, middle and lower graphs stand for alcohol and water contents, respectively.

Software Operation Example





Software Operation Example