ANALYTICAL APPLICATIONS OF TUNABLE DIODE LASER SPECTROSCOPY

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Introduction

First high resolution molecular spectra using Diode Lasers (DL) were obtained in [1]. [1] E.D.Hinkley, HIGH RESOLUTION INFRARED SPECTROSCOPY WITH A TUNABLE DIODE LASER, Appl. Phys. Lett. 16, 351 (1970).

During its history TDLS passed the same steps as atomic and molecular spectroscopy: measurements of line frequency, intensity, broadening and shift.

Now analytical applications are most attractive. In TDLS there are 6 main players:

Diode Laser (DL), Photo detector (PD), Molecule, Optics, Electronics, Operation mode.

Simultaneous analysis of physical properties of all above mentioned players is necessary to achieve fundamental limits. Such analysis can result in nontraditional solutions (see below).

Diode Lasers



DL types available now operate from UV to THz, where different molecules have absorption features. Hence, different molecules can be detected in different spectral ranges using different DL types. **Question: what** spectral range is optimal?

Optimal spectral range

Answer is obvious for experts in molecular spectroscopy. Optimal spectral range is MIR where fundamental bands are located. Overtones and combination bands in NIR are **significantly weaker** in comparison with fundamental bands.

Question: what means significantly weaker?

Molecular spectra

Question: what means significantly weaker?

The answer one can find in adiabatic theory of molecular spectra. Significantly weaker is determined by Born-**Oppenheimer** parameter $\sqrt{(m/M)}$. Here m – electron mass, M – effective mass of vibration. So all molecular bands can be divided in 3 groups.

1. M~1 (Hydrogen bond). 2. M~10 (C-O, N-O, ...) 3. M~100 (heavy spherical tops: UF_6 , OsO_4 , ...)



Spectra of the groups representatives (HF, CO_2 , UF_6). Here **significantly weaker** means 0.03, 0.01, 0.003, respectively.

Optimal spectral range

Traditional approach: optimal spectral range – signal (absorption) maximum. It means fundamental bands in MIR. Wrong answer.

Correct answer: optimal spectral range - maximum of S/N ratio.

Conclusion: noise properties of PD and DL have to be analyzed.

Molecule + PD



Comparison of molecular spectra with PD noise spectral dependence (classical paper F.Jones, et.al. Detection and measurement of IR radiation, Oxford University, London, (1957).

For Hydrogen bonds NIR (overtones) has significant detection advantage in comparison with MIR (fundamentals). For second group S/N ratio is similar both for fundamentals and overtones. Choice depends of researcher qualification. We use NIR to measure CO_2 . For third group MIR is preferable. We've measured UF₆ isotope content in MIR.

Molecule + PD + DL

From previous slide it looks like that the higher Hydrogen bond overtone the higher advantage in S/N. It is not true because of DL noise. Comparison of PD noise (red) and DL noise (blue) with signal - HF absorption (black).

<u>Conclusion: optimal</u> <u>spectral range for trace</u> <u>molecular absorption</u> <u>detection (hydrogen</u> <u>bonds) is NIR where</u> <u>overtones are located.</u>



<u>S/N advantage in NIR in comparison with MIR can</u> <u>achieve 200 (HF).</u>

Molecules and DLs in NIR



Practically all molecules have absorption between 1 and 2 μ (NIR). Overtones, located here, are characteristic for C-H, N-H, O-H, etc. bonds. For this spectral range commercial DL with 60 years lifetime are available. For practical applications it is important that NIR spectral range under consideration is eye-safe. Circles – GPI DLs set.

Applications classification

Classification of different applications can be done using photocurrent noise origins.



Photocurrent noise spectral density g(i) as function of photocurrent value i for NIR. Small signal (red) – PD noise is dominant. $g_{PD} = const$; Large signal (green) – photocurrent shot noise dominates. $g_{SN} = (ei)^{05}$. DL noise (blue) is proportional to i $g_{DL}=RIN^*i$.

<u>NIR Applications classification: for photocurrent below 0.1 μ A PD noise dominates, between 0.1 – 100 μ A – photocurrent shot noise, above 100 μ A – DL noise. For MIR PD noise dominates and is 4 orders of magnitude larger.</u>

Topography reflector



Several applications need topography reflector. DL light is collimated in parallel beam and directed to topography reflector - TR (wall, grass, trees, etc). Small part $(10^{-3} - 10^{-9})$ of DL light scattered by TR is collected by receiving optics and recorded by PD. Requirement for TP is related to NEP (Noise Equivalent Power). For present system NEP \sim 1pW. This application is small signal detection.

Based on DL power (20 mW), NEP, final efficiency - 0.3, receiving optics diameter - 20 cm, and requirement for S/N \ge 1000, maximum operation distance for TR can be estimated \le 250 m.

DL systems with TR

A lot of applications needs UAV (Unmanned aerial vehicle), helicopter or airplane based instruments. Main problem in this case is related to minimum allowed altitude of their flights (for helicopter more than 80 m).

1k -

— GPI DL+fiber amplifier



Because of system elements optimization, final efficiency was improved more than 50 times. For the first time DLS instrument with TR was developed for helicopter installation.





Using Raman fiber amplifier operation distance of DLS instrument can be increased up to 4.4 km (airplane).

Remote detection using TR



Remote detection of ammonia and methane when sample gases were injected in vehicle located at 100 m from the instrument. Receiving optics with 20 cm diameter was used. Because of small scattered signal from TR, sufficiently high concentrations are necessary for remote detection. <u>Application of TDLS with TR – detection of hazard situations.</u>

Leakage from gas pipeline



Example of hazard situation leakage from gas pipelines. **TDLS** instrument was installed on helicopter. Example of test flight (140 m.) Peak - methane leakage from low pressure pipeline. Leakage coordinates were determined. Surface presents background of methane concentration and its spatial variations.

Question: is detected leakage hazard with respect to regulations? TDLS instrument was calibrated with MosTransGas and leakage rate was estimated – 4 l/sec. It is dangerous inside building and is not dangerous in open air. High pressure pipelines - for some leakages, significantly higher rates were detected (hazard).

Heterodyne

- Next application: Heterodyne in NIR. Requirement: operation within photocurrent range $0.1 100 \mu$ A when photocurrent shot noise dominates.
- Heterodyne is well-known technique for remote sensing. Two radiations reach PD: coherent radiation from Local Oscillator (LO) and broad band radiation from signal source (S). PD detects intensity.

$$\left|\vec{E}_{LO} + \vec{E}_{S}\right|^{2} = \left|\vec{E}_{LO}\right|^{2} + \left|\vec{E}_{S}\right|^{2} + \left|\vec{E}_{LO}\vec{E}_{S}^{*} + \vec{E}_{LO}^{*}\vec{E}_{S}\right|$$

- The intensity has two constant components (LO and S) and heterodyne (in brackets). Heterodyne is noise and is measuring near f = 0. Main heterodyne problem is alignment of LO and S wave fronts within radiation wavelength. Even in MIR it is difficult – only few MIR Heterodyne systems are available in the world. In NIR this problem is extremely difficult.
- NIR Heterodyne. We've used single mode fiber coupler (A.Rodin) to fix the alignment problem. Single mode fiber do alignment procedure automatically because it is single mode.

Heterodyne in Near IR

First demonstration of laboratory heterodyne radiometer operation in Near IR.



Photocurrent noise variance - D(i) vs. I - DL excitation current (black circles). LO and S – two DLs above and below threshold, respectively. S radiation passed cell with low pressure of water vapor. Red – photocurrent shot noise (SN). Difference is HET.

$$HET = G_{S}(v_{LO})i_{LO}B$$
$$SN = ei_{LO}B$$
$$\frac{HET}{SN} = \frac{G_{S}(v_{LO})}{e}$$

Both HET and SN have similar dependences on experimental parameters. Hence HET can be measured in unites of SN. $G_{S}(v_{LO})$ is spectral density of signal source for LO frequency.

Near IR Heterodyne radiometer

Simple, portable NIR radiometer for Sun radiation was developed.



It contains module to follow automatically Sun position (left); small (2 cm) objective to focus Sun on single mode fiber (middle), and module with DL, fiber optics, reference channel, and electronics (right). Left module was installed on our building roof. Right module was installed in our office. Both modules were connected by 100 m single mode fiber cable.

Near IR Heterodyne radiometer test Example of measurement March 7, 2013.



Recorded spectrum of heterodyne dispersion (HET) normalized to shot noise (SN), averaging time -10 min. Sun irradiance is highest at noon.

Several absorption features can be found in spectral range under consideration. Some are due to absorption by Earth atmosphere $(CH_4 \text{ and } CO_2)$. Sun Fraunhofer line can be also observed.

Heterodyne data retrieval

Heterodyne spectra are using for atmosphere parameters retrieval. Observed atmosphere line shape is superposition of absorption of layers of all altitudes with different pressures and temperatures.



In present case CH_4 line shape for zenith angle was used to retrieve altitude dependence of methane concentration.



A.Rodin, et.al., Optics Express, 2014, 22, 13825 (see C5).

Heterodyne data retrieval

10.03.2014



Doppler shift (black circles) as function of observation time.

$$Doppler _ shift = -\frac{\left(\vec{k}\vec{V}\right)}{c}$$

CO₂ line can be used to obtain information about wind velocity in stratosphere -Doppler shift.



For known observation time, Doppler shift can be calculated. Red curve corresponds to Doppler shift calculations for wind speed V(W-E) = 105 m/sec.

Noise Equivalent Absorbance (NEA)

Previous two applications consider small signal detection in presence of sufficiently high molecular absorbance.



Next application is detection of trace molecular absorbance for large signal. Requirement – NEA (Noise Equivalent Absorbance) = relative photocurrent noise = RIN (Relative Intensity Noise).

For photocurrent i above 0.1 mA (0.5 % of total DL emission in NIR), noise is proportional to i (blue line), NEA is constant. Hence, this noise is generated inside DL.

DL Quantum Noise



Noise dependence vs. excitation current near threshold. It is DL quantum noise: excitation current shot noise; electrons and photons Poison noises; quantum noise of electromagnetic field inside laser due to spontaneous emission.

DL model (red curve) was developed and tested (see next slide).

Inter-comparison

Noise properties of many DLs were investigated. Part of these results is presented.



Model describing DL noise was developed. It has three parameters: Photons number at threshold $-N_{p}(I_{th})$ (experiment). Two fitting parameters: photons and electrons lifetimes are close to physical estimates (traveling time and scattering by acoustic phonons).

In NIR, for correct TDLS system (no technical noises), NEA origin is DL quantum noise. *It is NEA fundamental limit*. For further NEA improvement recorded signal averaging is necessary.

Origins of NEA limitation NEA Allan plot as function of averaging time.



White noise (red), Flicker noise (green), and drift (blue) determine NEA. For white noise fundamental limit due to DL quantum noise is achieved. Flicker noise and drift limit NEA and can not be reduced by averaging time increase.

Physical origins of both Flicker noise and drift have to be identified to reduce their influence.

DL flicker noise origin

DL flicker noise has fundamental origin: excitation current density fluctuations and nonlinear DL behavior. It is known that combination of these two processes results in flicker noise.

Result - flicker fluctuations of DL near field pattern: position (red) and width (blue). This noise has important characteristic: its integral over DL active area is constant (current is constant).



 $E(t,\theta) = \int_{-\infty}^{\infty} E(t,x) \exp[kx\sin(\theta)] dx$ Far field is Fourier transformation of near field.

Near field flicker noise of position and width will result in frequency and intensity noises, respectively. *Important result: there is direction in DL diagram (\theta = 0) where both frequency and intensity flicker noises are equal 0 (total intensity is constant).*

DL flicker noise



As PD records only part of DL radiation, flicker noise is presenting (black open circles).

Traditional experimental scheme with objective.



DL flicker noise suppression



As PD records only part of DL radiation, flicker noise is presenting (black open circles).

Traditional experimental



scheme with objective.



PD records small part of DL radiation (~ 0.5 %) where flicker noise is equal 0 (red solid circles).

Correct experimental scheme: no objectives.

Correct experimental strategy based on flicker noise origin and its properties provides possibility for total flicker noise suppression.

Origins of NEA limitation NEA Allan plot as function of averaging time.



White noise (red), Flicker noise (green), and drift (blue) are limiting NEA. For white noise fundamental limit due to DL quantum noise is achieved. Flicker noise and drift limit NEA and can not be reduced by averaging time increase.

Physical origins of both Flicker noise and drift have to be identified to reduce their influence.

Flicker noise suppression

NEA Allan plot as function of averaging time.



Flicker noise origin is identified and method of its suppression was developed.

NEA is limited by baseline drift

Baseline

Eight baseline origins were identified and their properties were investigated:

- B1 DL active area conductivity inhomogeneity;
- B2 Excitation current density fluctuations;
- B3 Light scattering inside DL chip;
- B4 Light scattering inside DL module;
- B5 Light scattering inside fiber;
- B6 Optical feedback;
- B7 Interference in TDLS optical scheme;
- B8 Interaction of DL photons and electrons with phonons.

Methods of above mentioned baseline origins subtraction were developed.

Flicker noise suppression

NEA Allan plot as function of averaging time.



Flicker noise origin is identified and method of its suppression was developed.

NEA is limited by drift.

Drift suppression

NEA Allan plot as function of averaging time.



Baseline origins were identified and methods of their suppression were developed.

NEA is limited by DL quantum noise (fundamental limit).

Inter-comparison



Inter-comparison of best results achieved in the world for NEA. GPI has several orders of magnitude advantage. It was achieved because origins of main fundamental processes of limitation were identified and strategy to suppress them was developed.

Comments if necessary.

For 6 sec averaging time NEA achieved is 6 10^{-8} . Using very stable Chernin cell (0.5 m, 600 passes, total length = 300 m) following parameters can be achieved: Noise equivalent absorption coefficient = 2 10^{-12} cm⁻¹. Noise equivalent molecular concentration (HF) = 0.8 ppt (10^{-10} %).

IAEA safeguards

Backpack modification of TDLS instrument was developed for IAEA to detect illegal UF_6 enrichment activity.

For field experiments we use Chernin cell (25 cm * 156 passes = 39 m). The instrument detects HF presence in atmosphere.





Noise Equivalent Concentration (NEC) for HF as function of averaging time. The instrument can be also used for monitoring near aluminum and plastic plants.

Additional requirements

For many applications molecular absorbance is significantly (orders of magnitude) higher NEA (Noise Equivalent Absorbance). For such applications there are other requirements:

Long-term unattended monitoring.

Industrial control.

Detection of several molecules.

Fast concentration measurements.

High accurate measurements.

Etc.

Examples of several applications will be briefly presented below.

Long-term unattended monitoring

DL beam passed open atmosphere (100 m), was reflected, and received by 10 cm telescope. Three parameters were recorded: Sun illumination (black), DL light (blue), and CO_2 concentration (red). Graph presents one year monitoring with 1 hour averaging.



Day – night as well as summer – winter variation of Sun illumination intensity can be observed.

DL signal variation is due to optics misalignment as well as changes of transparency due to snow and rain.

Observed CO_2 concentration variations is not noise. It is due to daily concentration variations.
Industrial control





High purity hydrides

Now four rectification columns are in operation at NPO "Salut" (NN). Present list of impurities of interest: H_2O , CH_4 , CO_2 , H_2S , NH_3 , C_2H_4 , C_2H_2 . To control different impurities in purification processes of different high purity hydrides 15 TDLS complexes were developed and installed. These complexes were prepared for long-term unattended operation. Goal of the complexes was to control purification process.



Example of AsH₃ purification control. NH₃ in present case was impurity under control. Measurements were done in 3 points. Raw and pure materials – green and red, respectively. White - Light Fraction.

End of purification process can be easily recognize. Result – significant reduction of purification time. See also O3, A15, C14.

Airplane – laboratory

Russian State Program: ROSHYDROMET airplane laboratory IAK – 42D. Now it is in operation. Part of the laboratory is TDLS complex to measure methane, CO_2 , water and its isotope content in real time.





TDLS complex: DLs and electronics; gas module and computer.



Electronics and reference channels for 3 DLs and fiber optics.



Gas module: Chernin cell – 39 m. Pressure – 50 mBar.

TDLS complex

ROSHYDROMET has program of environment monitoring using airplane-laboratory. TDLS complex is part of this laboratory.



Monitoring campaign June 2014. Goal: investigation of the ability to identify pollution from industrial centers of Europe in the Yamal-Nenets Autonomous District. Results for June 24, 2014 flight.



Monitoring campaign February 2015 near Novaya Zemlya. Goal: identification of results of oil gas burning on oil derricks located around oil fields. Trajectory of Feb.28, 2015 flight. See also B3, C4.

Non-contact explosives detection

Traditionally explosive molecules presence in atmosphere is considered as main signature for remote explosives detection. I don't know any positive result of this approach. From our point of view it is dead end: for main explosives saturated vapor concentration is dramatically smaller in comparison with available techniques Detectivity. In real life situation is even worse because of explosive sample wrapping. Explosive molecules flow from hole in wrapping can be estimated and is too small:

 $\frac{\partial N}{\partial t} = \pi D dN_0 = 10^5 \, mol \, / \, \text{sec}$

Physics is saying: this flow can not be detected. What sniper dogs smell?

Explosives belongs to energetic materials producing energy after defragmentation, their energy is higher than energy of products of defragmentation. Such systems are known as metastable. Explosives have characteristic half life time around tens years. Estimation of decay product molecules flow for 100 kg explosive sample in wrapping is: It is 13 orders of magnitude higher $\frac{\partial N}{\partial t} = 310^{18} \, mol \, / \sec$

Explosives decay products were identified and several TDLS instruments for remote explosives detection were developed.

Remote explosives detection

Several TDLS instruments were developed to detect explosives for different scenarios. As example, field tests of two instruments for two scenarios are presented



Remote explosive sample (20 kg) detection inside moving vehicle.



Remote explosives detection: 200 kg explosive sample in wrapping was detected at 120 m distance down wind.

Medical screening diagnostics

The possibility of medical screening diagnostics using TDLS was considered decades ago [A.I.Nadezhdinskii, et.al, Infrared Physics & Technology, 37, 181-192 (1996)]. Idea was rather simple: for healthy patient molecular concentration has to be normal, otherwise significant difference from equilibrium can be observed.

It is not disease diagnostics. It is more like temperature measurement: 36.6 °C – normal; above 37 °C – problem.

- Next step: human can be considered in similar way as explosives. Human body is metastable system. There is a lot of chemical reactions inside us.
- Following list of molecules for medical screening diagnostics is under consideration at the moment H_2O , NH_3 , H_2S , CO_2 , and CH_4 .

Clinical test of TDLS complex

TDLS complex to measure H_2O , NH_3 , H_2S , CO_2 , and CH_4 both from breath and hands of patient was developed. This complex was tested in Moscow City Clinical Hospital Nº12.



Results of clinical tests

TDLS complex to measure H_2O , NH_3 , H_2S , CO_2 , and CH_4 both from breath and hands of patient was developed. This complex was tested in Moscow City Clinical Hospital Nº12. 78 patients with known diagnoses passed these measurements. As example we are presenting preliminary results of CO_2 and CH_4 measurements.



One can see normal (constant value) and abnormal (orders of magnitude difference) behavior due to particular diseases – subject of medical screening diagnostics.

See also C15.

Fast measurements

Next application – fast processes investigation. Requirements: high both spectral and time resolution.

Fundamental limit for this application is related to uncertainty $\Delta\omega\Delta t \sim 1$. This effect is well-known in radio spectroscopy as adiabatic (fast, rapid) resonance passing. In MIR for the first time it was experimentally observed in: M.Spiridonov, et.al., Optics and Spectroscopy, 65, #6, 706-709 (1988).

We had several examples of fast processes investigation: molecules (ethanol, explosives) detection inside passing vehicle, gas leakage detection (vehicle, helicopter, Unmanned aerial vehicle based TDLS instruments), turbulence channel for airplane laboratory, combustion zone investigation of mixing supersonic flows of fuel and oxidizer. Characteristic times of these measurements are between 50 μ sec – 50 msec depending on application, as well as hardware and software in use.

Turbulence channel

Turbulence channel developed test is considered below as example of fast processes investigation. The instrument measured H_2O concentration and was installed on vehicle.



Moscow ringroad was used for this test (driving speed around 80 – 100 km/h). Stable water concentration can be observed with variations - subject of present slide.

Allan plot of this graph. GPS data were used to transform time dependence to spatial one. Smoothed peak can be observed near 4 m. For higher distances one can see drift. Both are due to turbulence.



Measurements with high accuracy

Several TDLS applications (UF₆ enrichment, greenhouse gases, accurate spectral line parameters, gas mixture standards, etc.) require high accurate absolute measurements below 0.1 % level.

	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

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, etc. See A1.

Total accuracy estimation is 0.06 %.

Integral intensity test

To test achieved measurements accuracy, isolated CO_2 line (6953.467 cm⁻¹) was selected. For isolated spectral line integral intensity has to be constant.



Spread of experimental data is in agreement with vertical bar - our accuracy estimation (0.06 % - A1). Horizontal red constant is HITRAN integral intensity for analytical line. HITRAN accuracy estimation for this line is 1 - 2 %. Vertical red bar corresponds 1 %. Our data can confirm HITRAN accuracy. The reverse is not valid. **Conclusion: absolute TDLS** accuracy 0.06 % was confirmed experimentally (see B2).

Gas mixture standard

Example of high accurate measurements is gas mixture standard. Requirement: absolute concentration accuracy < 0.1%.



TDLS system was developed to measure CO_2 concentration in $CO_2:N_2$ gas mixtures. To test its absolute accuracy, several calibrated gas mixtures were prepared (C_0) and measured (C).

Result of TDLS system accuracy test is in agreement with TDLS accuracy estimation (0.06 %).

UF₆ enrichment

Measurement of UF_6 enrichment is important part of IAEA safeguards. Requirement for enrichment measurement accuracy is very hard < 0.003 %.

Possibility to measure UF₆ enrichment using TDLS technique was considered in [1]. Specially developed QCL to measure UF₆ enrichment was investigated in [2]. The same fine structure due to molecule rotation was observed for both ²³⁵UF₆ and ²³⁸UF₆ [3].

[1] A.Berezin, S.Malyugin, A.Nadezhdinskii, D.Namestnikov, Ya.Ponurovskii, D.Stavrovskii, Yu.Shapovalov, I.Vyazov, V.Zaslavskii, Yu.Selivanov, N.Gorshunov, G.Grigoriev, Sh.Nabiev, UF6 enrichment measurements using TDLS techniques, Spectrochimica Acta, A 66, 796–802 (2007)

[2] A.Nadezhdinskii, Ya.Ponurovskii, I.Popov, Yu.Shapovalov, D.Stavrovskii, Investigation of quantum cascade laser developed to measure UF6 enrichment, Abstracts of TDLS 2011, Zermatt, Switzerland, p.63.

[3] A.Nadezhdinskii, Ya.Ponurovskii, I.Popov, V.Semenov, Yu.Shapovalov, D.Stavrovskii, A.Babichev, G.Grigoriev, Sh.Nabiev, 238UF6 and 235UF6 spectra and enrichment measurement in mid IR spectral range, Abstracts of TDLS 2013, Moscow, Russia, p.26.

Isotope shift

Cross sections of $v_1 + v_3$ band for ²³⁸UF₆ (N) and ²³⁵UF₆ (E).



Involvement of U atom in vibration motion results in isotope shift 0.59(1) cm⁻¹ (left graph).

After taking into account this shift (right graph), spectra of both samples coincided. It is important for applications: measure $^{238}UF_6$ spectrum and using isotope shift obtain $^{235}UF_6$ spectrum. Spectra fine structure can be observed.

UF₆ spectra fine structure

To intensify fine structure, cross-sections logarithmic derivatives were calculated ${}^{238}\text{UF}_6$ – black, red; ${}^{235}\text{UF}_6$ – blue, green (left).



After taking into account isotope shift (right graph), spectra of both samples coincided. This fine structure of Q-branch is known from literature for spherical top molecules.

This fine structure is due to molecule rotation. It is similar for both isotopomers because U atom is not included in rotation motion and has no influence on rotational structure.

S pressure dependence

Accuracy improvement achieved provides possibility to detect new physical effects (see C1).



High accurate CO₂ data were fitted by convolution of Lorenz and Doppler (Hard and Soft). Normalized integral intensity S/S_0 is presented. Here S_0 is integral intensity for high pressure. Significant (0.15%) difference can be observed in intermediate pressure range. For zero and high pressures both Hard and Soft are approaching to 1. More careful analysis of line shape model is required.

Phase and velocity correlation

In classical paper [1] several line shape models were considered. Line shape was obtained for model when phase and velocity are changing in the same collision and hence have correlation (**COR**). It was predicted theoretically and its main characteristics were analyzed. **COR**: Its influence is negligible both for low (no collisions) and high pressures (for high number of collisions, the process is normal – no correlation). Line shape is not convolution of Doppler and Lorenz profiles.

Conclusion (see C1): Correlation between phase and velocity changes during collision was experimentally observed for the first time. CO_2 molecule is good candidate for this effect observation because both broadening and narrowing cross sections have close values.

 S. G. Rautian and I. I. Sobel'man, "Effect of collisions on Doppler broadening of spectral lines," Sov. Phys. Usp. 9, 701–716 (1967), УΦΗ, 90, 209-236 (1966) (in Russian).

Conclusion

- TDLS analytical application classification based on dominant noise type was presented.
 Additional requirements for special applications were considered.
- Several instruments for different TDLS analytical applications were developed.
 Test results of several instruments for different
 - TDLS analytical applications were discussed.

Thank you

DL history

Here we are speaking about spectroscopy using Diode Lasers (DL). For Diode Laser all laser components (active media, excitation and resonator) are in the same package of DL chip.

Milestones:

First publications: Semiconductor as laser active media [1] and p-n junction usage for excitation [2], <u>N.Basov</u> Nobel lecture [3]
[1] N.G. Basov, B.M Vul and Yu.M. Popov, Soviet JETP (U.S.S.R.), 37, 585, (1959).
[2] N.G. Basov, O.N. Krokhin and Yu.M. Popov, Soviet JETP (U.S.S.R.), 40 (1961) 1897.
[3] NIKOLAI G. BASOV, Semiconductor lasers, Nobel Lecture, December 11, 1964.

DL history

From theoretical prediction to practical realization – 3 years. Stimulated emission in semiconductors [4]. [4] A.Rogachev, etc, "Recombination radiation of galium arsenic", Soviet Physics- Solid State (USA), 4, pp. 782 (1962). First semiconductor injection laser (Diode Laser) [5]. [5] R. H. Hall, etc. "Coherent light emission from GaAs junction", Phys. Rev. Lett, 9, pp. 366-378 (1962). First DL in USSR was developed at the same time (*A.Shotov*). Hetero-structures [6] are base of recent DL technology. [6] **Zh.Alferov**, etc., A characteristic feature of injection into heterojunctions, Sov.Phys.Solid State, 8, 2480 (1967), Zh.Alferov, Nobel lecture December 8, 2000. New $A^{V}B^{V}$ (PbTe) DL for Mid IR [7]. [7] J.F.Butler, etc., PbTe Diode Laser, Appl.Phys.Lett., 5, 75 (1964). In USSR ~1975 – A.Shotov, I.Zasavitskii, A.Britov, G.Kaluzhnaya, Yu.Kosichkin.

TDLS History

First high resolution molecular spectra using Diode Lasers (DL) were obtained by <u>**E.D.Hinkley</u>** [1]. [1] E.D.Hinkley, High resolution IR spectroscopy with a tunable diode laser, Appl.Phys.Lett., 16, 351 (1970). It was beginning of TDLS.</u>

First commercial DL spectrometer was developed by Prof. <u>*A.W.Mantz*</u>.

In USSR - first spectra were obtained in 1977.

1985 - USSR State Prize: Tunable A^{IV}B^{VI} semiconductor

lasers and high resolution molecular spectroscopy;

A.Britov, I.Zasavitskii, A.Shotov, A.Nadezhdinskii,

Yu.Kuritsyn, etc.



Molecular spectra

- Maximum molecular absorption is in fundamentals (MIR). Overtones are many times weaker.
- For adiabatic (Born-Oppenheimer) approximation: "Many times" is determined by - $\sqrt{(m/M)}$,
- Here m and M are electron mass and effective mass of vibration, respectively.
- Using this classification all molecular absorption bands can be divided in three groups:
- 1. M~1 (Hydrogen bond).
- 2. M~10 (C-O, N-O, ...)
- 3. M~100 (heavy spherical tops UF_6 , OsO_4 , ...)



Spectra of HF, CO_2 , UF_6 – representatives of above mentioned groups. "Many times" for them are 30, 100 μ 300 times, respectively.

Molecular spectra and PD

Comparison of PD noise with signal (absorption) for three above mentioned groups of molecules leads to principal conclusion: overtones (NIR) are optimal for molecules with hydrogen bonds (M=1) detection.

For second group (M~10) S/N ratio is similar for both fundamentals and overtones. The choice depends on researcher qualification.



For third group (heavy spherical tops) MIR spectral range is preferable. So to measure UF_6 enrichment we are using MIR spectral range.

Heterodyne

Heterodyne is well-known technique for remote sensing.



Two radiations reach PD: coherent radiation from Local Oscillator (LO - black) and broad band radiation from signal source – S (red).

PD detects intensity.

$$\left| \vec{E}_{LO} + \vec{E}_{S} \right|^{2} = \left| \vec{E}_{LO} \right|^{2} + \left| \vec{E}_{S} \right|^{2} + \left| \vec{E}_{LO} \vec{E}_{S}^{*} + \vec{E}_{LO}^{*} \vec{E}_{S} \right|$$

Receiving intensity has two constant components (LO and S) and HET heterodyne component (in brackets). Heterodyne transfers signal source spectrum to small frequency range (blue). Heterodyne component is noise and is measuring near f = 0.

Applications classification ??

Different applications have different requirements. Applications classification can be done using classification of noise origins.



Noise origins classification for NIR. Classification of PD people: small signal range (red) – PD noise is dominant. $g_{PD} = const;$ large signal range (green) photocurrent shot noise dominates. $g_{SN} = (ei)^{05}$. DL quantum noise (blue) is proportional to i - $g_{DI} = RIN^*i$. Here **RIN** is Relative Intensity Noise. For MIR, PD noise dominates and is above presented scale. The last is in agreement with analysis presented above.

Next application: Heterodyne in Near IR.

Applications requirement: operation within photocurrent range 0.1 – 100 μ A where photocurrent shot noise dominates.

Heterodyne

- Traditional Heterodyne usage of quick PD+Preamp (several GHZ) and Fourier Transformation of recorded noise.
- Main problem of heterodyne is alignment of LO and S wave fronts within radiation wavelength. In radiofrequency range it is simple. In Mid IR it is very difficult – only few Mid IR Heterodyne systems are available in the world. In Near IR this problem is extremely difficult. No Near IR Heterodyne system is known for author.
- Near IR Heterodyne. We've used single mode fiber coupler (A.Rodin) to fix the alignment problem in Near IR. Single mode fiber do alignment procedure automatically because it is single mode. Our approach to measure noise inside low bandwidth (1 MHz) and use dependence of LO frequency vs. excitation current to obtain Heterodyne spectrum.

Receiving modules





Family of receiving modules was used for different applications with TR:
1. Handle - objective diameter 5 cm (distance up to 60 m)
2. Vehicle - objective diameter 10 cm (distance up to 120 m)
3. Helicopter - objective diameter 20 cm (distance up to 250 m)



Calibration

Calibration was performed with MosTransGas near Moscow where 5 high pressure gas pipelines are crossing.



View of the experiment location and instrument with 10 cm receiver installation. Forest was used as TR.





Gas leakage source was developed, calibrated, and connected to high pressure gas pipelines facility.

The source provided calibrated gas flow from 1 to 10 l/sec.



Calibration results



Cross sections of gas plume above calibrated gas leakage for leakage rate 1.2 l/sec (human breath). Similar to smoke over fire, they have fine random structure due to atmosphere turbulence. The cross sections integral parameter was determined giving ability to determine leakage rate.

Diagram of calibration experiment. DL beam was directed to forest (TR), scattered light was recorded by receiver. The receiver automatically scanned gas plume from the leakage source.



Using this calibration leakage rate for helicopter test flight was estimated -4 l/sec. It is dangerous inside building and is not dangerous in open air.

Water isotopologues



Isotopes content of these samples was measured with respect to standard one (#1). Significant variation of samples under investigation isotopes content can be observed. Water cannel provides possibility to measure isotope content of water vapor. Recorded signal with identification of H₂O isotopologues spectral lines for standard sample. Water samples were taken from Volga, Moscow, and Oka rivers, springs, wetlands, and artesian well.



Turbulence

Requirement of many applications is fast data recording. Time to measure molecular concentration in present case is 0.5 msec. Example of this application is turbulence channel of Airplane laboratory. This channel measures times dependence of water vapor concentration in atmosphere out of plain.



DL output is located close to illuminator (4). DL radiation is reflected by mirror (5) and detected by PD. Mirror (5) is located on TDLS complex air receiving module. Optical path out of plain is L = 40 cm.

Turbulence channel prototype



Turbulence channel prototype was developed for field tests. For this prototype the same components and dimensions were used as for airplane turbulence channel.

Turbulence channel prototype was installed on vehicle roof. It measures water vapor partial pressure in air passing through prototype optical path (L = 40 cm).


Turbulence channel field test



Fragment of water partial pressure time dependence detected during test drive. H_2O partial pressure is constant with variations due to water spatial inhomogeneity – subject of present investigation.

Allan plot of fragment presented above. To obtain this graph GPS data were used to transform time dependence to spatial one.



Smoothed peak can be observed near 3-4 m (distance between vehicles). Longer turbulence dimension (above 100 m) also can be observed.

Explosives are metastable

Explosives belongs to energetic materials producing energy after defragmentation (for TNT it is 4.2 MJ/kg or 10 eV/mol). Hence, their energy is higher than energy of products of defragmentation. Explosives energy diagram (right) in some configuration space. Such systems are known as metastable. Decay channels are shown by arrows. Explosives are metastable objects with characteristic half life time around tens years.



Detection of explosives decay products in wrapping is determined by totally different process in comparison with previous one. <u>Concentration of explosive decay molecules inside wrapping will increase</u> <u>until their flow through wrapping hole will be equal to decay rate. For 100</u> <u>kg of explosive sample it means:</u>

3 10¹⁸ mol/sec

It is 13 orders of magnitude higher than explosive molecules flow.

Explosive decay products

Small explosives samples (~ 1g) were installed in container and remained in it at 60 °C for several hours. Explosive decay products in atmosphere above samples were investigated using GC/MS technique.







For all samples under investigation 3.66 min peak (marked by arrow) was observed (upper picture). Lower picture is MS of this peak. It is HNCO – isocyanic acid. Its interaction with atmosphere water leads to [1]:

 $HNCO+H_2O=NH_3+CO_2$

1. Fearon, Wm. Robt. And G.C. Dockeray, "A Note on the Hydrolysis of Cyanic Acid." *BioChem Journal*, November, 1925.

http://www.biochemj.org/bj/020/0013/0200013.pdf

<u>Resume: ammonia is signature of all N</u> <u>containing explosives.</u>

Some other peaks common for different samples were observed but not yet identified.