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TDLS of methane and its applications to study of methane emissions from natural structures to the atmosphere

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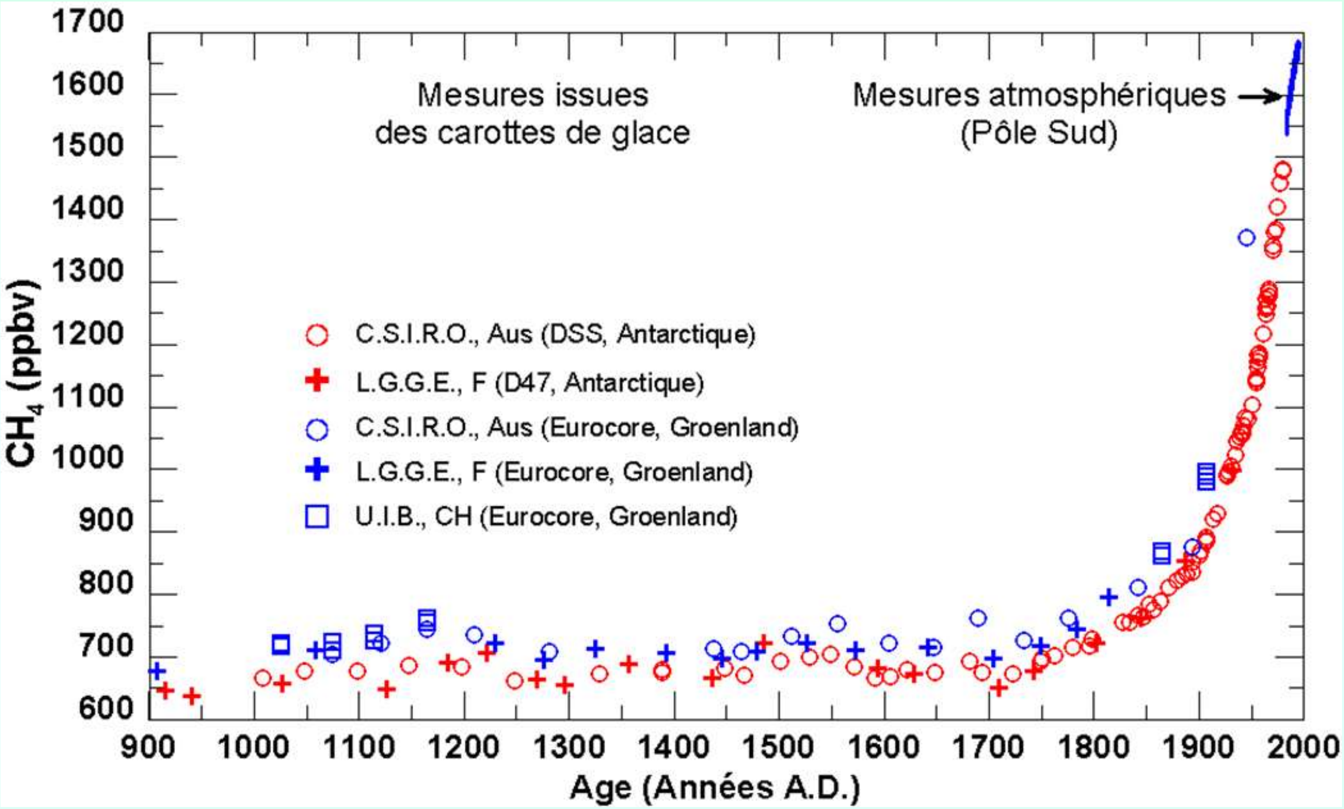
1. Motivation
2. PA TDLS spectrometers
3. Experimental study of CH_4 spectra
   - line positions and intensities
   - line broadening, shifting and interference
4. TDLS applications to study of methane emissions (hydrocarbons, coal, biological systems)
5. Summary

1.Motivation

1. Spectroscopic databases progress
2. Validation of spectral line shape models
3. Retrieval of methane profiles in Earth atmosphere from satellite data
4. Local and remote detection of methane emissions with TDL techniques

Changes of atmospheric methane total amount from 900 to 2000 year.



CH_4 increase

0,6 ⟶ 1,7 ppm

Change in radiative heating, W/m²

Atmospheric gas	Atmosphere	Surface
CH_4 doubling	0,43	0,21
CO_2 doubling	1,14	1,56

Contribution of CH_4 doubling = 38% of CO_2 doubling

PA TDL spectroscopy of CH_4 spectral line manifolds near 1.65 mkm

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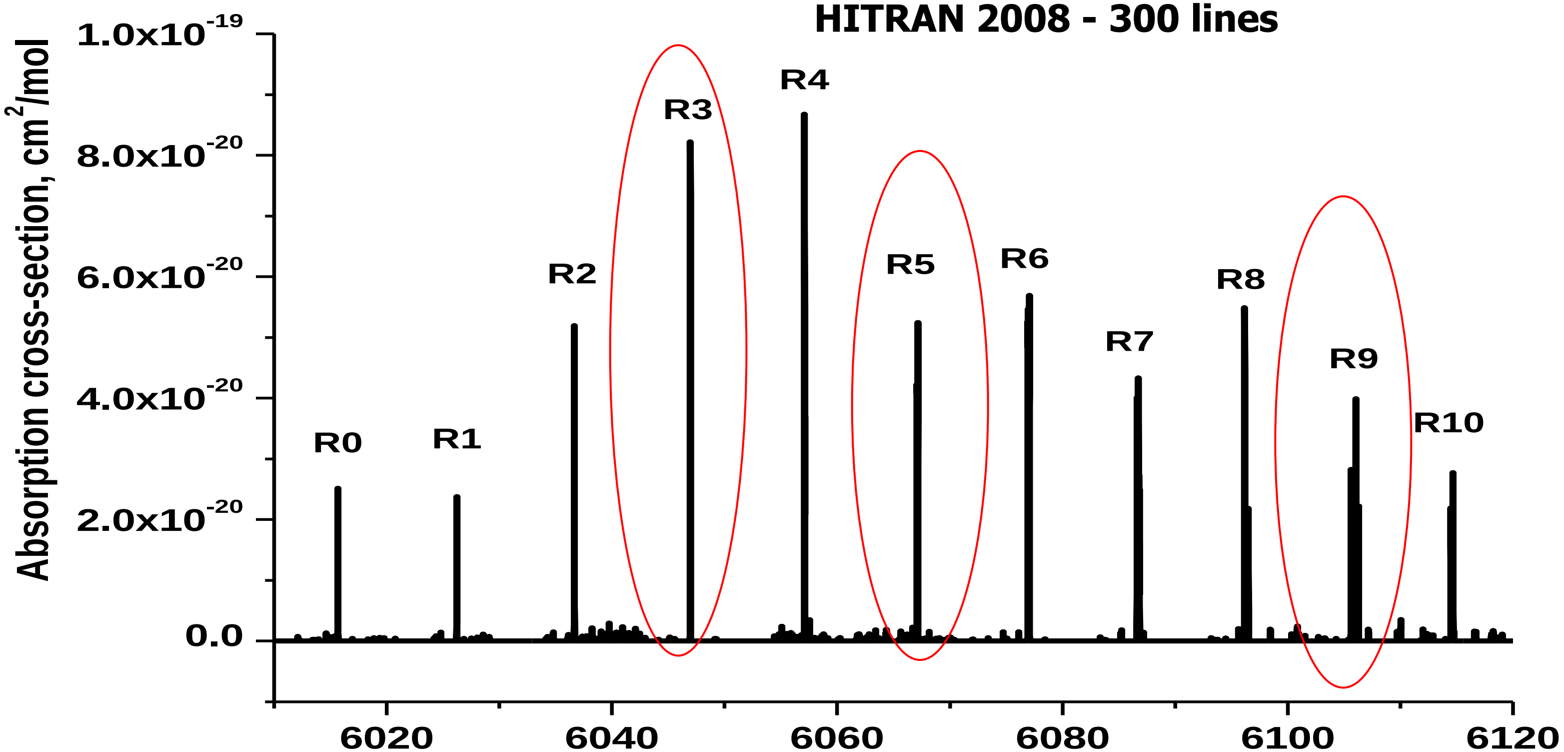
Methane $2\nu_3$ band spectrum

Kapitanov V.A., Ponomarev Yu.N., Tyryshkin I.S. and Rostov A.P. // Spectrochimica Acta Part A. 2007. V. 66, N 4-5, P. 811-818.

Our CH_4 Spectrum -more than 600 lines
HITRAN 2008 - 300 lines



http:\\spectra.iao.ru (HITRAN 2008)

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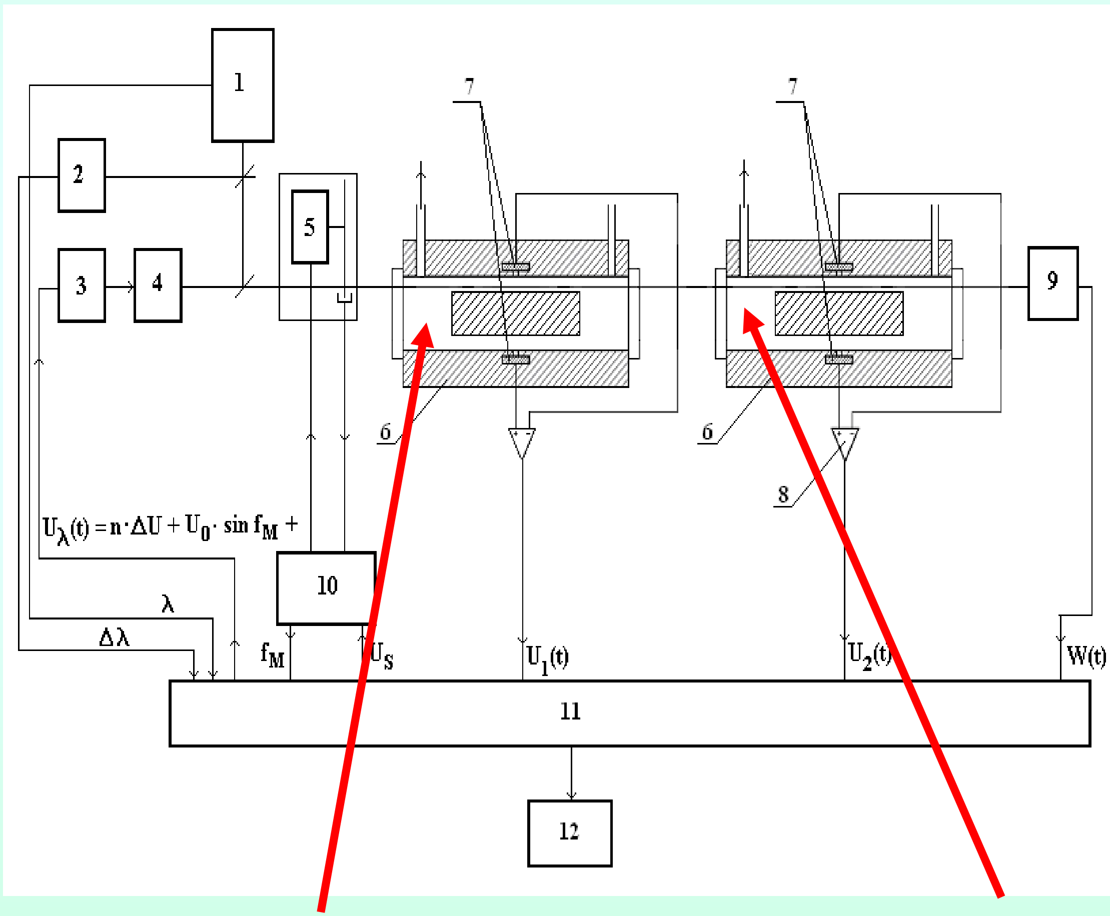
Two-channel diode laser OAD spectrometer

Kapitanov V.A., Ponomarev Yu.N., Tyryshkin I.S and Rostov A.P.: Spectrochimica Acta Part A, 66A, 4-5, 811-818 (2007)



laser:

$\Delta\nu$ - 6060-6250см$^{-1}$

$d\nu$ - 2,5-3 см-1

W - 3-7 мВт

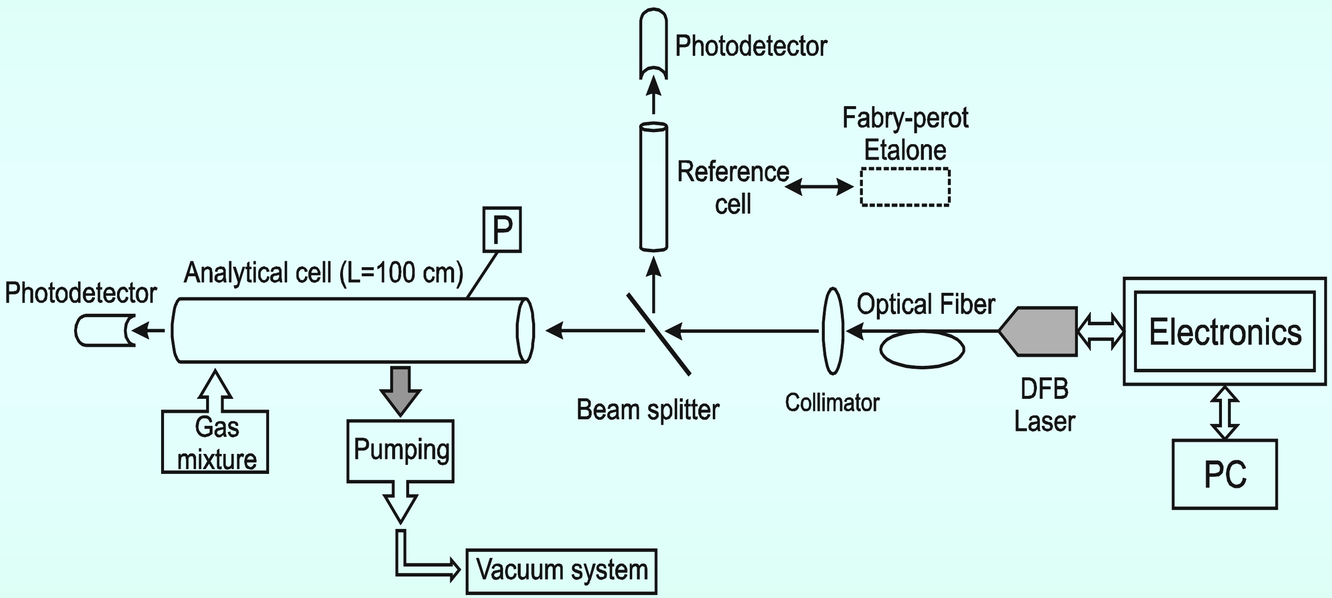
OAD:

$\Delta = (U_{ш}^2)^{1/2}/R =$ $4 \cdot 10^{-9}$ см$^{-1}$Вт

CH_4, low pressure — **Mixture, high pressure**

Block-diagram of the two channel DL spectrometer

K.Y. Osipov, A.E. Protasevich, V.A. Kapitanov, Y.Y. Ponurovskii: Appl.Phys. B. 2012. V. 106, No 3. P. 725-732



laser: Δν - 6066-6068см$^{-1}$, W - 15 мВт

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Fitting procedure

1. Spectrum by spectrum fitting
2. Multispectrum fitting

Multispectrum fitting procedure applied for all spectra simultaneously.

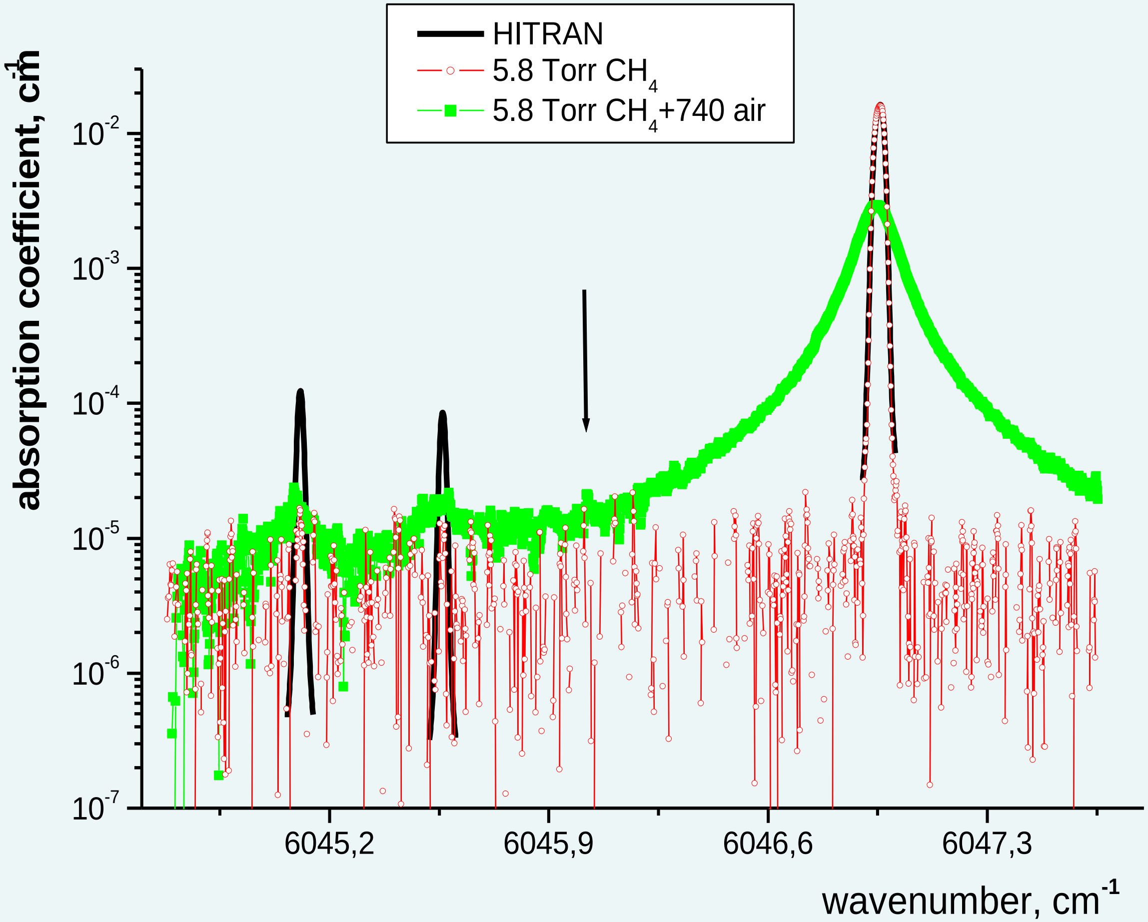
[Pine A. S. Line mixing sum rules for the analysis of multiplet spectra // JQSRT 1997. Vol. 57. № 2. pp. 145-155.]

$$K(\omega) = \frac{1}{\sqrt{\pi}} \sum_m \frac{\xi_m \operatorname{Re} P(x'_m, y_m, \zeta_m) + \eta_m \operatorname{Im} P(x'_m, y_m, \zeta_m)}{\sigma_m}$$

$\sigma_m = \omega_m^0 \sqrt{\frac{2k_B T}{Mc^2}}$ *- Doppler halfwidth of line numbered m at e^{-1} of line maximum, cm^{-1}*

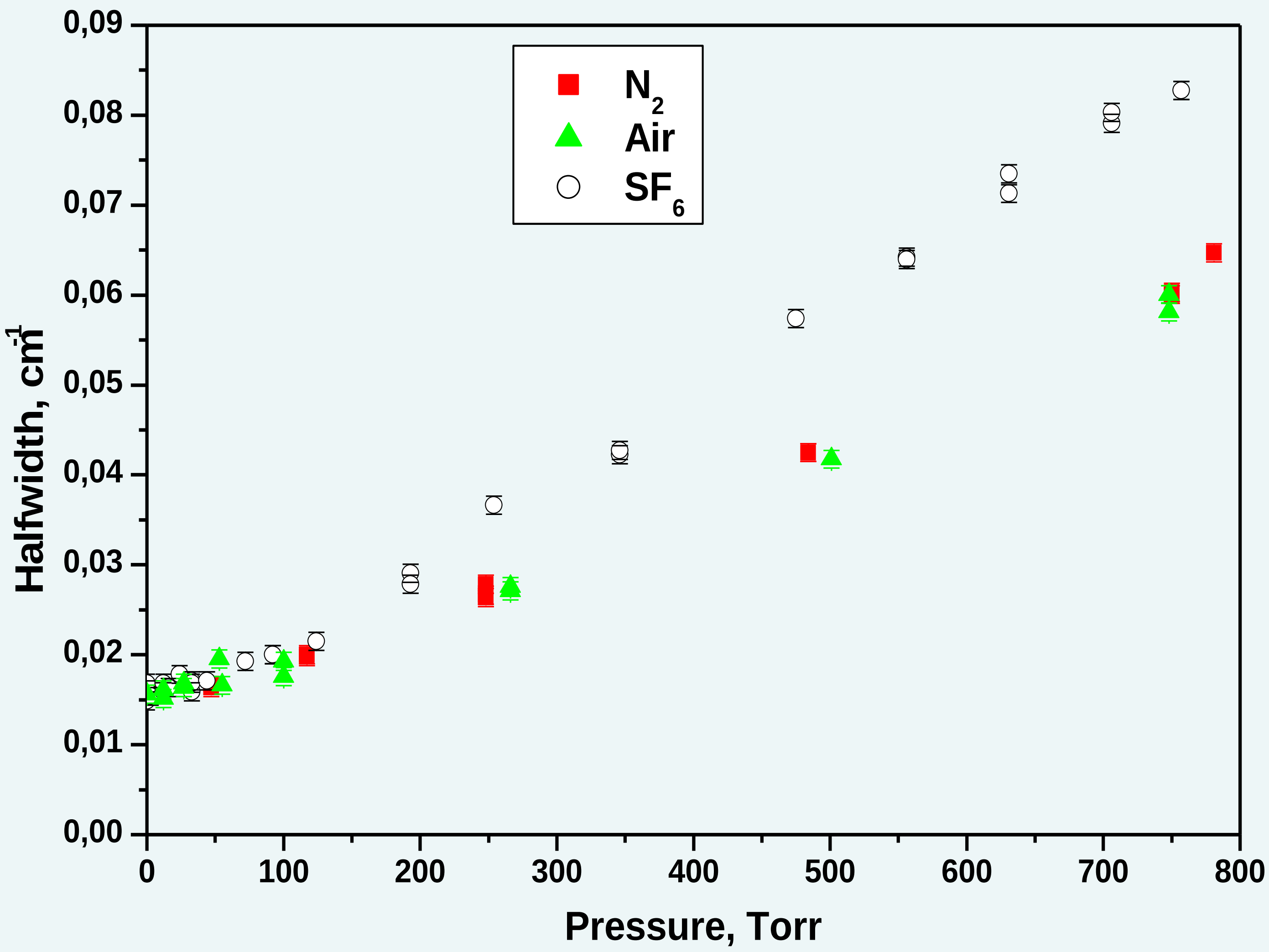
ω_m^0 *- line center at zero pressure, cm^{-1}*

Triplet R(3) of $2\nu_3$ methane absorption band, broadened by air pressure

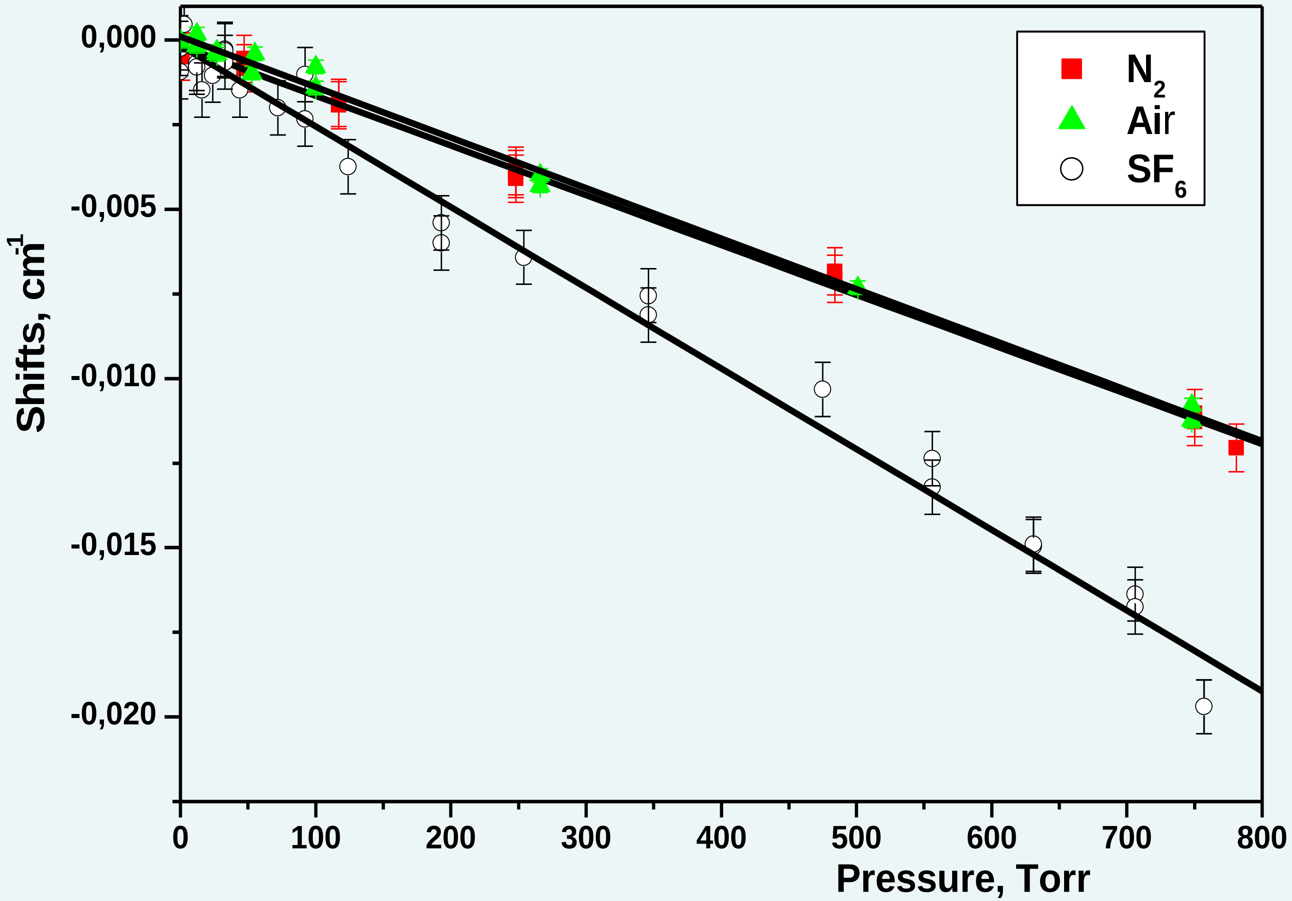


V. Zeninari, B. Parvitte D. Courtois V.A. Kapitanov, Yu.N. Ponomarev: Appl. Phys. B 72, 953–959 (2001

Halfwidth of the triplet R(3) vs CH_4 - N_2, -air and – SF_6 mixture pressure



Mass center shift of the triplet R(3) vs CH_4 - N_2, -air and – SF_6 mixture pressure



Kapitanov V.A., Ponomarev Yu.N., Tyryshkin I.S ., Bykov A.D., Savel'ev V.N.: Atmos.Oceanic Optics, 2008, Vol.21, No.7, 493-499

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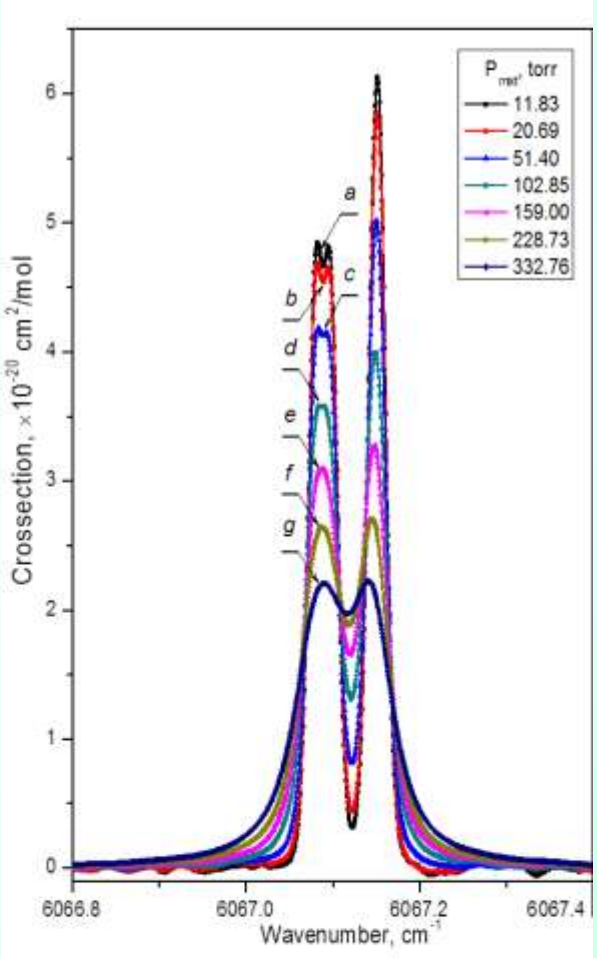
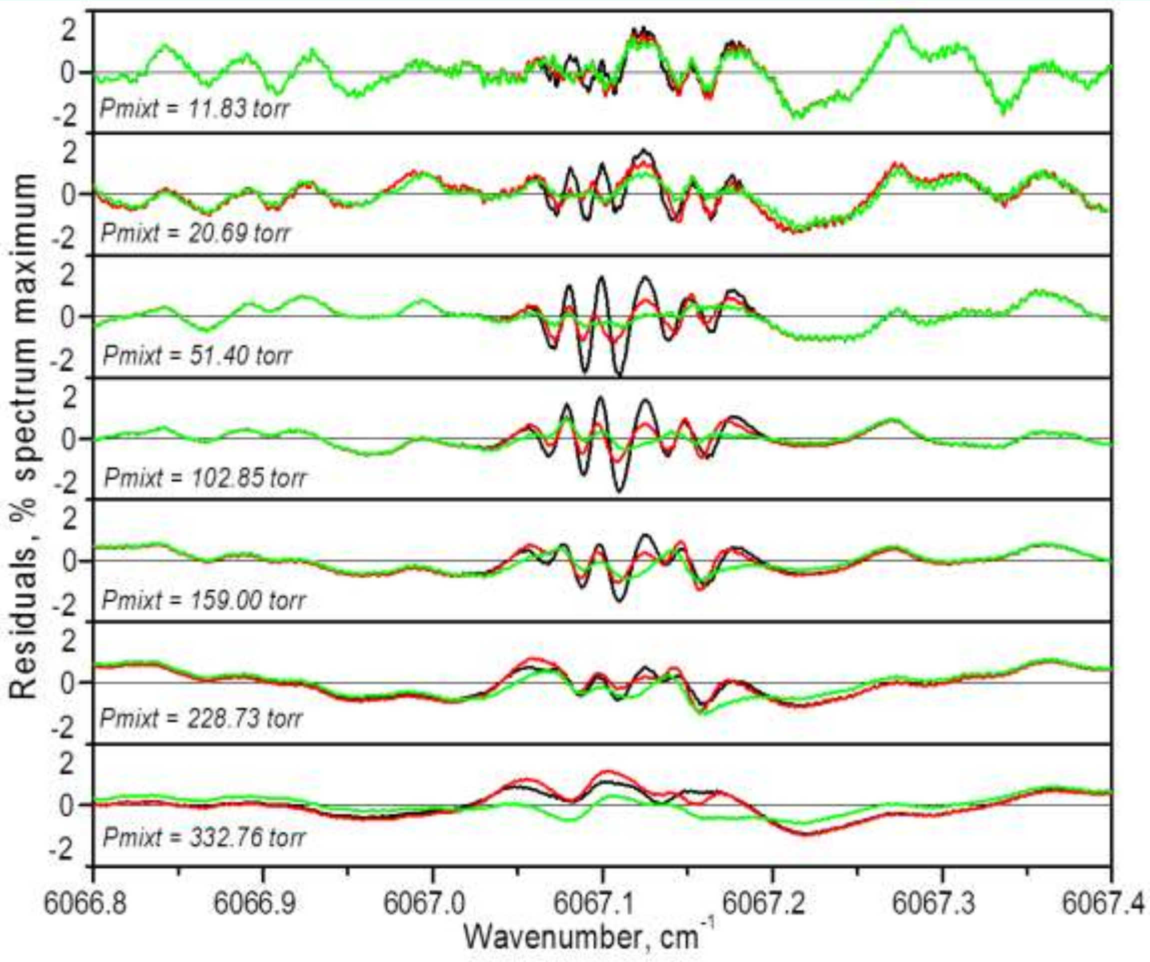
Methane R5 spectra broadened by N_2 pressure

Residuals: black – Voigt, red – RS, green – Pine profiles





K.Y. Osipov, A.E. Protasevich, V.A. Kapitanov, Y.Y. Ponurovskii: Appl.Phys. B. 2012. V. 106, No 3. P. 725-732

Parameters of the methane R5 multiplet spectral lines

#	This work (Pine model [2])	This work (Rautian-Sobelman model [8])	This work (Voigt profile)	GOSAT data [7]	Frankenberg data [15]
Line center position, ω^0, cm^{-1}					
1	**6067.0818703(72)**	**6067.0818708(77)**	**6067.0817706(73)**	**6067.08186**	**6067.0816**
2	**6067.0999781(72)**	**6067.0999762(77)**	**6067.0998809(73)**	**6067.09982**	**6067.0997**
3	**6067.148138(35)**	**6067.148114(36)**	**6067.147999(33)**	**6067.14848**	**6067.1485**
4	**6067.157028(26)**	**6067.157032(26)**	**6067.156913(22)**	**6067.15554**	**6067.1570**
Line intensity, S, cm/mol $\times 10^{-22}$					
1	**9.2089(57)**	**9.2296(58)**	**9.1506(53)**	**8.874**	**8.803(12)**
2	**9.1754(56)**	**9.1854(58)**	**9.2490(56)**	**9.020**	**8.440(11)**
3	**6.465(45)**	**6.468(45)**	**6.322(40)**	**5.842**	**6.316(10)**
4	**8.603(45)**	**8.644(45)**	**8.779(39)**	**8.750**	**7.844(10)**
Broadening coefficient, γ (N_2), cm^{-1}/atm					
1	**0.05706(27)**	**0.05676(11)**	**0.057334(81)**	**0.067**	**0.0597(2)**
2	**0.06258(30)**	**0.06748(14)**	**0.064283(97)**	**0.067**	**0.0630(4)**
3	**0.05809(40)**	**0.06149(26)**	**0.06006(23)**	**0.061**	**0.0518(6)**
4	**0.06149(33)**	**0.05414(14)**	**0.05581(15)**	**0.058**	**0.0597(3)**
Shifting coefficient, δ (N_2), cm^{-1}/atm					
1	**-0.00620(29)**	**-0.006133(84)**	**-0.007040(82)**	**-0.0085**	**-0.0075(1)**
2	**-0.01315(31)**	**-0.002897(99)**	**-0.003108(93)**	**-0.0065**	**-0.0056(1)**
3	**-0.009577(59)**	**-0.01890(26)**	**-0.00885(26)**	**-0.0165**	**-0.0148(1)**
4	**-0.01307(34)**	**-0.01543(18)**	**-0.02080(17)**	**-0.0125**	**-0.0158(2)**
Dike narrowing parameter, β (N_2), cm^{-1} /atm					
1	**0.00980(50)**	**0.00174(40)**	**–**	**–**	**–**
2	**0.01430(56)**	**0.02142(57)**	**–**	**–**	**–**
3	**0.02442(14)**	**0.0310(12)**	**–**	**–**	**–**
4	**0.0202(10)**	**0.01719(77)**	**–**	**–**	**–**
Line mixing parameter, ζ (N_2), atm^{-1}					
1	**-0.511(Depend)**	**–**	**–**	**–**	**–**
2	**0.874(49)**	**–**	**–**	**–**	**–**
3	**0**	**–**	**–**	**–**	**–**
4	**-0.385(68)**	**–**	**–**	**–**	**–**

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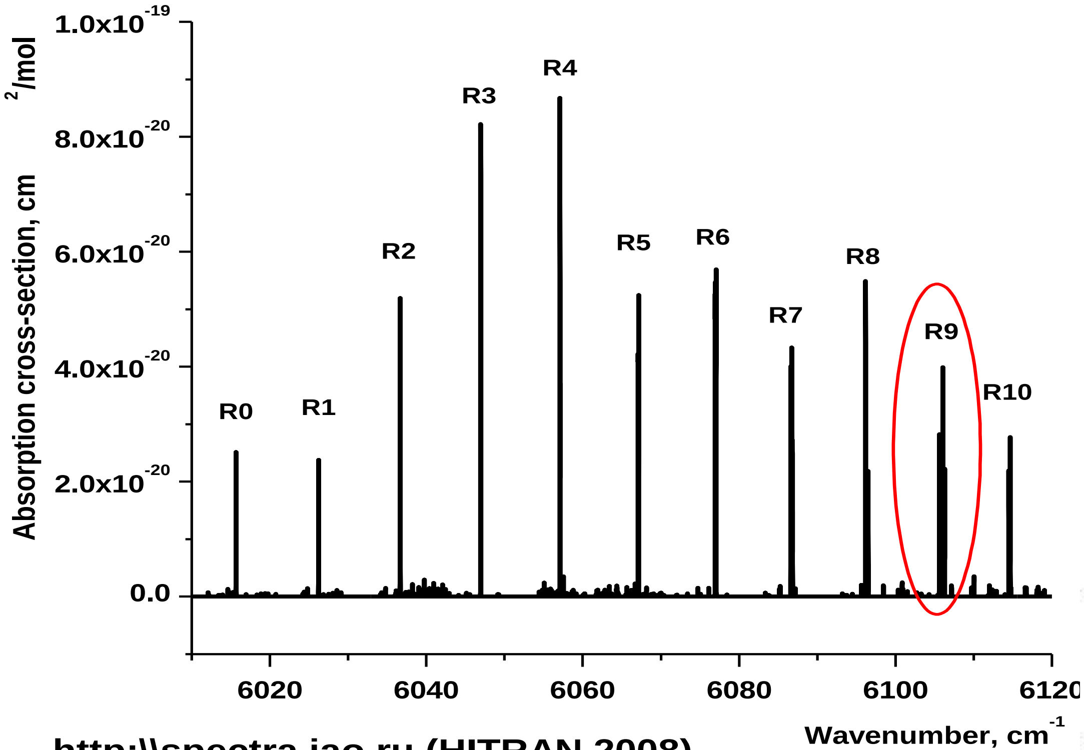
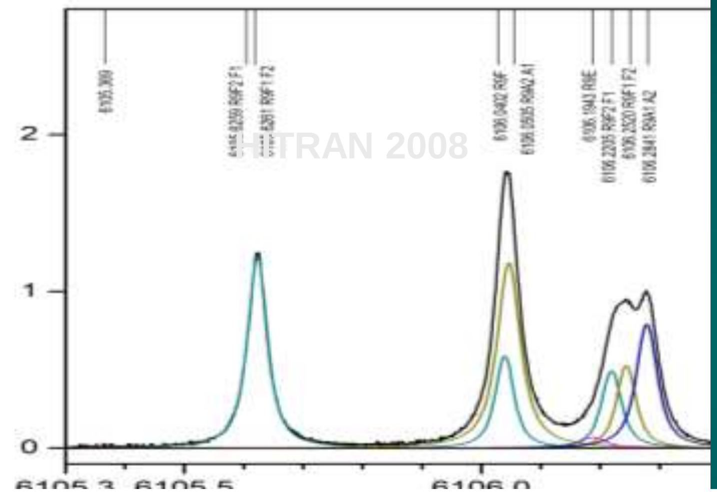
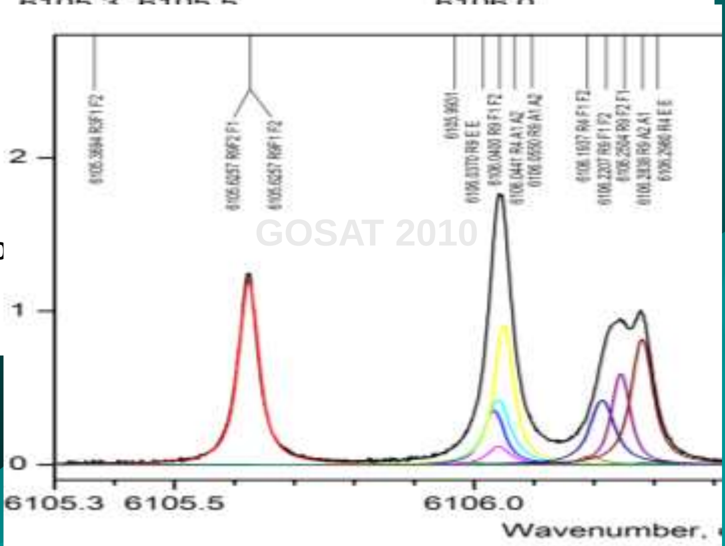
Methane spectrum in the 6010-6200 cm^{-1}

CH_4 absorption spectra are registered by two-channels diode laser OA spectrometer (IAO SB RAS, Tomsk) *[Kapitanov V.A., Ponomarev Yu.N., Tyryshkin I.S. and Rostov A.P. // Spectrochimica Acta Part A. 2007. V. 66, N 4-5, P. 811-818.]*

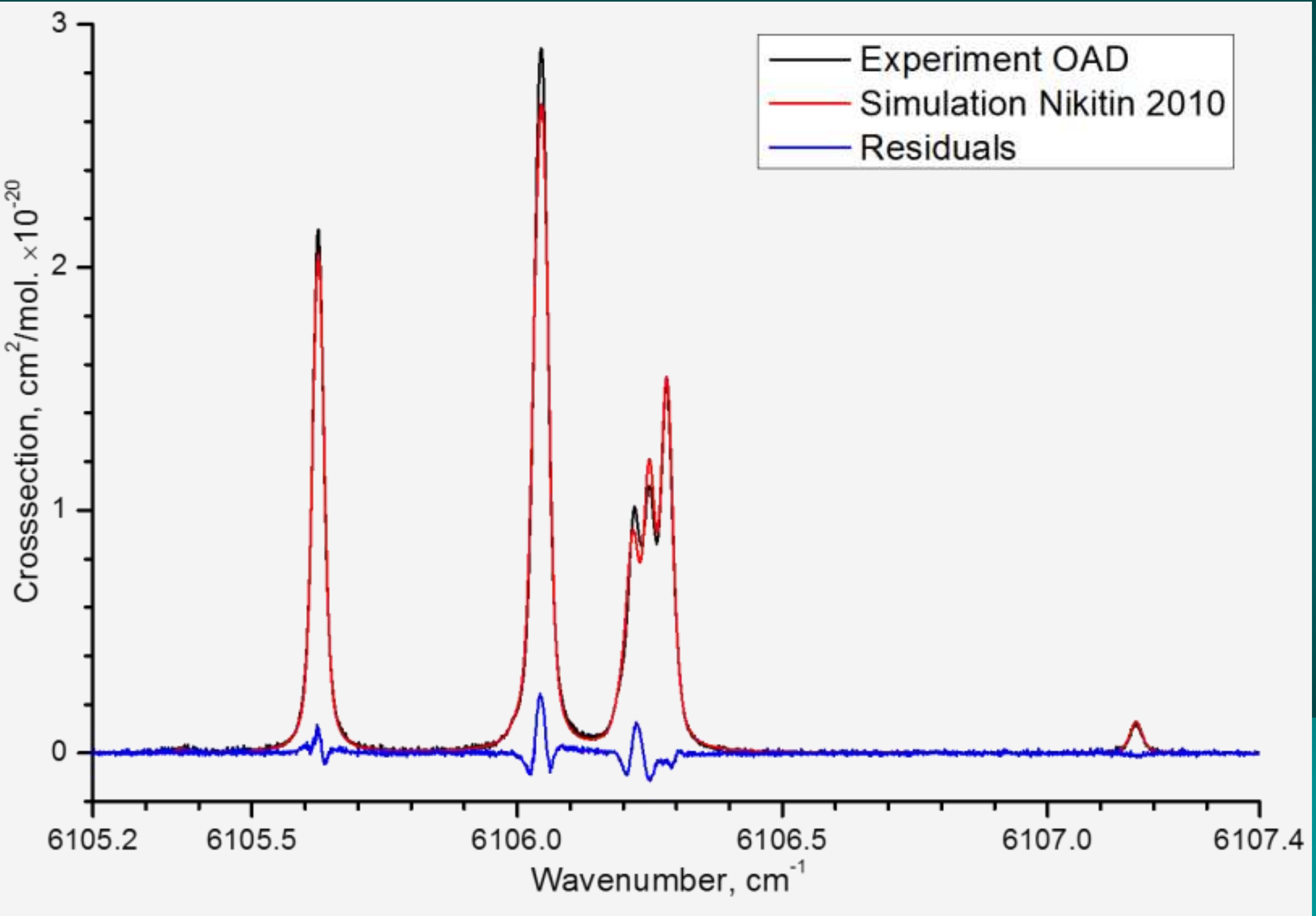


http:\\spectra.iao.ru (HITRAN 2008)





OAD spectrum+GOSAT simulatoin



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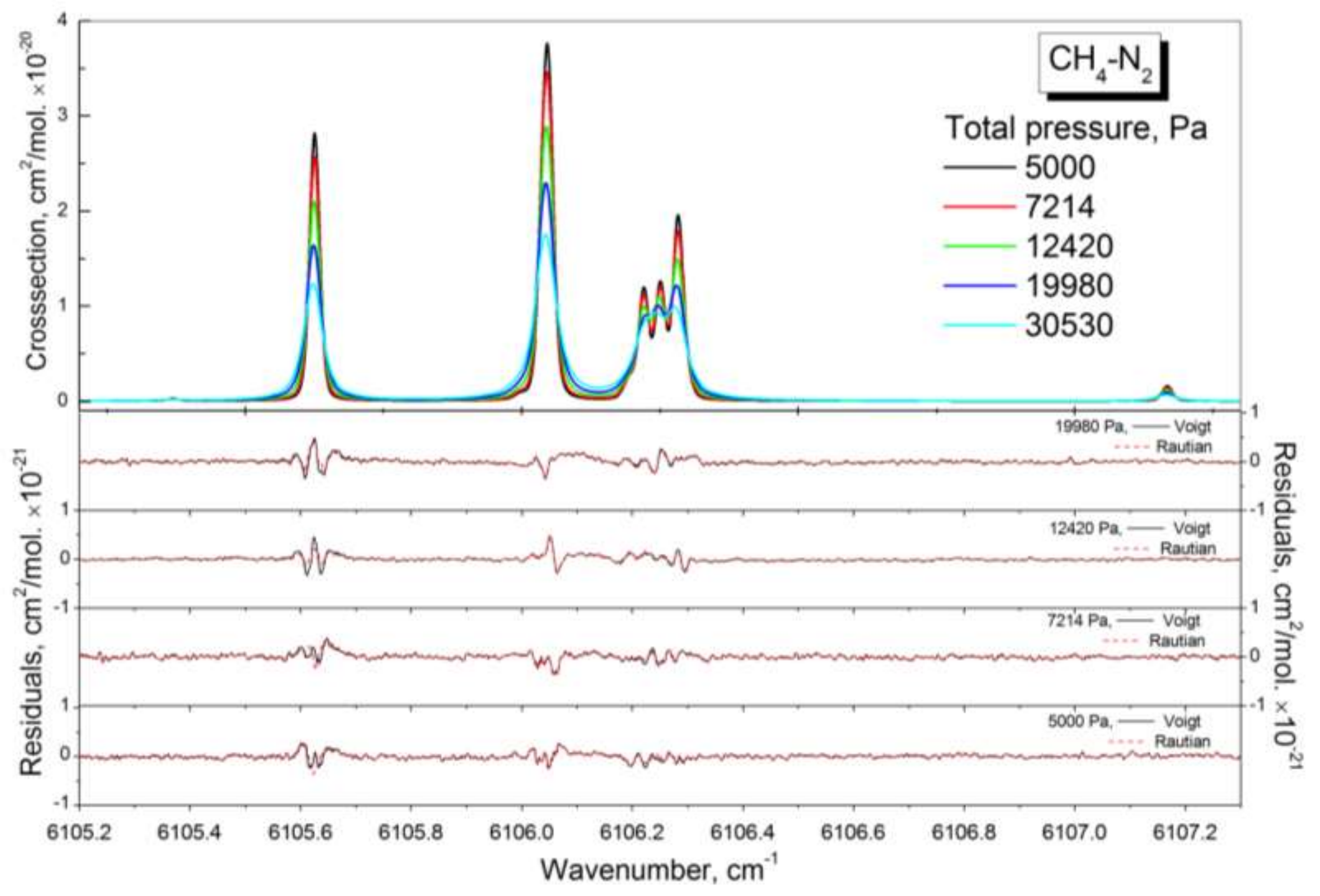
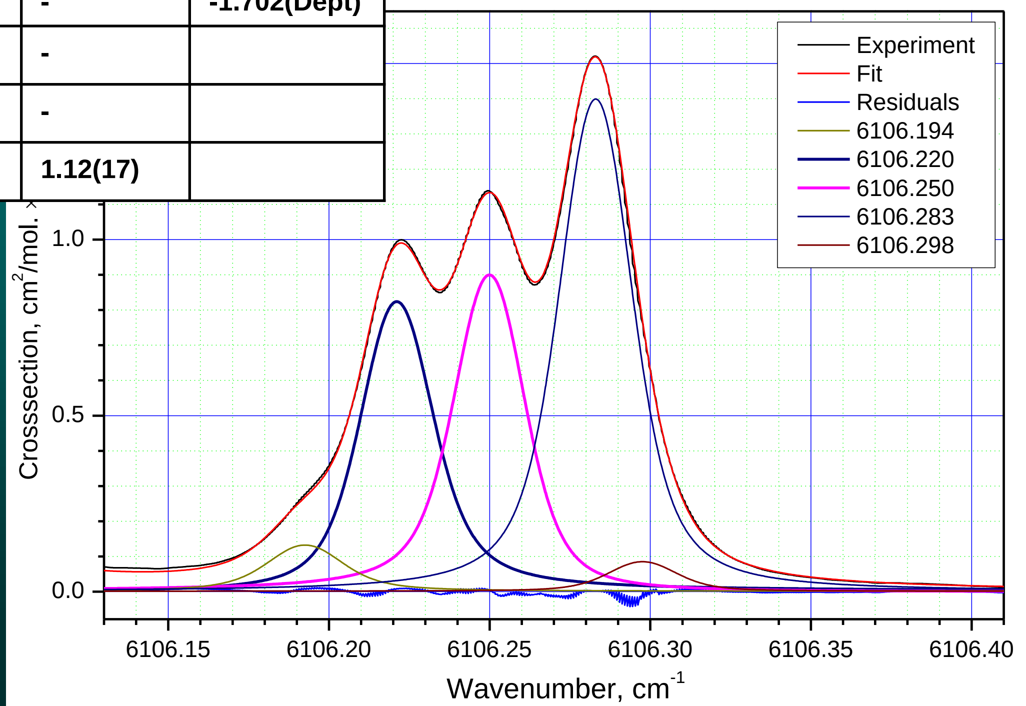
Simultaneous fitting of experimental spectra, registered by OA spectrometer at T=296^{0}C and different partial pressures of CH_4:N_2 (1:14) mixture. Model spectrum consists of 11 lines with S_i>*6E-24 cm/mol*



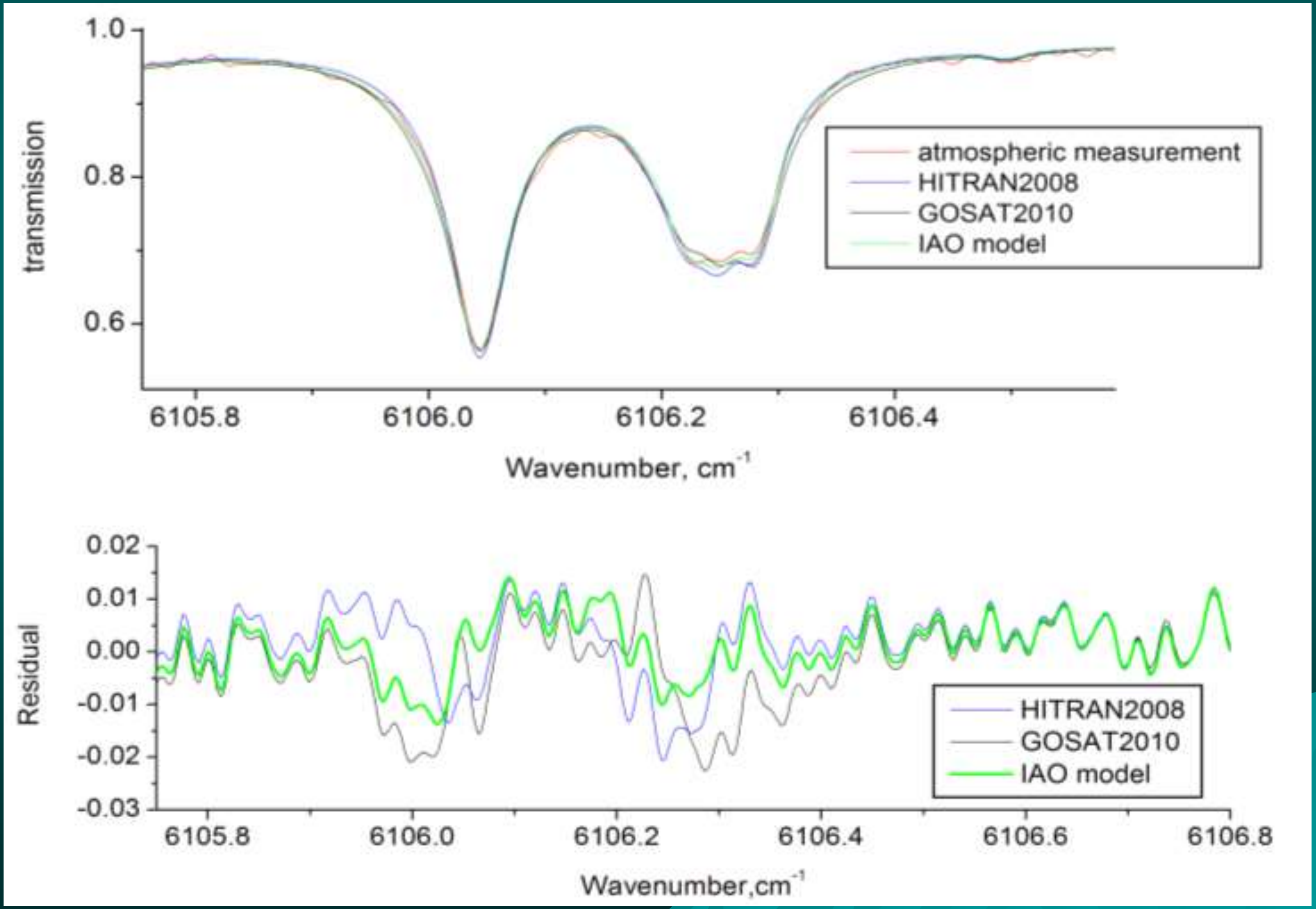
ν_0, cm^{-1}	S, cm/mol $\times 10^{-22}$	γ_L, Ne, cm^{-1}/atm $\times 10^{-2}$	δ, Ne, cm^{-1}/atm $\times 10^{-2}$	β, cm^{-1}/atm $\times 10^{-2}$	η, cm^{-2}/atm$\times 10^{-3}$
6105.36875(27)	0.0750(13)	5.34(25)	-0.00(27)	-	
6105.6258930(27)	7.0457(12)	3.3746(25)	-0.1415(21)	1.0824(94)	
6105.99560(13)	0.1079(11)	3.5(Fixed)	-0.5 (Fixed)	-	
6106.039566(16)	4.438(10)	3.8459(85)	0.6985(97)	-	
6106.050820(10)	6.652(10)	4.1899(58)	-0.5090(69)	-	
6106.194805(51)	0.4934(17)	4.210(43)	-1.225(52)	-	
6106.2205803(86)	2.8876(17)	3.6599(99)	0.087(16)	-	1.702(95)
6106.2519971(75)	3.0585(16)	3.4237(85)	-0.930(15)	-	-1.702(Dept)
6106.2839776(49)	4.9943(19)	3.7921(64)	-0.5230(62)	-	
6106.300823(95)	0.2716(Fixed)	3.051(71)	-1.770(99)	-	
6107.168209(44)	0.4797(14)	4.004(44)	-0.492(38)	1.12(17)	

Line parameters of R9 multiplet of $2\nu_3$ band, retrieved from the spectra, measured by OA spectrometer. Broadening gas is Ne. Line mixing is taken into account.

Line mixing model (*Pine A. S. JQSRT 1997. Vol. 57. № 2. pp. 145-155.*)



Comparison of atmospheric spectra, measured by ground-based Fourier spectrometer (FTS) and spectra, modeled with HITRAN2008, GOSAT CH_4 line list and our CH_4 line parameters, retrieved from OA spectrometer measurements (IAO model) (FTS July 1st, 2010. Solar zenith angle is 52.9º,Kourovka Ekaterinburg, Russia http://www.remotesensing.ru/fts_sta.html)

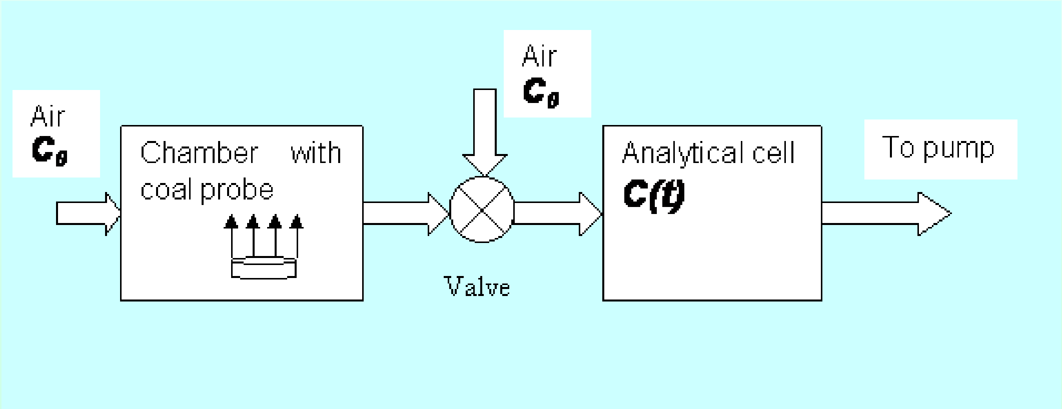


Methane line mixing

- **The neglecting of the CH_4 line-mixing effects in the modeled spectra in the 1,6-1,7 µm can give an error in the methane column amount determination from the solar spectra, measured by ground—based Fourier spectrometer, up to 0.05 ppm for large solar zenith angles (H.Tran et al, JQSRT,11, 2010)**
- **Taking CH_4 line mixing into account in the spectral region of 7-10 µm allows to decrease the difference between calculated emitted radiance and values measured in the Jupiter atmosphere from 0,5 $W/m^2 sr$ (10%) to 0,02 $W/m^2 sr$ (0,3%). [*H. Tran et al. JQSRT. 2006. V.101*]**
- **Neglect of CH_4 line mixing in the inversion model of CH_4 concentration retrieval from the atmospheric limb transmission spectra, measured by FTIR spectrometer in the 3,4 µm spectral region, leads to an error of 7% in the retrieved methane concentration. [*D. Mondelain et al. JMS. 2007. V.244*]**

Our preliminary studies found an effect of CH_4 line mixing in the measured spectra of methane in the 1,6-1,7 µm (R5 and R9 manifolds) at the pressures 0-1 atm.*[K.Yu. Osipov, V.A. Kapitanov, Yu.N. Ponomarev, Protasevich A.E. HRMS, Dijon 2011]*

TDLS applications to study of methane emissions (hydrocarbons, coal, biological systems)



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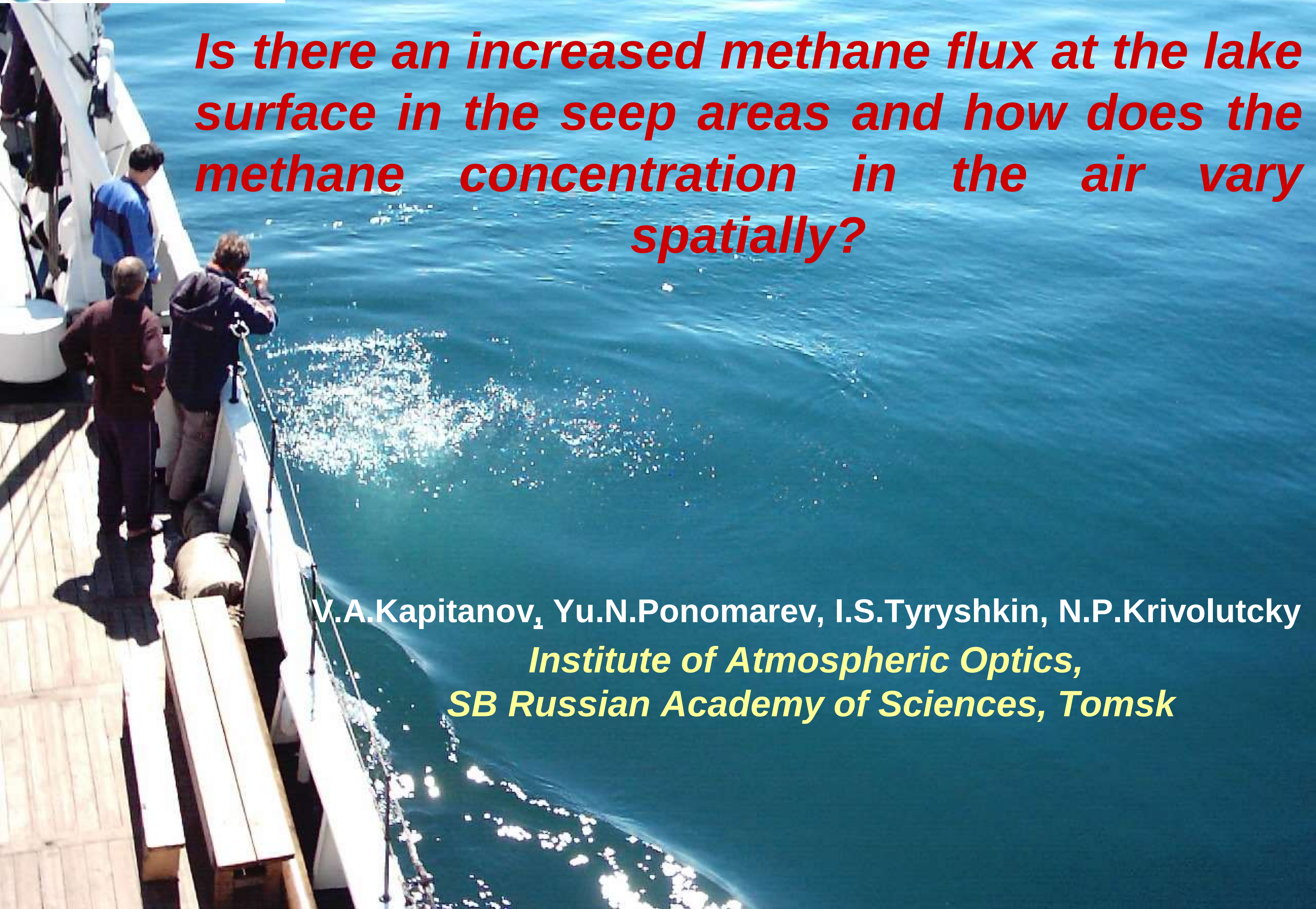
Is there an increased methane flux at the lake surface in the seep areas and how does the methane concentration in the air vary spatially?



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Institute of Atmospheric Optics,
SB Russian Academy of Sciences, Tomsk

v.VERESHAGIN air bleeding position

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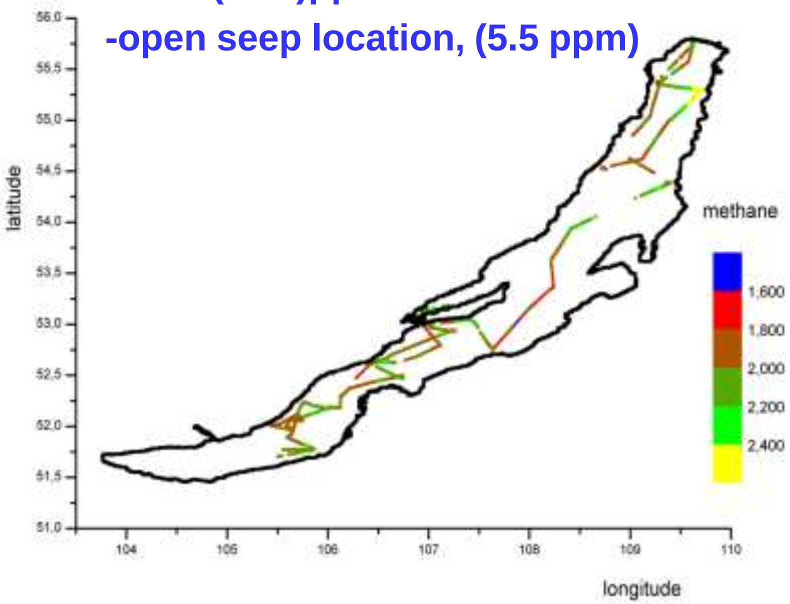
v.Verechagin

8-17 AUGUST 2003

-2.001(0.16)ppm

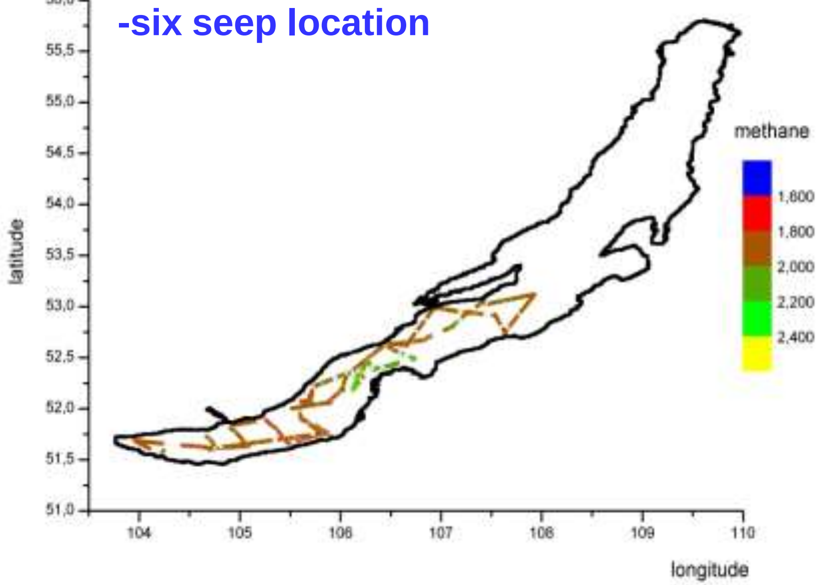
-open seep location, (5.5 ppm)



16-24 JUNE 2004

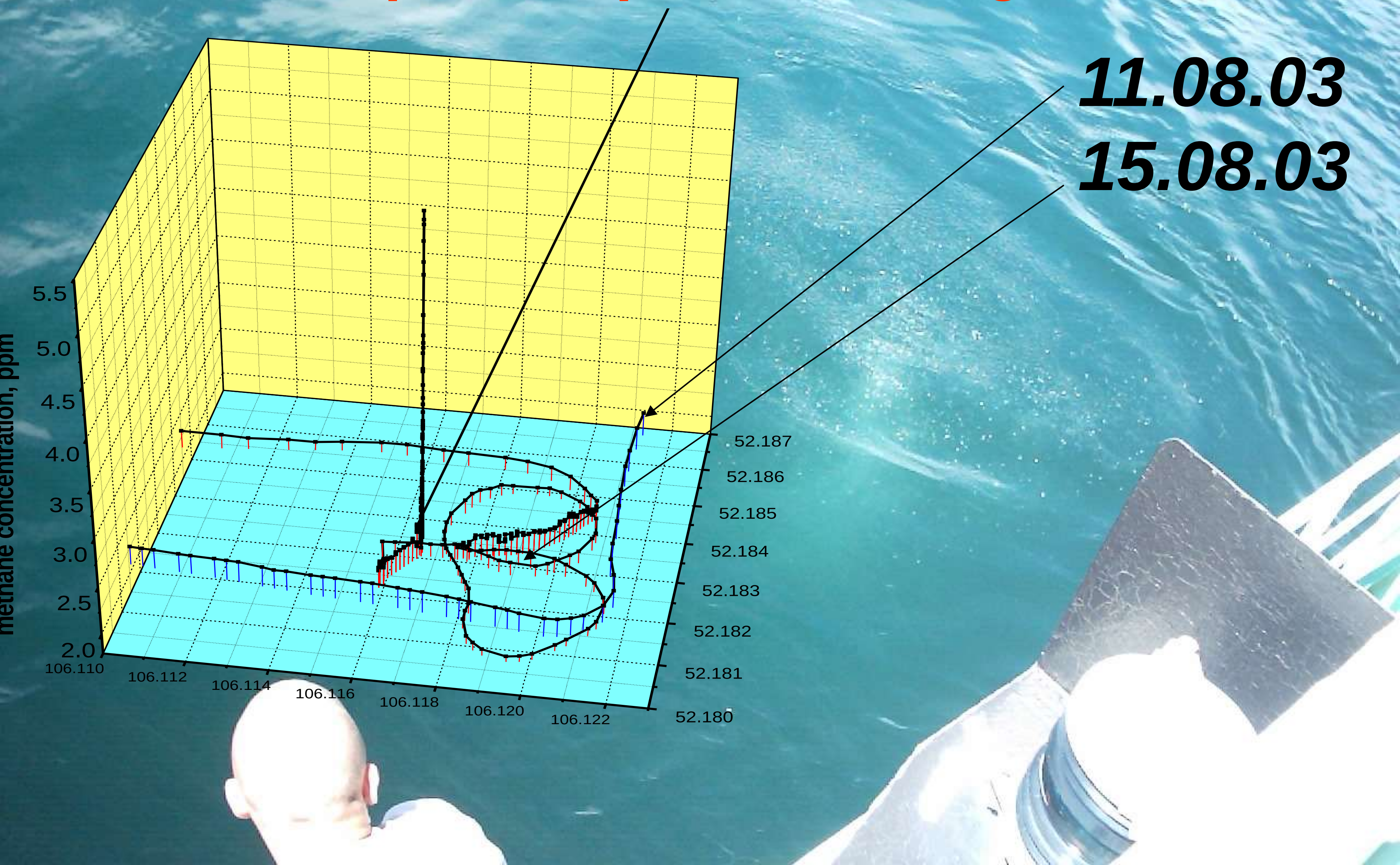
-1.91(0.07) ppm

-six seep location



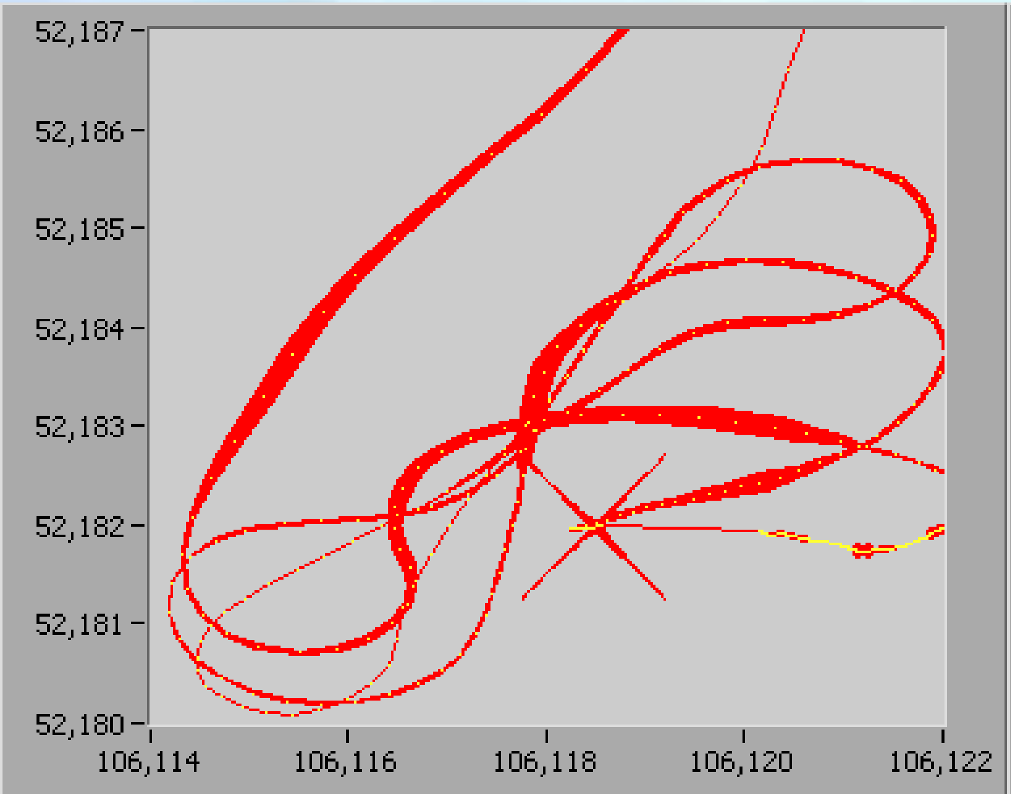
METHANE SEEP LOCATION

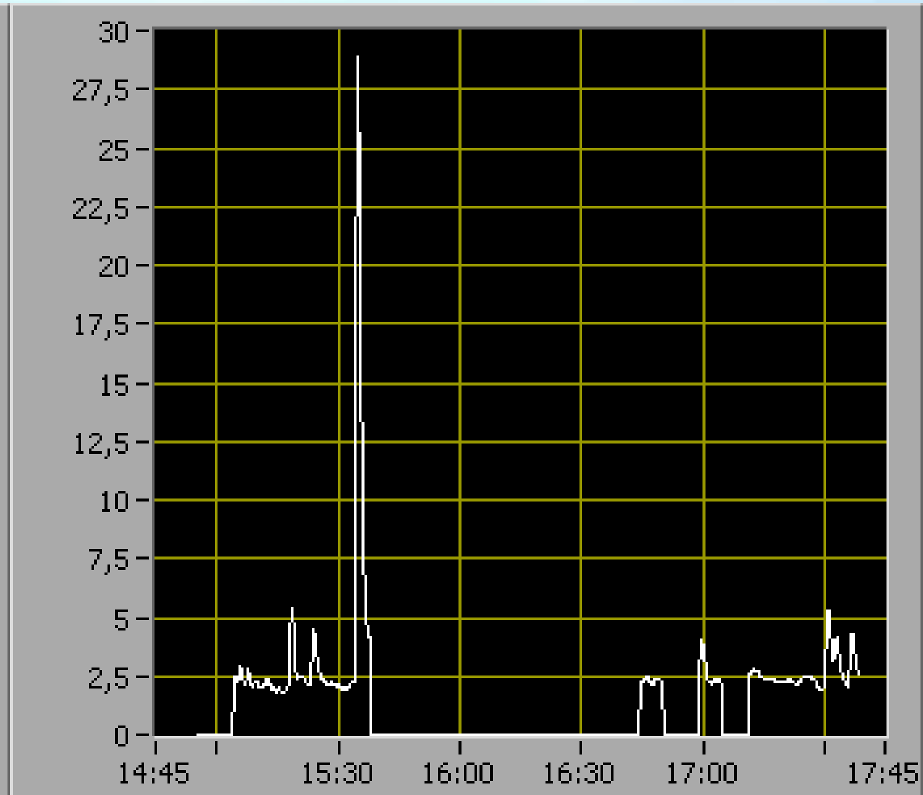
open seep near Selenga



OPEN SEEP (Selenga's entry),

22 June 2004





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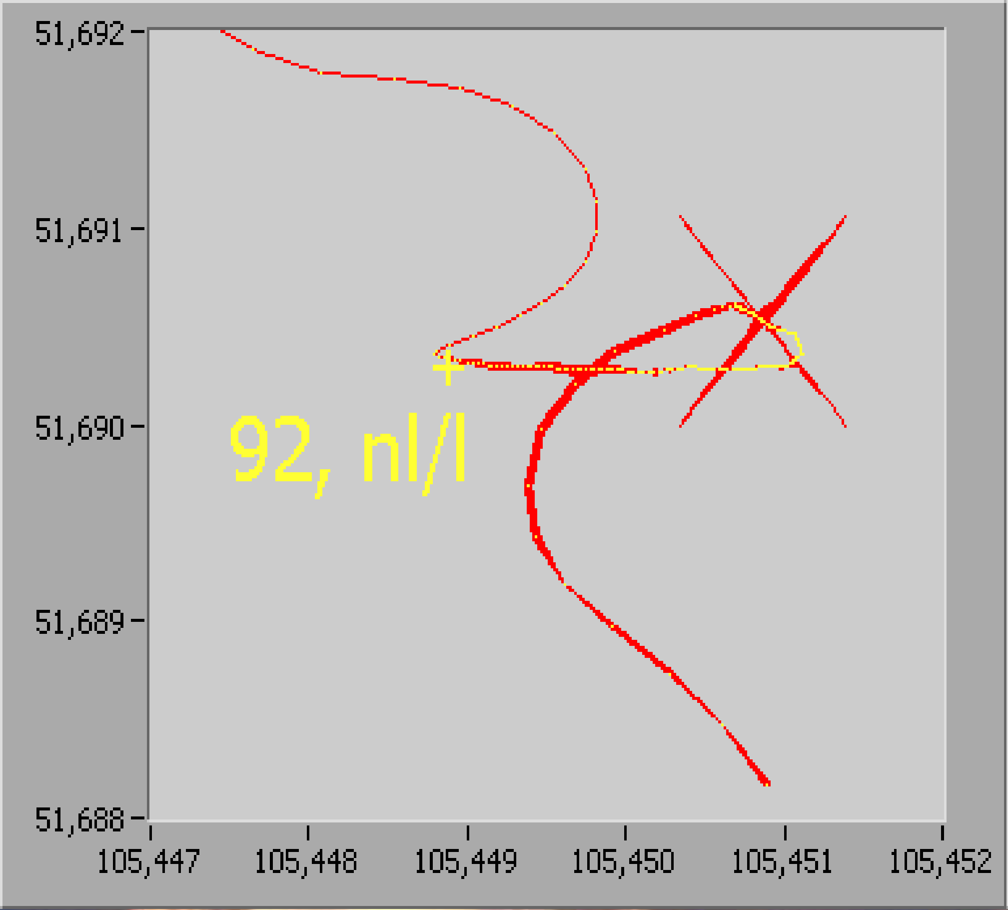
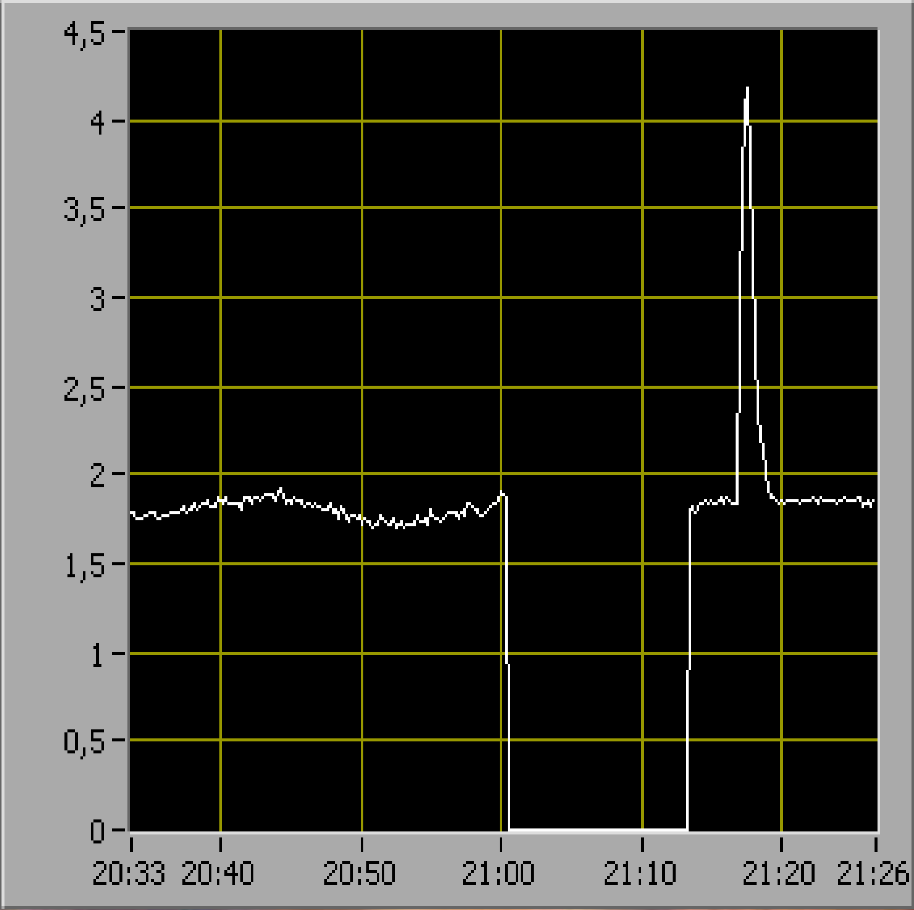
DEEP-SEA SEEP

18.08.04 June, near Mishicha, depth ~ 1000 m





TEAM WORK (IOA+POI)

- ***Intercomparison***

Air sample for gas chromatograph was bled directly from air tube near detector

21.06.04

GC five air samples	**- 1.89 (0.056) ppm**
Methane detector	**- 1.94 (0.054) ppm**

22.06.04

GC two air samples	**- 1.95 (0.056) ppm**
Methane detector	**- 2.02 (0.09) ppm**

23.06.04

GC one air sample	**- 8.98 (0.27) ppm**
Methane detector	**- 13.7 (0.09) ppm**

- Direct measurements and evaluation of water surface **methane fluxes** in South and Middle Baikal were carried out.
- High methane content in water or air within seep area is strongly located with scale ~ 100 m
- Singularity of air methane content like “seep” was detected near Mishicha, (depth > 1000 m)

Summary

- Progress of TDL provides the permanent perfection of all types of TDL spectroscopy (absorption spectrophotometry, CRDS, PAS, etc.), leads to sensitivity and tuning range increase.
- Due to high sensitivity and high resolution of TDLS methods the detail analysis of molecular spectra in gases requires:

— Application of multispectrum fitting instead spectrum by spectrum procedure;
— Perfection of line shape models;
— Taking into account even very weak neighbor spectral lines

- TDLS techniques could be efficiently applied to basic study of spectra structure and line shape parameters under pressure and temperature varying as well as for application to gas analysis and environmental monitoring.

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Acknowledgements

- The authors are very thankful TDLS division of IGP RAS and personally Prof. A.Nadezhdenskii and Dr. Ya.Ponurovskii, K. Osipov and A. Protasevitch (IAO SB RAS) for collaboration and help.
- This research program is supported by the project No 01201051379 SB RAS, and Program III.9 of RAS “Basic optical spectroscopy and its application”, Projects 10-05-00764-a and 11-02-93112-CNRS_a of RBRF