Line mixing effect in $2\nu_3$ band R9 methane lines

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Line mixing in methane ν_1, ν_2 and ν_3 bands spectra

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9. D. Pieroni, Nguyen-Van-Thanh, C. Brodbeck, and J.-M. Hartmann T. Gabard and J.-P. Champion D. Bermejo and J.-L. Domenech C. Claveau and A. Valentin Experimental and theoretical study of line mixing in methane spectra. IV. Influence of the temperature and of the band // J. Chem. Phys., 2000 V. 113, N 14, pp. 5776-5783
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11. D. Pieroni, Nguyen-Van-Thanh, C. Brodbeck, and J.-M. Hartmann T. Gabard and J.-P. Champion D. Bermejo and J.-L. Domenech C. Claveau and A. Valentin M. V. Tonkov, I. M. Grigoriev, and R. Le Doucen Experimental and theoretical study of line mixing in methane spectra. II. Influence of the collision partner (He and Ar) in the *v*3 IR band // J. Chem. Phys. 1999 V. 111, N 15, pp. 6850-6863
12. D. Pieroni, Nguyen-Van-Thanh, and C. Brodbeck, C. Claveau and A. Valentin , J. M. Hartmann , T. Gabard and J.-P. Champion D. Bermejo and J.-L. Domenech Experimental and theoretical study of line mixing in methane spectra. I. The N2-broadened ν3 band at room temperature // J. Chem. Phys. 1999 V. 110, N 16, pp. 7717-7732

Summary

The principal conclusion of these works is that spectral exchange becomes appreciable already at low pressures of a buffer gas, which leads to a significant deviation of absorption coefficients from the sum of Voigt profiles of individual lines.

This work

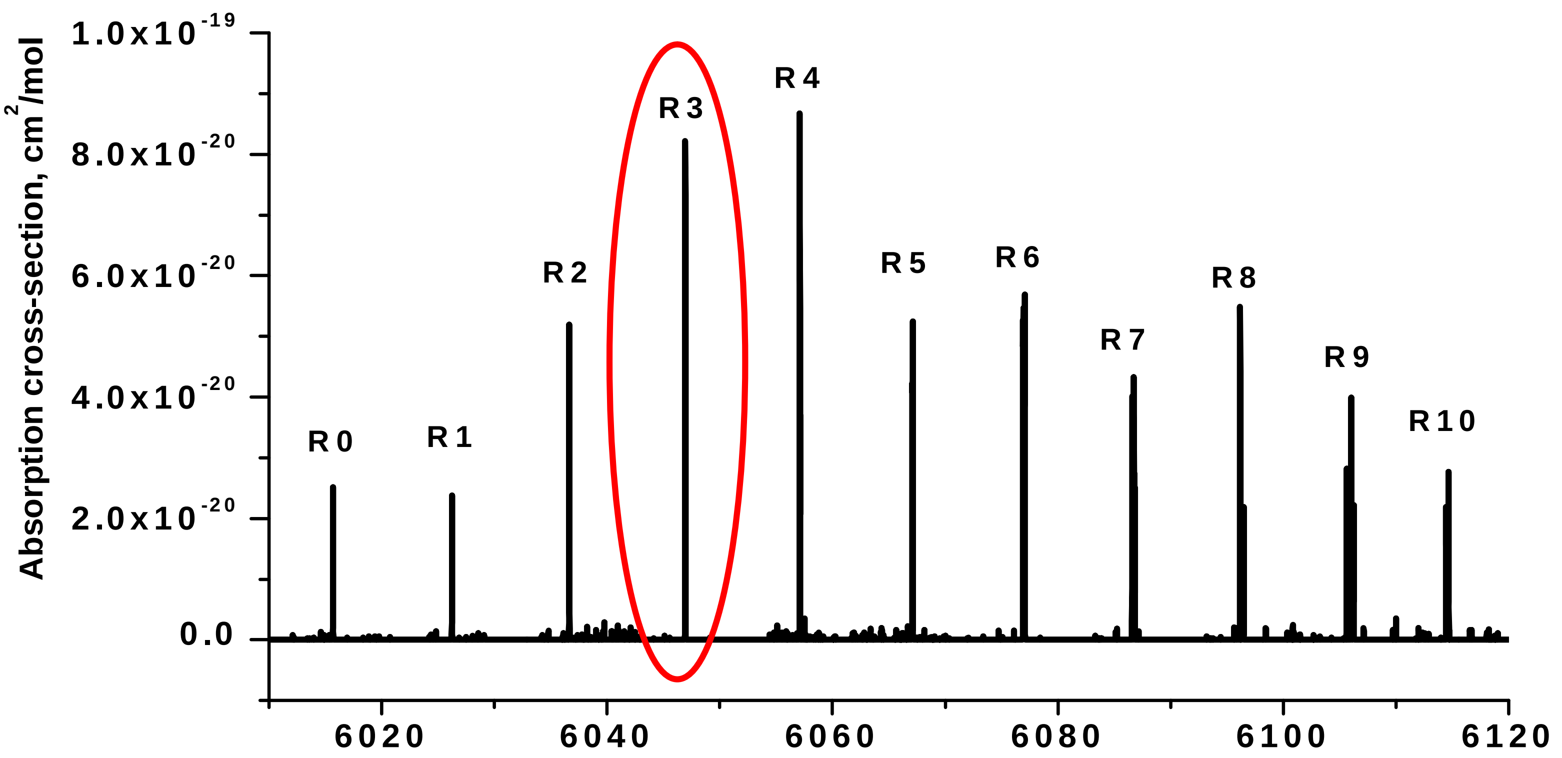
The subject of this work is the broadening and shift of lines of methane $2\nu_3$ band, induced by collisions of CH_4 molecule with N_2 ones

CONTENT

- Methane $2\mathbf{v}_3$ band spectrum
- Diode laser OA spectrometer
- Measurement procedure
- Experimental results and preliminary analysis
- Summary

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.

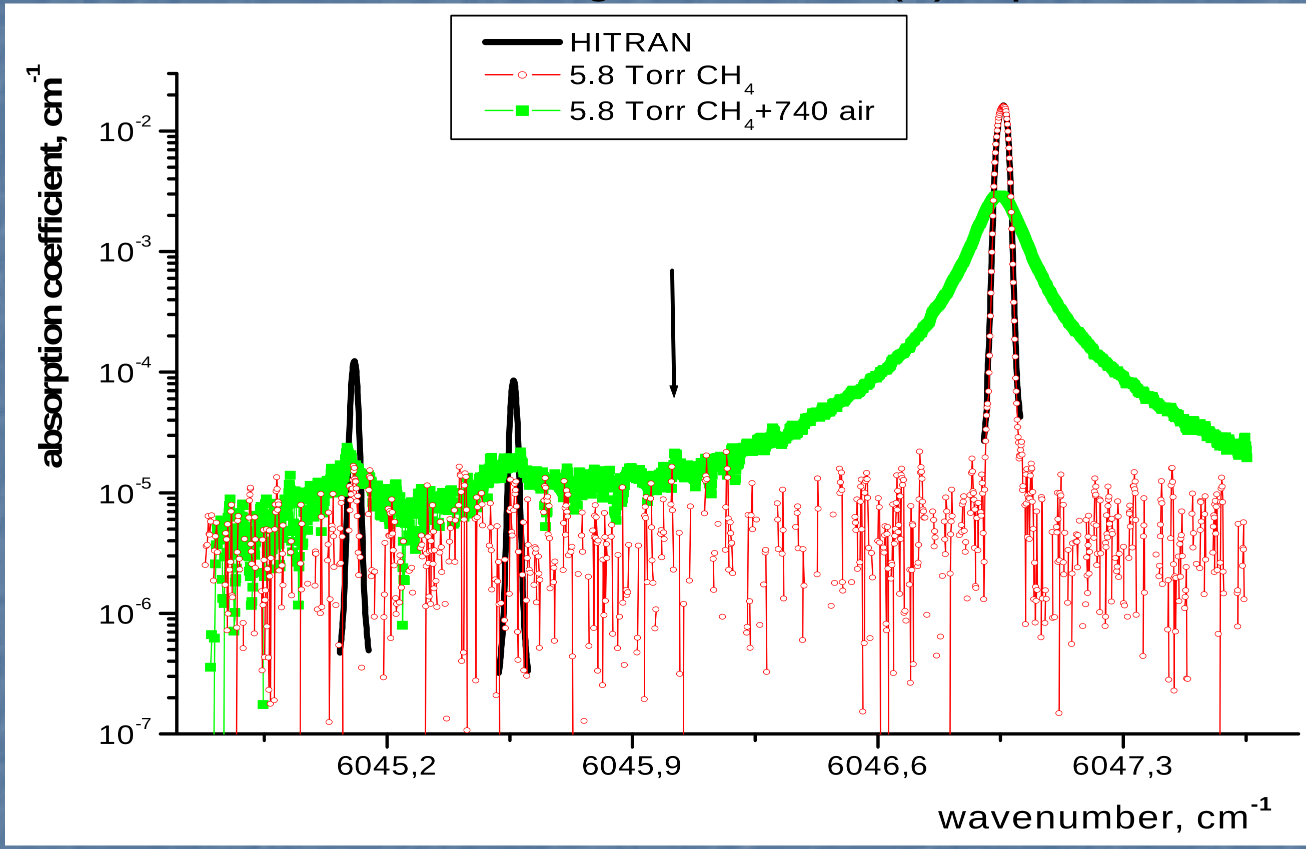


http:\\spectra.iao.ru (HITRAN 2008)

$2\nu_3$ Methane Spectrum -more than 600 lines
HITRAN 2008 - 300 lines

Triplet R(3) of $2\nu_3$ methane absorption band, broadened by air and SF_6 pressure

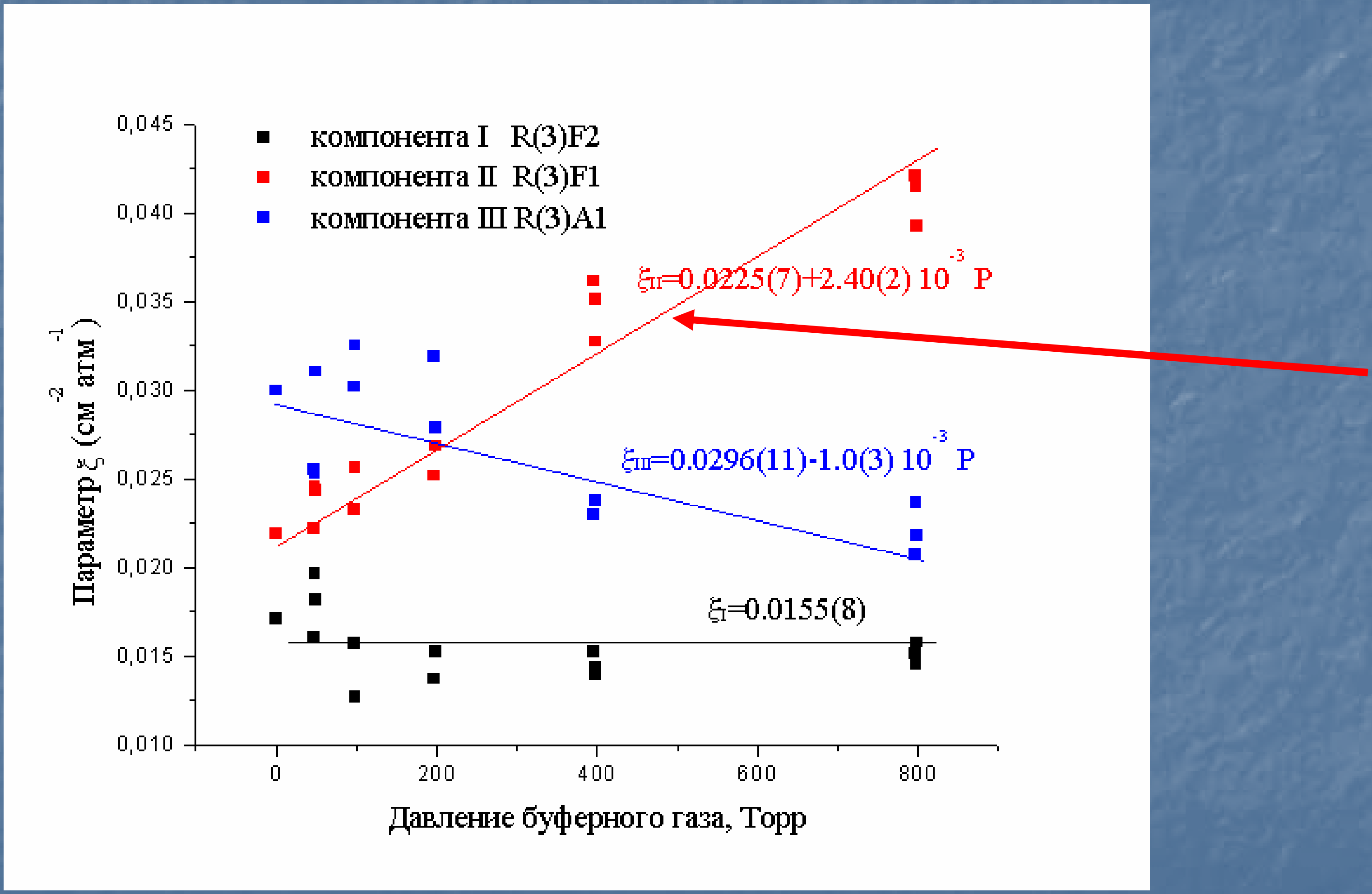
2007-2008 Line-mixing effect of R(3) triplet



Капитанов В.А., Пономарев Ю.Н., Тырышкин И.С.,Быков А.Д.,Савельев В.Н.// Оптика атмосферы и океана. 2008., Т.21, № 07, С.569-576.

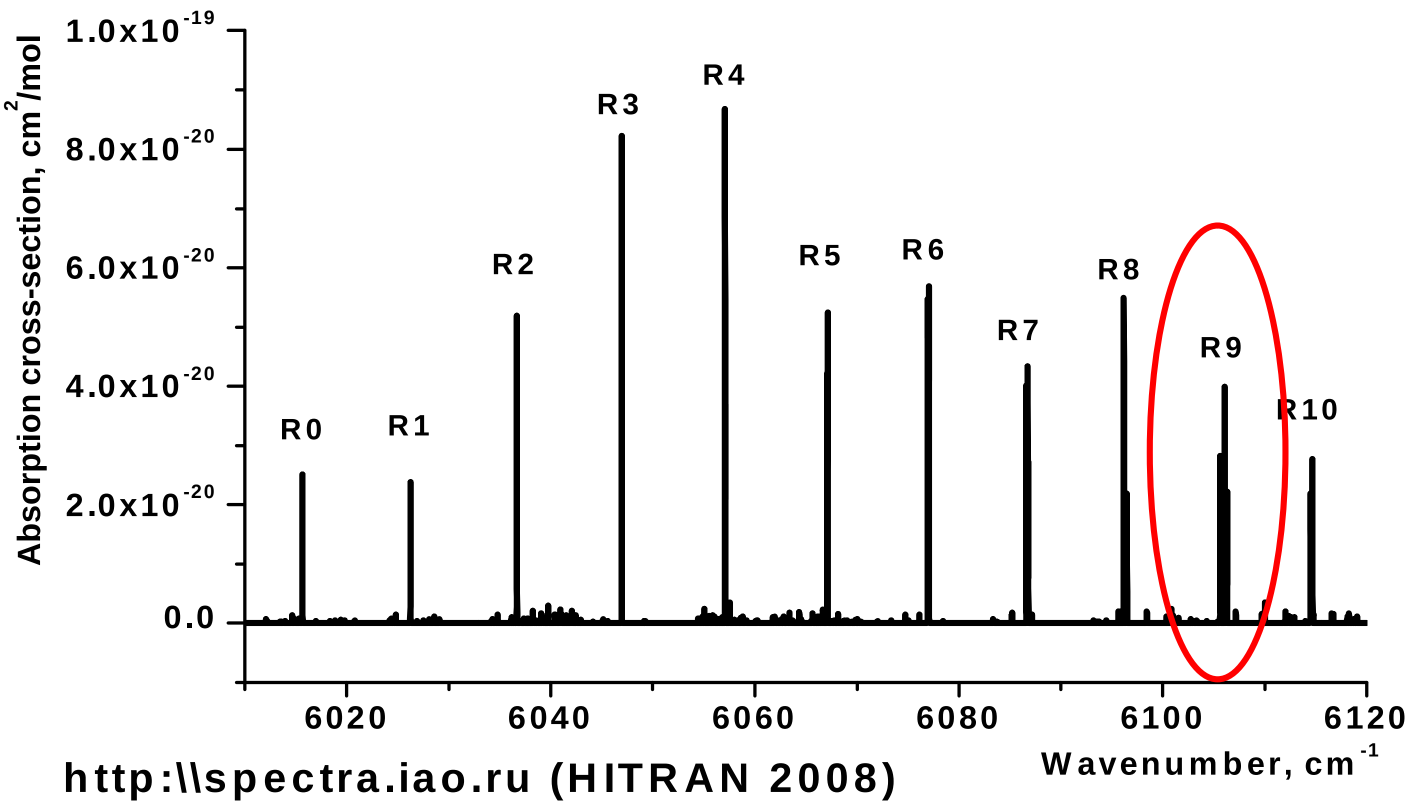
Triplet R(3) of $2\nu_3$ band, broadened by SF_6 pressure

Intensity, cm^{-2}/atm



Methane 2ν_3 band spectrum

September 2009



Two-channel diode laser OAD spectrometer

interferometer

Vacuum station

controller

Diode laser

Two OAD

Measurement procedure

- Lines centers measurements
- OAD calibration and
- Lines intensities measurements

Diode laser wavelength measurements

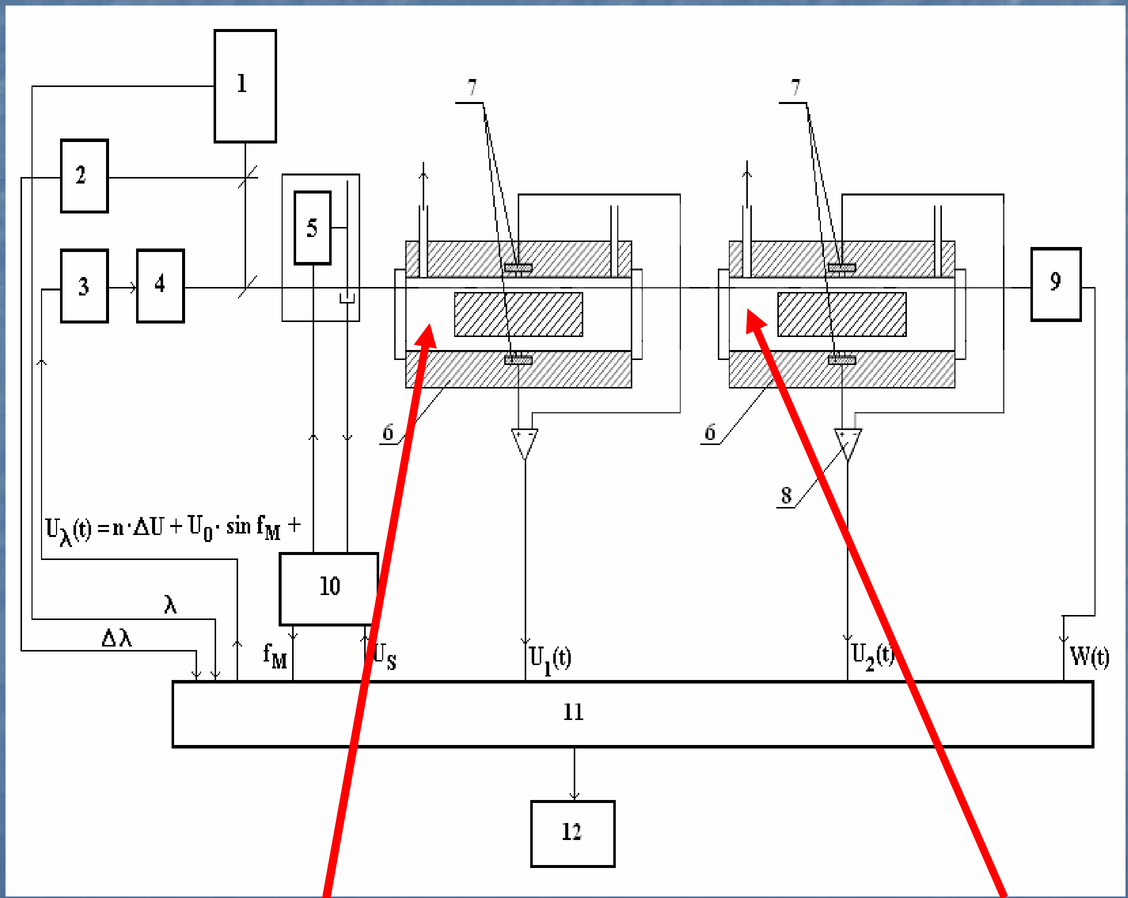
Angstrom WS7 Super-Precision Wavelength Meter

Technical Data		WS7
Measurement range (nm)	Standard (350 – 1120)	●
	UV (248 – 1100)	●
	IR (800 – 1750)	●
	UV-II (192 – 800)	●
	IR-II (1000 – 2250)	●
Absolute accuracy [7]	192 – 370 nm (pm) [1]	0.2
	370 – 1100 nm (MHz)	60
	1100 – 2250 nm (MHz)	40
Quick coupling accuracy (with MM fiber)		200
Resolution (MHz)		10
Linewidth option: [4]	Accuracy (MHz) [3]	5 % (>200) [4]
	Max. bandwidth (GHz)	20
Measurement speed (Hz) (depending on PC hardware and settings)	Wavelength	150
	Interferometer picture	40
	Linewidth option	10
Required input power (µJ)	Standard	0.06 – 15
	UV	0.03 – 60
	IR	3 – 200
	UV-II	50 – 1000
	IR-II	250 – 3000
Fizeau interferometers [2]	FSR (GHz)	15 (100)
Coupling fiber diameter (µm)		400 µm or SM fiberset

Absolute accuracy (1100-2250 nm): - 40 MHz(1.3*10^{-3} cm^{-1})

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:

Δν - 6060-6250см$^{-1}$

dν - 2,5-3 см-1

W - 3-7 мВт

OAD:

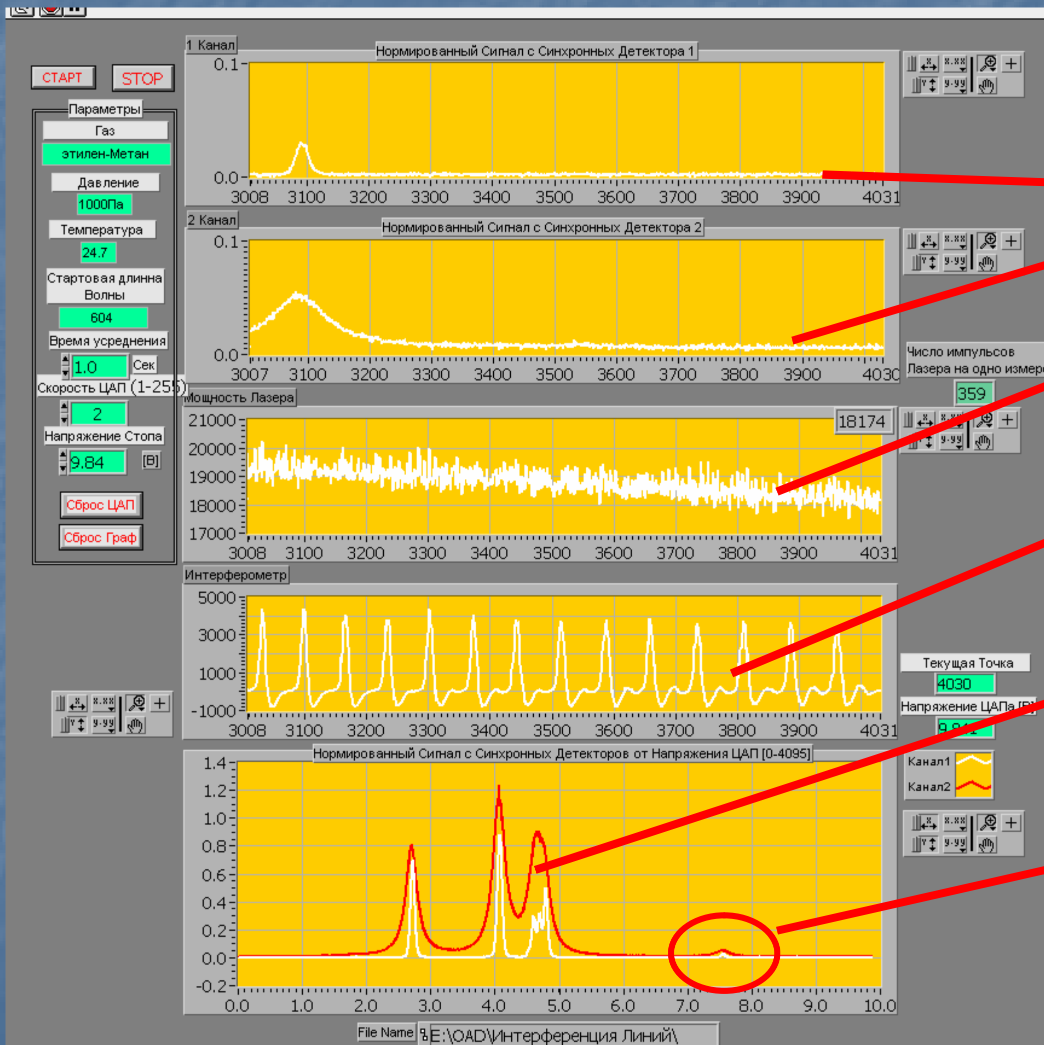
$\Delta = (U_ш{}^2)^{1/2}/R$

$4*10^{-9}$ см$^{-1}$Вт

CH_4, low pressure   Mixture, high pressure

Lines wavelength measurements

The display of the LabVIEW data acquisition system



OAD signals

Laser power

Interferogram
FSR = **0.05 cm^{-1}**

OAD signals/laser power

Secondary wavelength standard (CH_4 HITRAN)

$\Delta\nu = 3*10^{-5}\ cm^{-1}$

OAD calibration

$$\frac{U_{OAD}(\nu, P_{br})}{W_0(\nu)} = R(P_{br}) * \sigma(\nu, P_{br}) * n(P_{br})$$

$$\sigma(\nu, P_{br}) = \frac{1}{R(P_{br}) * n(P_{br})} * \frac{U_{OAD}(\nu, P_{br})}{W_0(\nu)}$$

$$\sum_i \int_{\Delta\nu} \sigma_i(\nu, P_{br}) d\nu = F(P_{br}) = const$$

$$\sum_i \int_{\Delta\nu} \sigma_i(\nu) \cdot d\nu = \frac{1}{R(P_{br}) * n(P_{br})} * \sum_i \int_{\Delta\nu} \frac{U_i(\nu)}{W_0(\nu)} \cdot d\nu = const$$

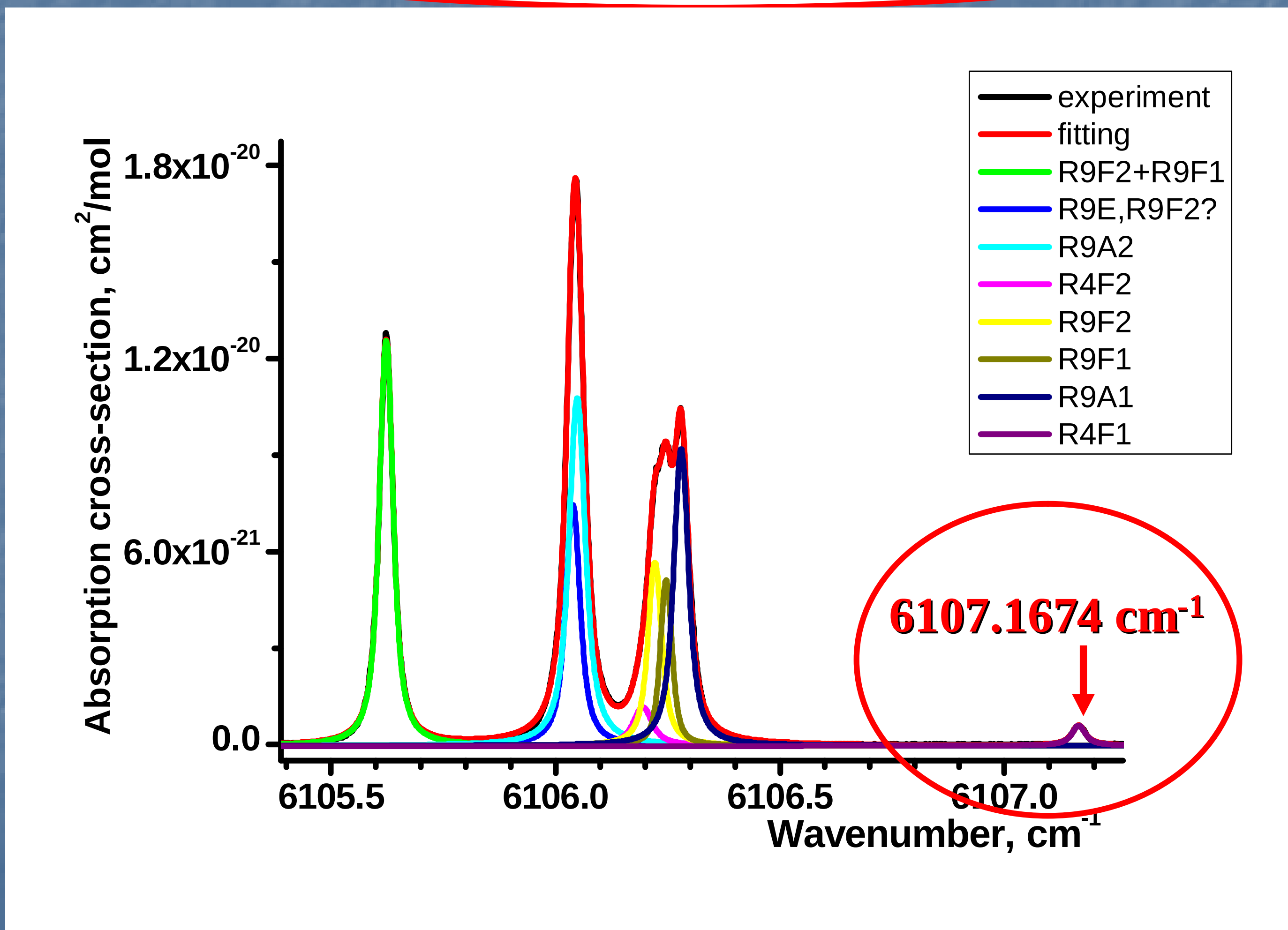
OriginPro 7.5 Multi-line fitting

Voigt profiles

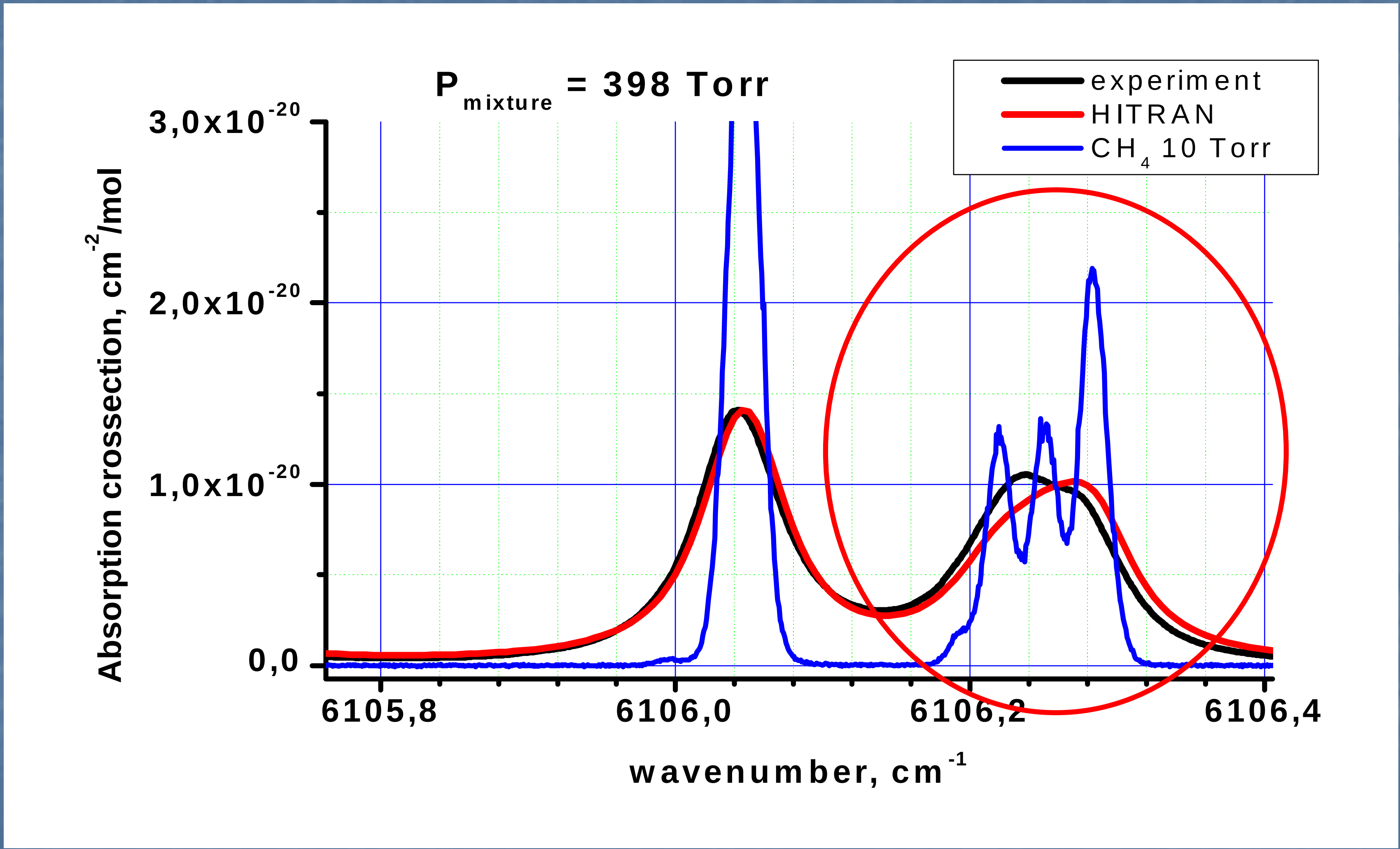
Wavenumber Experiment, cm^{-1}	Intensity, cm/mol	Broadening Coefficient, cm^{-1}/atm	Shifting Coefficient, cm^{-1}/atm	Wavenumber HITRAN, cm^{-1}	Intensity, HITRAN cm/mol	Broadening Coefficient, cm^{-1}/atm
6104.5808	8.14E-25					
6104.63041	8.73E-25					
6104.72345	1.1E-25					
6104.74925	1.41E-25					
6104.813	1E-24					
6104.879	3.8E-26					
6104.9306	1.2E-25					
6104.9903	2.9E-24					
6105.0963	6.5E-25					
6105.1668	2.2E-25					
6105.3693	6E-24			6105.3694	6.56E-24	0.082
6105.4185	1.41E-25			--	--	--
6105.4851	4E-25			--	--	--
6105.62511	6.82E-22	0.0506	-0.0106	6105.626*	6.63E-22	0.079
6105.7419	1E-25	--	--	--	--	--
6105.774	1E-25	--	--	--	--	--
6105.9135	1E-24	--	--	--	--	--
6105.99417	4.27E-24	--	--	--	--	--
6106.03768	3.5E-22	0.0641	-0.005	6106.0402	4.45E-22	0.079
6106.04902	7.47E-22	0.065	-0.004	6106.0505	6.91E-22	0.079
6106.1933	3.06E-23	0.06	0.016	6106.1943	4.63E-23	0.079
6106.22048	2.9E-22	0.048	0.002	6106.2205	2.92E-22	0.079
6106.25179	2.9E-22	0.035	-0.019	6106.252	3.04E-22	0.079
6106.28421	5.11E-22	0.055	-0.0113	6106.2841	5.2E-22	0.079
6106.3814	1E-24	--	--	--	--	--
6106.5136	3.8E-25	--	--	--	--	--
6106.593	9E-26	--	--	--	--	--
6106.732198	7E-26	--	--	--	--	--
6106.78665	1E-24	--	--	--	--	--
6106.819368	5.8E-25	--	--	--	--	--
6106.893401	4E-25	--	--	--	--	--
6106.979283	5E-26	--	--	--	--	--
6107.167741	4.05E-23	0.064	-0.01	6107.167741	4.88E-23	0.083
6107.24575	2E-25					

Methane R9 spectrum

$\sum_i \int \sigma_i(v)dv = 2.9378*10^{-21}$cm/mol

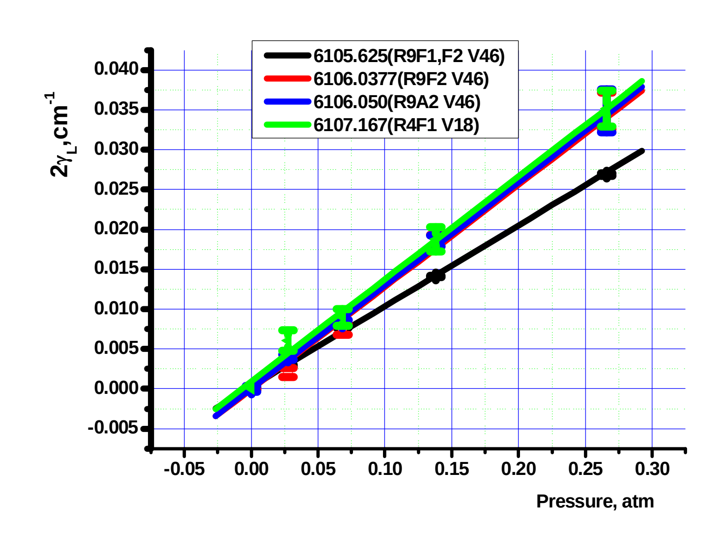


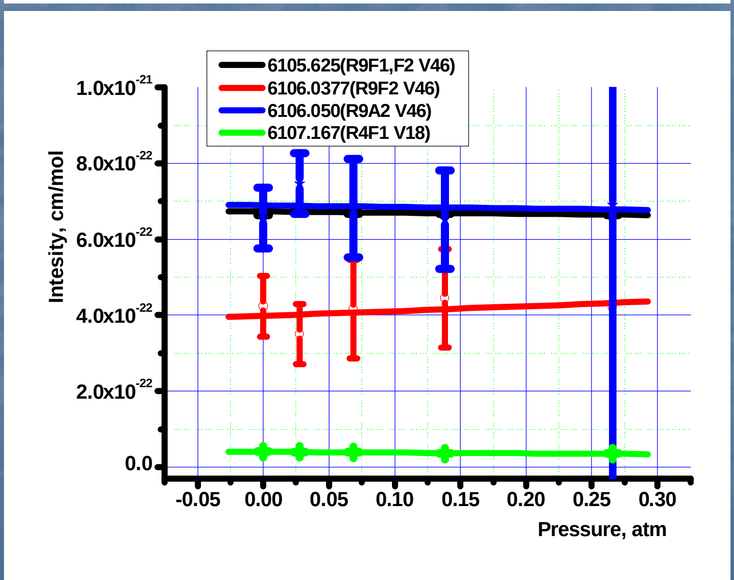
Experimental results and Preliminary analysis



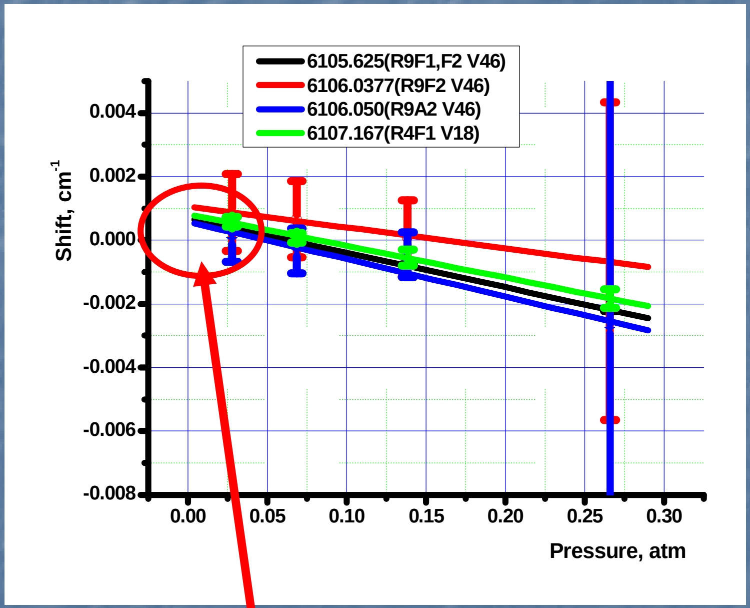
Collision partners: Ar, SF_6, N_2

Experimental results and preliminary analysis



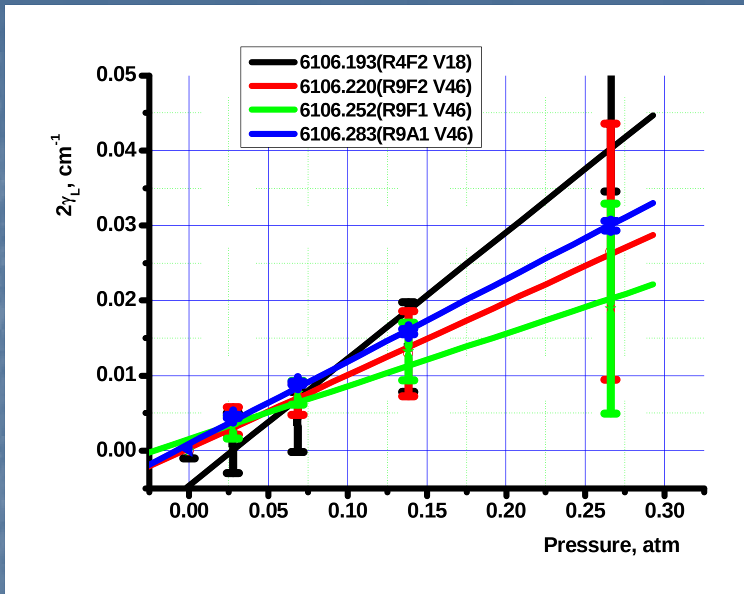


Mixture CH_4:N_2=1:15

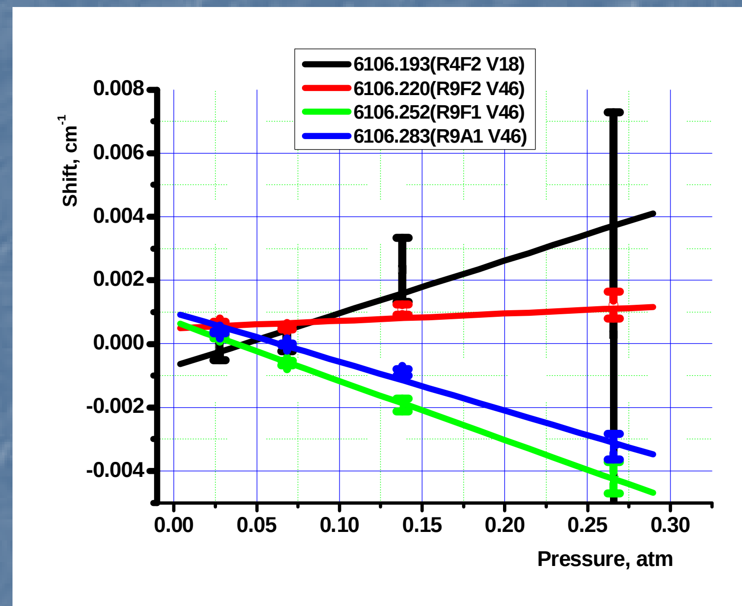


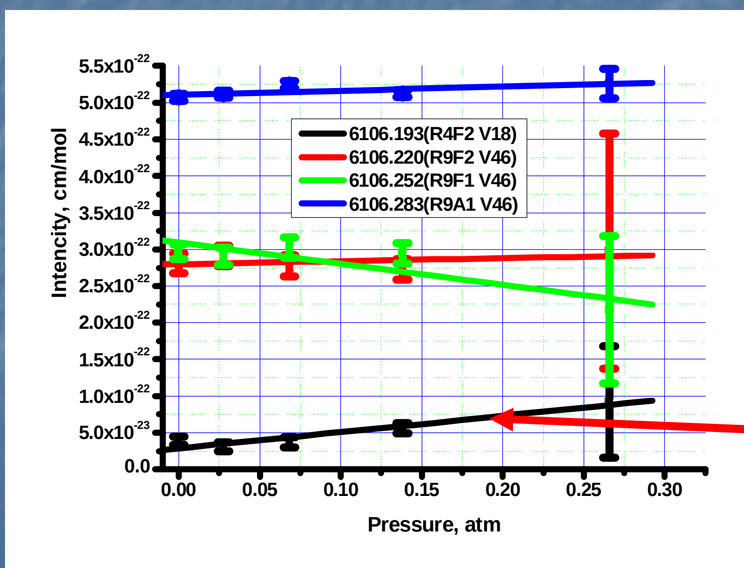
δ (CH_4-CH_4)= -0.051 (2) cm^{-1}/atm

Experimental results and preliminary analysis



Mixture $CH_4:N_2=1:15$





$I = 2.3(7)*10^{-23}+2*10^{-22}*P$

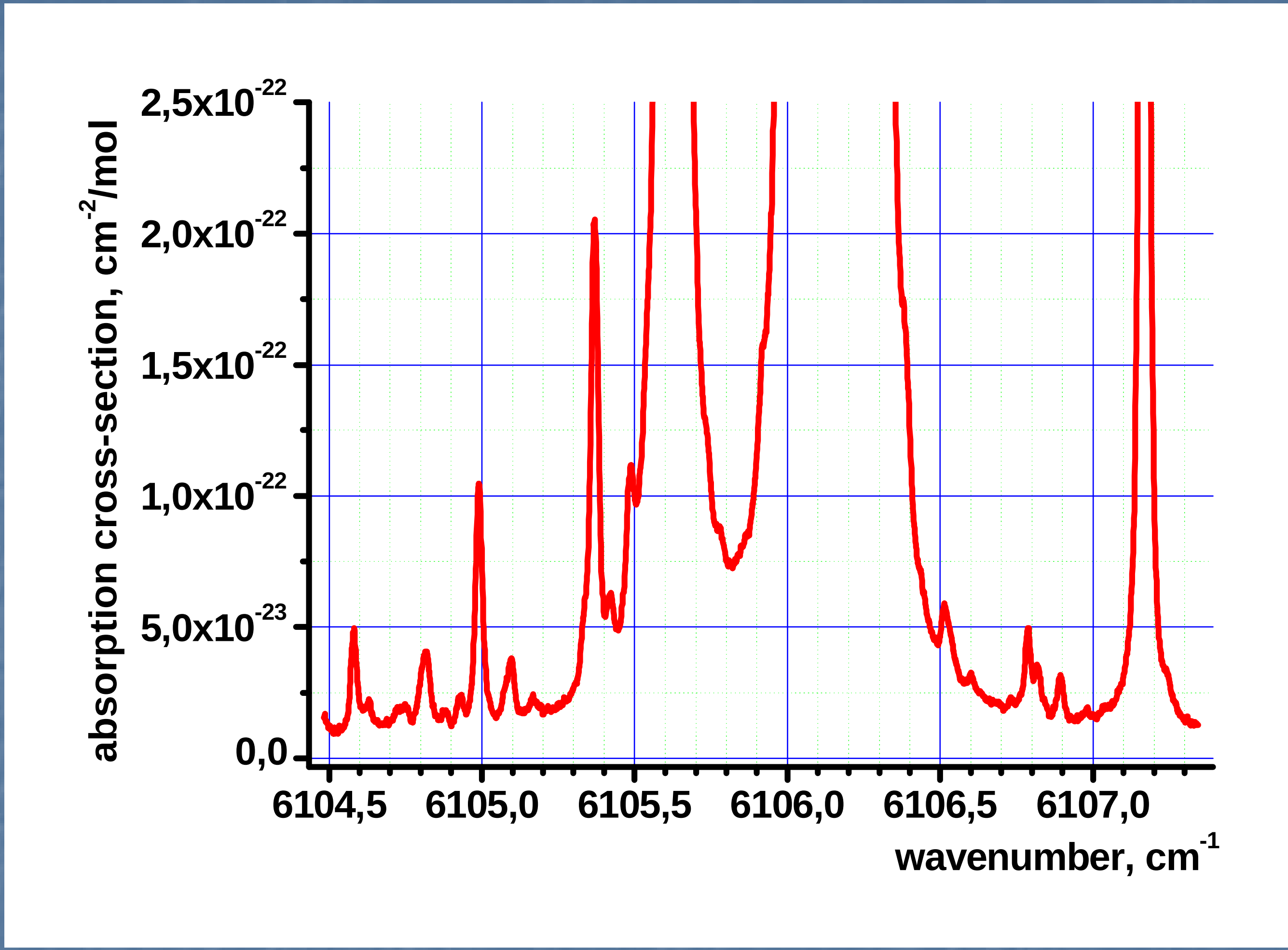
Wavenumber Experiment, cm^{-1}	Intensity, cm/mol	Broadening Coefficient, cm^{-1}/atm	Shifting Coefficient, cm^{-1}/atm	Wavenumber Lyulin et.all cm^{-1}	Intensity, Lyulin et.all cm/mol	Broadening Coefficient, cm^{-1}/atm	Shift cm^{-1}/atm
6104.5808	8.14E-25			6104.5812	1.6e-24		
6104.63041	8.73E-25			6104.633	2e-25		
6104.72345	1.1E-25			6104.724	1e-25		
6104.74925	1.41E-25			6104.749	2.7e-25		
6104.813	1E-24			6104.8088	3.e-25		
6104.879	3.8E-26			6104.883	2.0e-25		
6104.9306	1.2E-25			6104.930	2e-25		
6104.9903	2.9E-24			6104.9908	3.35e-24		
6105.0963	6.5E-25			6105.0959	7.e-25		
6105.1668	2.2E-25			---	---		
6105.3693	6E-24			6105.3694	6.2e-24		
6105.4185	1.41E-25			6105.420	2e-25		
6105.4851	4E-25			6105.4848	4e-25		
6105.62511	6.82E-22	0.0506	-0.0106	6105.6257	7E-22		
6105.7419	1E-25	--	--	6105.7419	2E-25		
6105.774	1E-25	--	--	6105.784	2E-25		
6105.9135	1E-24	--	--	6105.9135	1.1E-24		
6105.99417	4.27E-24	--	--	6105.99417	1.11E-23		
6106.03768	3.5E-22	0.0641	-0.005	6106.03700*	5.2E-22		
6106.04902	7.47E-22	0.065	-0.004	6106.055	5.16E-22		
6106.1933	3.06E-23	0.06	0.016	6106.1936	3.9E-23		
6106.22048	2.9E-22	0.048	0.002	6106.22072	3.1E-23	0.0534	-0.0172
6106.25179	2.9E-22	0.035	-0.019	6106.25035	3.12E-22	0.0423	-0.0268
6106.28421	5.11E-22	0.055	-0.0113	6106.2838	5.21E-22	0.0598	-0.0183
6106.3814	1E-24	--	--	6106.3863	9.95E-25	--	--
6106.5136	3.8E-25	--	--	6106.5144	6.56E-25	--	--
6106.593	9E-26	--	--	6106.534	2E-25	--	--
6106.732198	7E-26	--	--	--	--	--	--
6106.78665	1E-24	--	--	6106.7862	1.3E-24	--	--
6106.819368	5.8E-25	--	--	6106.8182	7.2E-25	--	--
6106.893401	4E-25	--	--	6106.8887	4E-26	--	--
6106.979283	5E-26	--	--	6106.943	5E-26	--	--
6107.167741	4.05E-23	0.064	-0.01	6107.16692	4.7E-23	0.0641	-0.0098
6107.24575	2E-25			6107.242	1e-25		

O.M.Lyulin, A.V.Nikitin, et al. Measurements of N_2-and O_2 broadening and shifting of methane spectral lines in the 5550-6236 cm^{-1} region // IQSRT, (2009), 654-668

Data processing perfection

- Rosenkrantz profile + multiline and multispectra fittitg
- Weak lines contribution – high dynamic range

Methane weak absorption lines



Conclusions

- Even at low pressure spectral line mixing affects the absorption spectra shape of $2v_3$ band of CH_4
- The using of isolated line model and Voigt profile results in significant error in lines intensities, shift and broadening coefficients

Acknowledgement

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Project of RAS “Laser spectroscopy and frequency standards”.
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