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$^{238}UF_6$ and $^{235}UF_6$ spectra measurement in mid IR spectral range

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Abstract

Measurement of UF_6 enrichment is important part of IAEA safeguards. In [1] it was demonstrated that TDLS is efficient technique for such application. In present paper next step of development of UF_6 enrichment monitor to be used in IAEA safeguards is presented. There were two main goals of this development: precision and accuracy improvement.

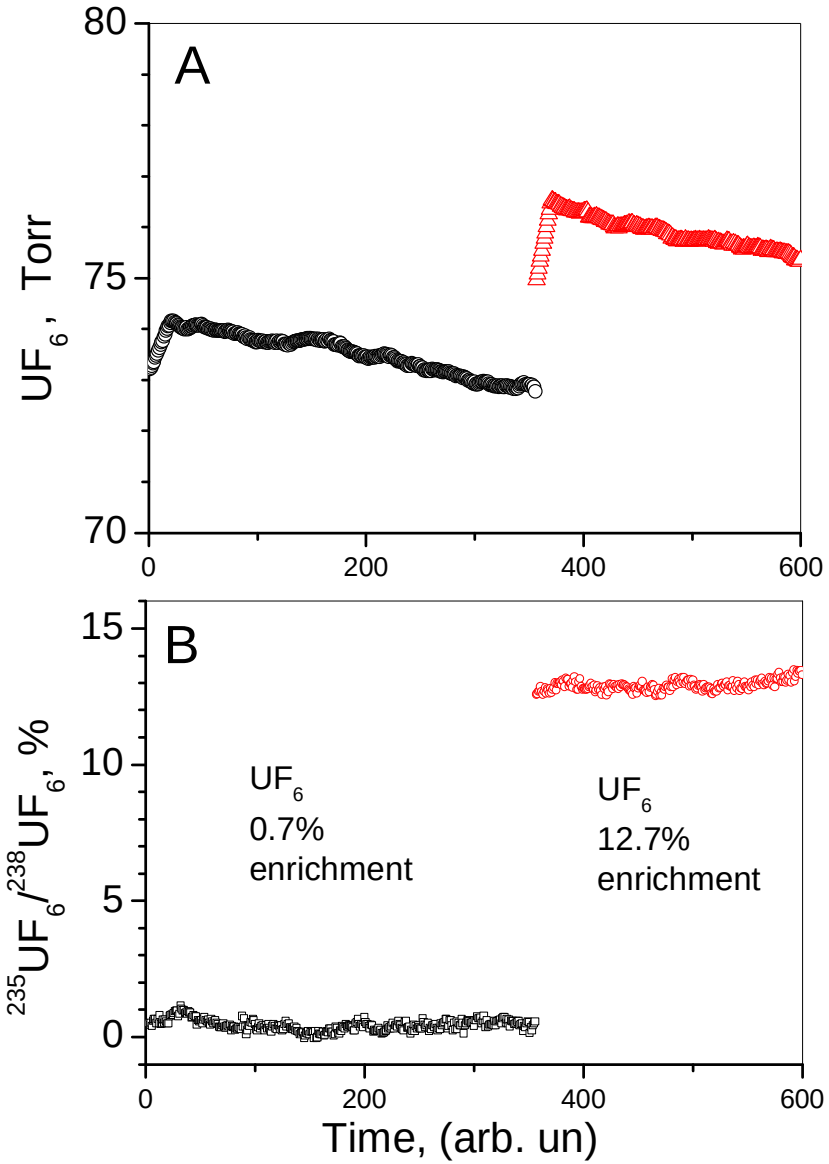
The first one was to develop instrument with higher sensitivity. Laboratory prototype of the instrument was developed. Analysis of the instrument sensitivity are presented.

To achieve high accuracy of enrichment measurement absorption cross-sections of UF_6 isotopomers have to be obtained very accurately. The instrument developed was used to measure absorption cross-sections of $^{238}UF_6$ and $^{235}UF_6$. Spectra obtained and their analyses are presented.

References:

[1] A.Nadezhdinskii, Ya.Ponurovskii, D.Stavrovskii, D. Bolyasov, G.Grigoriev, N.Gorshunov, S.Malyugin, Sh.Nabiev , in TDLS 2005, Abstracts of papers, Florence, Italy, 2005, p.121

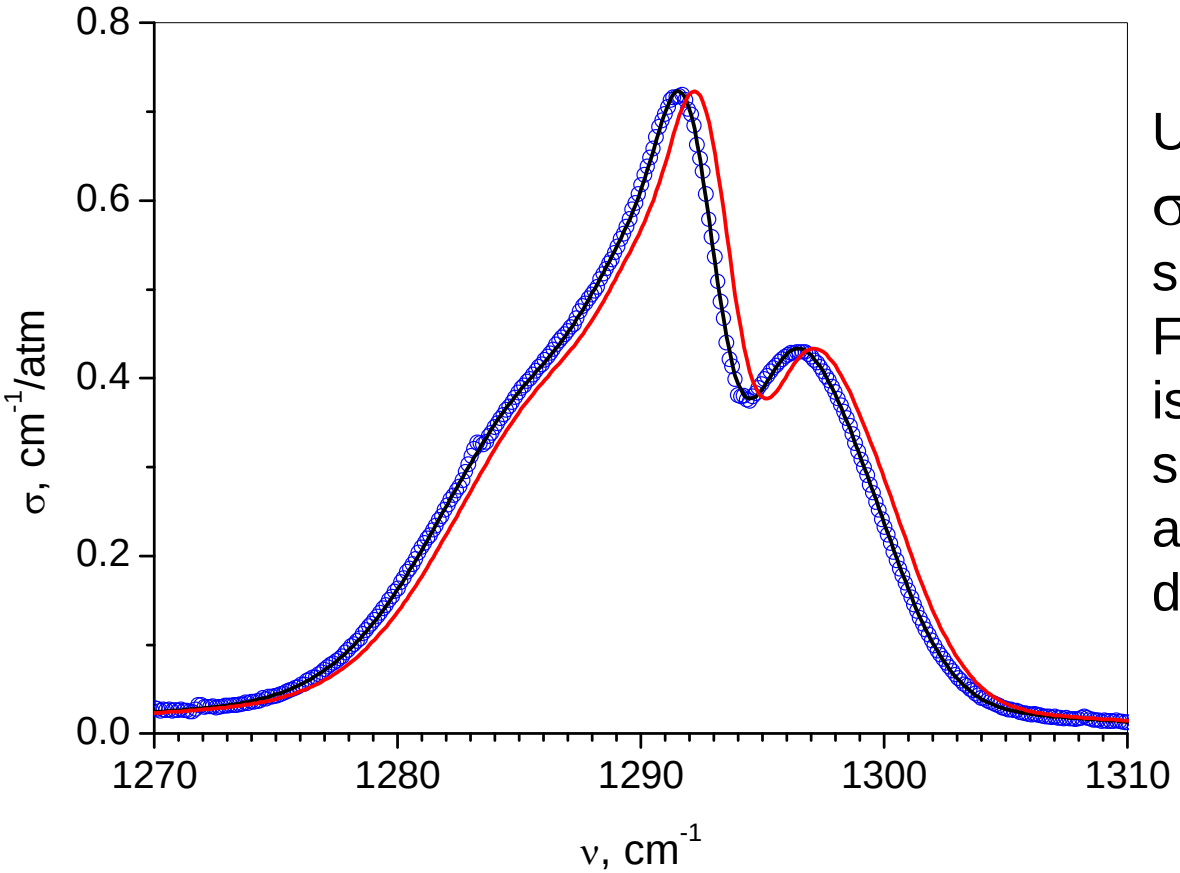
Introduction



Preliminary test of instrument and prove of the concept was performed at IAEA UF_6 Loop in Seibersdorf in 2002.
Several UF_6 samples with calibrated enrichment were used. Figure shows results obtained for two calibrated samples: natural and high enriched ones. Sample cell was filled with calibrated gas and measurement procedure was started. Fig.A and Fig.B presents measured partial pressure and enrichment, respectively.

Precision in this experiment was limited by low quality of diode laser and photo-diodes in use; to improve enrichment measurement accuracy $^{235}UF_6$ spectrum has to be obtained.

UF_6 absorption cross-section

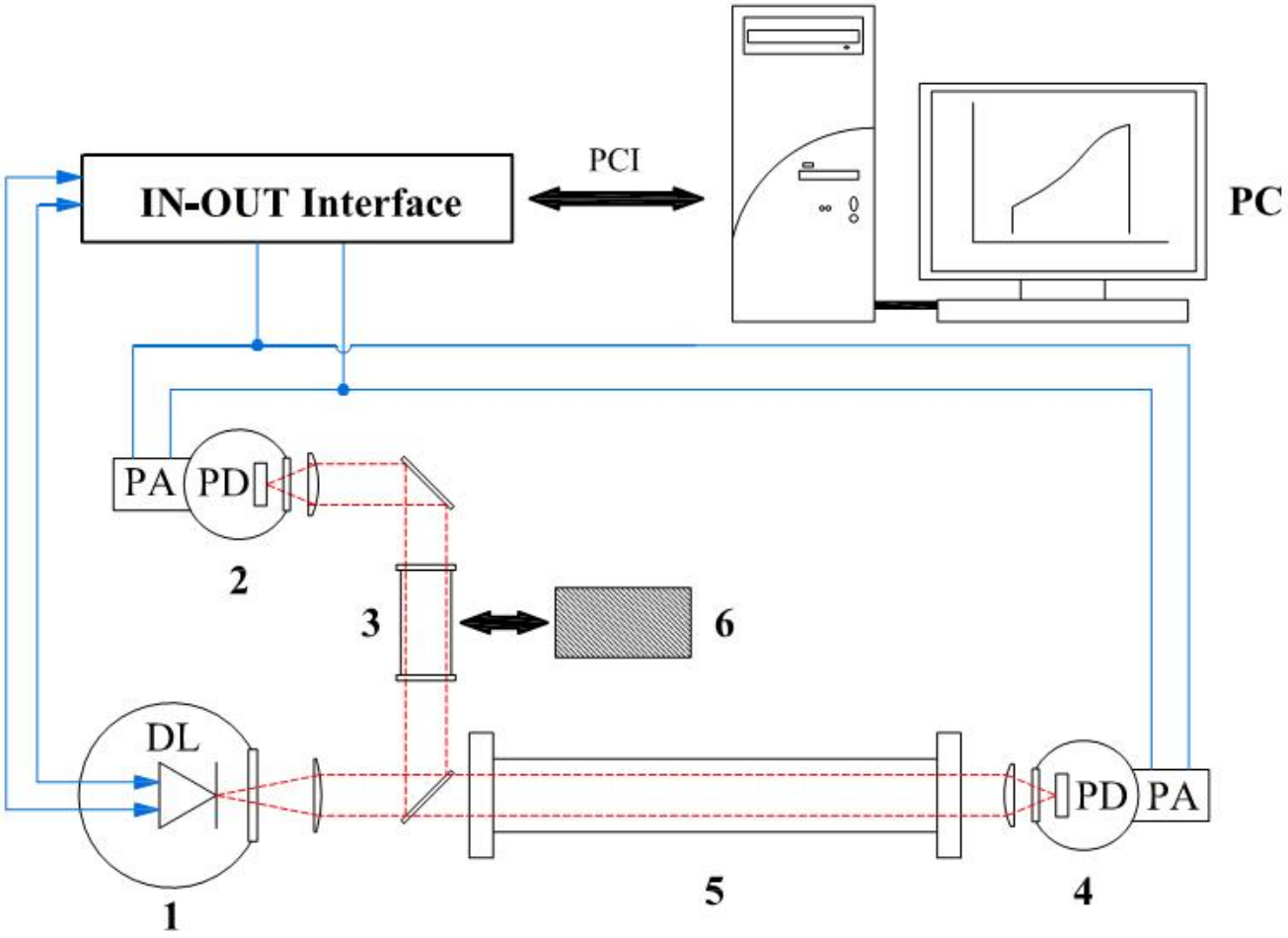


UF_6 absorption cross-section - σ (circles) of $\nu_1+\nu_3$ band. The spectrum was recorded by FTS for sample with natural isotopes abundance. Model spectra of $^{238}UF_6$ (black line) and $^{235}UF_6$ (red line) [2] demonstrates isotope shift [3].

[2] A.G.Berezin, S.L.Malyugin, A.I.Nadezhdinskii, D.Yu.Namestnikov, Ya.Ya.Ponurovskii, D.B.Stavrovskii, Yu.P.Shapovalov, I.E.Vyazov, V.Ya.Zaslavskii, Yu.G.Selivanov, N.M.Gorshunov, G.Yu.Grigoriev, Sh.Sh.Nabiev, UF_6 enrichment measurements using TDLS techniques, Spectrochimica Acta , A 66, 796– 802 (2007)

[3] R.S. McDowell, L.B. Asprey, R.T. Paine, Vibrational spectrum and force field of uranium hexafluoride. -J. of Chemical Physics, Vol. 61, No. 9, 1974.

Block-scheme

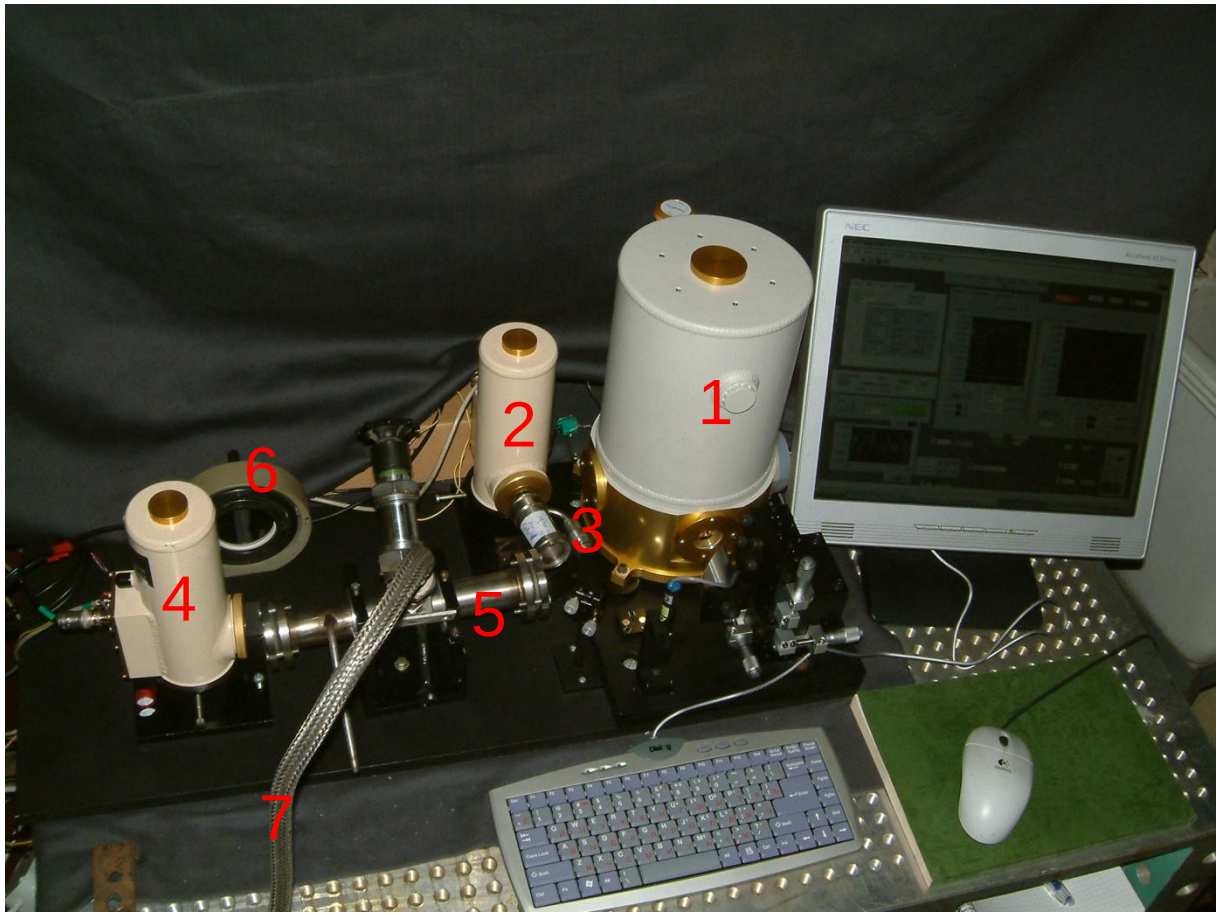


1. DL in cryostat;
2. Reference PD;
3. Reference gas cell;
4. Analytical PD;
5. Analytical gas cell;
6. FP etalon;

Analytical channel with gas cell (5) containing gas under investigation. Reference channel with cells (3) containing methane and acetylene, and with Fabry-Perot etalon (6) were used to determine laser frequency tuning.

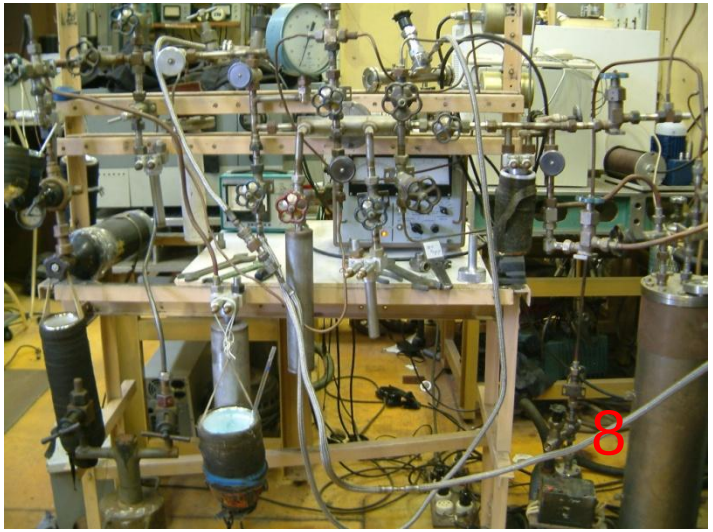
Experimental setup view

For present experiments the instrument was installed in Kurchatov Institute



View of TDLS system developed:

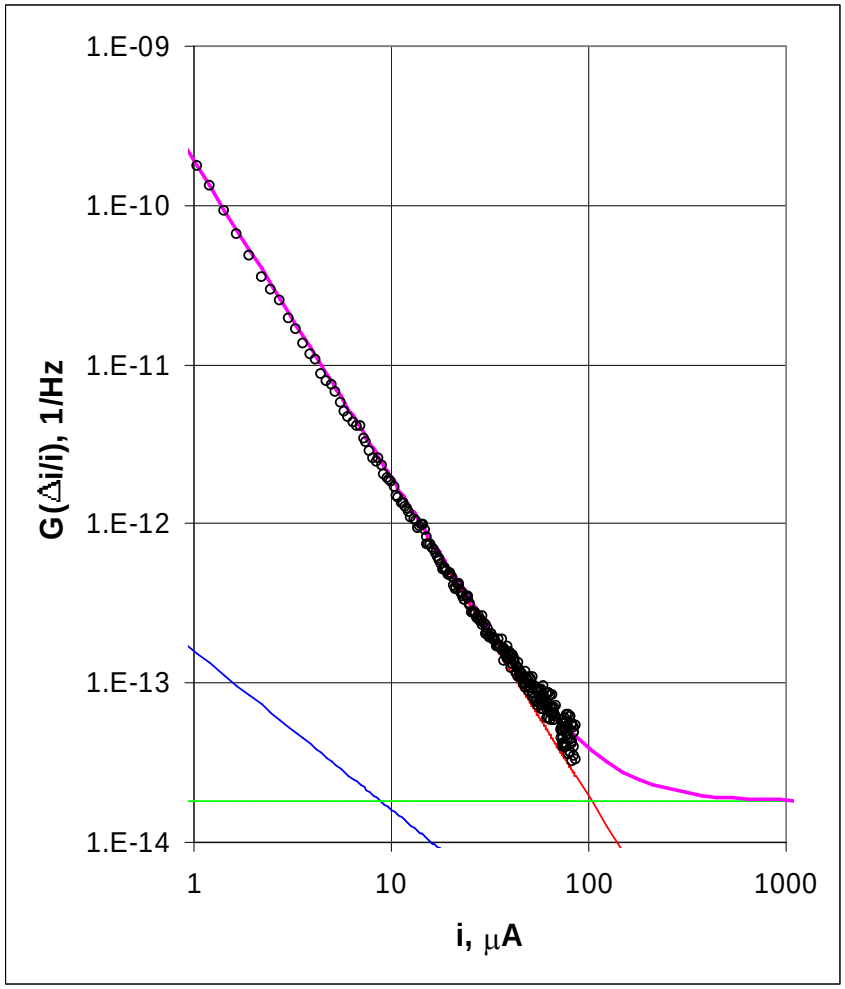
1. DL in cryostat;
2. Reference PD;
3. Reference gas cell;
4. Analytical PD;
5. Analytical gas cell;
6. FP etalon;
7. Connection to UF_6 gas distribution system.

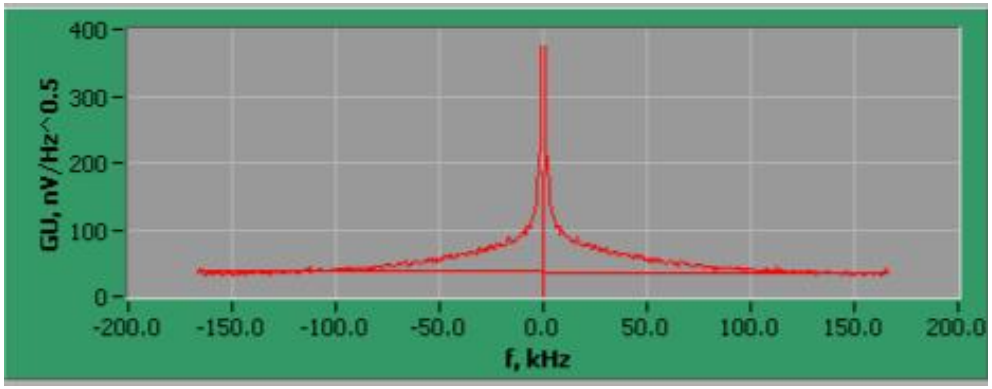


View of UF_6 gas distribution system

8. Connection to TDLS system

Noises of PD and DL





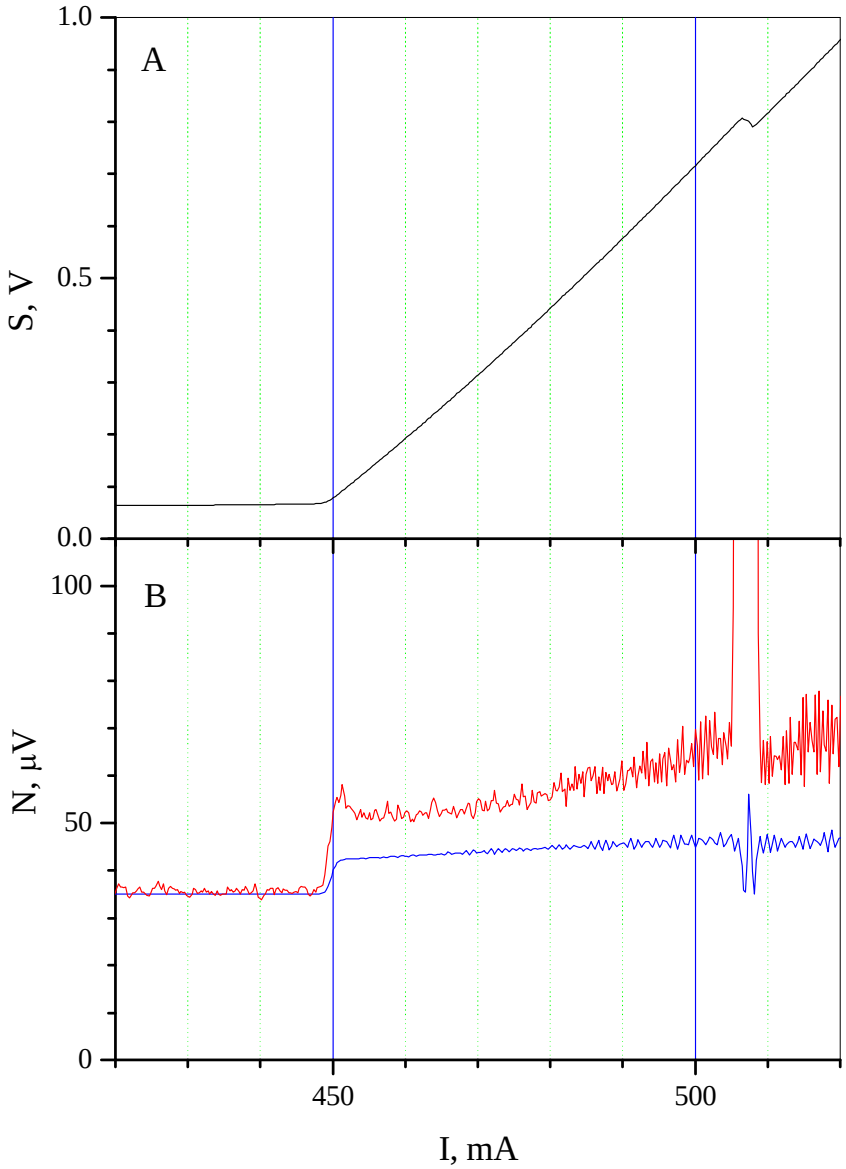
Noise spectrum of recorded signal

Main physical mechanisms of photo-current noise: red line – PD + preamplifier noise (small signal); blue line – photo-current shot noise (large signal); green line – DL intensity quantum noise.

Photo-current relative noise spectral density as function of photo-current value – i (black open cycles), total photo-current relative noise spectral density - thick line.

For mid IR spectral range PD + preamplifier thermal noises dominate.

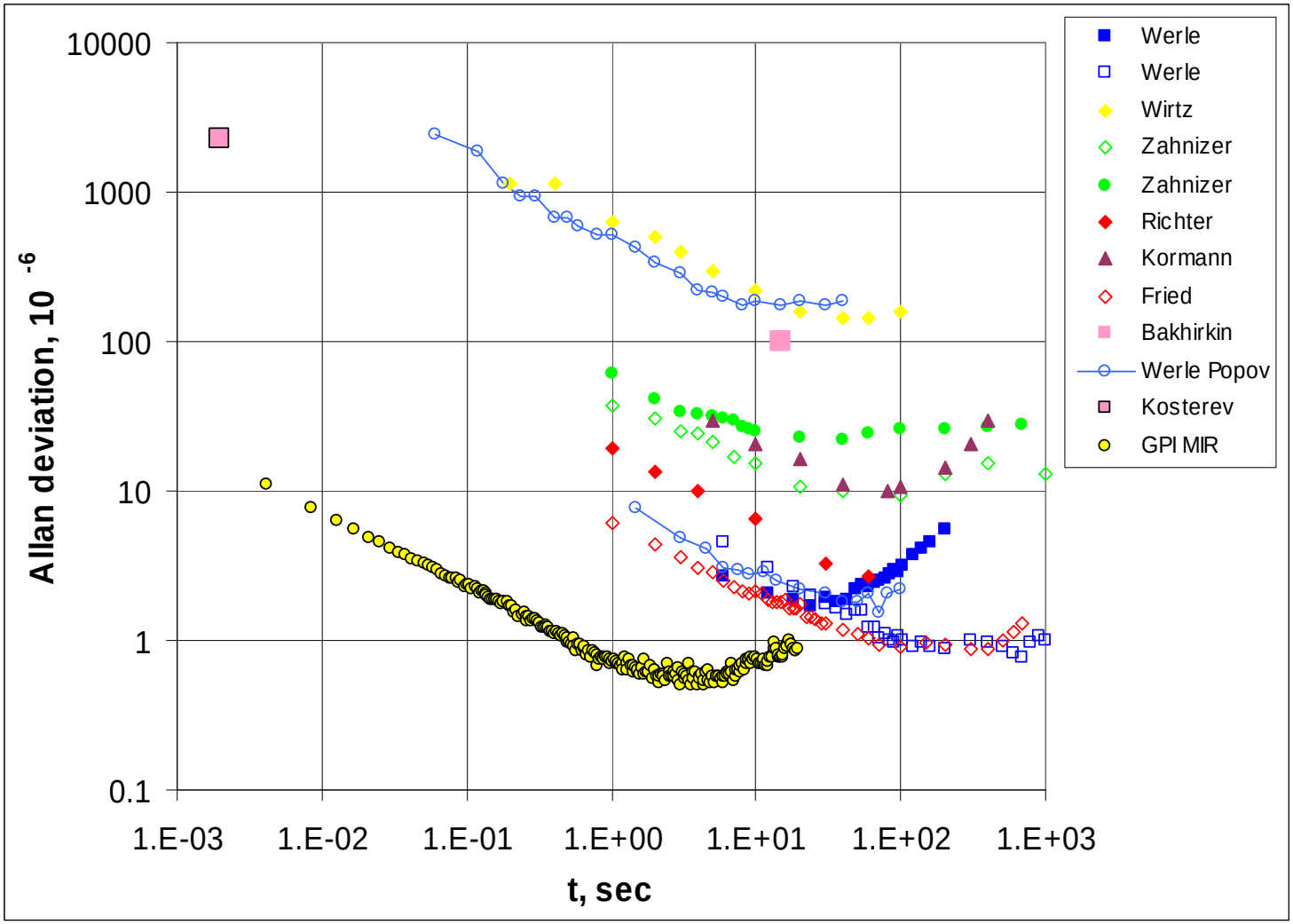
DL noise



A - recorded signal as function of excitation current for DL under investigation (Laser Components - 448-HV-1-17).
Presence of mode hop can be observed near 507 mA.

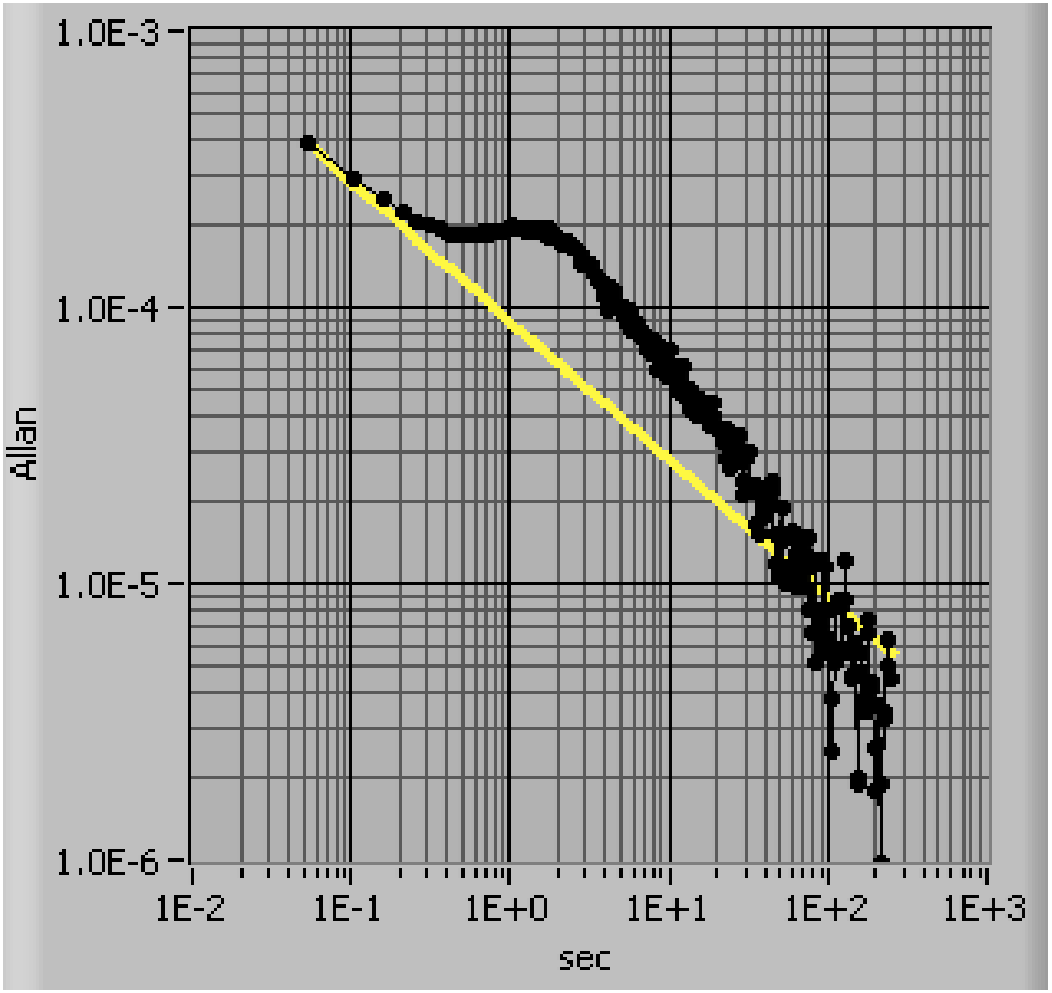
B – signal noise as function of excitation current (red); PD noise + current noise (blue). Difference between red and blue is due to DL noise.
There are 3 DL noise mechanisms: noise peak near threshold is due to DL quantum noise; near 507 mA DL modes competition noise can be observed; additional noise proportional to DL intensity also takes place.

Allan plots



Comparison of minimum detectable absorption obtained in present work (GPI MIR) with best published results in mid IR spectral range.

Temperature stabilization



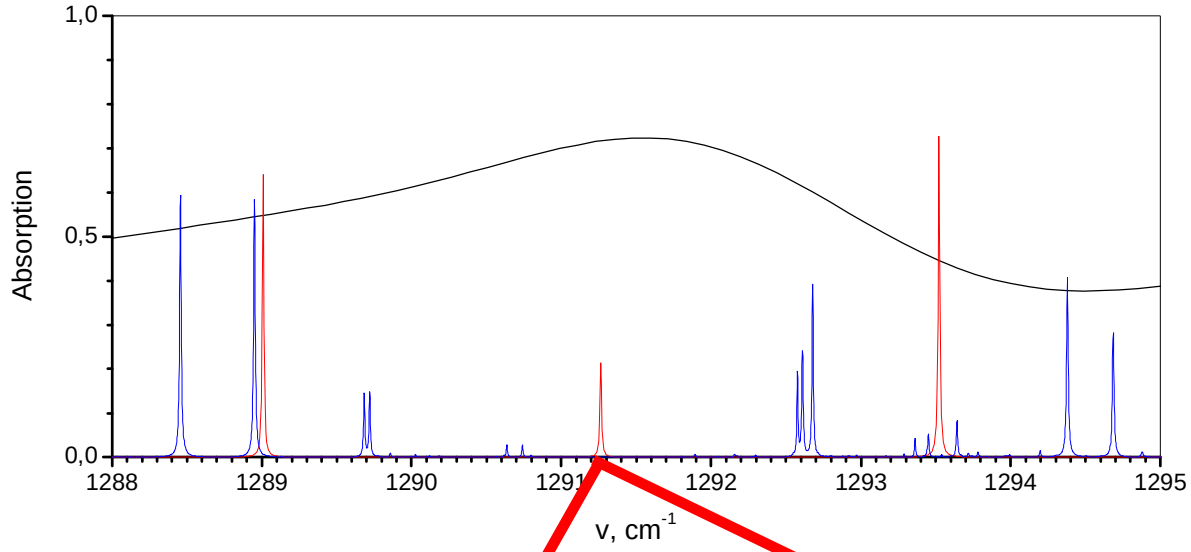
DL was installed in LN2 cryostat L5736 (Laser Components s/n 1070).

Temperature stability level achieved (2 10^{-4} K) is one order of magnitude better than other results obtained for this system by other authors. Nevertheless, it is order of magnitude worse in comparison with our results obtained for similar optimized system [3].

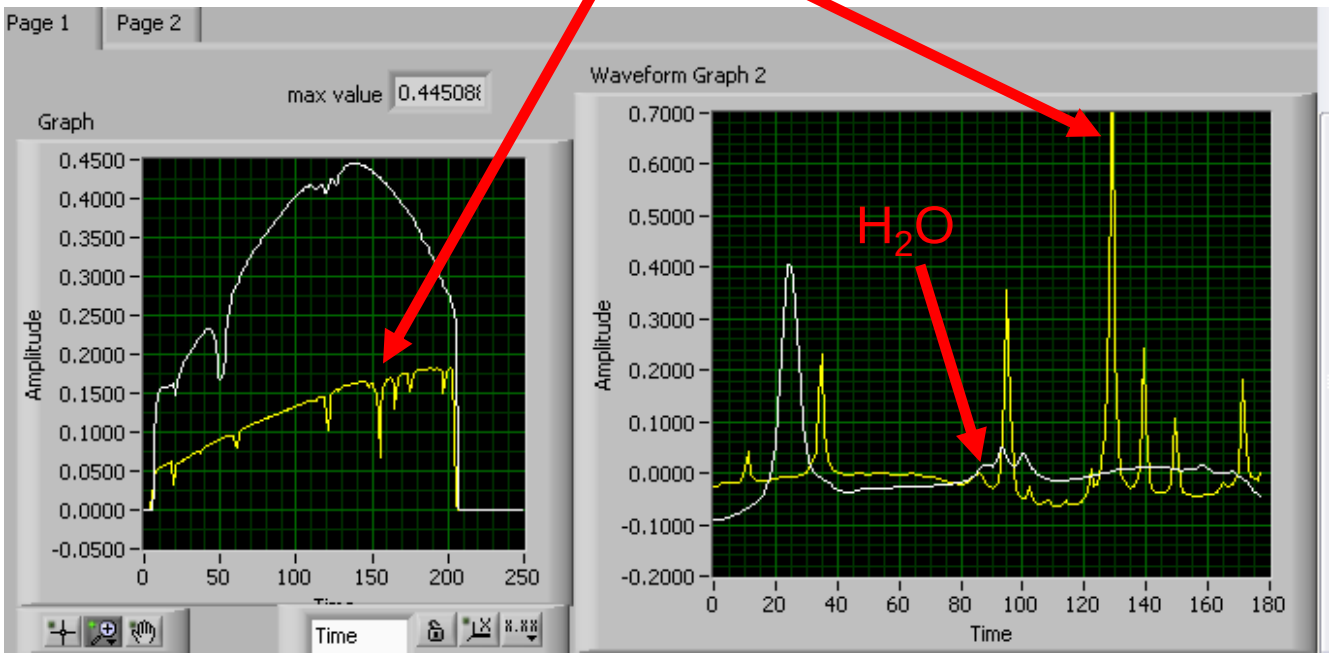
[3] A.Nadezhdinskii, Diode laser spectroscopy of polyatomic molecules, Doctor of Sciences Thesis, Moscow, 1986.

Requirements of temperature stabilization in present work are very high, because temperature stability determines accuracy of isotopic ratio measurements. In future improvement of the system will be necessary.

DL frequency tuning curve calibration

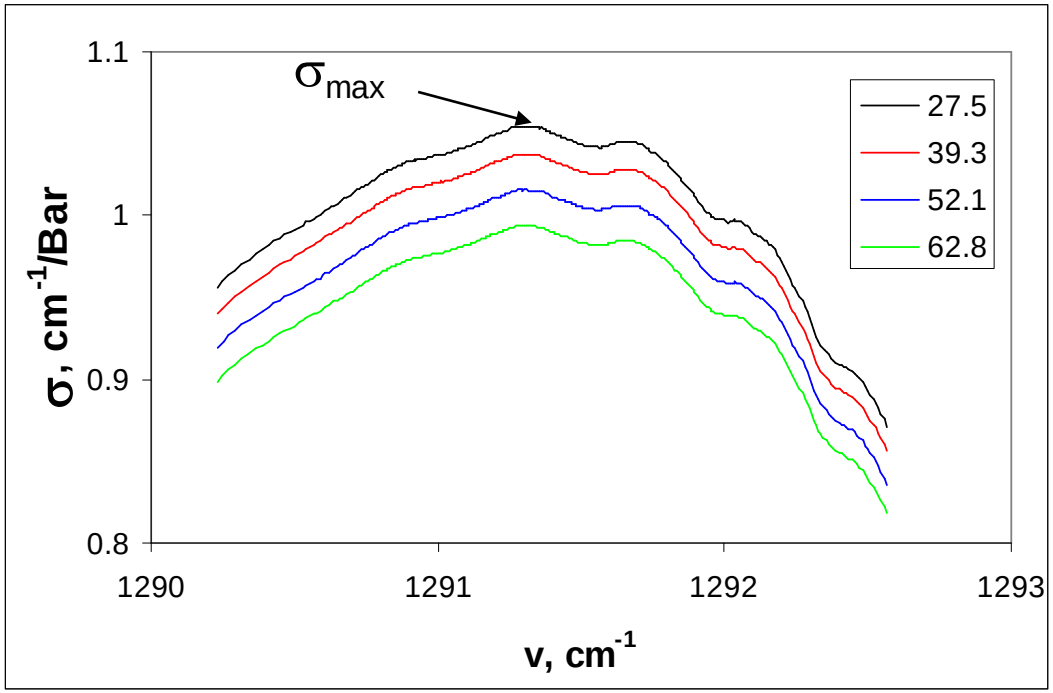


Absorption spectra of $^{238}UF_6$ (black), C_2H_2 (red), and CH_4 (blue).

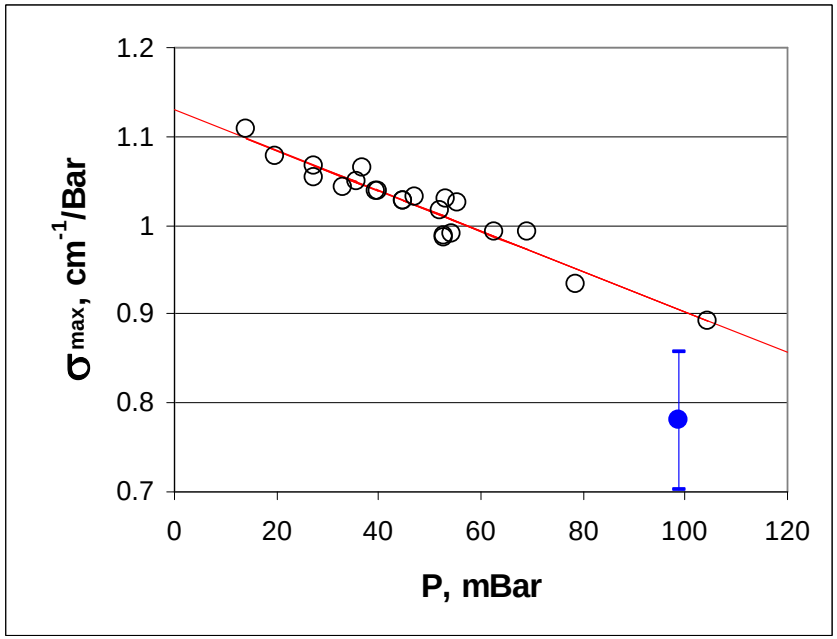


DL operation regime Channels with cells containing C_2H_2 (yellow) and CH_4 (white). There are some weaker C_2H_2 lines not included in HITRAN as well as water line.

Absorption cross-section



Absorption cross-section - σ of UF_6 sample with natural isotopes abundance for different pressures [mBar] as measured by TDLS. Spectra fine structure can be observed.

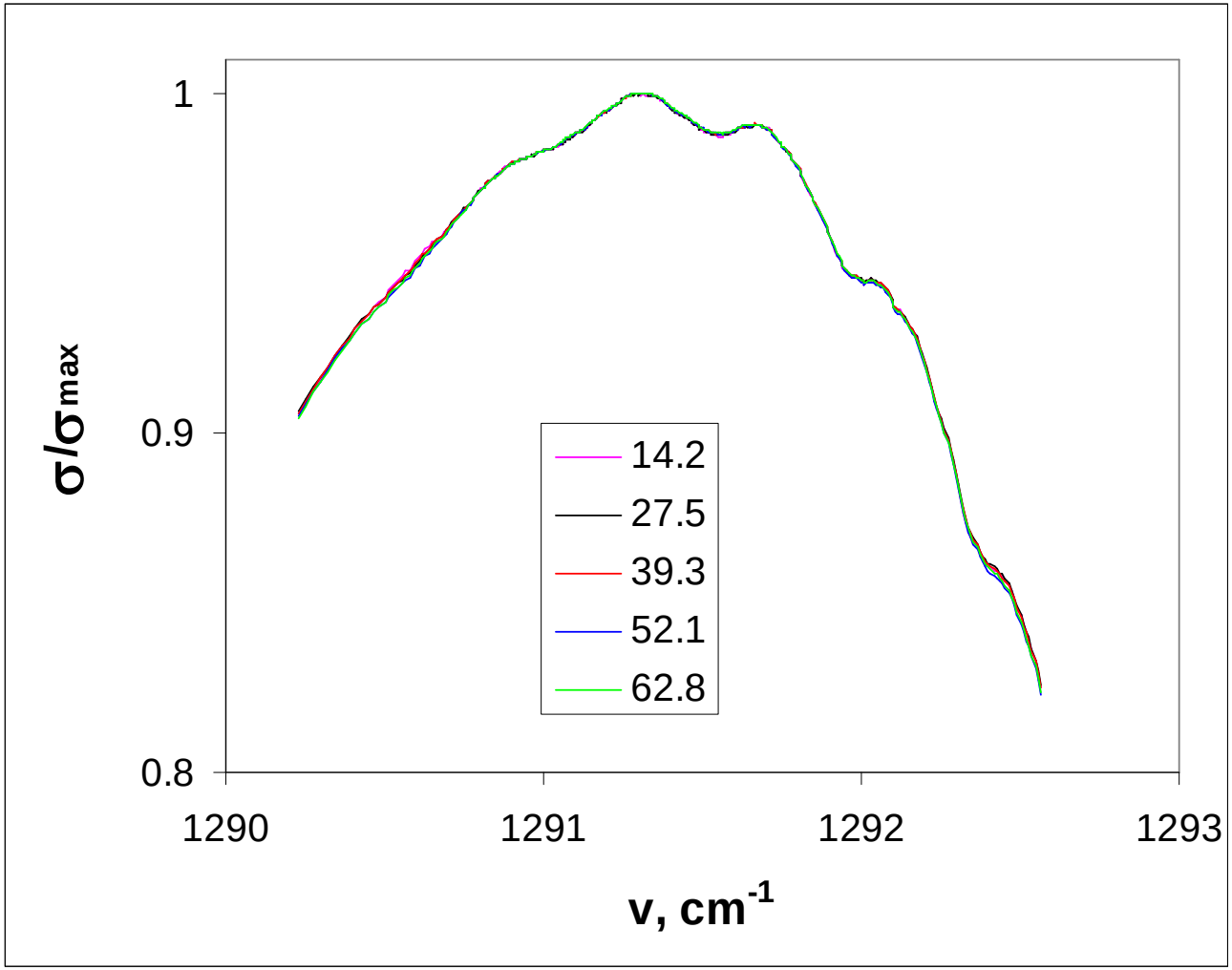


σ_{max} as function of UF_6 partial pressure P: black open cycles - present work; blue solid cycle – [3]; red line - linear regression

$$\sigma_{\max} = \sigma_0 + \frac{\partial \sigma}{\partial P} P = 1.129 \frac{\mathrm{cm}^{-1}}{\mathrm{Bar}} - 2.27 \frac{\mathrm{cm}^{-1}}{\mathrm{Bar}^2} P$$

To explain this graph presence of UF_6 dimers has to be assumed.

UF_6 cross-section shape

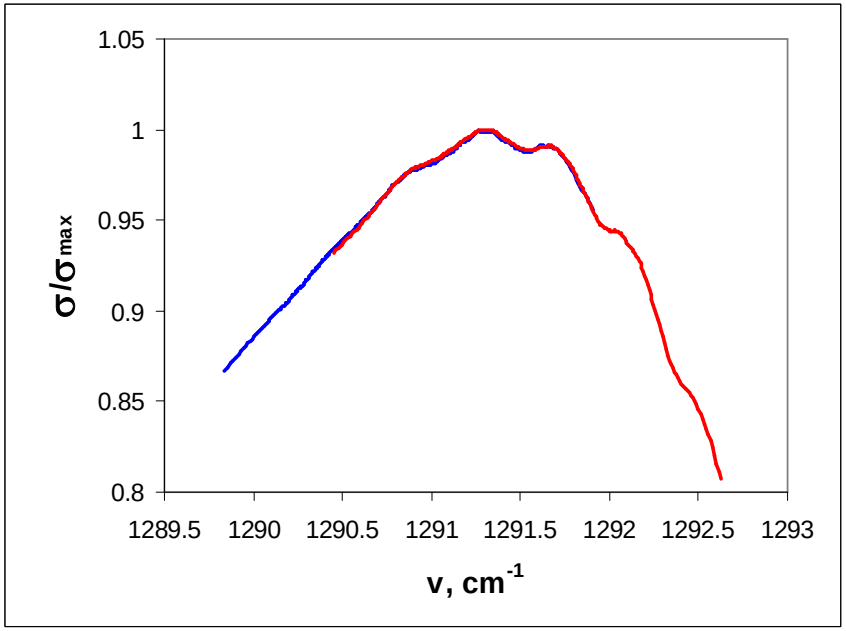


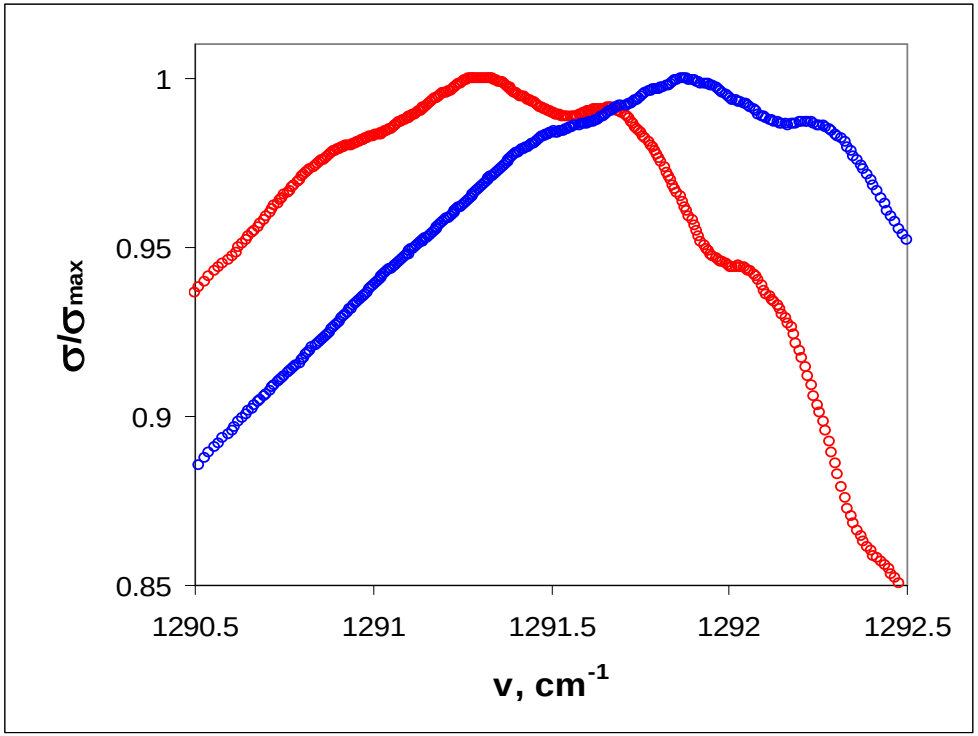
Normalized absorption cross-section – σ/σ_{max} (the same results as on previous slide) of UF_6 sample with natural isotopes abundance for different pressures [mBar] as recorded by TDLS.

Graph demonstrates good reproducibility of recorded normalized absorption cross-sections σ/σ_{max} with relative std = 0.00027. Spectrum fine structure can be observed. No pronounce pressure dependence of the shape was found.

Isotope shift

Spectra of two UF_6 samples were measured using TDLS: sample with natural isotopes abundance and sample with 89 % enrichment. Using data obtained normalized absorption cross-section of $^{238}UF_6$ (red open cycles) and $^{235}UF_6$ (blue open cycles) were obtained.



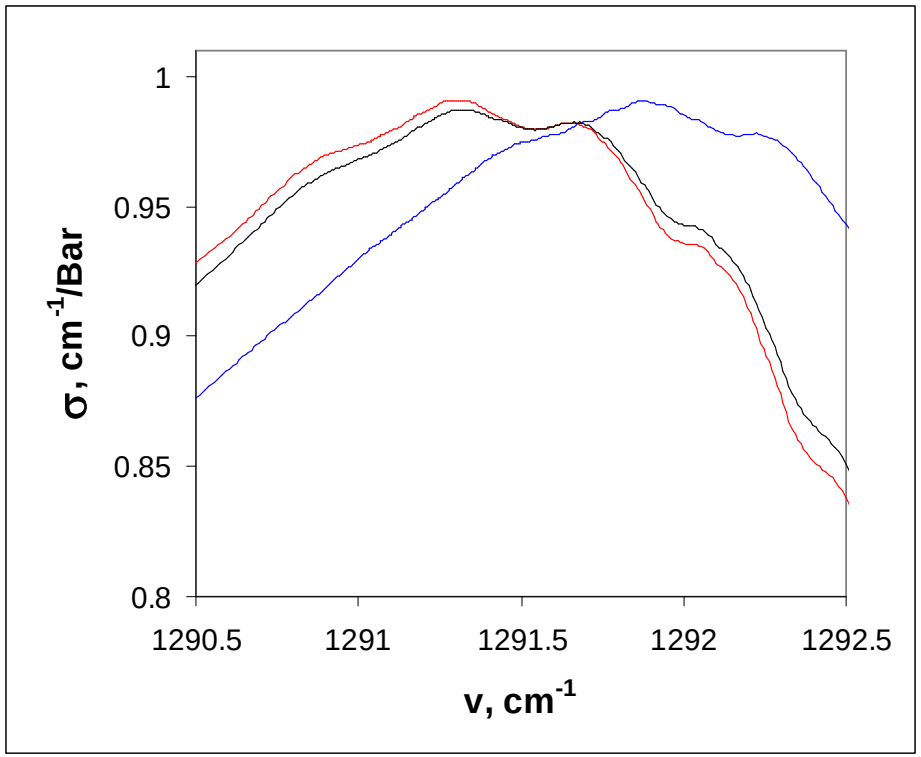


σ/σ_{max} of $^{238}UF_6$ (red line) and $^{235}UF_6$ (blue line) (the same as above) when $^{235}UF_6$ spectrum was shifted by isotope shift obtained - 0.61 cm^{-1}. The results demonstrates that spectrum shape doesn't depend on Uranium isotopes. Difference between spectra of isotopes is determined only by isotope shift.

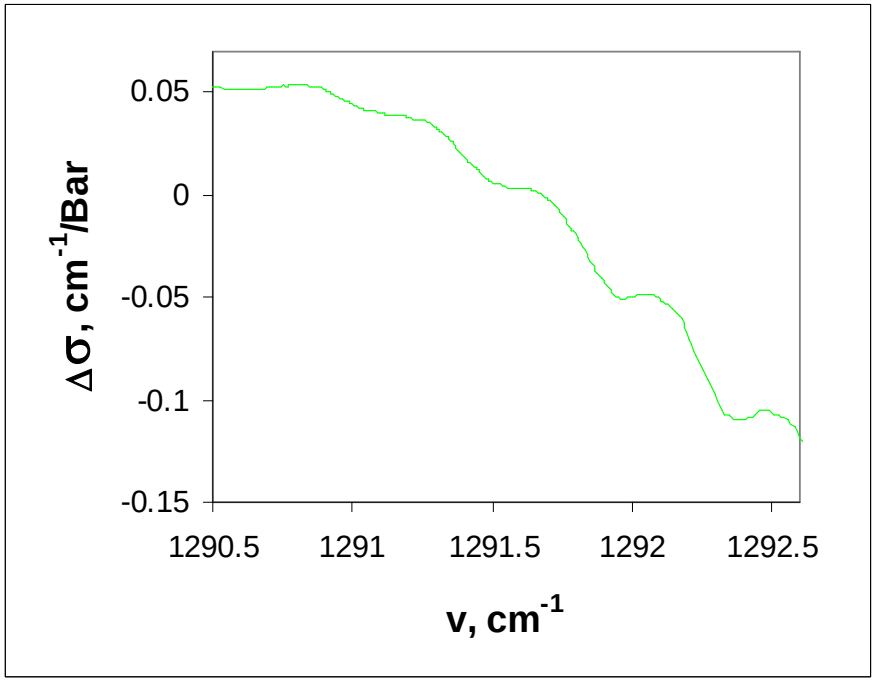
Enrichment measurement

Measured absorption cross-section σ is superposition of both UF_6 isotopomers; its difference with cross-section of $^{238}UF_6$ is direct measure of enrichment - R.

$$\sigma(\nu) = R\left[\sigma_5(\nu) - \sigma_8(\nu)\right] + \sigma_8(\nu) = R\Delta\sigma(\nu) + \sigma_8(\nu)$$



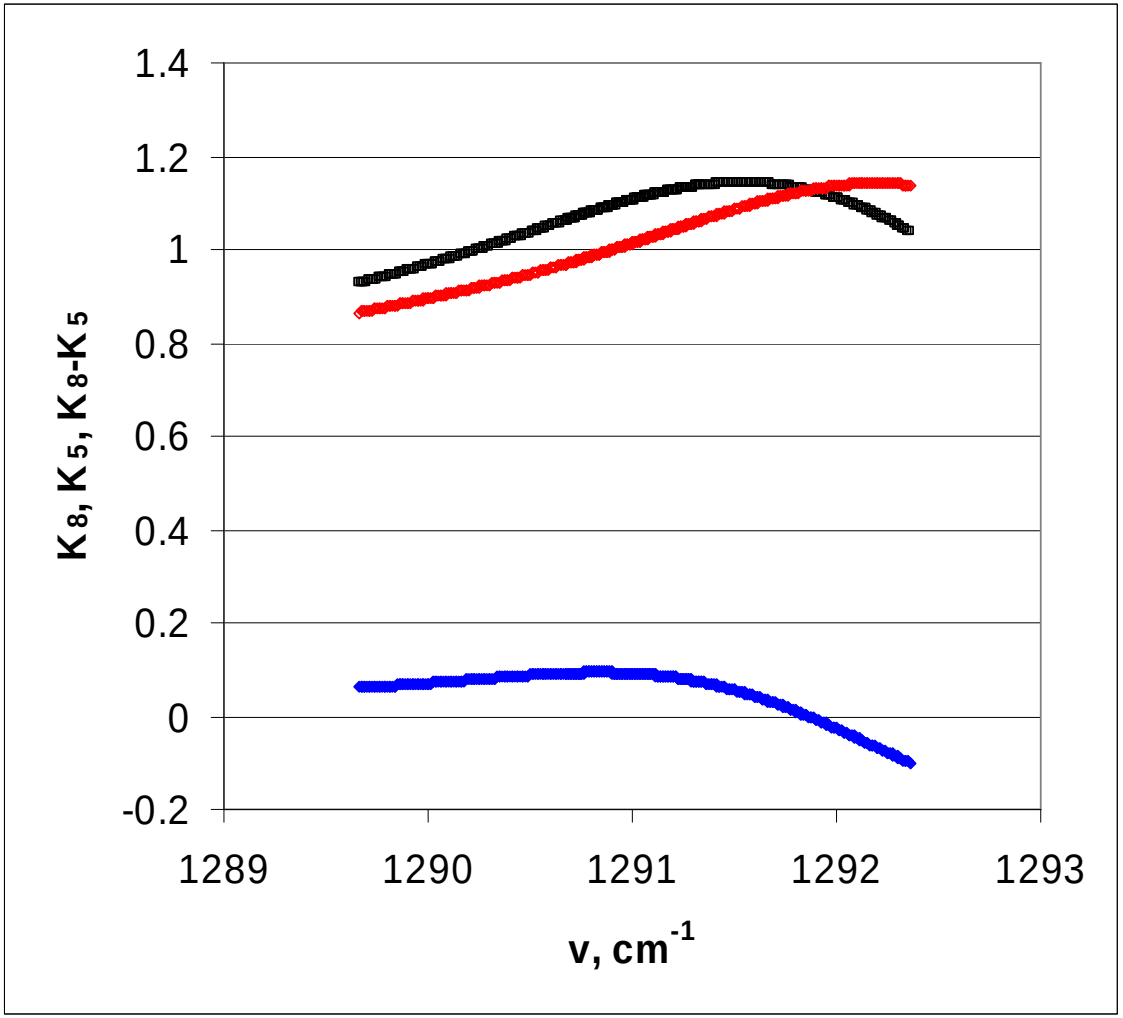
Absorption cross-section σ (P = 40 Torr): $^{238}UF_6$ (red), $^{235}UF_6$ (blue), sample under investigation with R = 14.3 % (black).



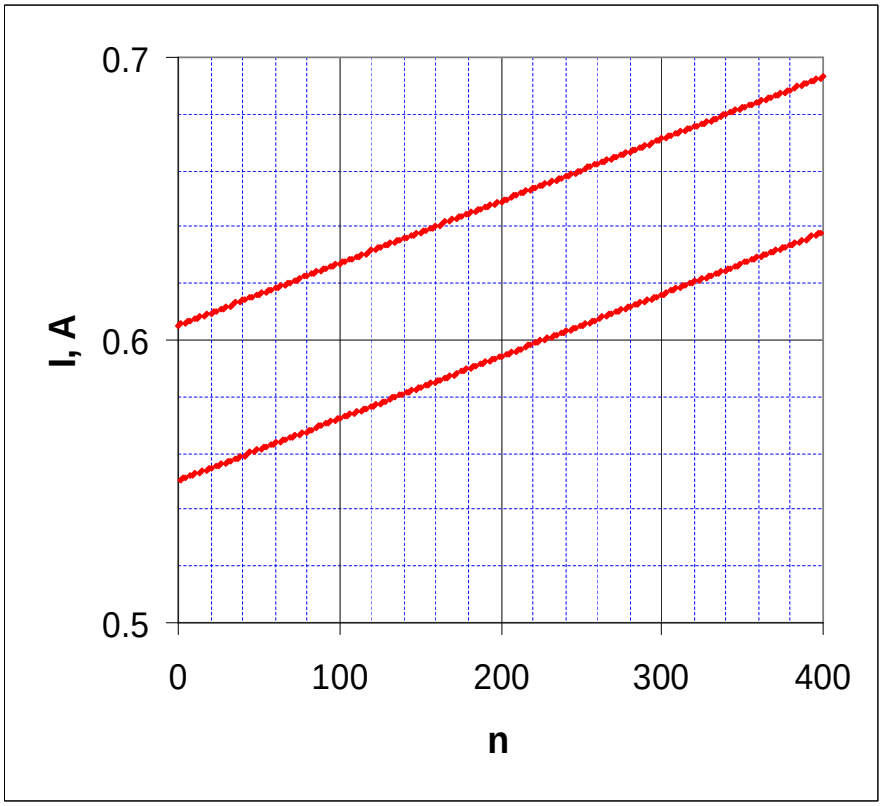
Δσ as measured by TDLS (P = 40 Torr)

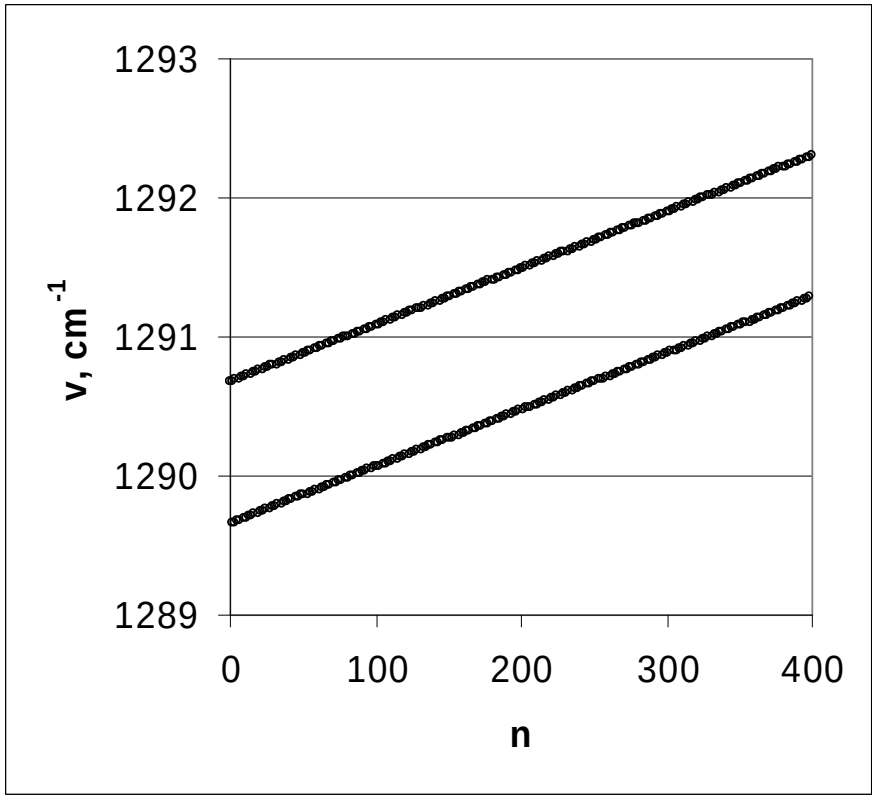
UF6 absorption

$$K(\nu) = P\left[(1-R)\sigma_8(\nu) + R\sigma_5(\nu)\right]L$$



Modulation regime



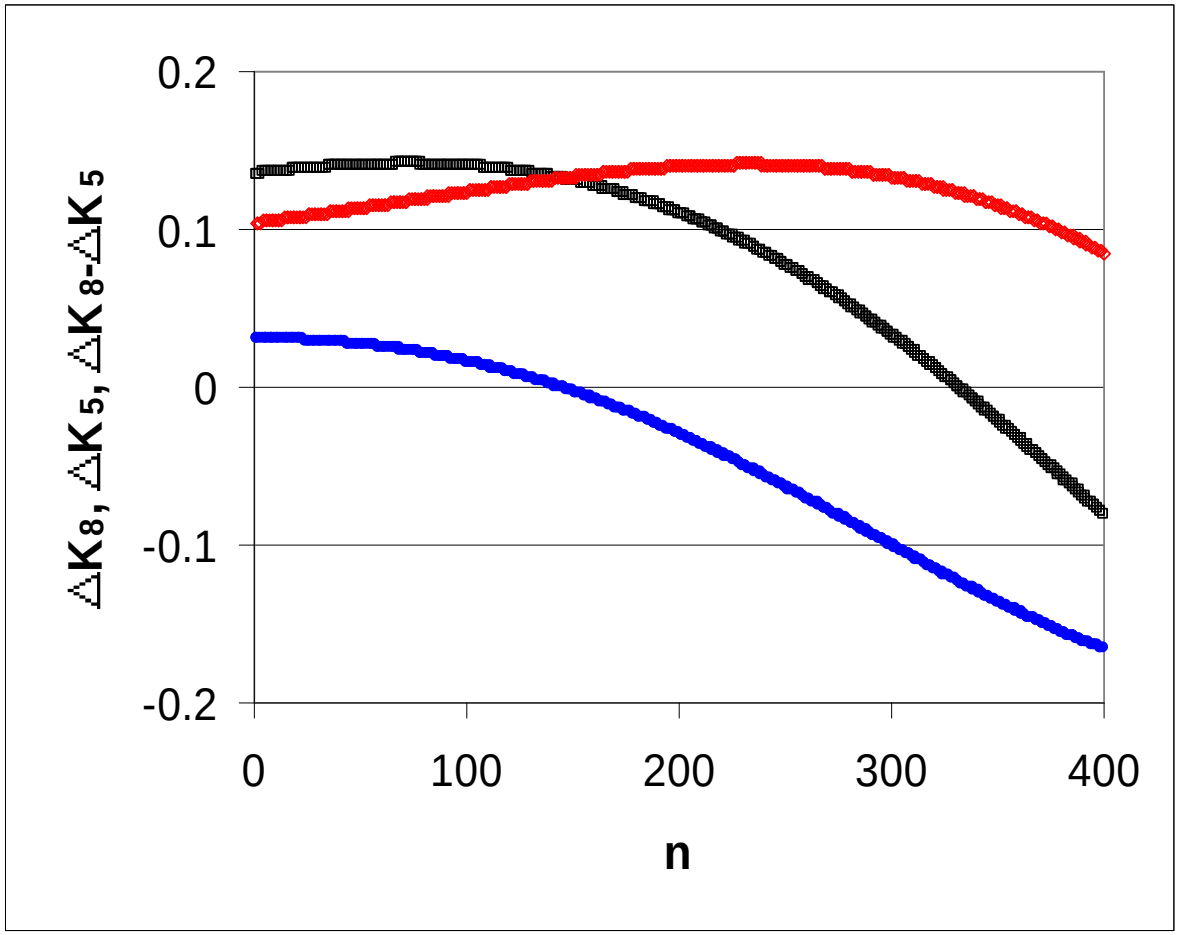


$$I_n = I_0 + \frac{\partial I}{\partial n} n \pm \Delta I$$

$$\nu_n = \nu_0 + \frac{\partial \nu}{\partial n} n \pm \Delta \nu$$

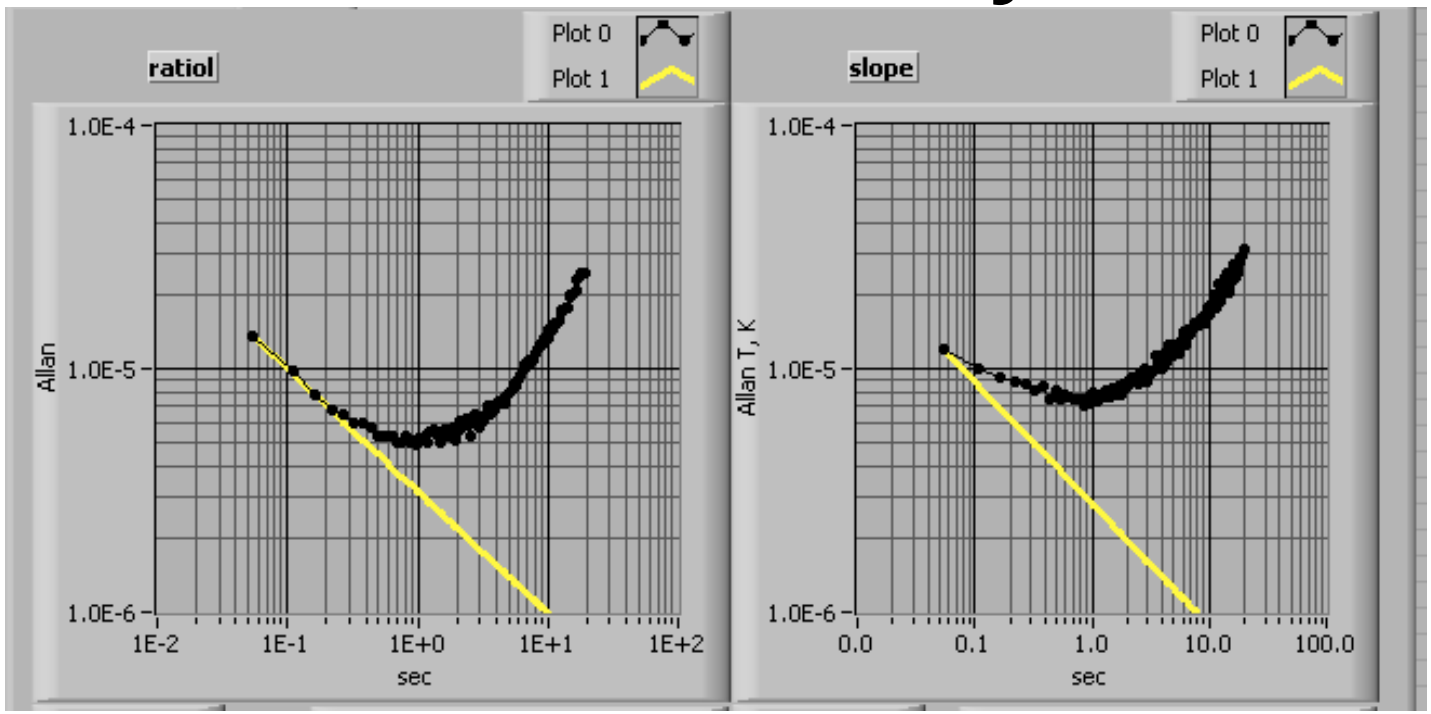
Enrichment measurement

$$\Delta K(\nu) = P\{(1-R)[\sigma_8(\nu+\Delta\nu)-\sigma_8(\nu-\Delta\nu)]+R[\sigma_5(\nu+\Delta\nu)-\sigma_5(\nu-\Delta\nu)]\}L$$



$$Dif(\Delta K) = R\{[\sigma_5(\nu+\Delta\nu)-\sigma_5(\nu-\Delta\nu)]-[\sigma_8(\nu+\Delta\nu)-\sigma_8(\nu-\Delta\nu)]\}PL$$

Precision and accuracy estimation



Preliminary results 8 10^{-5}, limitation DL diagram flicker noise (due to particular DL and operation mode in use).

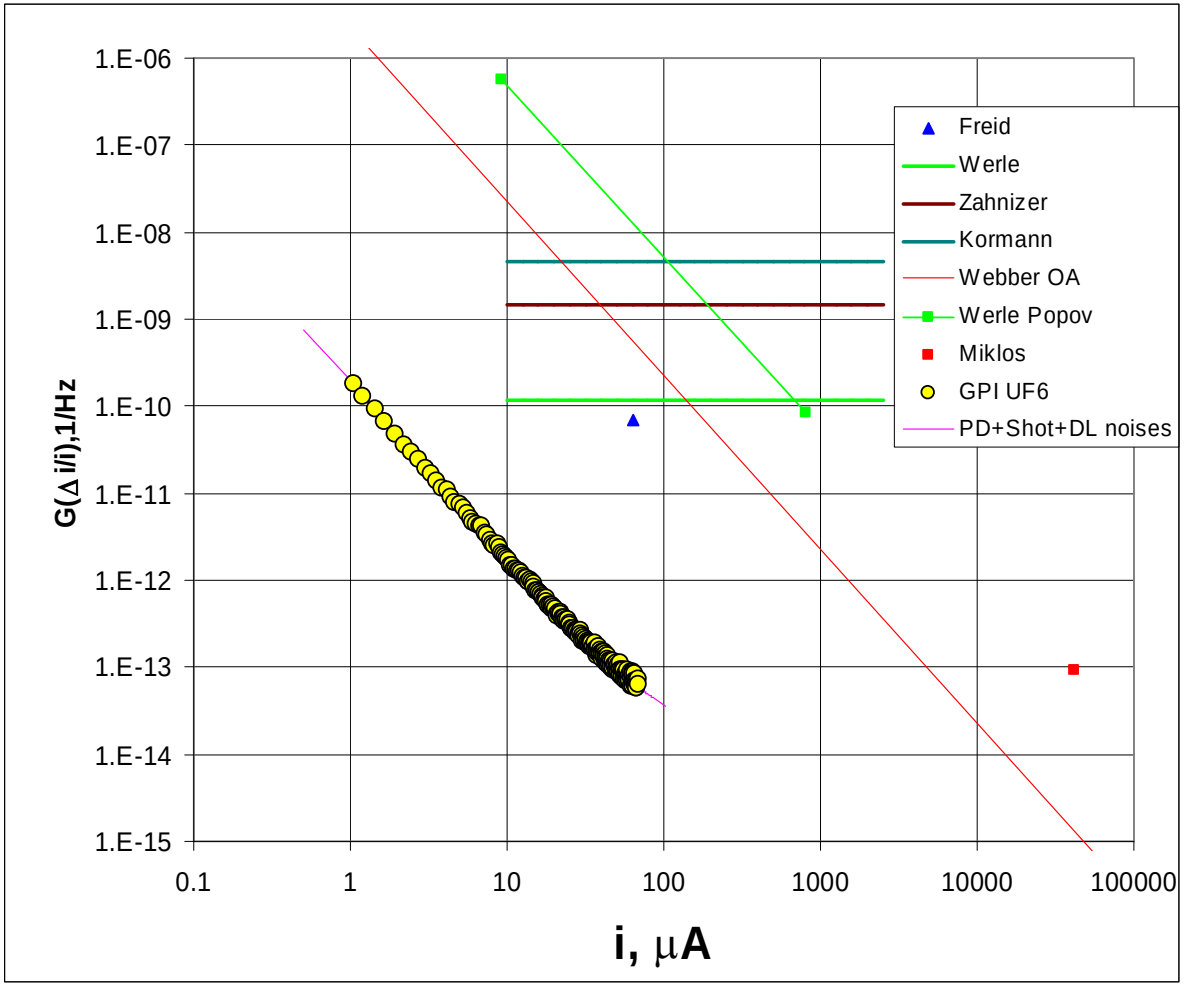
By changing operation regime (reducing tuning range) it can be reduced 4 times – 2 10^{-5}

Correct DL – 5 10^{-6}. UF_6 spectra fine structure is another option.

1 % of 0.3 % - 3 10^{-5}; 1 % of 0.7 % - 7 10^{-5}

Accuracy is determined by accuracy of calibration: accuracy of $^{238}UF_6$ cross-section measurement = accuracy of reference sample

Noise spectral density



Comparison of noise spectral density obtained in present work (GPI UF_6) with best published results in mid IR spectral range. Thick line represents fundamental limit due to PD, shot, and DL noises.