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

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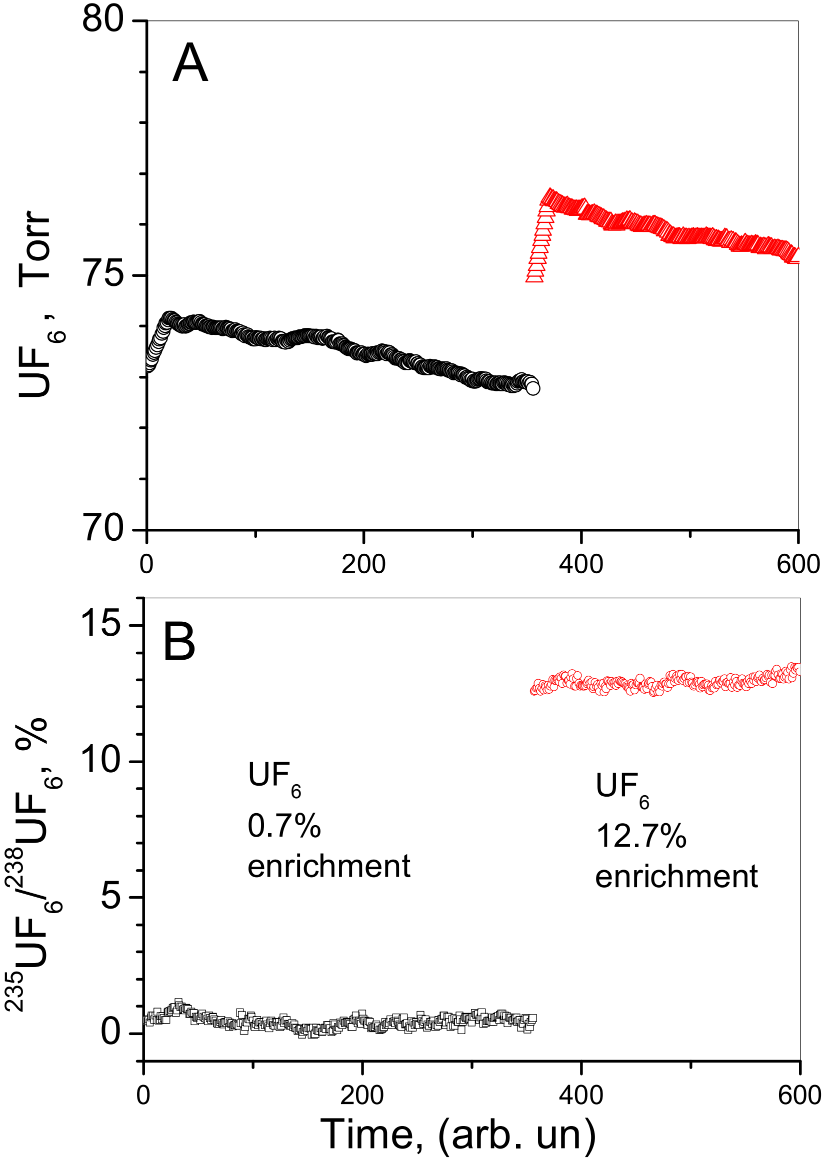
Introduction



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 Bands in mid IR

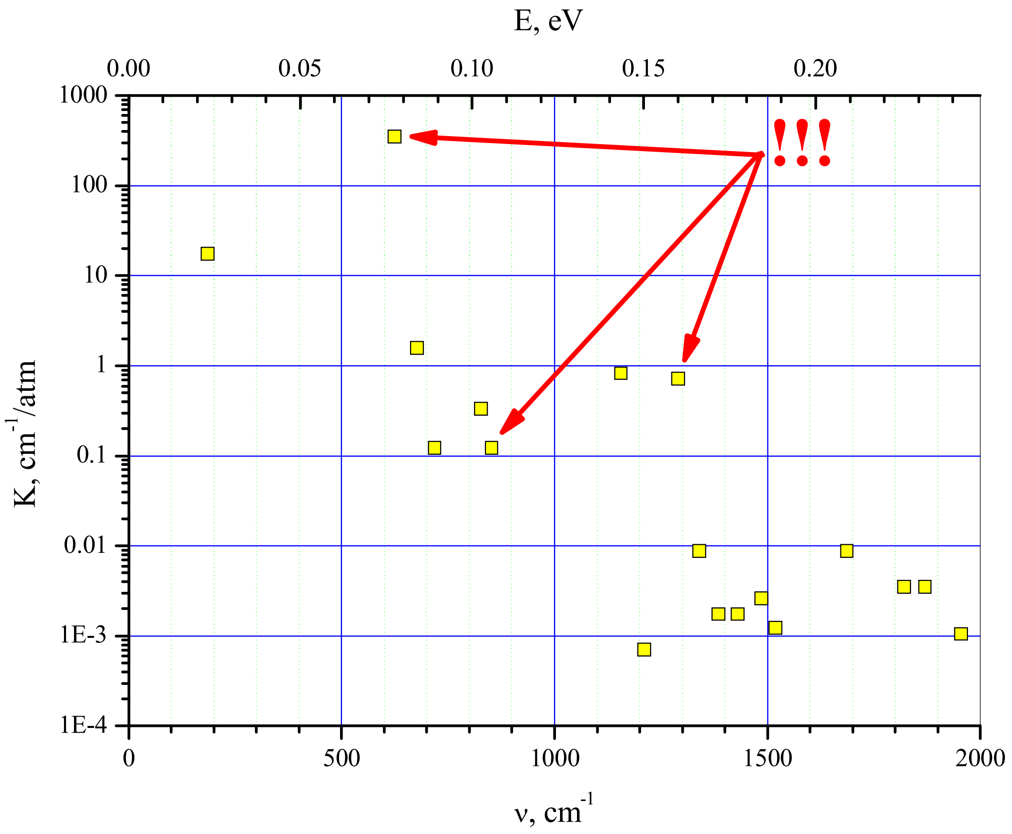
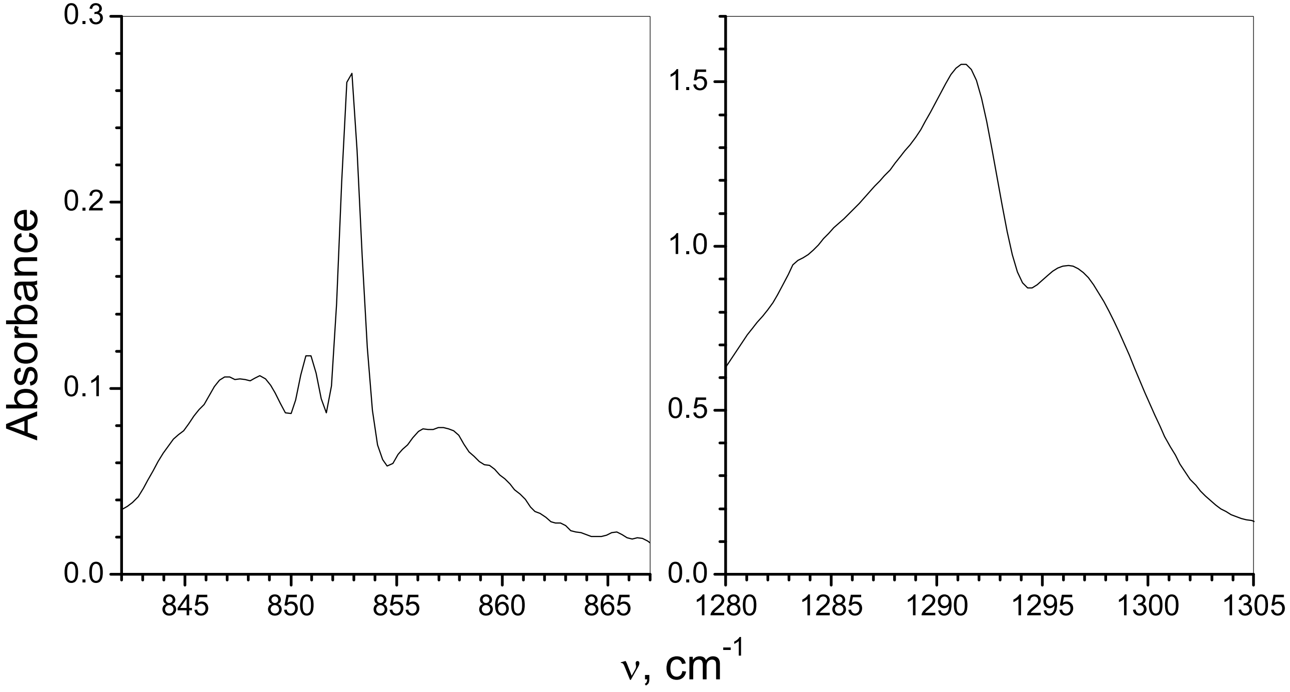


Figure presents absorption cross section of UF_6 molecule in mid IR.

Perspective absorption bands for enrichment measurement and trace uranium hexafluoride detection are marked by red arrows.

v_1+v_3	1291	0.72	Enrichment measurement
v_1+v_4	853	0.12	Enrichment measurement
v_3	625	350	Trace detection

Analytical band selection



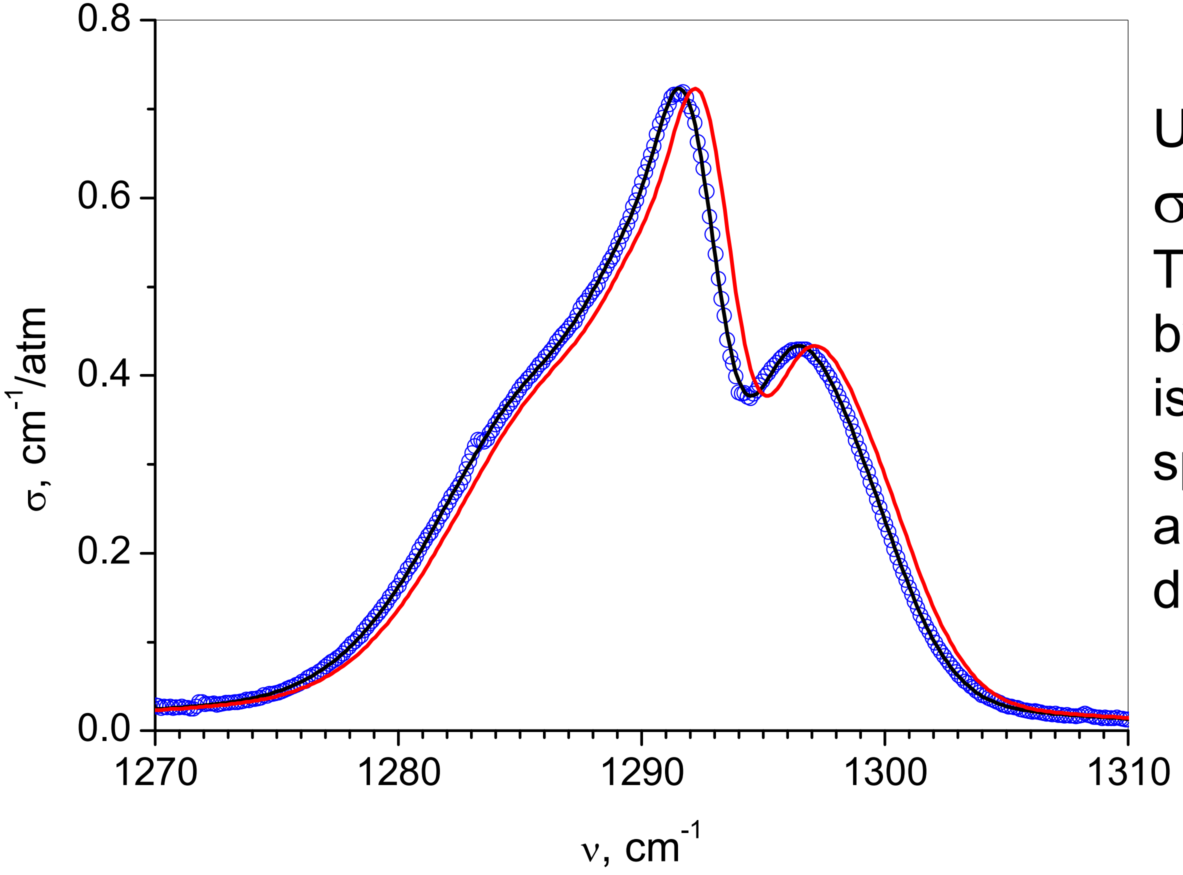
Combination bands v_1+v_4 (left) and v_1+v_3 (right) of UF_6 molecule

Isotope shifts for several UF_6 normal vibration modes [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]

Isotope shifts,cm^{-1}	$^{235}UF_6$-$^{238}UF_6$
ν_1	0
ν_3	0.65±0.09
ν_4	0.16±0.09

Combination band v_1+v_3 was chosen for present experiment.

UF_6 absorption cross-section

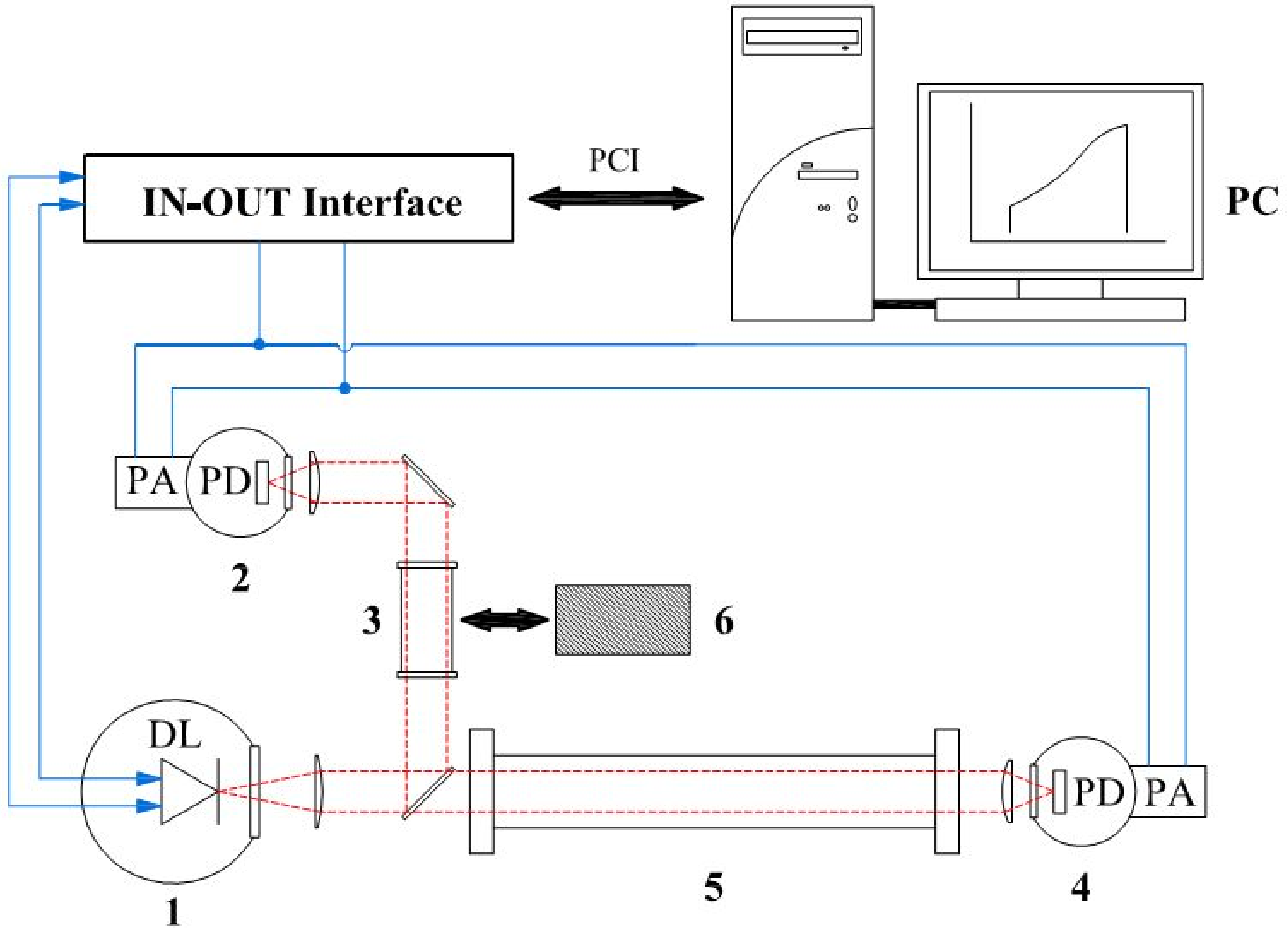


UF_6 absorption cross-section - σ (circles) of v_1+v_3 band [1]. The spectrum was recorded by FTS for sample with natural isotopes abundance. Model spectra of $^{238}UF_6$ (black line) and $^{235}UF_6$ (red line) [1] demonstrates isotope shift [2].

[1] 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)

[2] 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

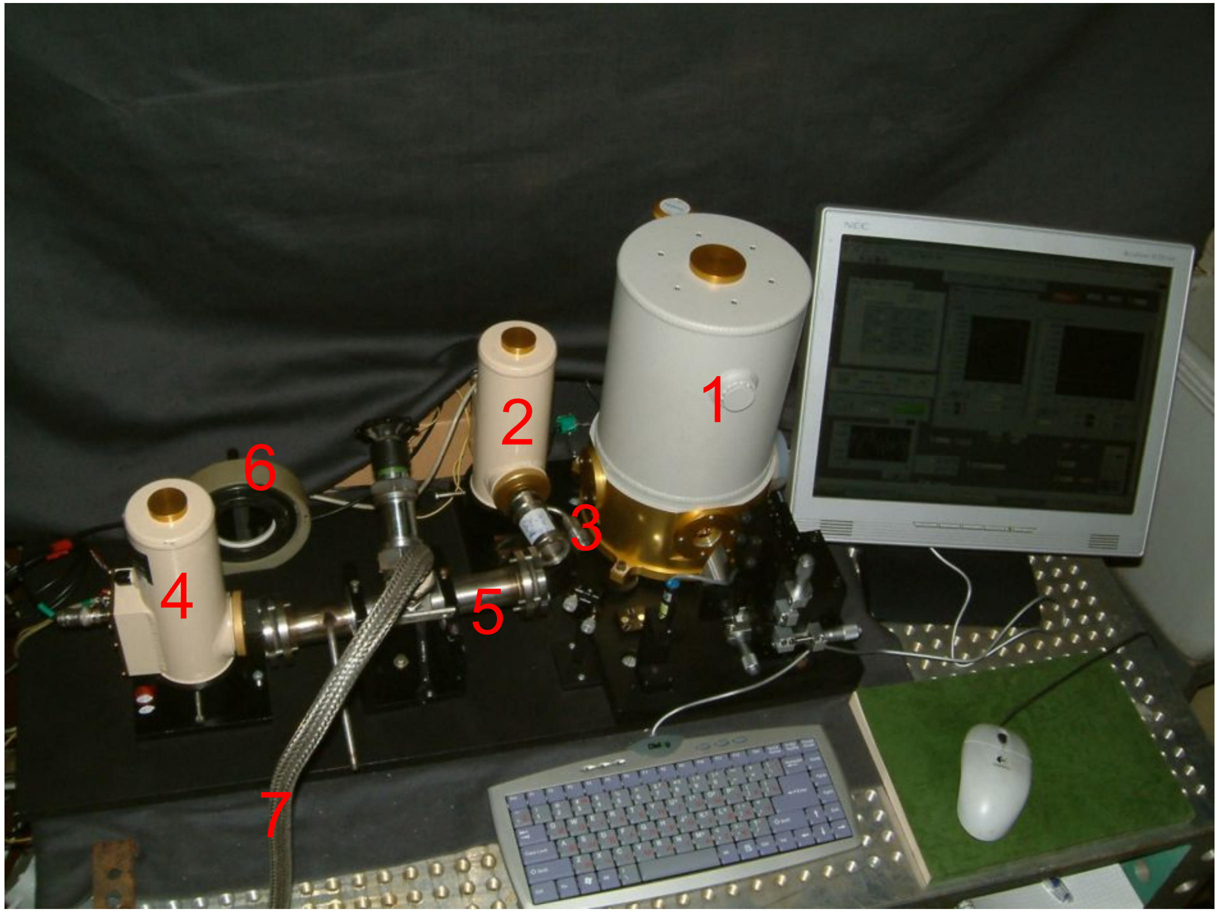


1. DL in cryostat;
2. Reference PD;
3. Reference gas cell;
4. Analytical PD;
5. Analytical gas cell;
6. FP etalon;

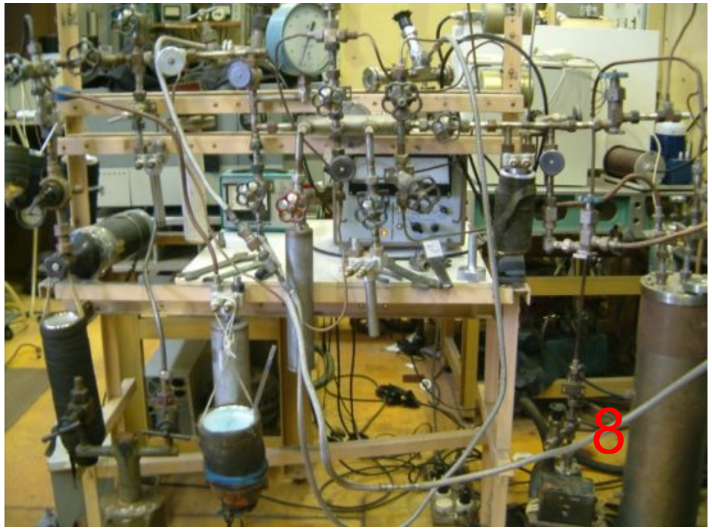
Analytical channel with gas cell (5) containing gas under investigation. Reference channel with cells (3) containing methane and acetylene, and with Fabry-Perot etalon (6) were used to determine laser frequency tuning.

Experimental setup view

For present experiments the instrument was installed in Kurchatov Institute

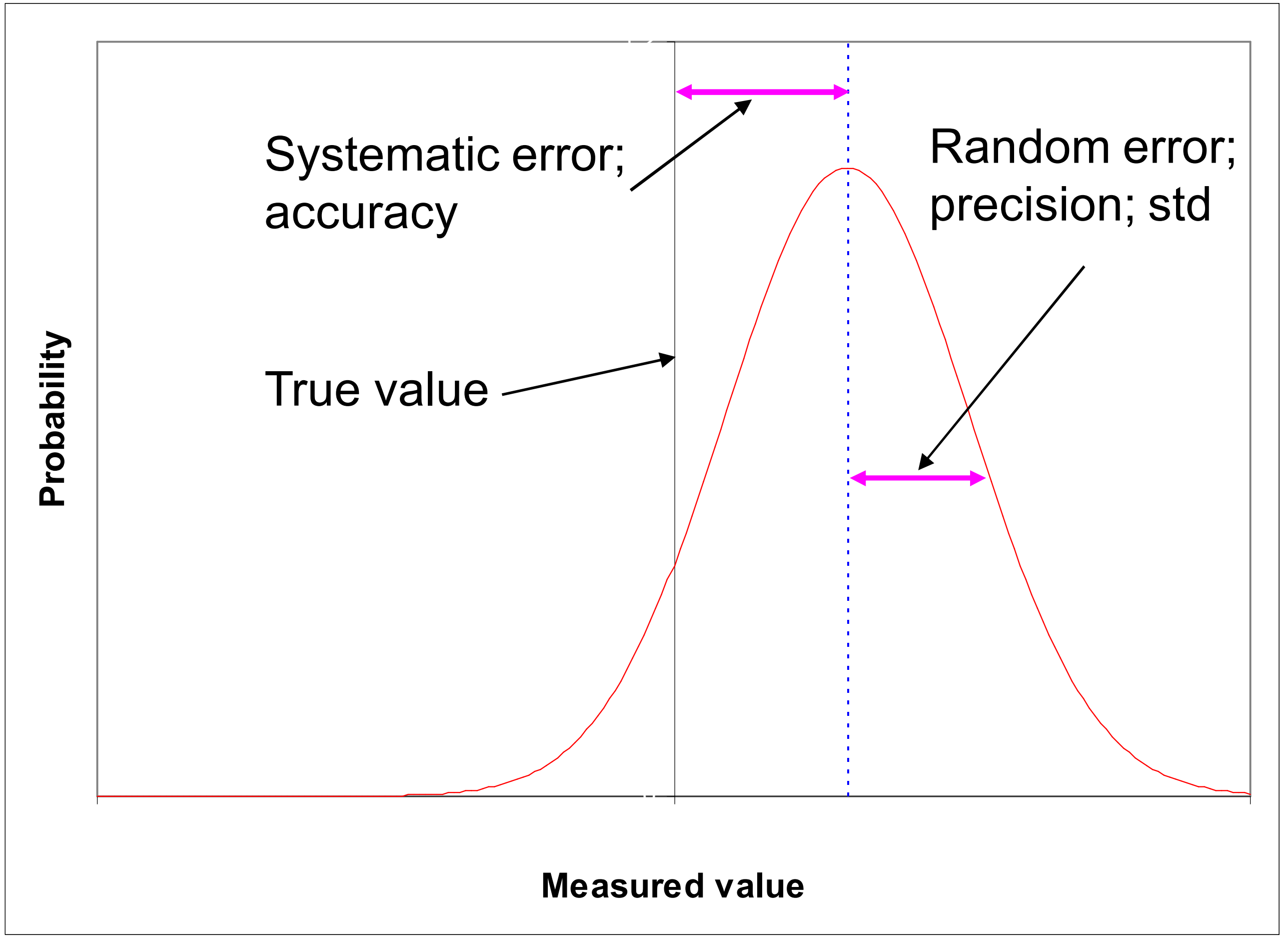


View of TDLS system developed:
1. DL in cryostat;
2. Reference PD;
3. Reference gas cell;
4. Analytical PD;
5. Analytical gas cell;
6. FP etalon;
7. Connection to UF_6 gas distribution system.



View of UF_6 gas distribution system
8. Connection to TDLS system

Definitions and requirements



Probability to measure particular value of parameter under investigation.

Accuracy and precision requirements for UF_6 enrichment measurements:

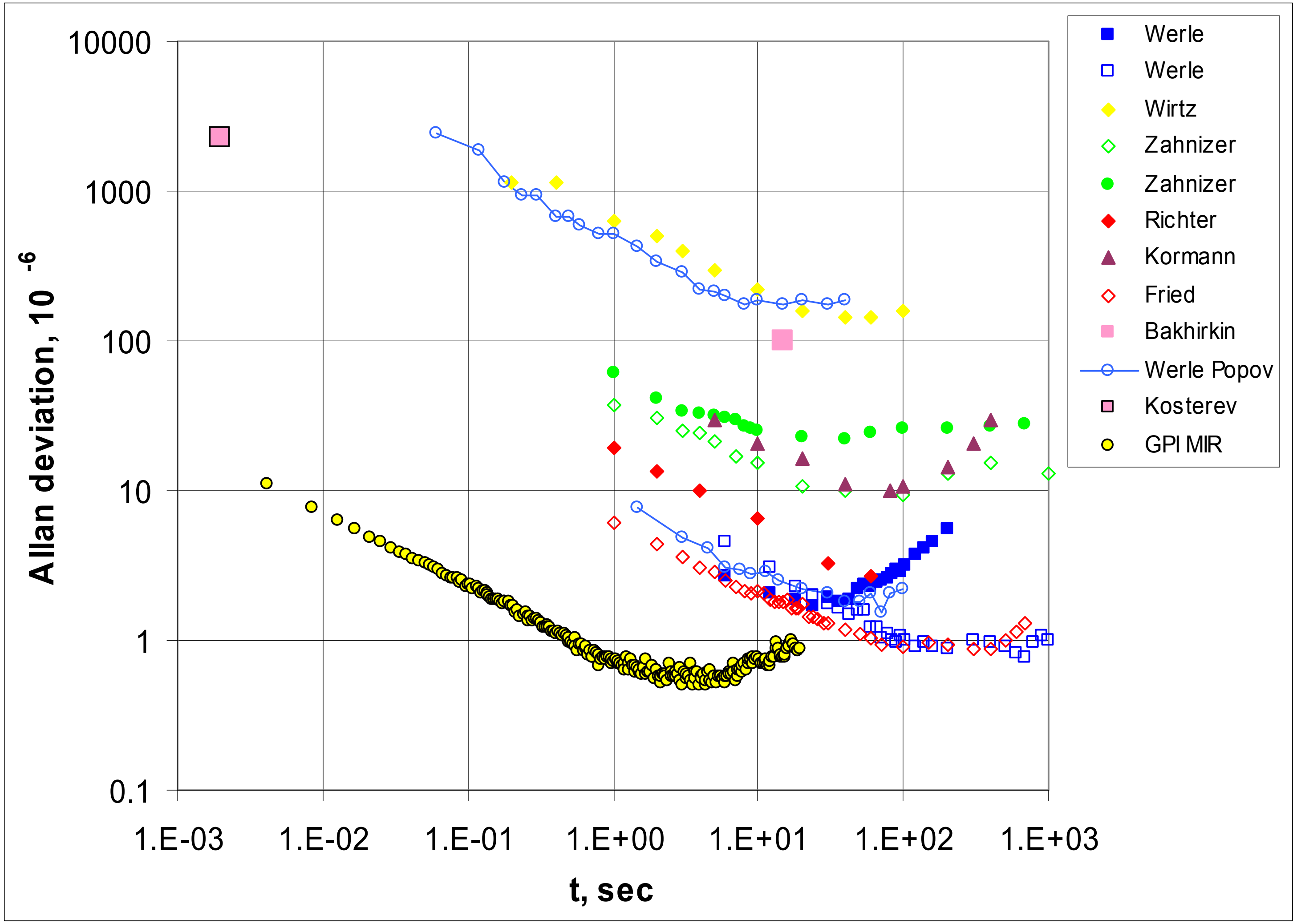
Enrichment < 0.01 %

Absorbance < 0.01 %

Frequency < $6\ 10^{-5}\ cm^{-1}$

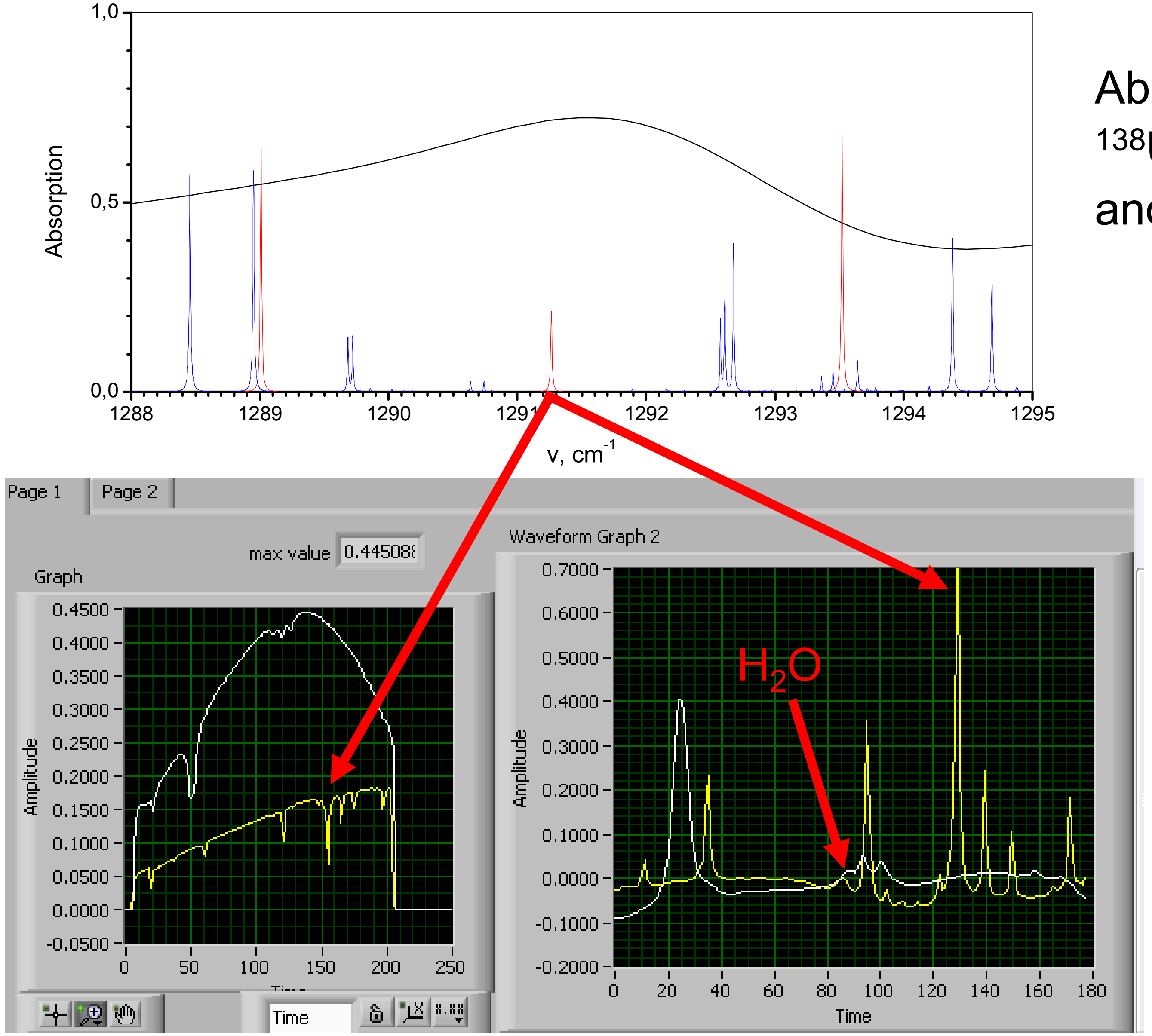
<u>For precision these requirements are achievable. However, for accuracy nobody in the world was able to work on this level yet.</u>

Allan plots



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

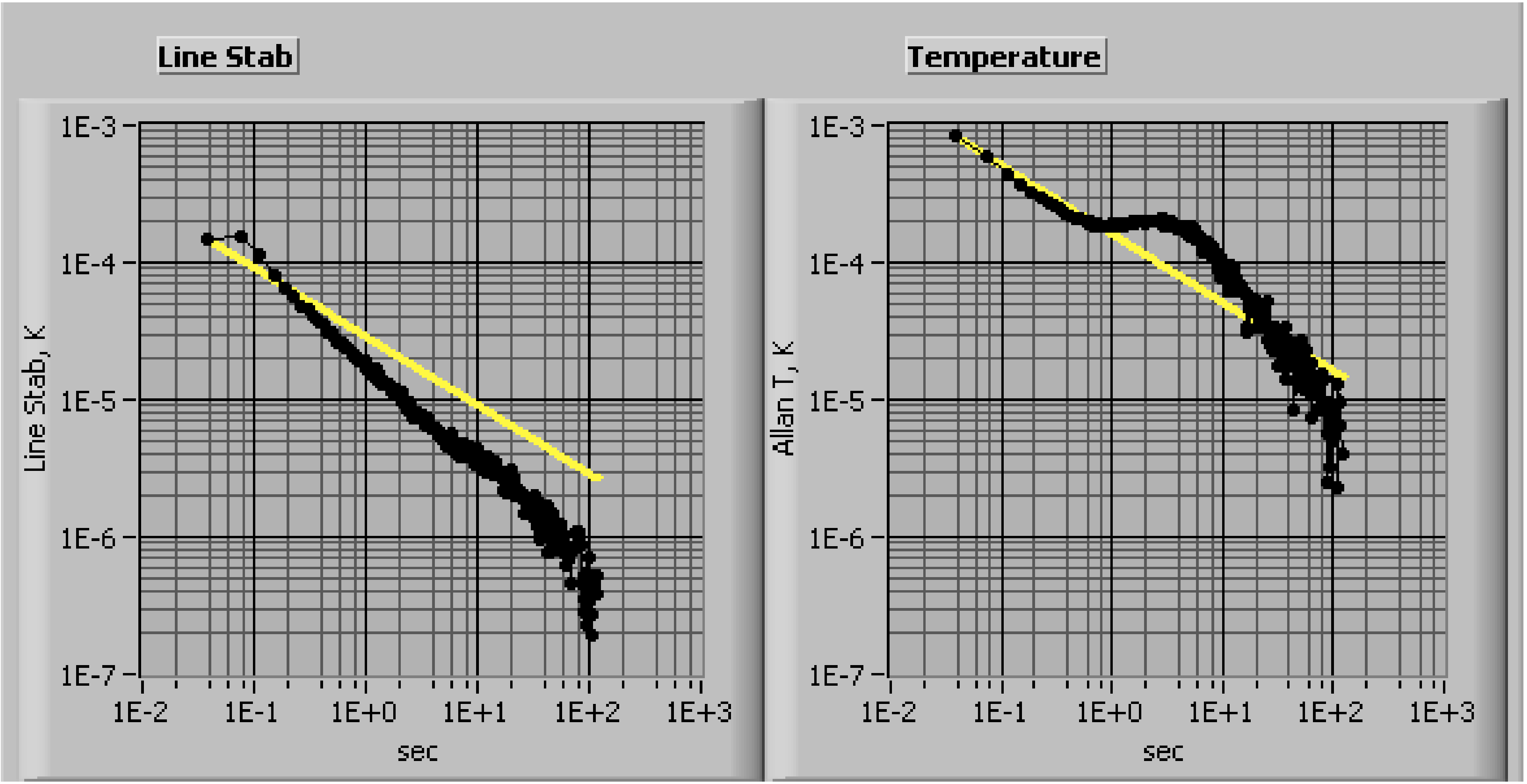
DL frequency tuning curve calibration



Absorption spectra of $^{138}UF_6$ (black), C_2H_2 (red), and CH_4 (blue).

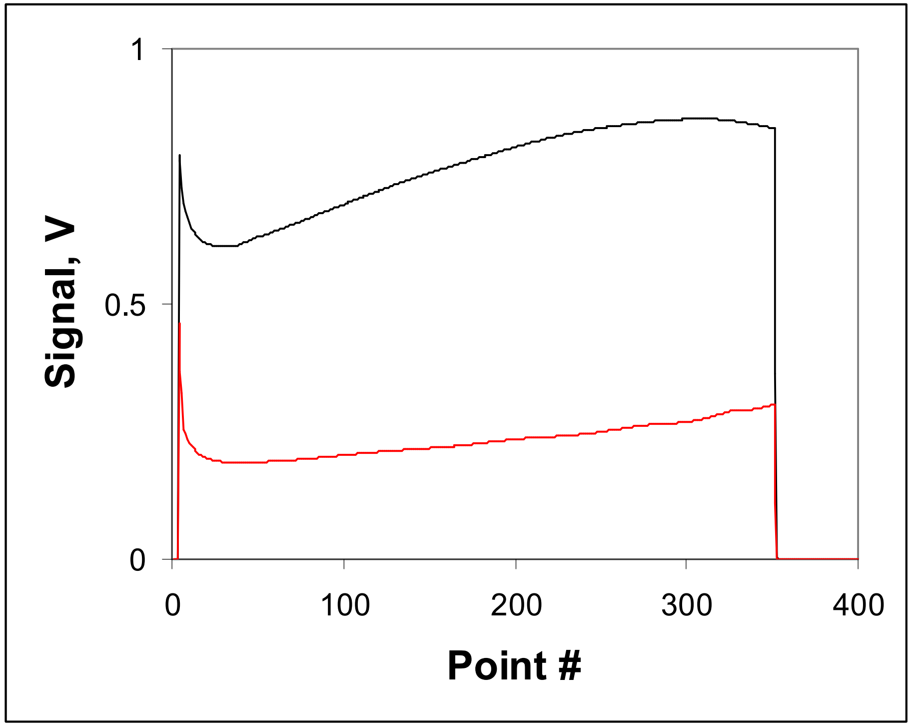
DL operation regime Channels with cells containing C_2H_2 (yellow) and CH_4 (white). There are some weaker C_2H_2 lines not included in HITRAN as well as water line. C_2H_2 line marked by red arrow was used for ***DL frequency cycles stabilization.***

DL frequency tuning stabilization

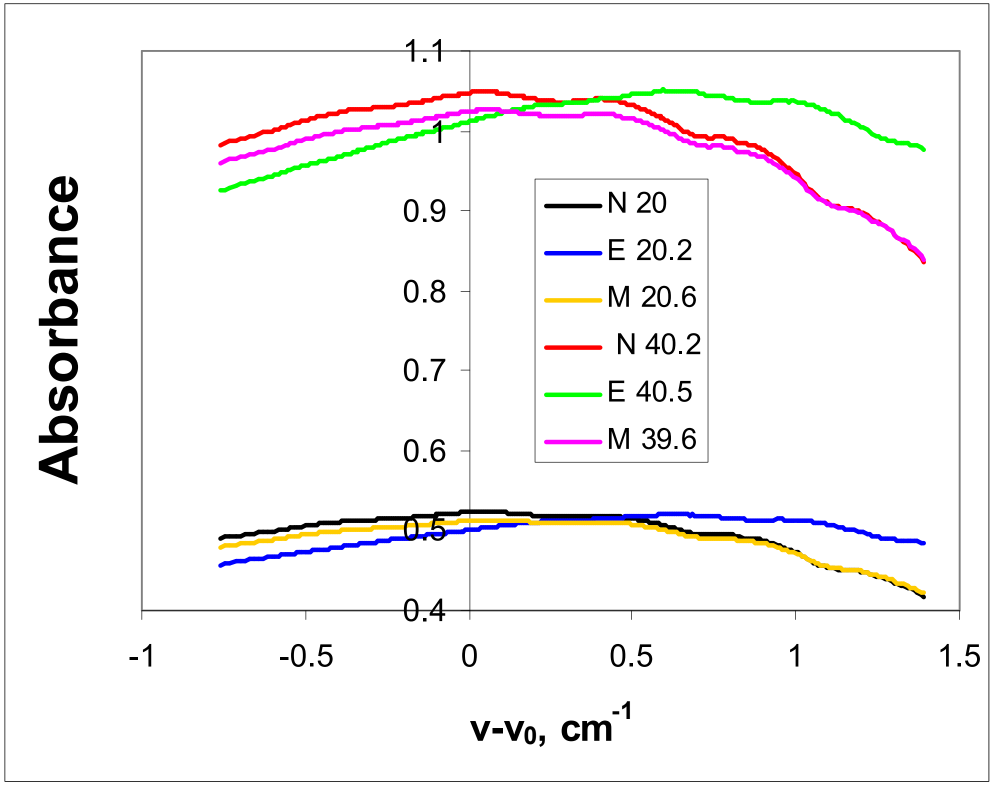


Allan’s graphs of thermal stability obtained by thermal sensor (right) and from the position of absorption line (left) when DL frequency tuning cycles stabilization was in use. ***This corresponds requirements of frequency stability < 6 10^{-5} cm^{-1}.***

Absorbance



Recorded signals shapes for empty cell (black) and for cell filled with 40 Torr of UF_6 sample under investigation. Sample cell with L = 20 cm was used.



Absorbance at two pressures close to 20 and 40 Torr for three UF_6 samples with different enrichment R:

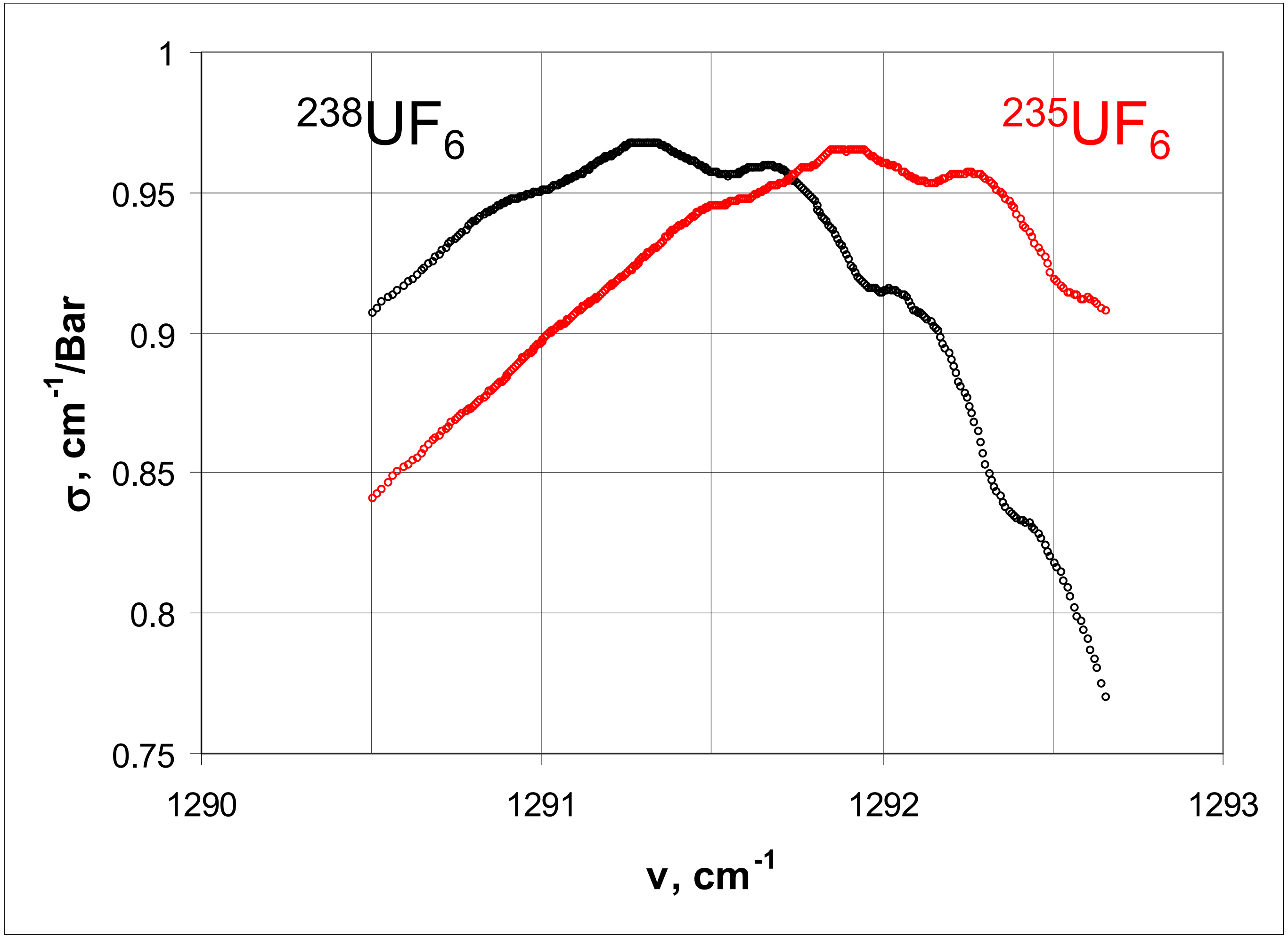
N - sample with natural abundance (R=0.7%);

E – enriched sample (R=90 %);

M – mixture of two above samples (R=12 %).

Cross-section

Using absorbance data of UF_6 samples under investigation absorption cross-section of different isotopomers can be determined.

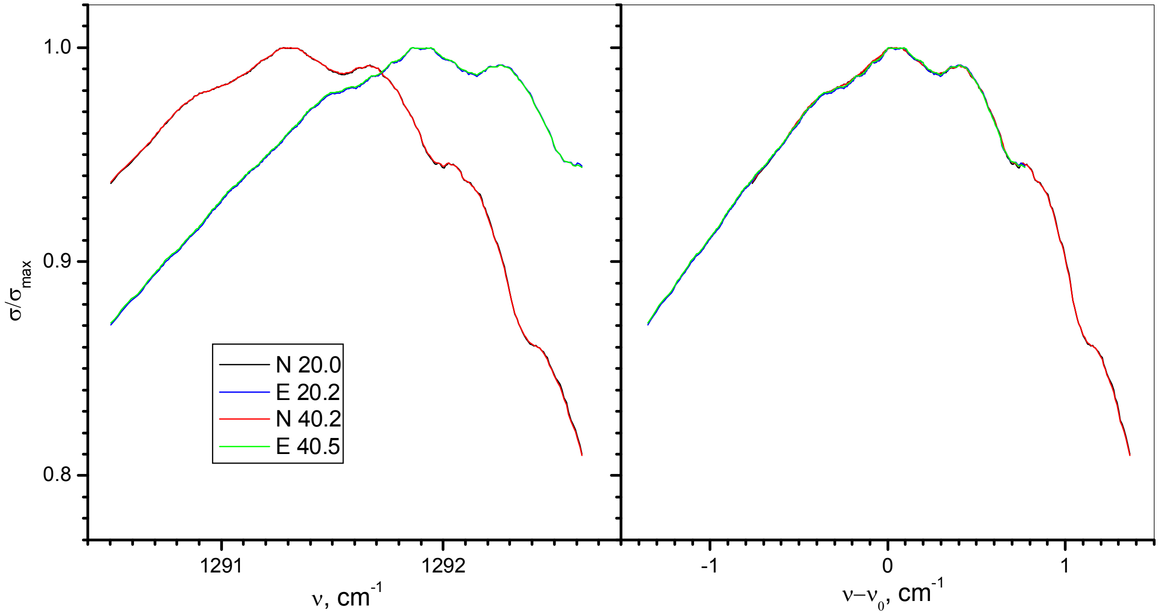


Absorption cross-section of $^{238}UF_6$ (black) and $^{235}UF_6$ (red). Both cross-sections have close maximum values. Fine structure can be observed.

<u>It seems as spectra are similar and are only shifted with respect to each other.</u>

UF_6 cross-section shape

Cross-section shape is determined by vibration and rotation motion of the molecule. U atom is included in vibration motion leading to isotope shift. As rotation is considered, one has to take in mind that UF_6 molecule is spherical top with U atom located in its center. Hence, it is not included in molecular rotation motion and rotation structure has to be the same for both UF_6 isotopomers.



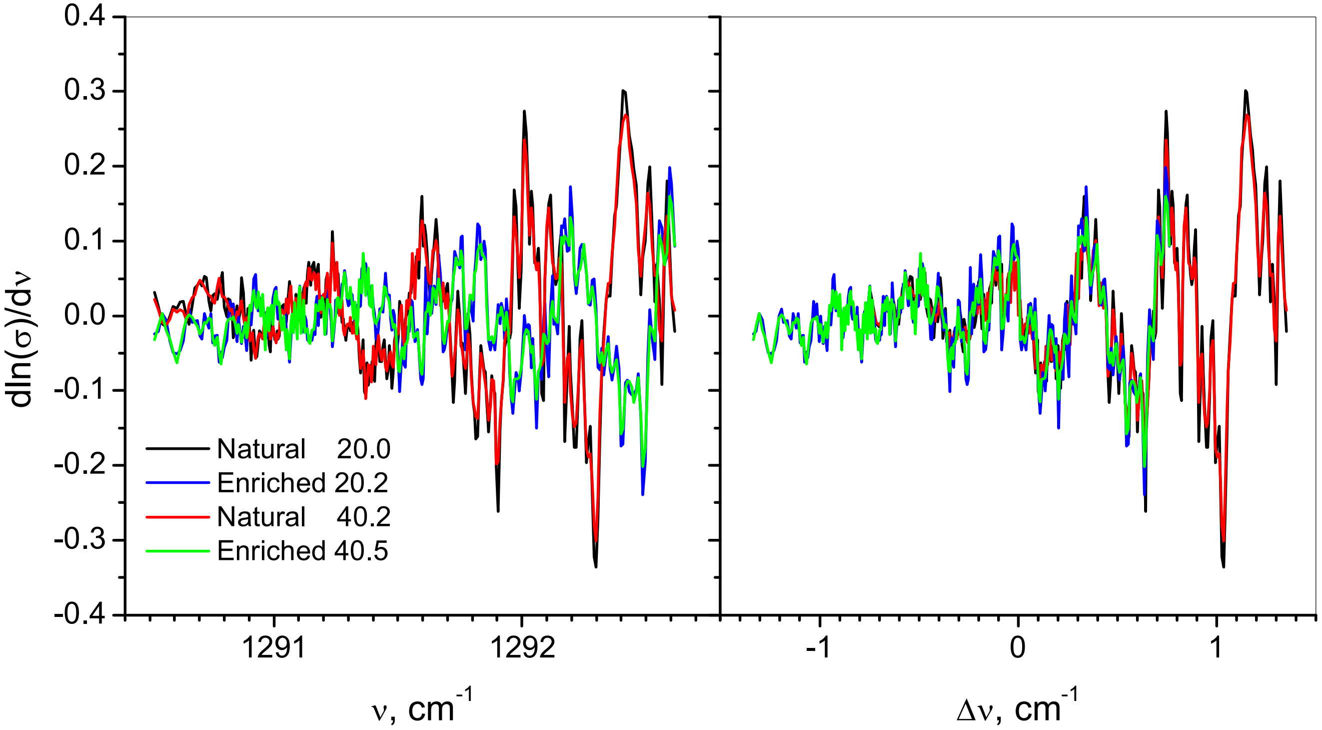
Left - normalized cross-section – σ/σ_{max} of two UF_6 isotopomers obtained from different recorded spectra (see above). Graph demonstrates good reproducibility of σ/σ_{max} with relative std = 0.00027.

After isotope shift is determined – 0.59 cm^{-1} (see next slide) all recorded spectra can be presented in one scale as shown on right graph with excellent reproducibility.

Conclusion – if one measures with high accuracy in broad spectral range $^{238}UF_6$ cross-section, $^{235}UF_6$ one can be determined straightforward using isotope shift value.

Spectra fine structure

To intensify fine structure, cross-section logarithmic derivative was calculated (left graph) as its measurements had high S/N ratio.

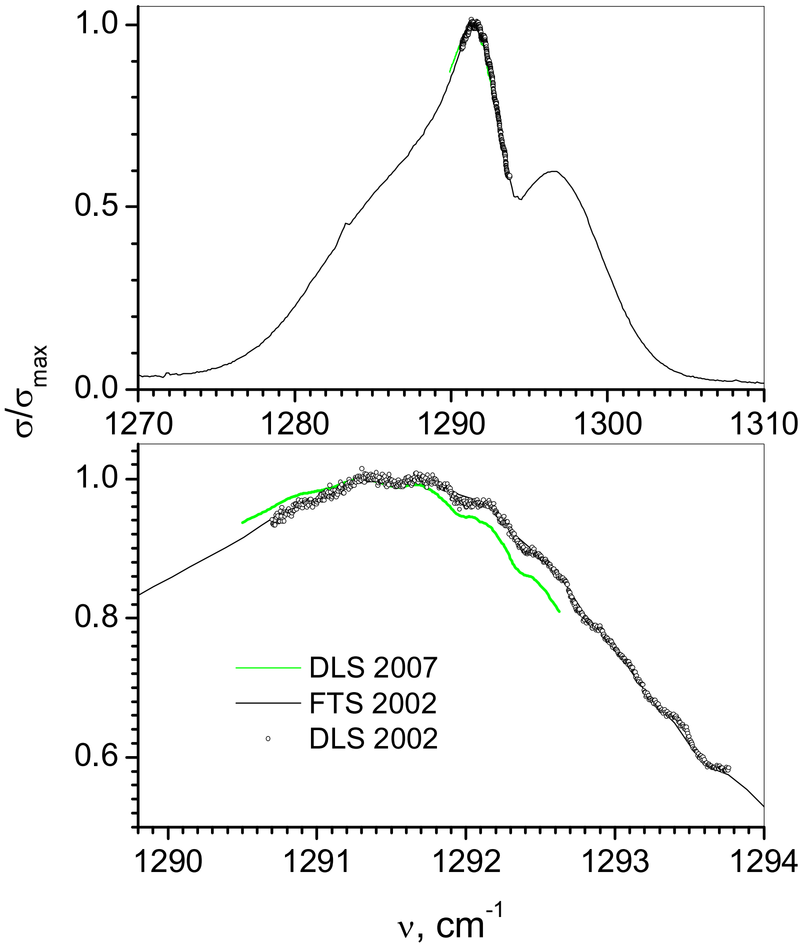


UF_6 cross-section logarithmic derivative for different isotopomers obtained from different spectra:
$^{238}UF_6$ – black and red;
$^{238}UF_6$ – blue and green.

For each isotopomer reproducible fine structure can be observed being more shaper for smaller pressure due to collision broadening. This fine structure of Q-branch is known from literature for spherical top molecules. It is similar for both isotopomers (see above) and allow one to determine isotope shift:

Isotope shift for v_1+v_3 band = 0.59(1) cm^{-1}

Data comparison



Comparison of normalized $^{238}UF_6$ cross-section obtained in 2002 by FTS (black curve) and TDLS (black open circles) with results of present work (green line).

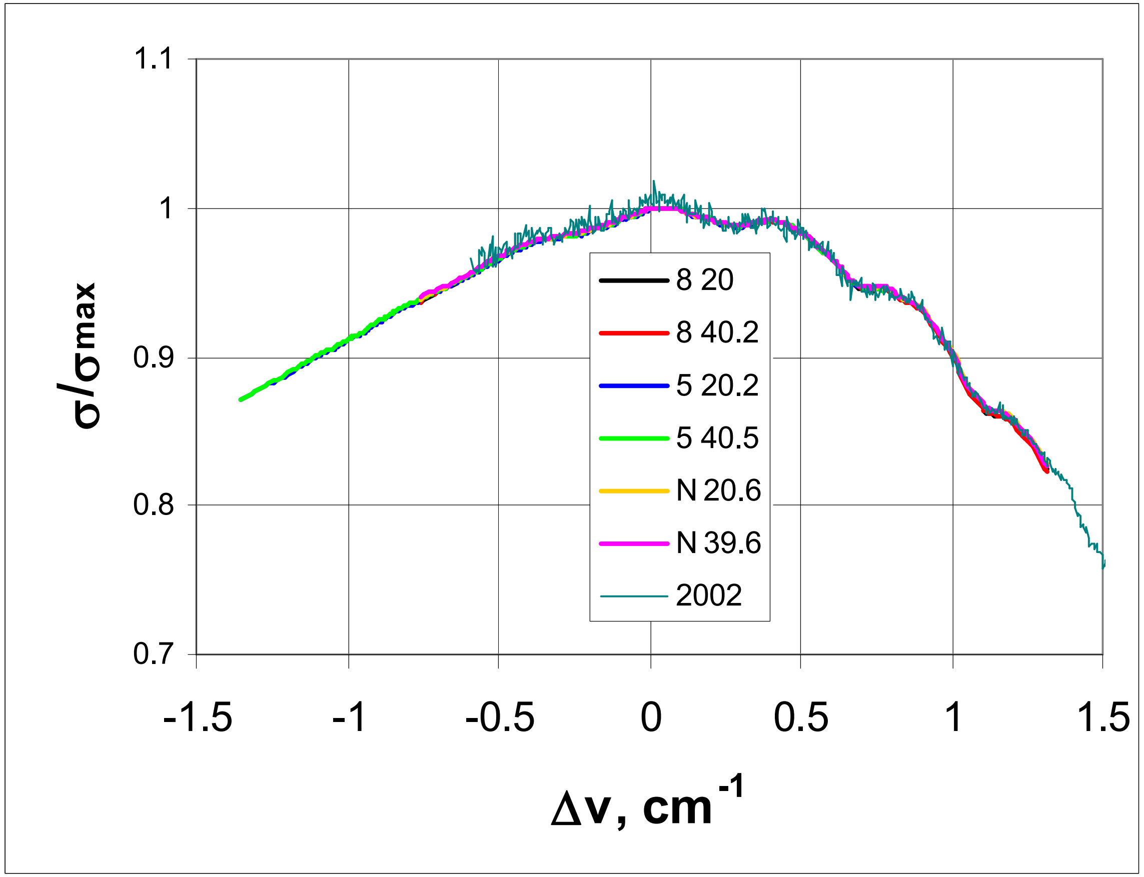
1. Dramatic improvement in precision was achieved.
2. However, tuning range of present DL is significantly smaller and spectral range of DL operation is not optimal.
3. Fine structure is presenting being similar for all spectra.
4. However, significant difference between spectra under consideration can be observed. It is due to temperature dependence of cross-section. Spectra in 2002 were obtained during winter, while in 2007 during hot summer time.

Conclusions:

Improvement of DL (larger tuning range, proper spectral range) is necessary.

Cross-section temperature dependence has to be determined and temperature has to be measured during enrichment determination.

Temperature dependence correction



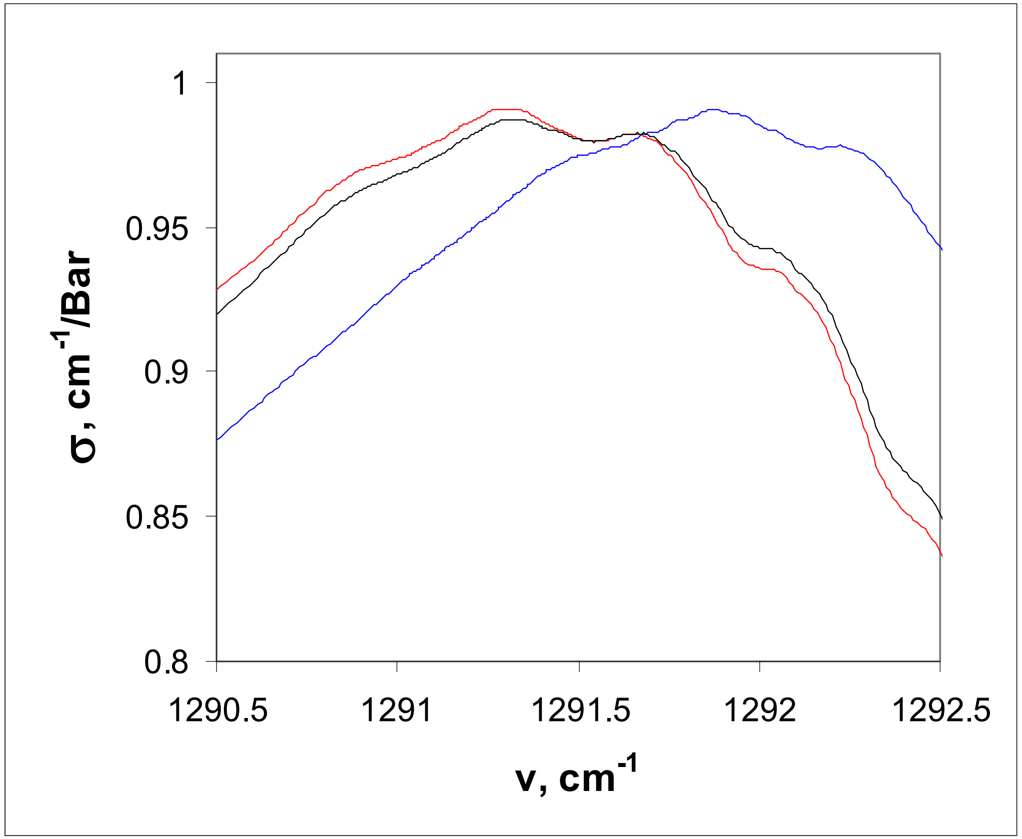
After empirical exponential correction of measured cross-sections

$$\sigma_T(\nu) = \sigma_{T_0}(\nu)\exp\left[\alpha\Delta\nu\left(-\frac{1}{T}+\frac{1}{T_0}\right)\right]$$

good agreement can be observed.

Enrichment measurement

Measured absorption cross-section σ (P ≅ 40 Torr) of $^{238}UF_6$ (red), $^{235}UF_6$ (blue), and sample under investigation (black).



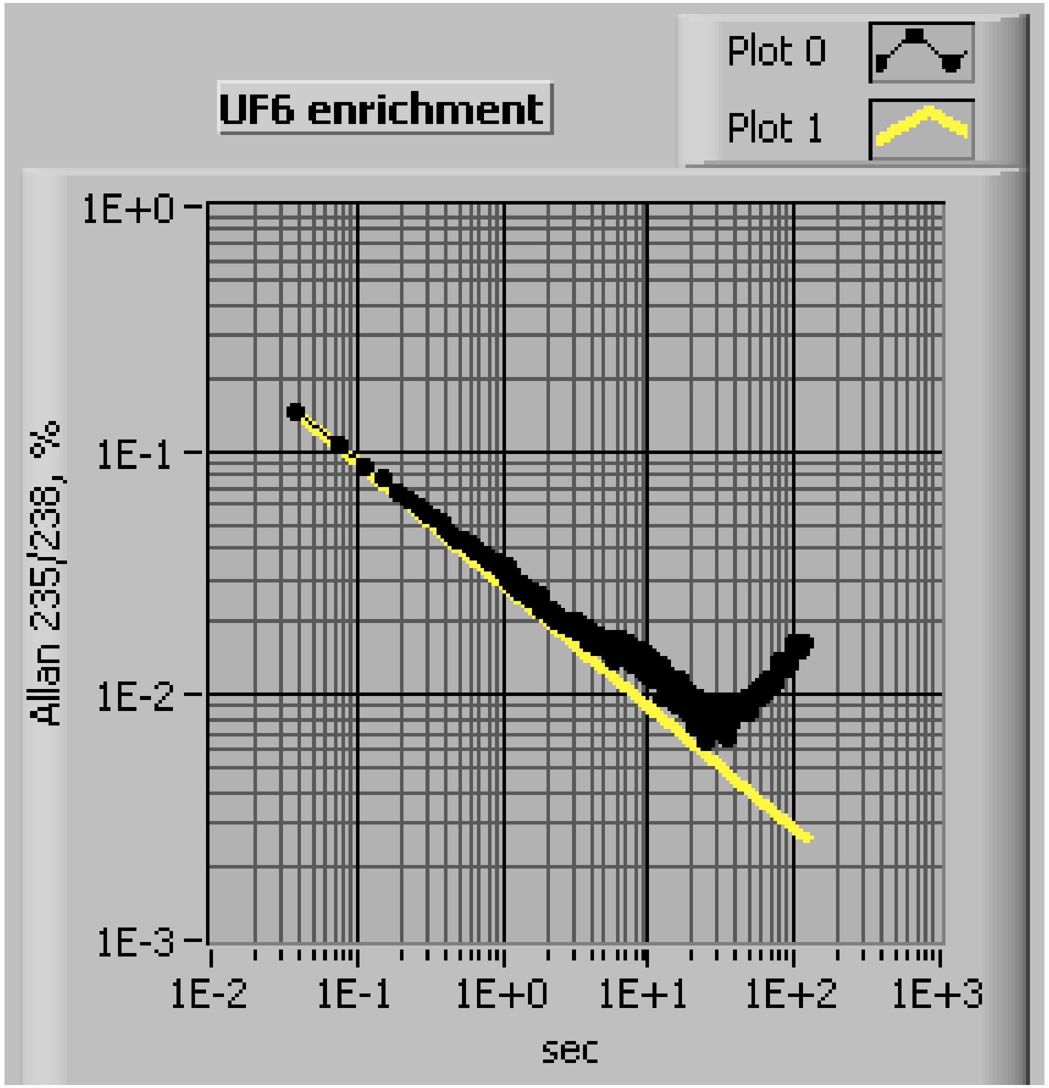
Measured absorption cross-section σ is superposition of both UF_6 isotopomers; its difference with cross-section of $^{238}UF_6$ is direct measure of enrichment - R.

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

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

When UF_6 isotopomers cross-sections were measured with high **accuracy** and stored in computer, enrichment of the sample under investigation can be determined.

Precision of enrichment measurements



Allan plot of minimum detectable UF_6 enrichment as function of averaging time.

Precision below 0.01 % (UF_6 enrichment measurement requirements) can be achieved at 30 sec averaging time with present setup and algorithms.

Accuracy of enrichment measurements

Accuracy of UF_6 enrichment measurement is determined by several physical processes:

-Limitation due to DL fundamental physical properties is solved.

-Quality of DL in use. Has to be improved by usage of more stable DL with larger tuning. Alternative: to use DL in 12 μ spectral range.

-Quality of DL temperature stabilization. Cryostat in use has to be improved.

-Quality of DL frequency cycles stabilization corresponds to requirements.

-Accuracy of $^{238}UF_6$ cross-section measurement. Now it is self-educated process. More calibrated samples will be measured, more accurate cross-section will be obtained.

-Accuracy of ^{235}UF6 cross-section measurement is enough for enrichment in range 0-5 %.

-Problem of memory effects during gas sample cell filling have to be solved.

-Problem of environment water and absorption due to HF presence in the sample under investigation has to be solved.

-Requirement for gas sample under measurement temperature reproducibility < 0.01 K. Has to be solved. Alternative: to determine cross-section temperature dependence and record gas sample temperature during measurement.