

$^{238}\text{UF}_6$ and $^{235}\text{UF}_6$ spectra and enrichment measurement in mid IR spectral range

*A.Nadezhdinskii, Ya.Ponurovskii, I.Popov, V.Semenov,
Yu.Shapovalov, D.Stavrovskii*

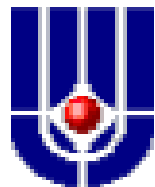
DLS

LAB

*A. M. Prokhorov General Physics Institute of RAS
38 Vavilov str., 119991 Moscow, Russia.
E-mail: Nad@nsc.gpi.ru*

A.Babichev, G.Grigoriev, Sh.Nabiev

*Institute of Molecular Physics of RRC "Kurchatov Institute"
Kurchatov sqv.1, 123182 Moscow, Russia*



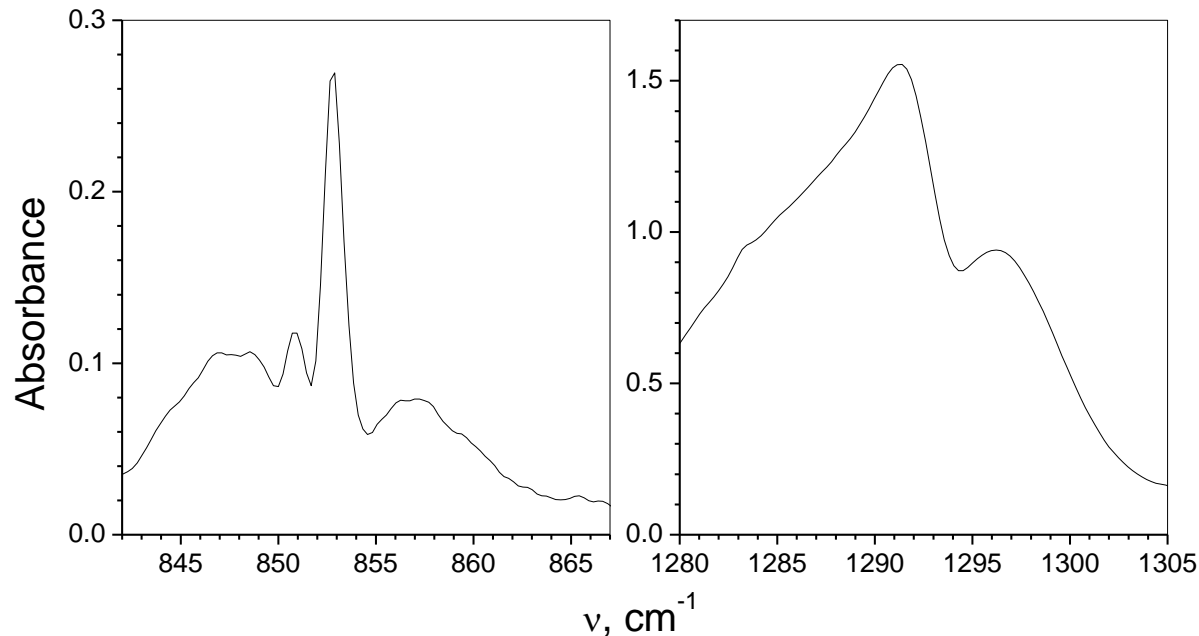
Introduction

Measurement of UF_6 enrichment is important part of IAEA safeguards. Requirements for enrichment measurement accuracy are very hard – 0.03 %. Possibility to measure UF_6 enrichment using TDLS technique was considered in [1]. In this paper spectra of UF_6 sample with natural isotopes abundance were recorded. Specially developed QCL to measure UF_6 enrichment was investigated in [2]. Investigation of $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$ cross sections using TDLS is subject of present paper.

[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, UF_6 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 UF_6 enrichment, Abstracts of TDLS 2011, Zermatt, Switzerland, p.63.

Analytical band selection



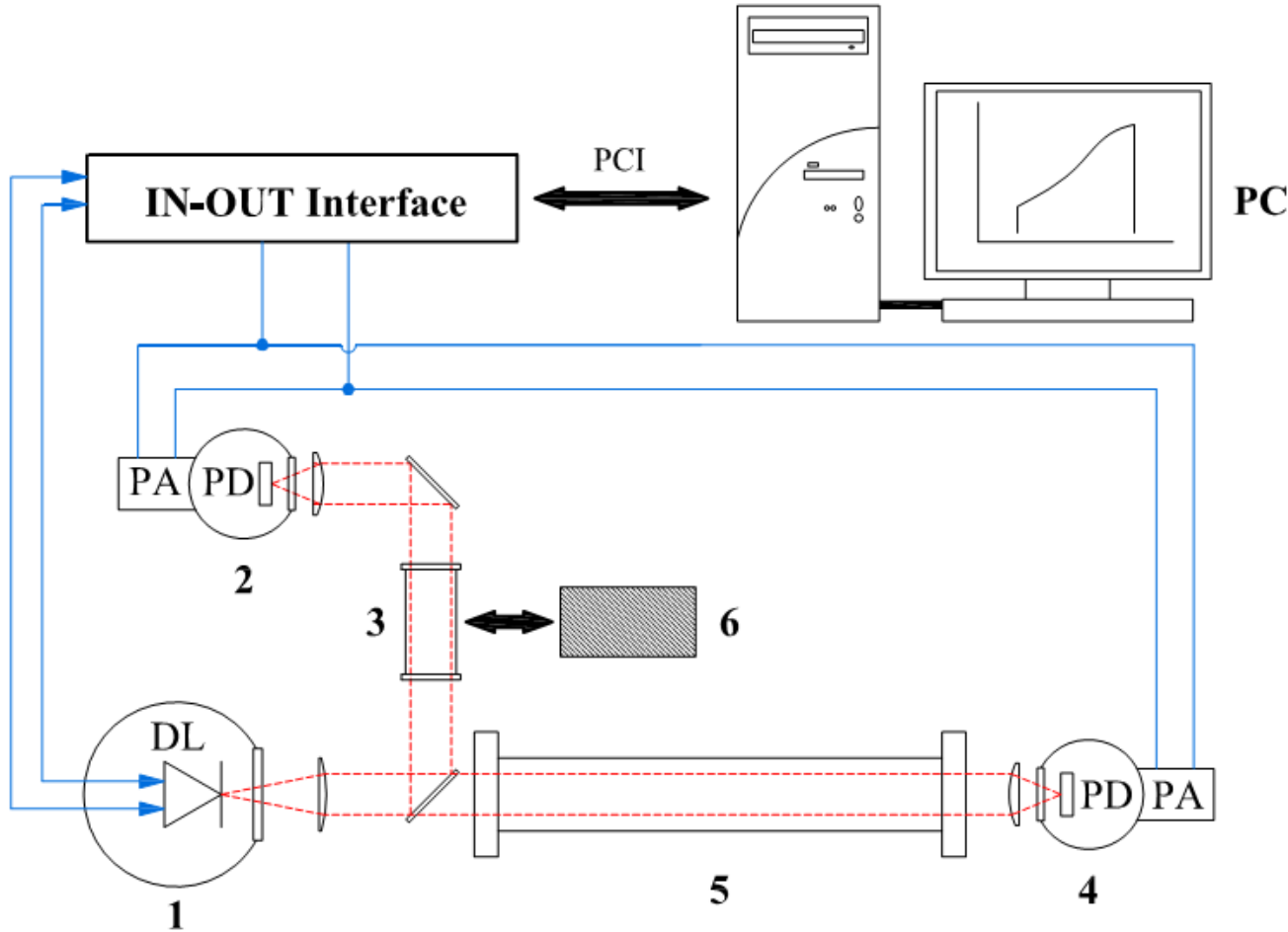
Combination bands $\nu_1 + \nu_4$ (left) and $\nu_1 + \nu_3$ (right) of UF_6 molecule

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}	$^{235}\text{UF}_6 - ^{238}\text{UF}_6$
ν_1	0
ν_3	0.65 ± 0.09
ν_4	0.16 ± 0.09

Combination band $\nu_1 + \nu_3$ was chosen for present experiment.

Block-scheme

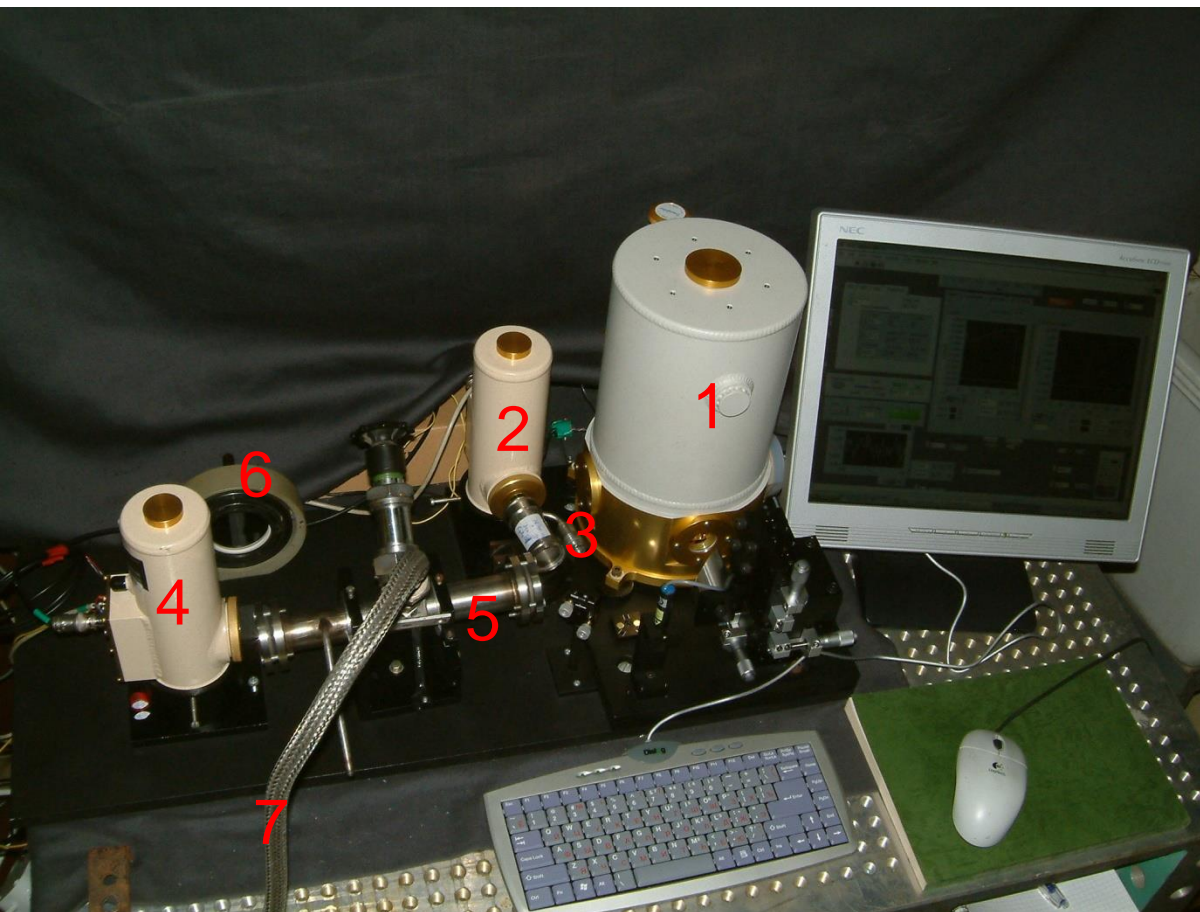


1. DL;
2. Reference PD;
3. Reference gas cell;
4. Analytical PD;
5. Analytical gas cell;
6. FP etalon;

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

For present experiments several TDLS instruments were installed in Institute of Molecular Physics of RRC "Kurchatov Institute"

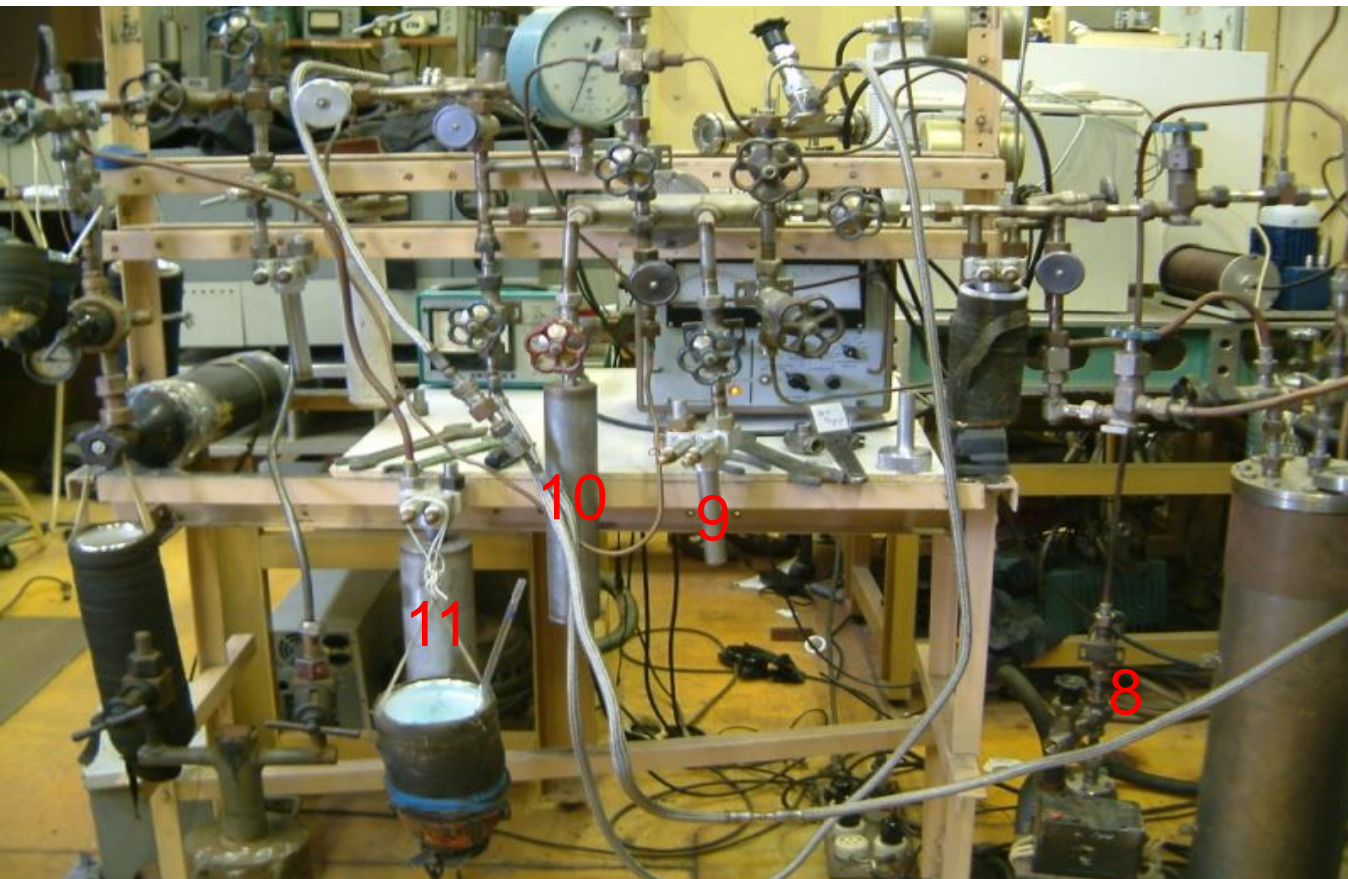


View of TDLS system with A^{IV}B^{VI} DL:

1. DL in cryostat;
2. Reference PD;
3. Reference gas cell;
4. Analytical PD;
5. Analytical gas cell;
6. FP etalon;
7. Connection to UF₆ gas distribution system.

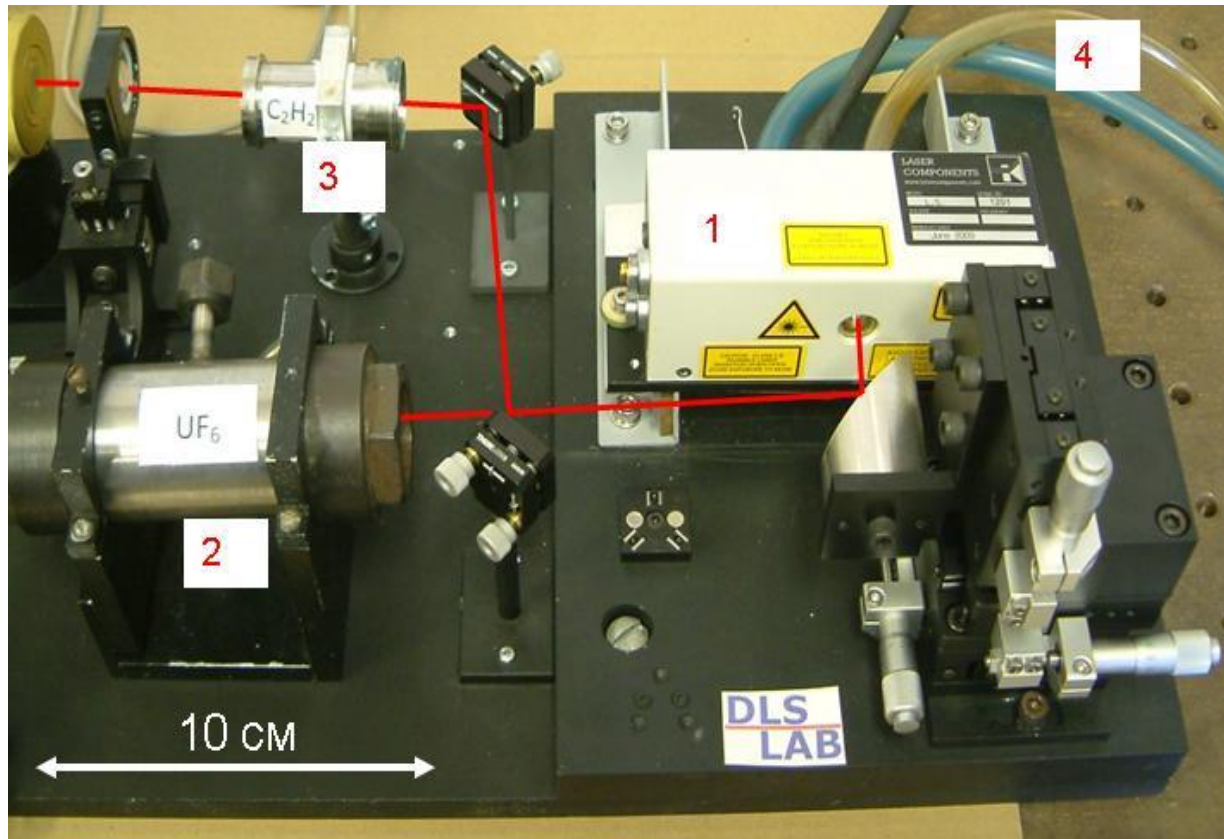
UF₆ gas distribution system

For present experiments the several instruments were installed in Institute of Molecular Physics of RRC "Kurchatov Institute". View of UF₆ gas distribution system developed at "Kurchatov Institute" for present work.



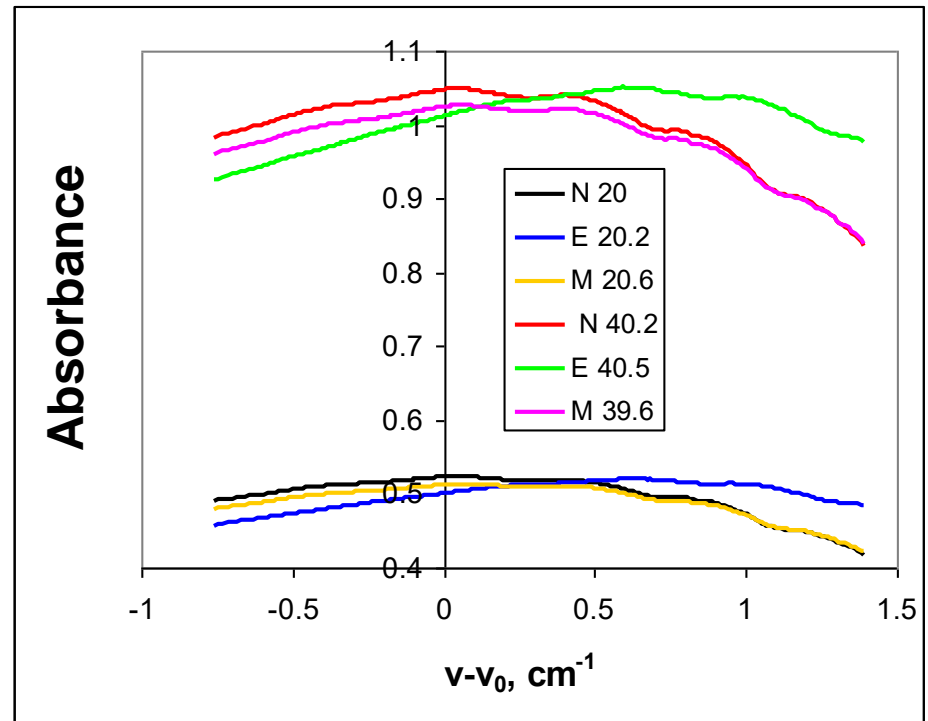
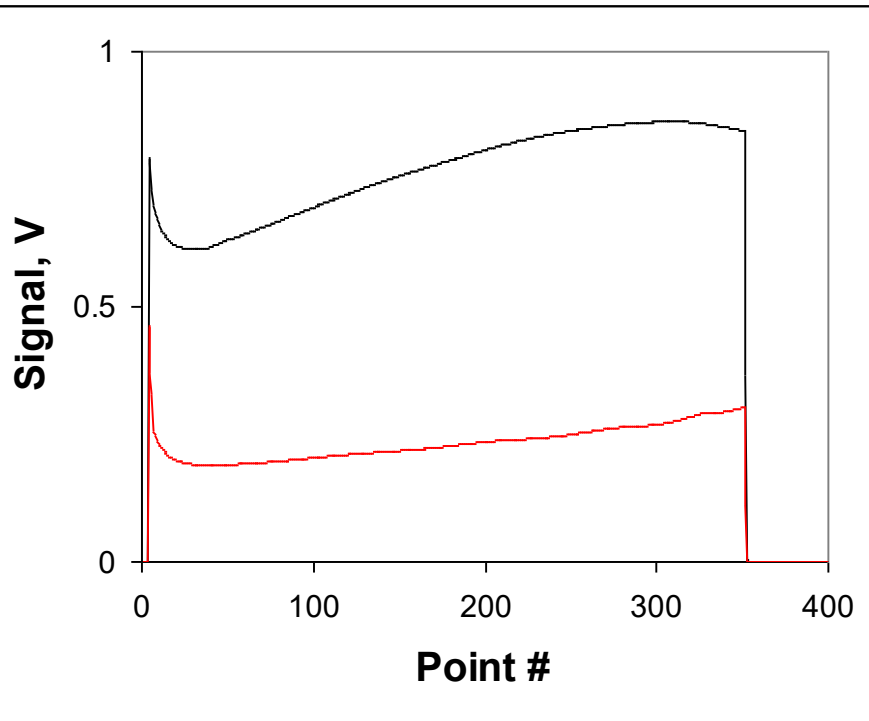
8. Connection to TDLS system.
9, 10, 11 – containers with samples with calibrated UF₆ enrichment.

Experimental set up with QCL



QCL (1) radiation (red) was divided into two beams, passed gas cells (2, 3), and was directed to two PD of analytical and reference channels. QCL module water cooling (4) was used.

Absorbance

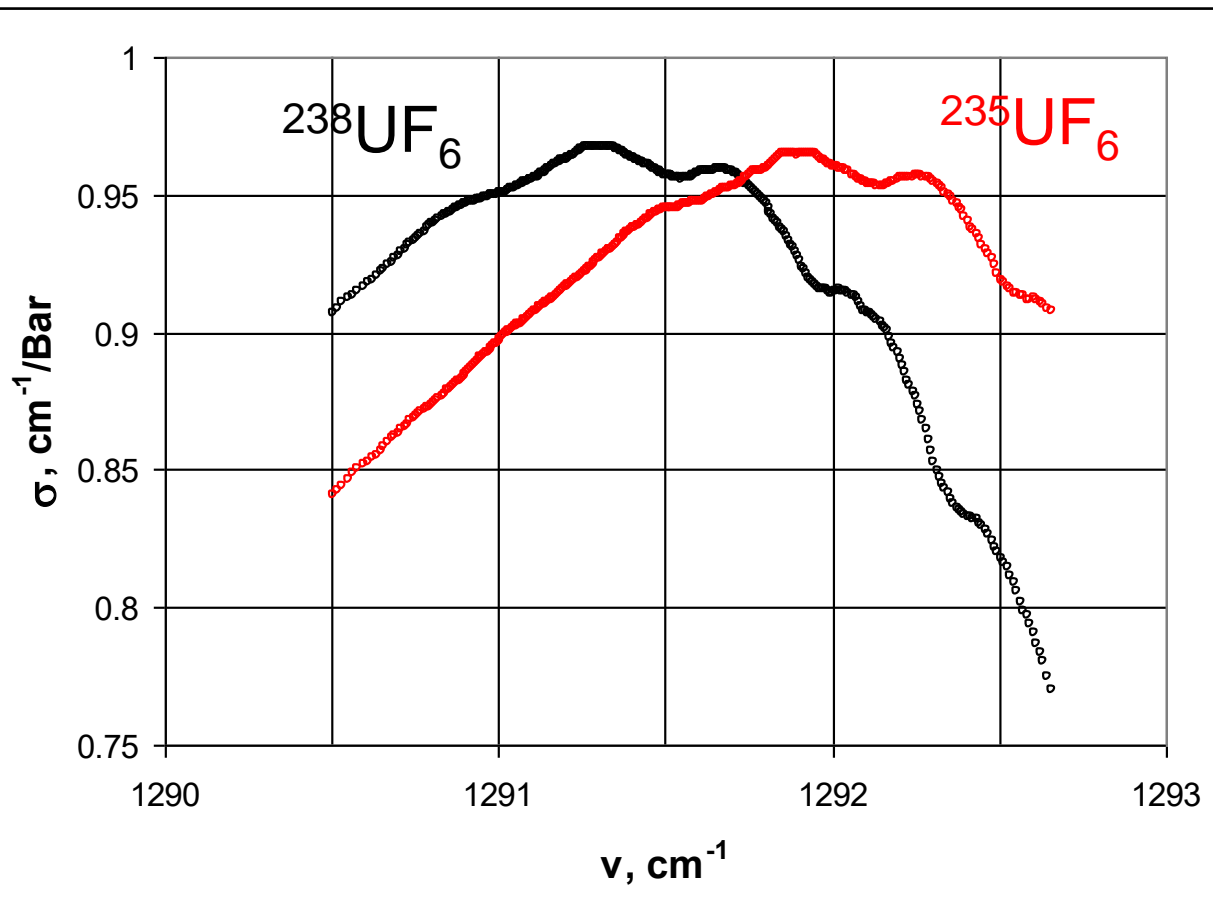


Recorded signals shapes for empty cell (black) and for cell filled with 40 Torr of UF_6 sample under investigation (red). Sample cell length $L = 20$ cm.

Absorbance at two pressures (20 and 40 Torr) for three UF_6 samples with different enrichment enrichment R: N - natural abundance ($R=0.7\%$); E – enriched sample ($R=90\%$); M – intermediate ($R=12\%$).

Cross-section

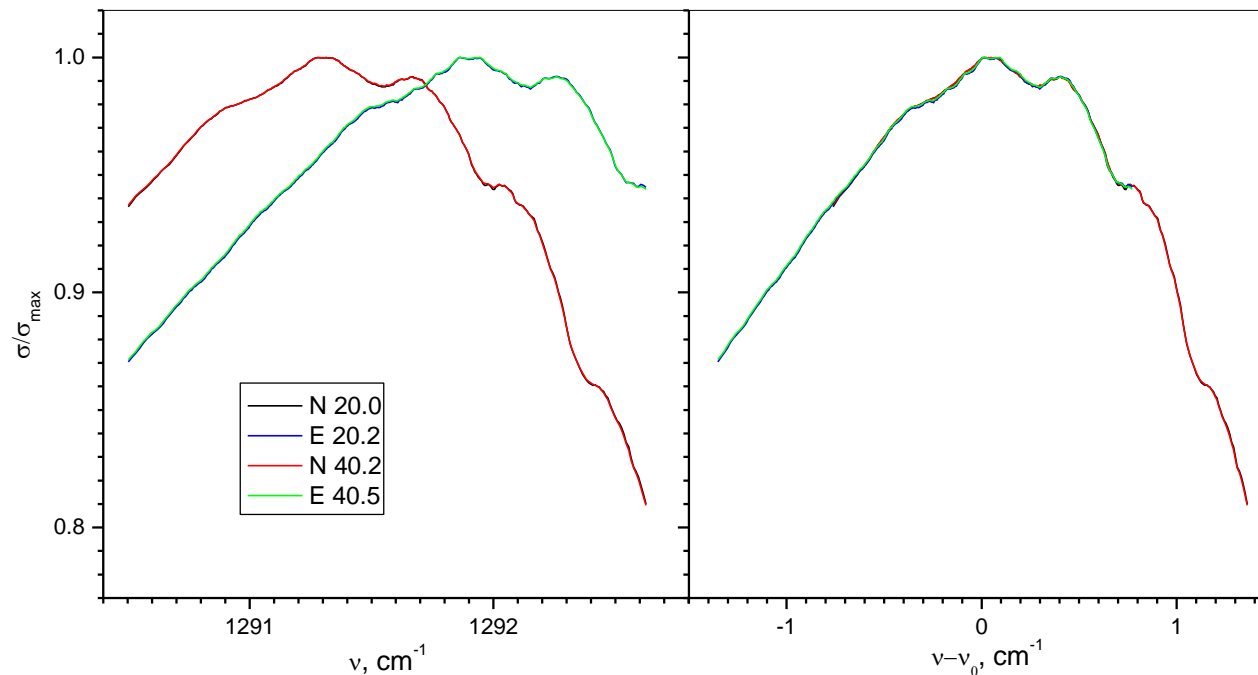
Using absorbance data obtained for UF_6 samples under investigation with known enrichment, absorption cross-section of different isotopomers can be determined.



Absorption cross-section of $^{238}\text{UF}_6$ (black) and $^{235}\text{UF}_6$ (red). Cross-sections for both isotopes have close maximum values and have fine structure. It seems that this fine structure is similar for both U isotopes and is only shifted with respect to each other.

Isotope shift

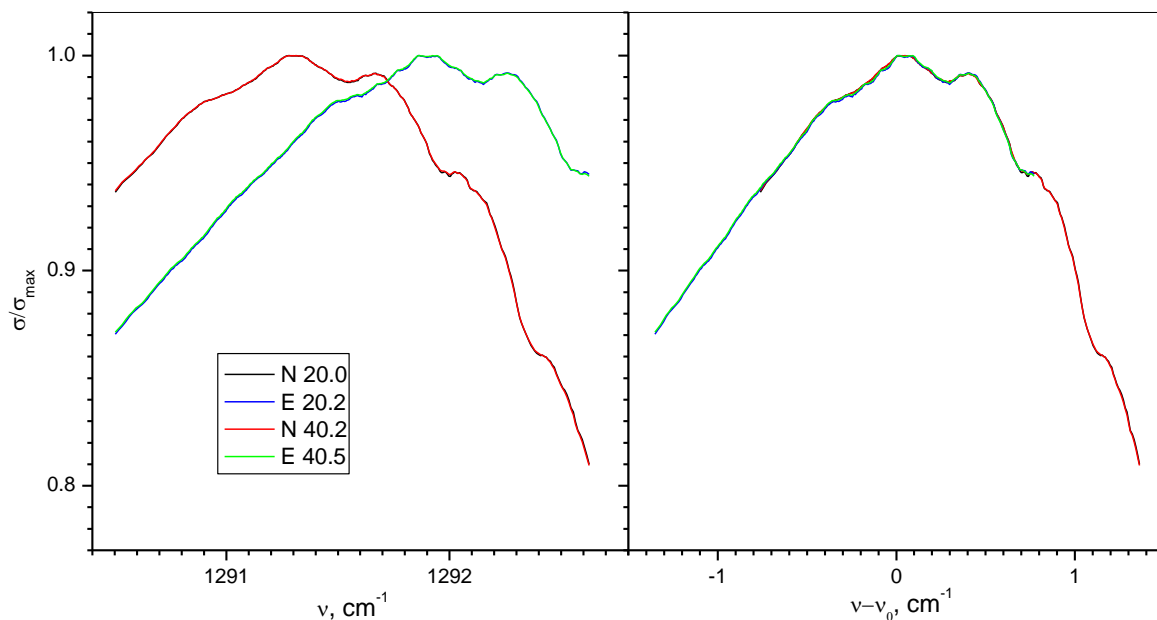
Cross section shape is determined by vibration and rotation of UF_6 molecule. U atom involvement in vibration motion results in isotope shift (left graph).



For $\nu_1 + \nu_3$ band under consideration isotope shift was determined – $0.59(1) \text{ cm}^{-1}$. After taking into account this shift (right graph), spectra of both samples coincided totally with $\text{std} = 0.027 \%$.

UF₆ cross-section shape

Cross section shape is determined by vibration and rotation of UF₆ molecule (left graph).

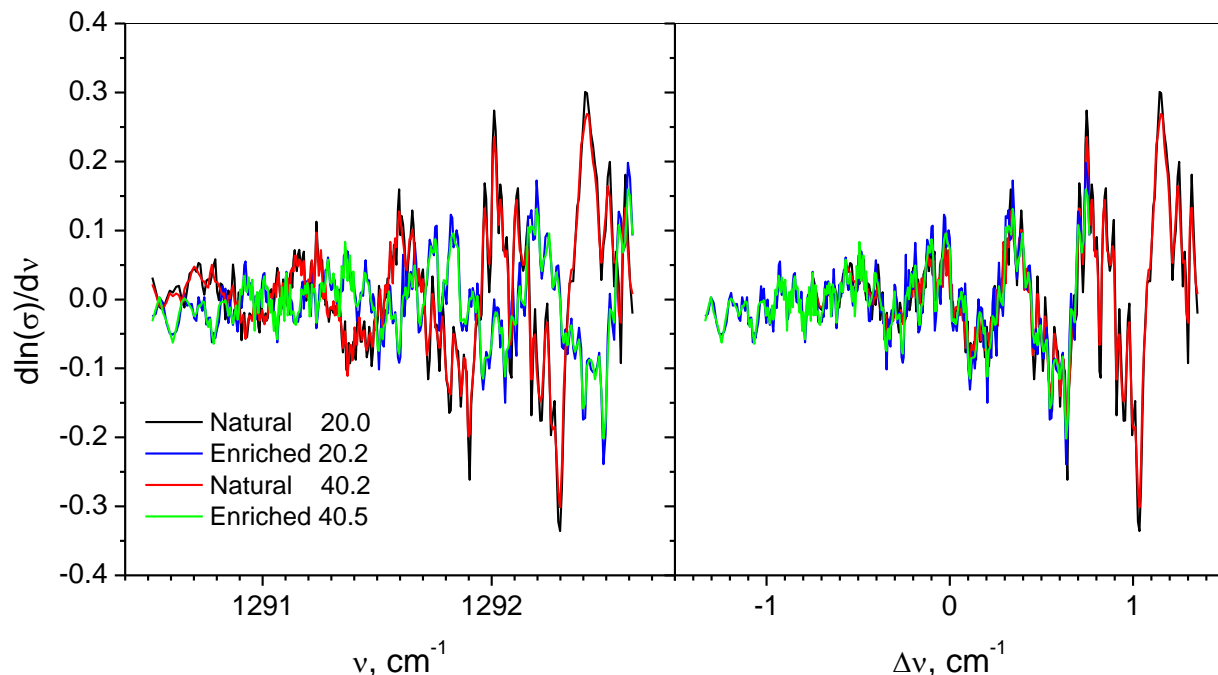


After taking into account isotope shift (right graph), spectra of both samples coincided.

Remained fine structure is due to UF₆ molecule rotation. It is the same for both isotopes because U atom is located in spherical top molecule center and is not involved in rotation. **Conclusion – if ²³⁸UF₆ cross-section was measured with high accuracy in broad spectral range, ²³⁵UF₆ one can be determined straightforward using isotope shift value.**

Spectra fine structure

To intensify fine structure, cross-section logarithmic derivative was calculated (left graph).



UF_6 cross-section logarithmic derivative for different isotopomers obtained from different spectra:

$^{238}\text{UF}_6$ – black and red;
 $^{235}\text{UF}_6$ – blue and green.

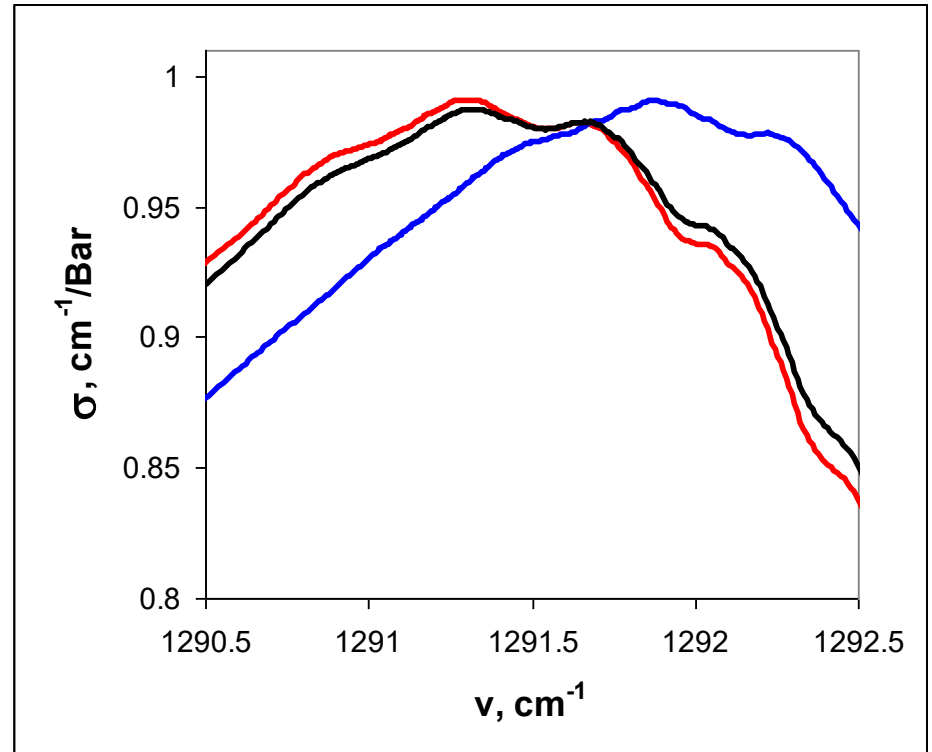
For each sample reproducible fine structure can be observed being sharper for smaller pressure due to collision broadening. This fine structure of Q-branch is known from literature for spherical top molecules. It is similar for both isotopomers (see above) and allow one to determine isotope shift:

Isotope shift for $\nu_1+\nu_3$ band = $0.59(1) \text{ cm}^{-1}$

Enrichment measurement

Measured absorption cross-section σ of $^{238}\text{UF}_6$ (red), $^{235}\text{UF}_6$ (blue), and sample under investigation (black). Black is superposition of both UF_6 isotopomers; its difference with cross-section of $^{238}\text{UF}_6$ is direct measure of enrichment - R.

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

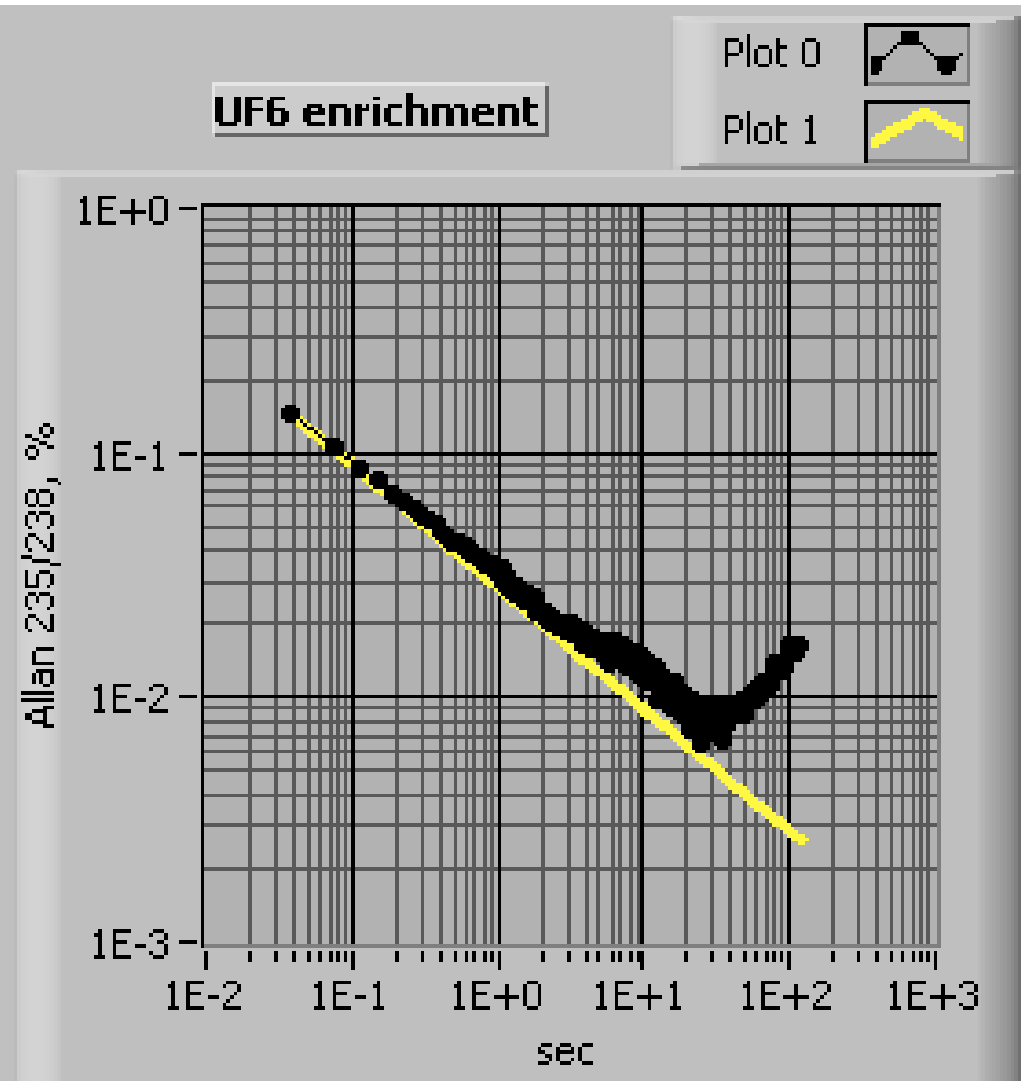


Procedure of enrichment measurement takes several minutes:

1. $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$ cross-sections were measured and stored in computer;
2. record baseline;
3. fill cell with sample under investigation;
4. wait some minutes (gas temperature);
5. record and calculate cross section;
6. determine enrichment.

Precision of enrichment measurements

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



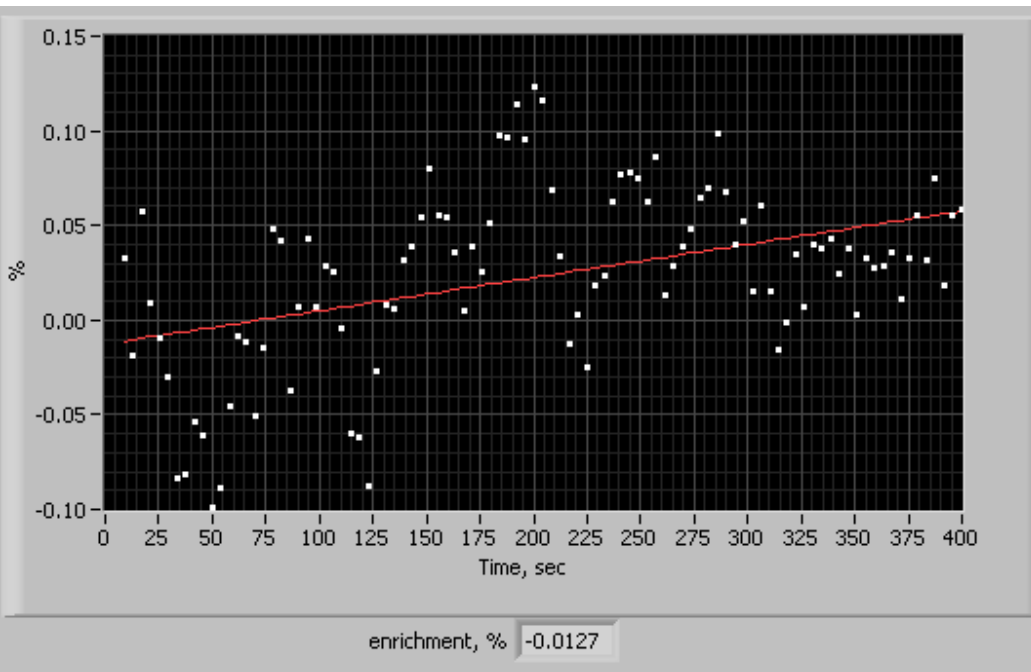
Precision below 0.01 % (UF_6 enrichment measurement requirements) can be achieved at 30 sec averaging time with present setup and algorithms.

For longer averaging times necessary for measurement procedure drift can be observed.

This drift can limit enrichment measurement accuracy for 600 sec averaging time to 0.1 % level (**unacceptable**).

Drift compensation

Drift of measured UF_6 enrichment is due to drift of DL baseline. The baseline drift is caused by DL fundamental processes. Important feature: this drift is slow in comparison with time of measurement procedure.



Sample with natural abundance (0.7 %) was used. At $t = 0$ baseline was saved and enrichment measurement started. Drift is more than 0.05 %. However, intercept is close to 0.01 % - UF_6 enrichment measurement requirements.

Conclusion: Drift problem related to fundamental DL physical properties was solved. Results achieved are in agreement with IAEA requirements.

Conclusion

- Experimental setup to investigate UF_6 in mid IR was developed
- UF_6 spectra of samples with different enrichment (0.7 – 90 %) were recorded
- $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$ cross sections were obtained
- Isotope shift for $\nu_1+\nu_3$ band - $0.59(1) \text{ cm}^{-1}$ was determined
- The same fine structure due to molecule rotation was observed for both $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$
- Enrichment measurement procedure was proposed and tested
- Achieved accuracy of enrichment measurement 0.01 % agree with IAEA requirements