\(^{238}\text{UF}_6\) and \(^{235}\text{UF}_6\) 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 photodiodes in use; to improve enrichment measurement accuracy $^{235}$UF$_6$ spectrum has to be obtained.
**UF₆ Absorption Bands in mid IR**

Figure presents absorption cross section of UF₆ molecule in mid IR.

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

| v₁+v₃ | 1291 | 0.72 | Enrichment measurement |
| v₁+v₄ | 853  | 0.12 | Enrichment measurement |
| v₃    | 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]

<table>
<thead>
<tr>
<th>Isotope shifts, cm$^{-1}$</th>
<th>$^{235}$UF$_6$</th>
<th>$^{238}$UF$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$v_3$</td>
<td>0.65±0.09</td>
<td>0.65±0.09</td>
</tr>
<tr>
<td>$v_4$</td>
<td>0.16±0.09</td>
<td>0.16±0.09</td>
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Combination band $v_1 + v_3$ was chosen for present experiment.
UF₆ absorption cross-section - σ (circles) of v₁+v₃ band [1]. The spectrum was recorded by FTS for sample with natural isotopes abundance. Model spectra of ^{238}UF₆ (black line) and ^{235}UF₆ (red line) [1] demonstrates isotope shift [2].

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.
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

Accuracy and precision requirements for UF$_6$ enrichment measurements:

- Enrichment $< 0.01\%$
- Absorbance $< 0.01\%$
- Frequency $< 6 \times 10^{-5}\text{ cm}^{-1}$

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

Probability to measure particular value of parameter under investigation.
Allan plots

Comparison of minimum detectable absorption obtained in present work (GPI MIR) with best published results in mid IR spectral range.
Absorption spectra of $^{138}$UF$_6$ (black), C$_2$H$_2$ (red), and CH$_4$ (blue).

DL operation regime
Channels with cells containing C$_2$H$_2$ (yellow) and CH$_4$ (white). There are some weaker C$_2$H$_2$ lines not included in HITRAN as well as water line. C$_2$H$_2$ 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 $< 6 \times 10^{-5}$ cm$^{-1}$. 
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 UF₆ samples under investigation absorption cross-section of different isotopomers can be determined.

Absorption cross-section of $^{238}$UF₆ (black) and $^{235}$UF₆ (red). Both cross-sections have close maximum values. Fine structure can be observed. 

*It seems as spectra are similar and are only shifted with respect to each other.*
**UF₆ 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 UF₆ 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 UF₆ isotopomers.

Left - normalized cross-section \( \sigma/\sigma_{\text{max}} \) of two UF₆ isotopomers obtained from different recorded spectra (see above). Graph demonstrates good reproducibility of \( \sigma/\sigma_{\text{max}} \) 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 \(^{238}\text{UF}_6\) cross-section, \(^{235}\text{UF}_6\) 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 $^{238}\text{UF}_6$ 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 $\sigma$ (P $\approx$ 40 Torr) of $^{238}$UF$_6$ (red), $^{235}$UF$_6$ (blue), and sample under investigation (black).

Measured absorption cross-section $\sigma$ is superposition of both UF$_6$ isotopomers; its difference with cross-section of $^{238}$UF$_6$ is direct measure of enrichment - R.

$$\sigma(v) = R\sigma_5(v) + (1 - R)\sigma_8(v) = R[\sigma_5(v) - \sigma_8(v)] + \sigma_8(v)$$

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

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 $\mu$ 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.