Express measurements of the degree of uranium hexafluoride enrichment and UF$_6$ and HF trace quantities in atmosphere based on near- and mid-infrared diode lasers

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Application of diode-laser spectroscopy principles is shown to ensure reliable measurements of the isotopic content of gaseous uranium hexafluoride and trace quantities of HF and UF$_6$. A DL-based laboratory prototype that provides for measurements of gaseous UF$_6$ isotopic content with inaccuracy less than 0.27% has been built and calibrated. The measurable concentration threshold for HF with the use of a Chernin multipass cell and a near-infrared range DL (ν_2 band) is shown to be less than 2 ppb. For UF$_6$ detection with mid-IR DL ($\lambda \sim 7.6\ \mu m$), the minimum value of the detected absorption was evaluated in terms of optical path ~ 50 m long and gave the concentration value of ~ 250 ppb. Assessment has been made of gas analyzer sensitivity to UF$_6$ with the use of 16 μm DL (ν_3 absorption band), which turned out to be less than 30 ppt at $L \sim 50$ m. A conclusion has been drawn that the concentrations obtained for the molecules under study are suitable for atmospheric monitoring in the vicinity of atomic industry facilities.

Introduction

The problem of measuring the isotopic composition of uranium being in the chemical form of uranium hexafluoride has been solved for long ago. At separating plants, the isotopic composition is measured by specialized mass-spectrometers with a high accuracy. The method of measuring the uranium enrichment degree by its γ-spectrum is also well elaborated. Therefore, at first glance, efforts to measure the uranium hexafluoride isotopic composition by diode laser spectroscopy methods seem to be of little utility. However, it turns out that there is no sufficiently reliable, exact, and, that is the most important, express method for estimation of the UF$_6$ enrichment degree, when checking different researching laboratories and plants being under IAEA control. To check such objects, inspectors have to perform sampling, send the samples for analysis, wait for and receive the result, and only after that make a conclusion on conducting additional tests or other actions. In order to exclude some actions of the party under checking during the expectation period, inspectors must have some instrumentation allowing an express *in situ* estimation of the UF$_6$ enrichment degree.

Apart from the above problem, analysis and protection of environment from pollution connected with serious emergencies at industrial enterprises become now of a particular concern. Primarily, these are the plants with nuclear fuel cycle (NFC), therefore, the control for gas and aerosol emissions from such plants into atmosphere and their fabrication facilities is of growing importance.

This fact can be explained by a complex ecologic situation in the vicinity of nuclear facilities and justified growing public concern relative to unfavorable impacts of such objects on the environment, associated with hazardous emissions both of radioactive matters and toxic compounds.[1] All this stimulates a search for new reliable methods and instruments for express measurements of concentrations of chemical and radioactive pollutants.

Recently, when constructing systems for monitoring the environment (basins of lakes, rivers, seas, oceans, green masses (forests), large industrial centers, ports), optical (laser) sensing methods are put in the forefront. These methods are distant (from several tens of meters to several kilometers), high sensitive (several ppb), and rapid (from several tens of seconds to several minutes). They allow a real-time obtaining of sufficient information about the medium under study, including the information from airborne instruments. This is very important for taking quick precautions, particularly, in the case of hazardous technogenic or natural catastrophes.

Most traditional contact monitoring methods are based on the sampling of air, water, soil, green mass, etc.

They require a dense and ramified net of specially equipped sites for simultaneous observations. Furthermore, to obtain the sampling results with the use of the available instrumentation, a prolonged and laborious work under laboratory conditions is needed, as a rule.

The diode laser spectroscopy (DLS) is at present one of the most prospective optical methods for on-line obtaining of reliable information on concentrations and chemical composition of emissions under conditions of their active interaction with atmospheric components. Estimates show that gas-analyzers of remote and local types, in particular, based on DLs of new generation (quantum-cascade and VCSEL lasers), can provide for sensitivity of 1 ppb and higher.

In this work, we present the results of studying the possibilities of reliable, accurate, and prompt estimates of the UF_6 enrichment degree with the use of mid-infrared diode lasers; describe the worked out instrumentation for express measurements of trace amounts of UF_6 and HF in atmosphere, and preliminary results of studying the process of UF_6 hydrolysis, using the near- and mid-infrared diode lasers under conditions maximally close to actual atmosphere.

1. Experiment

The UF_6 infrared absorption spectra were studied at the Vector 22 Fourier spectrometer (spectral resolution of 0.75 cm^{-1}) using a cell of 10 cm length with barium difluoride windows of 40 mm in diameter. Some spectra were obtained using the Bruker 66 Fourier spectrometer of a 0.2 cm^{-1} resolution. The spectrometer frequency scale was calibrated against CH_4 and C_2H_2 absorption spectra in the same range, as well as against the HITRAN-2004 spectral data.

The principle of measurement of the UF_6 isotopic composition is sufficiently close to that for CO_2 and H_2O (Refs. 2–4). Figure 1a shows a scheme of the setup for measuring the isotope content of uranium being in a chemical form of UF_6. Main difference from the methods described in Refs 2–4 is in measurements of intensity of the laser beam passed through three channels: measuring, referent, and interferometric.[5-8] In fact, the constructed setup is a high-resolution three-channel infrared spectrometer based on the mid-infrared diode laser.

The diode laser designed at the P.N. Lebedev Physical Institute RAS[9] generated at $\lambda = 7.68 \text{ μm}$. The laser was fixed on a copper refrigerated wire set inside a criosphere cooled by a liquid nitrogen. The DL radiation power was 300 μW. It was pumped by the trapezoidal current pulses at $I_w \sim 300 \text{ mA}$, pulse length of 4–10 ms, repetition frequency of 40 Hz. A fine frequency scanning ($\Delta\nu \sim 2 \text{ cm}^{-1}$) at such a generation regime was due to variation of effective index of refraction in the laser's active range during the pumping current pulse. The scanning in the whole range of the frequency tuning ($\sim 40 \text{ cm}^{-1}$) was performed by a smooth variation of the laser's crystal temperature through heating the refrigerated wire and was controlled by two thermostabilizing systems. The radiation receivers (CaHgTe photodiodes), efficiently operating in this wavelength range, were located inside the criospheres and cooled by the liquid nitrogen.

As it was mentioned above, two temperature-stabilizing systems were used in the DL gas-analyzer. In the first one (principal), the proportionally-integral law of temperature regulation was realized, which provided for long-term temperature stability of the laser crystal at a level of $5 \cdot 10^{-3} \text{ °C}$ in any point of the working temperature range ($\Delta T \sim 79$–115 K). Additional stabilization of the DL radiation frequency providing for prolonged frequency stability at a level better than $4 \cdot 10^{-4} \text{ cm}^{-1}$, was performed by absorption lines of the referent gas (CH_4).
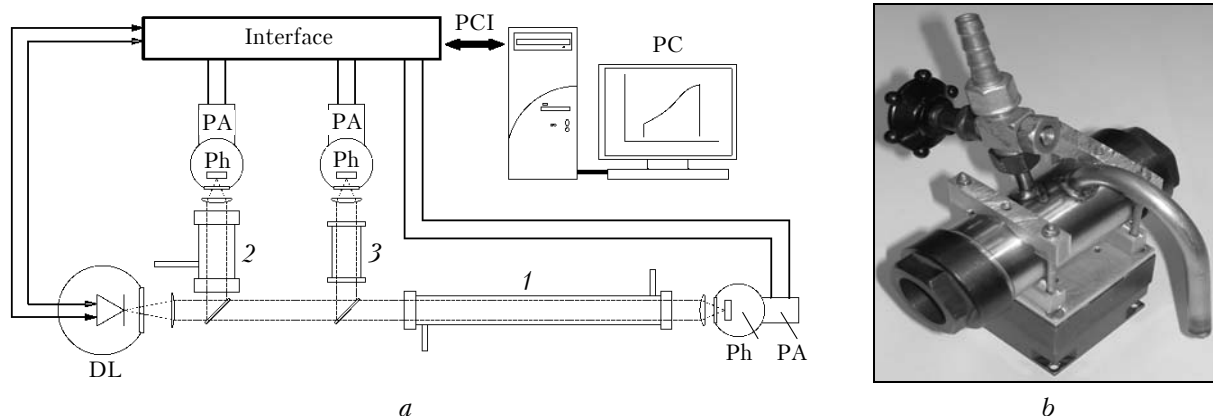
Fig. 1. A scheme of DL spectrometer for measurements of uranium isotopic composition (*a*) and an external view of the cell for measurements of UF_6 spectra (*b*): DL is diode laser in a cryostat; *1* is analytical channel for studying uranium hexafluoride absorption spectra and isotopic ratio $^{238}UF_6/^{235}UF_6$; *2* is reference channel for stabilization of radiation frequency by the referent gas (CH_4) absorption line and absolute assignment of frequency scale of absorption spectra; *3* is frequency calibration channel (linearization of frequency scale by Fabri–Perrot interferometer); Ph are photoreceivers in cryostats; PCI is data transmission bus; PA are preamplifiers; PC is personal computer.

The analytical channel (*1*) was intended for measurements of the UF_6 concentration and the $^{238}UF_6/^{235}UF_6$ isotopic ratio. It consisted of optical cell with $L = 10$ cm, vacuum-gas stand for preparing the gas mixture, filling the gas, and controlling for the gas pressure in optical cells.

The referent channel (*2*) was intended for performing absolute calibration of the frequency scale of the UF_6 absorption spectra and the radiation frequency stabilization against the referent gas absorption line. For absolute frequency assignment, isolated intense vibrational-rotational lines of CH_4 v_4 band were used. Parameters of CH_4 lines (frequency, intensity, coefficients of broadening and shift) were taken from the HITRAN-2004 database. The methane (99.9% purity class) was located in the optical cell of 5 cm length at a pressure of 1.5 mm Hg. The signal/noise ratio in the methane absorption spectra inside the referent channel exceeded 200 and then, after signal accumulating and averaging, increased more than an order of magnitude. High magnitude of the useful signal together with low pressure of the gas allowed finding centers of almost Doppler lines, not pressure-widened and not pressure-shifted, which were absolute frequency line references for linearization of the frequency scale of UF_6 absorption spectra.

An optical cell ($L = 10$ cm) with natural UF_6 (Fig. 1*b*) at a pressure of 75 mm Hg was located in the reference channel as well. It was used as a reference cell in determination of the UF_6 concentration in the gas sample of the uranium hexafluoride, as well as the magnitude of the isotope ratio $^{238}UF_6/^{235}UF_6$.

The frequency calibration channel (*3*) was intended for linearization of the frequency scale of absorption spectrum of the gas under study. It included Fabri—Perrot interferometer with the free dispersion range $D^* = 0.04965$ cm^{-1}. The linearization procedure consisted in constructing a rebuilding characteristic modifying the time scale of the absorption spectra into its frequency analogue. To do this, we used the values of centers of absorption maxima of the Fabri—Perrot resonator and D^*. In conclusion, the absolute assignment of the frequency scale to absorption lines of the reference gas was performed. Upon completion of linearization and frequency assignment, the error in determining a line center in any region of the working mode spectral range ($\Delta v \sim 2$ cm^{-1}) was better than $2 \cdot 10^{-4}$ cm^{-1}.

For controlling the DL pumping and thermostabilizing systems, as well as recording and processing signals, a many-functional DAC/ADC NI PCI-6110 board produced by "National Instruments" was used.

The frequency of sampling discretization in the gas-analyzer was 1 MHz; the sampling length varied from 800 to 2000, and a quantity of amassments was between 1 and 255. The input signal/noise ratio was $1–2 \cdot 10^4$. Control for the gas-analyzer and signal processing were performed using the programs written with the use of National Instruments drivers and a NI LabView 7.0 program package.[10]

The study of the process of UF_6 hydrolysis and measurements of trace amounts of the uranium hexafluoride and hydrogen fluoride was conducted under conditions maximally close to actual atmosphere. Figure 2 presents the setup scheme (*a*) and its photograph (*b*).

To simulate the conditions, a stainless steel closed box of 370 l volume, equipped with ventilator and filled with atmospheric air ($P = 720$ mm Hg, $T = 299$ K, humidity of 60%) was used, into which a mixture of UF_6 and pure nitrogen was injected, prepared beforehand in an individual tank ($P = 4$ atm, $V = 5$ l). After that, the pressure in the box increased to 750 mm Hg. Immediately afterwards, the ventilator was switched on for 10 s.

Measurements of the UF_6 concentration and HF formed in the process of hydrolysis were conducted via two individual optical channels. To determine accurately the UF_6 and HF concentrations, each channel was equipped with a reference cell. To analyze the HF concentration, a tunable diode laser (DL) of $\lambda \sim 1.31$ µm (HF $P2$ line) equipped with wave-guide output of radiation was used. To analyze the UF_6 concentration, just like in the case of measuring the isotope composition of uranium hexafluoride, a tunable DL of $\lambda \sim 7.68$ µm (absorption center of UF_6 $v_1 + v_3$ band) was used. The optical way length for each channel was 1.5 m.

To control for DL pumping and thermostabilizing systems, as well as for recording and processing signals, the input-output NI DAQ boards (National Instruments) were used. In the measurement control, a program functioning in the NI LabView 7.0 media was used.

The vacuum-gas stand made of stainless steel included gas valves of DU-4 and DU-10 types; needle leakers; receiver; a system for UF_6 filling in and discharge; reservoirs for keeping the gas under study, molecular fluoride, HF, and noble gases; calcareous chemical absorber; sensors for measuring pressure; and optical cells. All gaskets for valves and other stand's components were made of Teflon. Since UF_6 and HF are very active chemically and interact with inner surface of the stand, connecting pipelines, and optical cells, all they were thoroughly passivated by molecular fluoride and by the studied gases themselves at a pressure of 50–70 mm Hg. The passivation time was 6–7 days. Between measurements, the stand was under UF_6 pressure of 3–5 mm Hg.

Prior to each experiment, the UF_6 sample was additionally purified through a sequence of operations: freezing, pumping out, and defrosting. Gas pressure in the stand, as well as in analytical and reference cells was simultaneously controlled by DP-5 differential pressure sensors and VDG manometers. Additional errors of the sensors and manometers were eliminated before measurements at a pressure of $\approx 10^{-2}$ mm Hg via correcting their readings by readings of the manometer lamp. All measurements were conducted at an environmental temperature of 299 K and humidity of 60%.

a

b
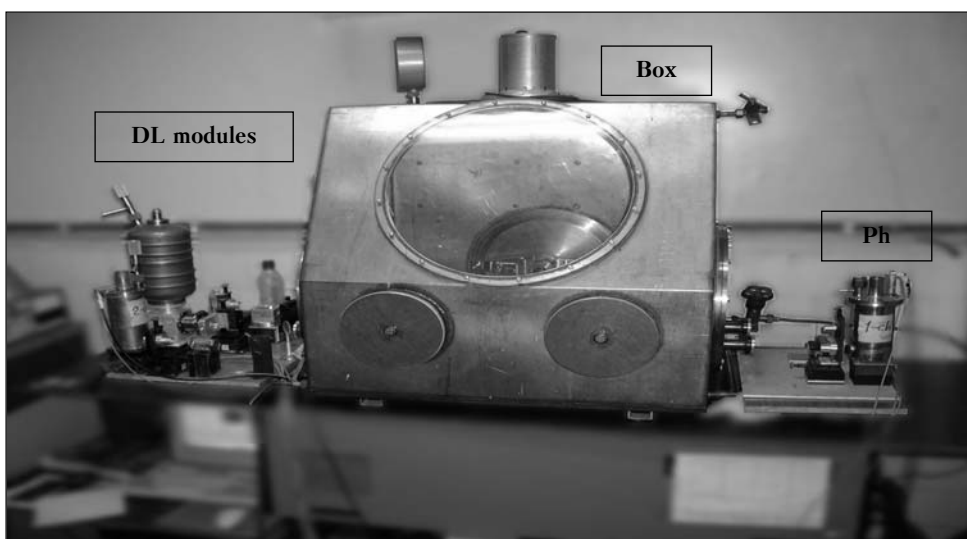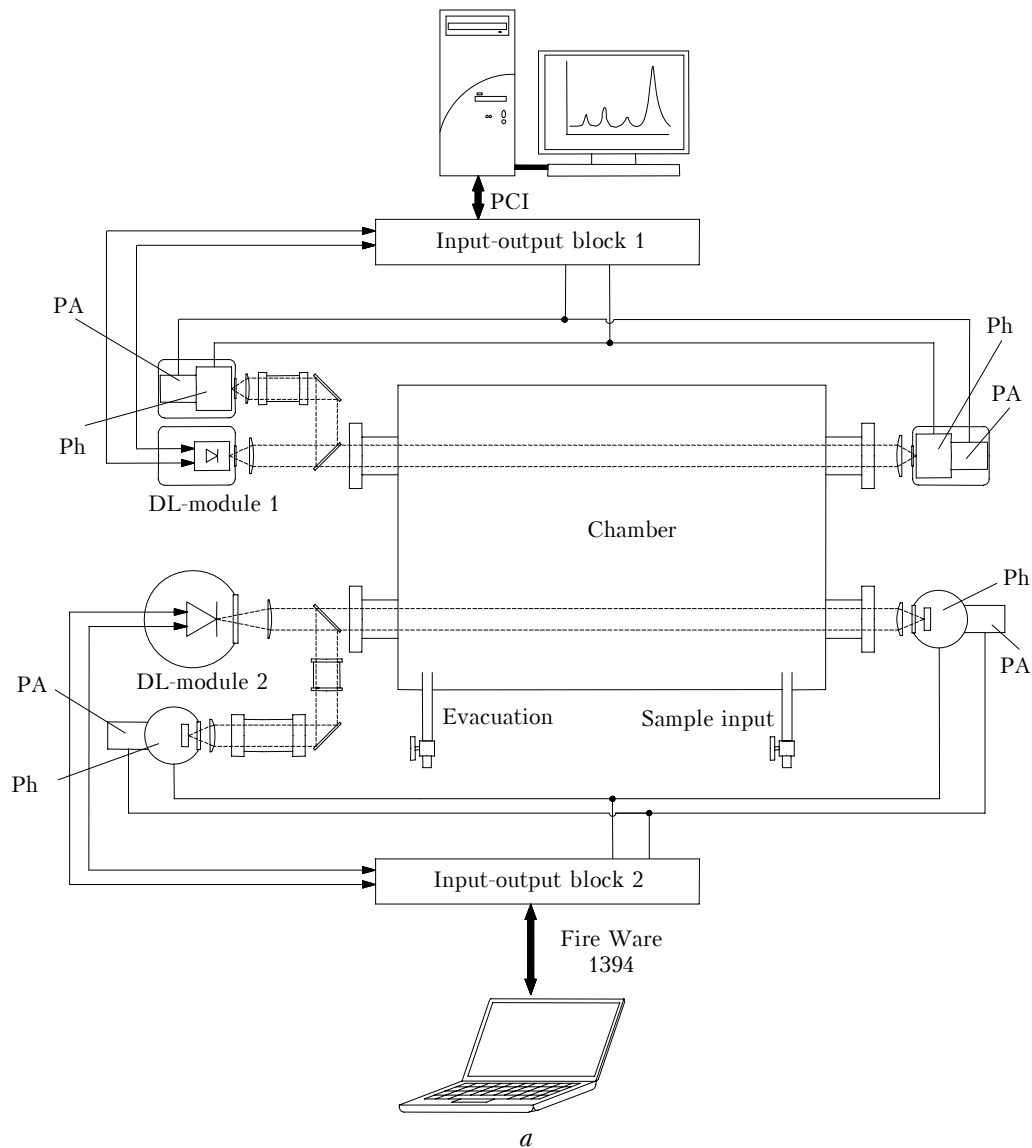
Fig. 2. A scheme of DL spectrometer for studying uranium hexafluoride hydrolysis and measurements of UF_6 and HF trace amounts (*a*) and the setup photo (*b*). Designations are the same as in Fig. 1. Fire Ware are data transmission buses.

The optical cells were made of stainless steel, all inner walls polished. The optical length of the cells was 10 cm. As the cell windows, plates of barium difluoride (for UF_6) and polyethylene (for HF) of 40 mm in diameter were used. The windows were sealed with viton located in special Teflon pockets to minimize interaction between viton and uranium hexafluoride. The cells were equipped with a cooled outlet ("finger") for express condensation of samples from them.

2. Results and discussion

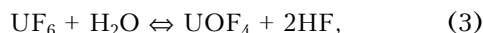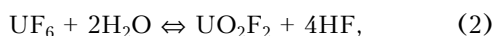## 2.1. A concise characteristic of UF_6 and HF physical-chemical properties

Uranium hexafluoride under standard conditions is a white crystal matter, which sublimates at a pressure of 1 atm and a temperature of 56.5°C (the temperature of UF_6 boiling at the atmospheric pressure). The temperature of the UF_6 triple point is 64.02°C and the vapor elasticity makes 1134 mm Hg. The critical temperature is 245 ± 5°C, and the critical pressure is 36000 mm Hg. The uranium hexafluoride sublimates without melting. The UF_6 pressure (P_{UF_6}) is strongly temperature-dependent. Thus, at $T = 0$°C $P_{UF_6} = 17.8$ mm Hg, at $T = 25$°C $P_{UF_6} = 112.7$ mm Hg, and at $T = 80$°C $P_{UF_6} = 1830.0$ mm Hg.

It is important to note that volatile UF_6 is the most chemically active compound of all fluoride-containing compounds of uranium and one of the most hazardous components of emergency emissions from the NFC-objects.[1]

In accordance with its reactive ability, UF_6 falls between actinide hexafluorides and elements of chromium subgroup[11]:

$$WF_6 > MoF_6 > UF_6 > NpF_6 > PuF_6. \qquad (1)$$
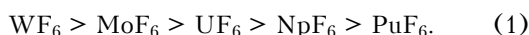
In the case of emergency emission, UF_6 actively interacts with atmospheric moisture, resulting in formation of UO_2F_2 and disproportioning to UOF_4. The UF_6 hydrolysis process can be described as

$$UF_6 + 2H_2O \Leftrightarrow UO_2F_2 + 4HF, \qquad (2)$$

$$UF_6 + H_2O \Leftrightarrow UOF_4 + 2HF, \qquad (3)$$

$$UOF_4 + H_2O \Leftrightarrow UO_2F_2 + 2HF. \qquad (4)$$

It is very important therewith that after UF_6 emission (leakage), a free (unreacted with atmospheric water) uranium hexafluoride can live in the atmospheric air for a rather long time.

The hydrogen fluoride is an achromatic gas very easily transformed into liquid. The HF liquefaction temperature is 19.54°C. At $T = 25$°C the HF vapor pressure is about 1 atm. Under these conditions, HF exists in the form of a mixture of monomers and association products of various composition (($HF)_2$, $(HF)_3$, etc.).

The HF monomer molecules are two-atom heteronuclear molecules characterized by one vibration at a frequency of 4141 cm^{-1} (band center). However, HF is able to polymerize both in condensed and gas phases. As a result, its valence vibration band during the polymerization noticeably shifts to low frequencies and makes 3962 cm^{-1} (band center).

The HF molecules can be formed almost at all stages of uranium hexafluoride interaction with products of its hydrolysis with water vapor, gaseous components of the emergency emission, and atmospheric gases. Although parameters of HF molecule are well known and can be found almost in all available spectroscopic databases (HITRAN, GEISHA, etc.), there is little reason for using these data in solving problems of laser control for emergency emission components. The thing is that HF molecules, when interacting with water vapor in atmosphere (H_2O content in atmosphere at low heights makes from 0.02 to 4% of mass) can form stable gas-phase complexes of $(HF)_m \ldots (H_2O)_n$ type ($n + m \geq 2$).[1]

These complexes, as a rule, are characterized by several types of movement of large amplitude (MLA),[12] that, in turn, results in transformation of vibration spectra of their components (spectral shift of relatively free molecules can reach several tens and even hundreds of inverse centimeters) and in appearance of new bands meeting intermolecular vibrations. The conducted estimates of the magnitude of variation of the complex-formation enthalpy show that the dissociation energy of the complexes can reach − 15 kcal · mol^{-1} (Refs. 1, 13–16).

2.2. Method of measurement of the UF_6 enrichment degree with the use of mid-infrared diode lasers

It is well known that the UF_6 molecule (O_h symmetry) has six standard vibrations, two of which (v_3 and v_4) are active in the IR absorption spectrum, and three (v_1, v_2, v_5) are active in the Raman scattering spectrum. The v_6 vibration is inactive in the both spectra, and its frequency is usually calculated from the frequency of composite bands or estimated by relation $v_6 = v_5\sqrt{2}$.

Frequency values for main vibrational absorption bands of the uranium hexafluoride molecules are given in Table 1. For comparison, Table 1 gives analogous values for some elements of actinides and chromium subgroup.

It follows from Table 1 that the absorption bands meeting the fundamental dipole-active vibrations of the both groups lay in a sufficiently far IR range, for which the diode lasers suitable for their quantitative analysis are unavailable.

Analysis of Fourier IR absorption spectra has led us to some conclusions allowing selection of the frequency working mid-infrared range of the used diode laser generation for measuring the UF_6 isotope composition and its trace amounts, as well as the uranium hexafluoride hydrolysis process under conditions maximally close to the actual atmosphere.

Table 1. Frequency values (ν, cm⁻¹) of fundamental vibrational absorption bands
of some hexafluoride molecules (O_h symmetry)

Molecule	ν_1 (A_{1g})	ν_2 (E_g)	ν_3 (F_{1u})	ν_4 (F_{1u})	ν_5 (F_{1g})	ν_6 (F_{2u})	Reference
UF_6	667	530	626	184	200	–	Refs. 1,17,19
NpF_6	654	535	624	199	208	(164)	Ref. 18
PuF_6	(628)	(523)	616	206	(211)	(173)	Ref. 18
CrF_6	(720)	(650)	790	(266)	(309)	(110)	Ref. 18
MoF_6	741.5	65.61	741.1	264	318	116	Ref. 18
WF_6	771.0	677.2	711.0	258	321	(127)	Ref. 18

1. The observed decrease in transmission in the long-wave spectral part is determined by transmittance of the cell windows (BaF_2), which are not transparent for $\nu < 700$ cm⁻¹.

2. There are two spectral ranges: 1080–1230 cm⁻¹ and 1410–2500 cm⁻¹, where the cell is also non-transparent because of absorption of non-volatile products of the cell passivation settled on the cell windows.

Thus, only three spectral ranges: 766–1080 cm⁻¹, 1230–1410 cm⁻¹, and > 2500 cm⁻¹ are accessible for studying uranium hexafluoride spectroscopic parameters in the used cells.

The range $\nu > 2500$ cm⁻¹ is the least informative. There the water vapor absorption takes place (3400–4000 cm⁻¹). Naturally, water vapor is absent in the cell, but it can be found in the spectrometer optical channel and its amount can change during the experiment. Another significant absorption in this range is caused by HF presence in the cell (3600–4300 cm⁻¹).

Range 1200–1400 cm⁻¹ includes water absorption lines (1300–1400 cm⁻¹) and two relatively narrow and partly overlapping UF_6 absorption bands with maxima at 1291 and 1254 cm⁻¹. Two narrow UF_6 absorption bands with maxima at 821 and 852 cm⁻¹ are in a 700–1100 cm⁻¹ band.

Table 2 presents frequencies and absorption coefficients of fundamental and some compound vibrational UF_6 absorption bands (Refs. 17–19).

Table 2. Frequency values (ν, cm⁻¹) and absorption
coefficients (σ_0, (atm · cm)⁻¹) of UF_6 fundamental
and some compound vibrational bands

Vibration type	ν, cm⁻¹	σ_0, (atm · cm)⁻¹
ν_3	626	350
$2\nu_3 + \nu_6$	1386 ± 2	0.00175
$\nu_1 + \nu_2 + \nu_6$	1341	0.00875
$\nu_1 + \nu_3$	1290.9 ± 0.5	0.717
$2\nu_2 + \nu_6$	1211 ± 2	0.0007
$\nu_2 + \nu_3$	1156.9 ± 0.5	0.822
$\nu_3 + 2\nu_6$	905 ± 2	0.0035
$\nu_1 + \nu_4$	852.8 ± 0.5	0.122
$\nu_3 + \nu_5$	821	0.332
Isotopic shift, cm⁻¹		$^{235}UF_6$–$^{238}UF_6$
ν_1		0
ν_3		0.65 ± 0.09
ν_4		0.16 ± 0.09

As is seen, the $\nu_1 + \nu_3$ band is the most suitable for the case, because the band with maximum at 821 cm⁻¹ refers to the compound vibration $\nu_3 + \nu_5$ with rather complex symmetry ($F_{1u} + F_{2u} + A_{2u} + E_u$), not allowing one to determine the isotopic shift $^{235}UF_6$–$^{238}UF_6$ with a sufficient accuracy.

The UF_6 absorption band with maximum at 852 cm⁻¹ refers to the compound vibration $\nu_1 + \nu_4$ (F_{1u} symmetry), the isotopic shift of which is one-fourth as much as of the compound vibration $\nu_1 + \nu_3$ (F_{1u} symmetry).

There is a laser, through frequency tuning of which it is possible to cover practically all band of the compound vibration $\nu_1 + \nu_3$. As it was mentioned above, there is an isotopic shift in this band, which is approximately equal to the shift in ν_3 band. Although the absorption coefficient for this band is two orders of magnitude lower comparative to the asymmetrical vibration band ν_3 (see Table 2), but it is sufficient for measuring IR absorption spectra in cells of 10–15 cm length.

The UF_6 absorption spectrum in the $\nu_1 + \nu_3$ band is presented in Fig. 3a. The experimental absorption spectrum of the uranium hexafluoride (circles), as well as model $^{238}UF_6$ (solid line) and $^{235}UF_6$ (dotted line) spectra are given in Fig. 3b.

A part of spectrum in the range 1291–1293 cm⁻¹, approximately coinciding with the right part of $^{238}UF_6$ Q-branch and sufficiently exactly coinciding with maximum of $^{235}UF_6$ Q-branch, can be used for measurements of the isotopic concentration.
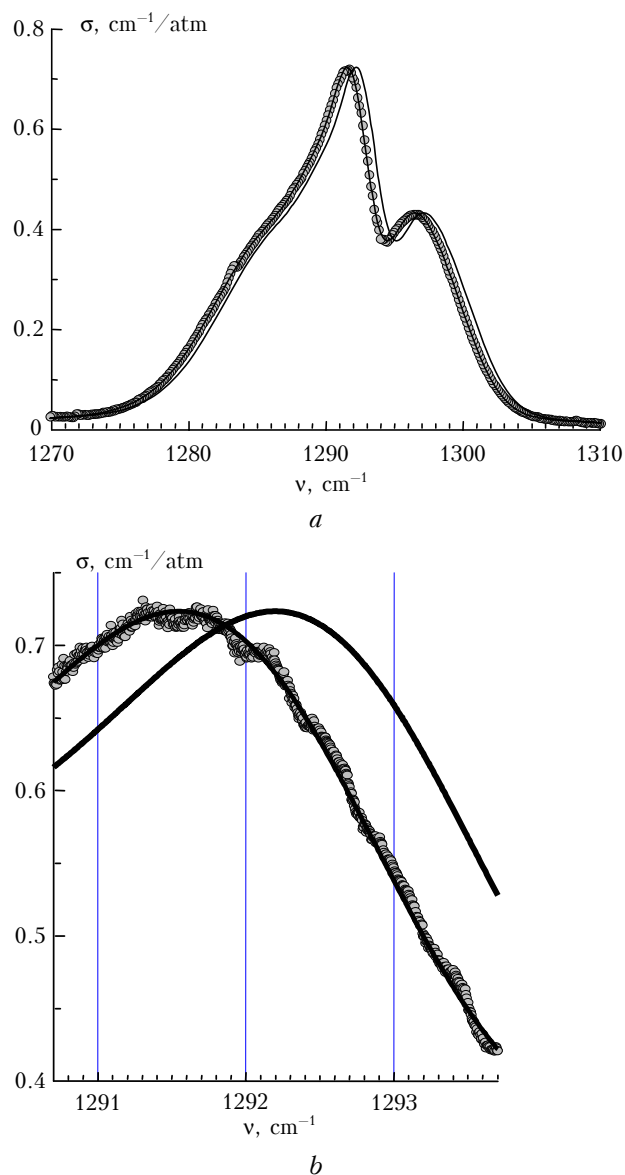
Variation of the absorption band relative intensity is described by formula (5), where σ is the absorption coefficient and ν is frequency:

$$T_i(\nu) = \frac{I_i}{I_0} = \exp\left[-A(\nu)\right] = \exp\left[-\sigma(\nu)PL\right]. \quad (5)$$

When measuring enriched samples, the spectrum changes; and the absorption coefficient change is described by formula (6):
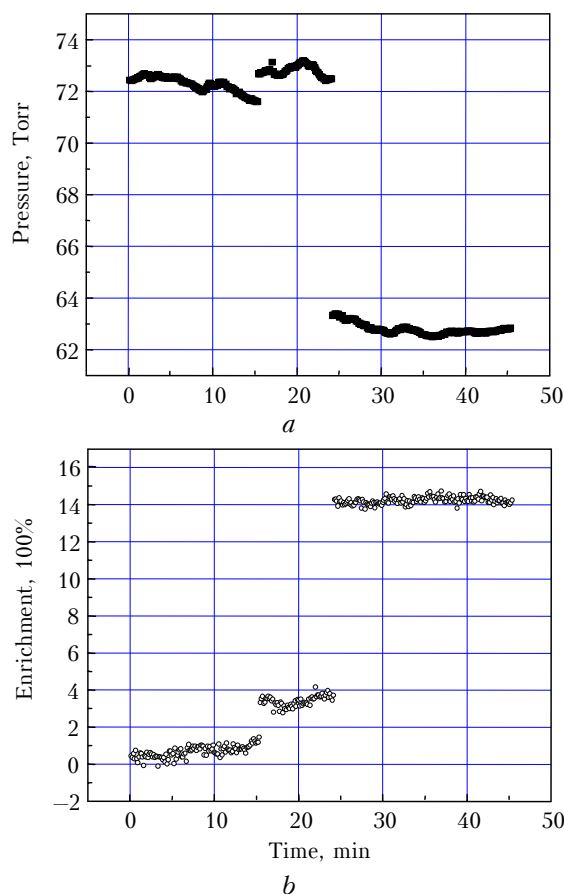
$$\Delta A = A - PL\sigma_{238} = PL(\sigma_{235} - \sigma_{238}). \quad (6)$$

In order to use formula (6) in calculations of the ^{235}U concentration in uranium hexafluoride, it is necessary to record the frequency dependence of absorption with a high accuracy. A change of the band shape at increase of ^{235}U concentration is insignificant, therefore, an exact measurement of absorption intensity and very accurate frequency assignment are needed, because the isotopic shift is small and the band structure is weekly expressed. Therefore, a three-ray scheme was used.

Fig. 4. Calibrating test of the gas-analyzer of isotope ratio of UF_6 calibrating samples.

The gas-analyzer determined automatically two mixture parameters: partial pressure (Fig. 4*a*) and isotope composition (Fig. 4*b*). To calibrate the device, three calibrating mixtures of isotopomers were used: $UF_6 - 0.73\%$ ^{235}U; 3.7% ^{235}U, 14.2% ^{235}U.

2.3. Determination of trace concentrations of uranium hexafluoride and hydrogen fluoride with the use of near- and mid-infrared diode lasers

In this section, the worked-out instrumentation for express measurements of UF_6 and HF trace concentrations in atmosphere is described.

For HF gas analysis, a multipass Chernin optical system with a 39 m total optical path-length was used. As it was mentioned above, although the HF molecular parameters are well-known and can be found in any available spectroscopic database, their use in solving the problems of laser control for emergency emission components is not always reasonable. This is due to the fact that HF molecules interacting with water vapor in atmosphere can form stable gas-phase complexes of $(HF)_m \ldots (H_2O)_n$ type ($n + m \geq 2$) (see Table 3).

To analyze UF_6 trace amounts, a Fabri–Perrot tunable diode laser with $\lambda \sim 7.68$ μm wavelength was used (UF_6 $\nu_1 + \nu_3$ absorption band center). The total

Fig. 3. Experimental absorption Fourier-spectrum of the uranium hexafluoride sample (circles), and obtained model spectra of $^{238}UF_6$ (solid line) and $^{235}UF_6$ (dotted line) (*a*). Experimental absorption spectrum of uranium hexafluoride (circles) and model spectra of $^{238}UF_6$ (solid line) and $^{235}UF_6$ (dotted line) recorded with the use of DL (*b*).

As a result, the device prototype allowed measuring absorption with ~ 1% accuracy when assigning to ~ 10^{-4} cm^{-1} frequency. In principle, such an accuracy allows determination of the $^{235}UF_6$ concentration in hexafluoride with the same accuracy as well, but the actual accuracy is much lower because of admixtures deforming the spectrum. At any case, the device prototype assures distinctions between the natural and enriched uranium hexafluoride, that fits the preset technical conditions. This is clearly seen in Fig. 4, where a calibrating test of the gas-analyzer of isotope ratio in UF_6 calibration samples is presented (IAEA, UF_6 Loop in Seibersdorf, Vienna).

length of the detection optical path was 1.5 m. The UF_6 measurements were conducted in a prepassivated closed box made of stainless steel.

Table 3. Values of experimental (ν_{exp}) and calculated (ν_{calc}) vibrational frequencies for complexes $(HF)_m...(H_2O)_n$ and their preliminary assignment[12,16]

ν_{exp}	ν_{calc}	Assignment
	3740	$HF...H_2O$,
3726 w	3720	$(HF)_2...H_2O$
	3740, 3750	$(HF)_2...(H_2O)_2$, $(HF)_3...(H_2O)_3$
3676 b	3670	$(HF)_2...(H_2O)_2$
	3690	$(HF)_2...H_2O$
3665 b	3670	$(HF)_2...(H_2O)_2$
3655 b	3650	$HF...H_2O$
3643 m	3645, 3635	$(HF)_2...(H_2O)_2$
3625 s	3623	$HF...(H_2O)_2$
3607 s	3610	$HF...H_2O$, $(HF)_2...H_2O$
3471 b	3534	$(HF)_2...(H_2O)_2$
3453 w	3527	$(HF)_2...(H_2O)_2$
3429 w	3430	$(HF)_2...H_2O$
3403 w	3425	$HF...(H_2O)_2$
1620 b	1622, 1628	$(HF)_3...(H_2O)_3$,
1612 m	1607, 1610	$HF...(H_2O)_2$
	1601, 1600	$(HF)_2...H_2O$, $(HF)_2...(H_2O)_2$
1594 b	1595	$(HF)_2...(H_2O)_2$
	1590	$(HF)_2...(H_2O)_2$
	1591	$HF...H_2O$, $(HF)_2...H_2O$

N o t e . s is strong, m is mean, w is weak band; b is branch.

The threshold of the HF measurable concentration was lower than 2 ppb. When detecting UF_6, minimally recorded absorption magnitude was recalculated to ~ 50 m optical path length and made the concentration value of about 250 ppb. When using a quantum-cascade diode laser of $\lambda = 16\ \mu m$ wavelength (ν_3 absorption band), the gas-analyzer's sensitivity to UF_6 was estimated, which at $L \sim 50$ m turned to be lower than 30 ppt.

2.4. Study of the uranium hexafluoride hydrolysis process

It was stated during the experiment that after UF_6 injection, a quick (≈ 2 s) mixing of the UF_6–N_2 mixture with initial atmosphere in the box took place, and the UF_6 pressure in the box reached 0.9 mm Hg. For 25 s the pressure fell to 0.1–0.2 mm Hg, while the HF pressure grew from 0 to ≈ 4 mm Hg. Thus, an approximate equilibrium of UF_6 and HF concentrations was observed during the hydrolysis process, which is described by relation (2).

Preliminary results on uranium hexafluoride hydrolysis under conditions close to actual atmosphere are presented in Fig. 5.

At the next stage of the research the authors plan to conduct experiments with the use of quantum-cascade diode lasers of $\lambda = 16\ \mu m$ wavelength ($\nu = 626\ cm^{-1}$), which will allow decreasing the threshold detection of UF_6 in atmosphere to several tens of ppt, because UF_6 ν_3 band center is located in this
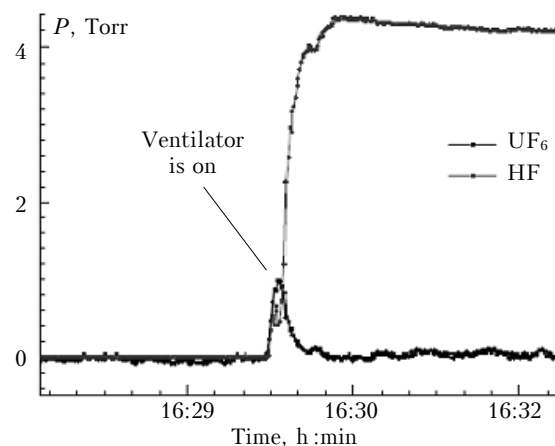
Fig. 5. Results of experiment on uranium hexafluoride hydrolysis.

range, where the integral absorption coefficient is almost three orders of magnitude higher then the same magnitude for the uranium hexafluoride $\nu_1 + \nu_3$ band.

Conclusion

Application of principles of diode laser spectroscopy allows us to advantageously conduct express room-temperature measurements of the uranium hexafluoride isotope composition, as well as HF and UF_6 trace amounts under conditions of actual atmosphere with sufficient reliability and accuracy.

A laboratory prototype of the device based on DL has been designed and calibrated. It allows measurements of gaseous UF_6 isotope composition with errors lower than 0.27% at close-to-room temperatures.

The measured threshold of HF concentrations, when using the Chernin multi-pass cell and near infrared DL ($P2$ line of HF ν_2 band; $\lambda = 1.31\ \mu m$), turned out to be less than 2 ppb.

When detecting UF_6 with mid-infrared diode laser ($\lambda \sim 7.6\ \mu m$), minimal magnitude of the recorded absorption was recalculated to a 50 m optical path length and the concentration value made about 250 ppb. The gas-analyzer sensitivity to UF_6 was estimated, when using a 16 μm DL (ν_3 absorption band), and at $L \sim 50$ m it turned out to be lower than 30 ppt. The concentrations of the molecules under study obtained by us, are acceptable for atmospheric monitoring in the vicinity of nuclear plants.

References

1. Sh.Sh. Nabiev and Yu.N. Ponomarev, Atmos. Oceanic Opt. **11**, No. 12, 1093–1098 (1998).
2. A.P. Babichev, G.Yu. Grigoriev, S.L. Malyugin, Sh.Sh. Nabiev, A.I. Nadezhdinskii, Ya.Ya. Ponurovskii, and D.B. Stavrovskii, in: *Abstracts of IX Conference on Physical-Chemical Processes at Selection of Atoms and Molecules,* Zvenigorod (2004), p. 64.
3. A.I. Nadezhdinskii, Ya.Ya. Ponurovskii, D.B. Stavrovskii, G.Yu. Grigoriev, and Sh.Sh. Nabiev, in: *Abstracts of Reports at Conference on Analytical Chemistry "Analytics of Russia,"* Moscow (2004), p. 116.

4. A.I. Nadezhdinskii, Ya.Ya. Ponurovskii, D.B. Stavrovskii, G.Yu. Grigoriev, and Sh.Sh. Nabiev, in: *Abstracts of Reports at Conference on Analytical Chemistry "Analytics of Russia,"* Moscow (2004), p. 124.
5. A.I. Nadezhdinskii, Ya.Ya. Ponurovskii, G. Bosler, R. Olsen, V. Ryjikov, Yu. Selivanov, N. Gorshunov, G. Grigoriev, and Sh. Nabiev, in: *Proceedings of VIII Conference on Physical-Chemical Processes at Selection of Atoms and Molecules* (CSRIAtominform, Moscow, 2003), p. 245.
6. A. Nadezhdinskii, Ya. Ponurovskii, G. Bosler, R. Olsen, V. Ryjikov, Yu. Selivanov, N. Gorshunov, G. Grigoriev, and Sh. Nabiev, in: *Abstracts of IV Int. Conf. on Tunable Diode Laser Spectroscopy,* Zermatt (2003), p. 105.
7. A. Nadezhdinskii, I. Vyazov, T. Moskalev, D. Namestnikov, Yu. Ponomarev, Ya. Ponurovskii, D. Stavrovskii, G. Grigoriev, and Sh. Nabiev, in: *Abstracts of XI Int. Symp. on Atmospheric and Ocean Optics. Atmospheric Physics,* Tomsk (2004), p. 53.
8. A. Nadezhdinskii, Ya. Ponurovskii, Yu. Selivanov, G. Grigoriev, Sh. Nabiev, G. Bosler, R. Olsen, and V. Ryjikov, in: *Abstracts of Conference on Analytical Chemistry "Analytics of Russia,"* Moscow (2004), p. 124.
9. E. Chizhevskii, V. Kopylov, S. Oskina, Ya. Ponurovskii, Yu. Selivanov, E. Stepanov, and V. Trofimov, in: *Proceedings of II International Conf. on Tunable Diode Laser Spectroscopy,* Moscow (1998), p. 41.
10. A. Nadezhdinskii, Ya. Ponurovskii, and M. Spiridonov, Kvant. Elektron. **29**, No. 1, 78–82 (1999).
11. I.V. Tananaev, N.S. Nikolaev, Yu.A. Luk'yanychev, et al., *Chemistry of Fluoride Compounds of Actinides* (Izd. Akad. Nauk USSR, Moscow, 1963), 227 pp.
12. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, *Structure and Properties of Water Molecular Complexes with Minor Gaseous Constituents of the Atmosphere* (Publishing House of IAO SB RAS, Tomsk, 2003), 139 pp.
13. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, in: *Abstracts of Int. Symp. on Current Problems in Atmospheric Radiation,* St. Petersburg (2000), p. 141.
14. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, in: *Abstracts of the NATO Advanced Research Workshop Spectroscopy from Space,* Bratislava (2000), p. 55.
15. Sh.Sh. Nabiev, N.A. Zvereva, S.K. Ignatov, Yu.N. Ponomarev, P.G. Sennikov, V.I. Starikov, K.M. Firsov, B.A. Fomin, and E.A. Zhitnitskii, in: *Abstr. of VII Int. Symp. on Atmospheric and Ocean Optics. Atmospheric Physics,* Irkutsk (2001), p. 94.
16. N.A. Zvereva, Sh.Sh. Nabiev, A.I. Nadezhdinskii, Yu.N. Ponomarev, D.B. Stavrovskii, S.M. Chernin, and T.A. Shubenkina, Atmos. Oceanic Opt. **14**, No. 12, 1009–1011 (2001).
17. R.S. McDowell, L.B. Asprey, and R.T. Paine, J. Chem. Phys. **61**, No. 9, 3571 (1974).
18. Sh.Sh. Nabiev, *"Vibrational spectra and structure of metal halides* (Hal = F, Cl) *in vapor state,"* Preprint No. 5310/12, IAE, Moscow (1991), 87 pp.
19. Sh.Sh. Nabiev and V.D. Klimov, Mol. Phys. **81**, No. 2, 395–408 (1994).