

Quantum cascade laser absorption spectroscopy of UF₆ at 7.74 μm for analytical uranium enrichment measurements

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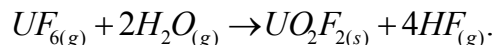
ABSTRACT

The $\nu_1+\nu_3$ combination band of uranium hexafluoride (UF₆) is targeted to perform analytical enrichment measurements using laser absorption spectroscopy. A high performance widely tunable EC-QCL sources emitting radiation at 7.74 μm (1291 cm⁻¹) is employed as an UF₆-LAS optical source to measure the unresolved rotational-vibrational spectral structure of several tens of wavenumbers (cm⁻¹). A preliminary spectroscopic measurement based on a direct laser absorption spectroscopy of methane (CH₄) as an appropriate UF₆ analyte simulant, was demonstrated.

Keywords: Laser absorption spectroscopy, quantum cascade laser, uranium hexafluoride (UF₆) enrichment, quartz enhanced photoacoustic spectroscopy

1. INTRODUCTION

Mid-infrared laser absorption spectroscopy (LAS) based on the state-of-the art quantum cascade laser technology offers the opportunity to detect, quantify and monitor, both in-situ and remotely, molecular species at trace gas concentration levels. The feasibility of non-contact isotopic measurements for reliable sensor platforms, capable of sensitive measurements of atmospheric releases from uranium enrichment plants, employing the LAS technique are of special interest to the US Department of Energy (DoE) and the International Atomic Energy Agency (IAEA) charged with detection and verification of nuclear materials and activities on a global basis [1,2]. The most widely used technologies for separating ²³⁵U isotope from ²³⁸U isotope involves either gaseous diffusion or centrifugation of UF₆ as the starting material. The uranium isotope separation process has a significant industrial importance in fabrication of the uranium fuel for nuclear power reactors and uranium based nuclear weapons. Industrial-scale production of enriched uranium is likely to generate UF₆ leaks into the environment. It is well known that UF₆ is a chemically aggressive species that can strongly react with water in the atmosphere. Moreover, in the presence of H₂O (including H₂O vapor) UF₆ forms HF gas and solid uranyl fluoride (UO₂F₂) through the following exothermic reaction:



Liquid UF₆ does not normally exist at atmospheric pressure and hence a release of liquid UF₆ from a tank will immediately convert into gaseous and solid forms which will continue to react exothermically, increasing the likelihood of human exposure or persistence in the atmosphere. In fact there are several documented cases of UF₆ releases due to leaks or cylinder ruptures that have resulted in loss of life due to HF inhalation [3]. Therefore, trace monitoring of both UF₆ and HF will provide safety for production and storage facilities as each species is indicative of possible uranium enrichment activities [4,5].

Currently, the IAEA verifies the ²³⁵U material balance at enrichment facilities using costly and time consuming environmental sampling, high resolution gamma spectroscopy systems, or destructive analysis by thermo ionization mass spectrometry at the IAEA Safeguards Analytical Laboratory. In-situ measurements with real time data analysis of ²³⁵U material by implementation of the LAS technique for an accurate uranium enrichment determination of UF₆

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samples appears to be an attractive replacement for the IAEA currently used methods. Therefore the IAEA initiated in 2006 the development of LAS technology for field deployable instrumentation for use at enrichment sites. To achieve this objective, the feasibility at the required level of accuracy has to be demonstrated and the technology needs to be robust, compact, sensitive and selective to meet IAEA and US DoE specifications. LAS was already demonstrated as a spectroscopic technique capable of accurate uranium enrichment determination on ^{235}U in UF_6 gas samples [4,6].

The UF_6 molecule has no absorption bands in the near infrared and unlike small molecules, the absorption spectrum of UF_6 is broadband with unresolved rotational-vibrational spectral structure covering several tens of wavenumbers (cm^{-1}). The UF_6 molecule has six fundamental bands located within $186\text{--}667\text{ cm}^{-1}$ region. Two mid-IR combination bands which can be potentially used for the uranium hexafluoride quantification are located at $\sim 852\text{ cm}^{-1}$ ($\nu_1 + \nu_4$) and $\sim 1291\text{ cm}^{-1}$ ($\nu_1 + \nu_3$). Hence, a mid-infrared spectroscopic source is needed for an optical UF_6 sensor. Currently available commercial quantum cascade laser (QCL) technology favors the $\sim 8\text{ }\mu\text{m}$ wavelength spectral region. Therefore, for this project the $\nu_1 + \nu_3$ combination band of UF_6 , centered at $\sim 1291\text{ cm}^{-1}$ ($\lambda = 7.75\text{ }\mu\text{m}$) was targeted. In the future mid-infrared QCL technology will allow us to access the longer wavelengths UF_6 combination band at $11.8\text{ }\mu\text{m}$ ($\nu_1 + \nu_4$) and the less congested fundamental band at $16\text{ }\mu\text{m}$ (ν_3).

The impact of the uranium isotope in the UF_6 molecule on its vibration characteristics is small and leads to an isotopic shift of only 0.59 cm^{-1} in the $\nu_1 + \nu_3$ combination band in the 1291 cm^{-1} region [4-6]. This means that the enrichment determination cannot be obtained from the ratio of absorption peaks but requires a linear convolution of the $^{235}\text{UF}_6$ and the $^{238}\text{UF}_6$ absorption cross-sections. This can be realized with the availability of mid-infrared continuous wave (CW) thermoelectrically cooled (TEC) QCLs with broadband tuning capabilities provided by external cavity (EC)-QCLs.

2. FP-QCL EVALUATION IN AN EXTERNAL CAVITY CONFIGURATION FOR UF_6 ANALYTICAL ENRICHMENT MEASUREMENTS

We developed a general purpose opto-mechanical platform for the evaluation of high performance Fabry Perot (FP) QCL chips (Fig. 1). A FP-QCL chip, placed in this testing platform, operates in a quasi-Littrow configuration, where the QCL front facet radiation is diffracted from a 135 grooves/mm and $10.6\text{ }\mu\text{m}$ blazed wavelength diffraction grating.

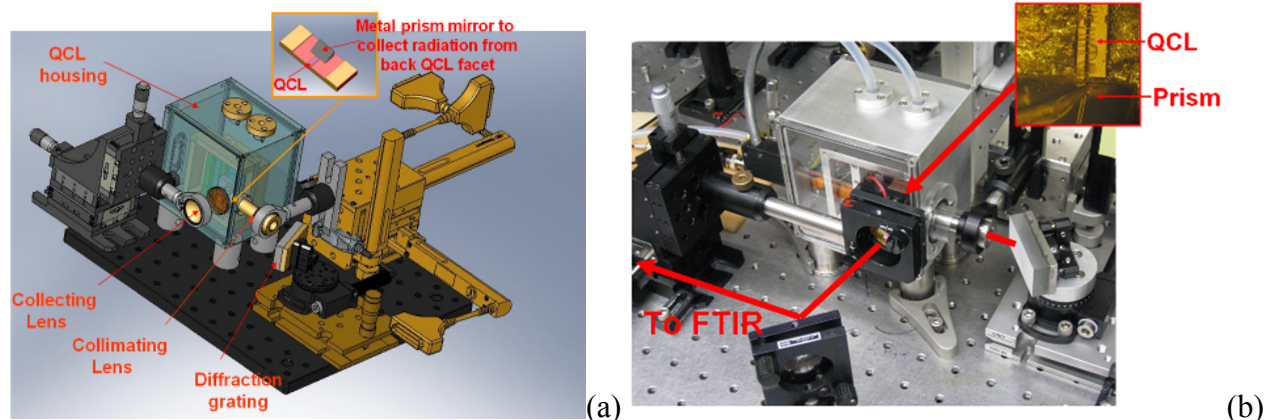


Figure 1. Schematic (a) and a completed design (b) of a user friendly opto-mechanical platform for testing mid-infrared high performance CW thermoelectrically cooled FP-QCL gain chips.

For this quasi EC configuration, the first order of diffraction provides feedback to the QCL, whereas the zeroth order of diffraction, which can be used as an output beam, is dislocated after each change of the diffraction grating angle. In addition we have access to the radiation emitted from the QCL back facet which can alternatively be used for evaluation of the mid-IR source. Access to the QCL back facet radiation is realized by a small $3\times 3\times 3\text{ mm}$ prism mirror located adjacent to the QCL surface. The laser beam, after reflection from a prism mirror, is collected by a 1.2 inch diameter ZnSe lens and sent to FTIR for spectral analysis. The housing was flushed continuously with pure nitrogen in order to avoid water condensation or ice formation on the FP-QCL chip, which was operated at -30°C . We tested several uncoated and high reflectivity (HR) coated $7.74\text{ }\mu\text{m}$ FP-QCL chips focusing on basic critical QCL parameters such as: wavelength tunability, optical power and threshold value for each analyzed QCL. The best performing laser chip, a HR coated 2 mm cavity length $7.74\text{ }\mu\text{m}$ FP-QCL (A758BH2_I) (see Fig. 2), has a frequency tuning range of 79.6 cm^{-1} . The

zeroth order optical power was $\sim 20\text{mW}$ at 500mA laser current, when laser frequency was set at 1301.55 cm^{-1} . For this optical power measurement the zeroth order of diffraction was used, because of the low intensity radiation emitted from the HR coated back facet of the FP-QCL and the limited prism mirror coupling efficiency. Currently some of the best performing FP-QCL chips undergo AR coating deposition processes. AR coating of the front facet increases the coupling efficiency of the EC which in turn increases the tuning range of the EC-QCL. By comparing QCL performance before and after AR coating deposition it will be possible to optimize conditions for the critical AR coating process. The acquired information should result in a significant reduction of QCL fabrication time and cost.

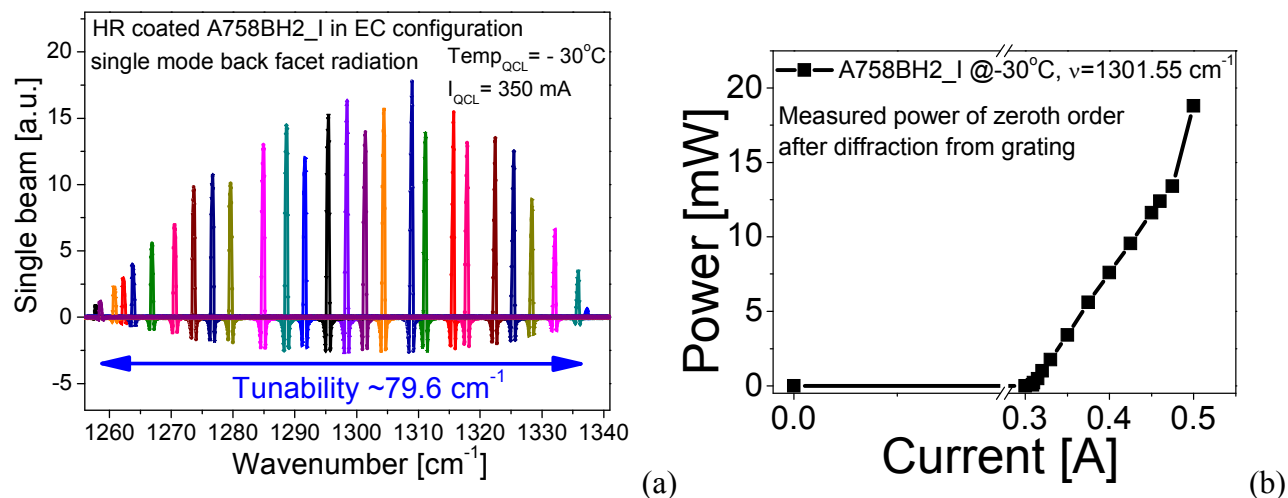


Figure 2. Single mode frequency tuning range (a) and zeroth order optical power (b) for HR coated CW $7.74\text{ }\mu\text{m}$ FP-QCL (A758BH2_I) in EC-configuration @ -30°C .

Figure 3 depicts a FTIR recorded multimode radiation spectrum of one of the tested FP-QCL chip (A758BHB1) without the EC compared to single mode radiation spectra for the same laser implemented into an EC configuration. The single mode spectral frequency tuning range of the tested FP-QCL (A758BHB1) covers the $\nu_1 + \nu_3$ UF_6 combination band at $\sim 1291\text{ cm}^{-1}$ and several methane (CH_4) and acetylene (C_2H_2) absorption lines. As mentioned above the spectroscopic detection of CH_4 and C_2H_2 molecules serve as an appropriate simulant for UF_6 . The uranium hexafluoride absorption spectrum [4] and HITRAN simulated spectra for 100 ppm of CH_4 and C_2H_2 concentrations within the available wavelength tuning range are shown in Figure 4.

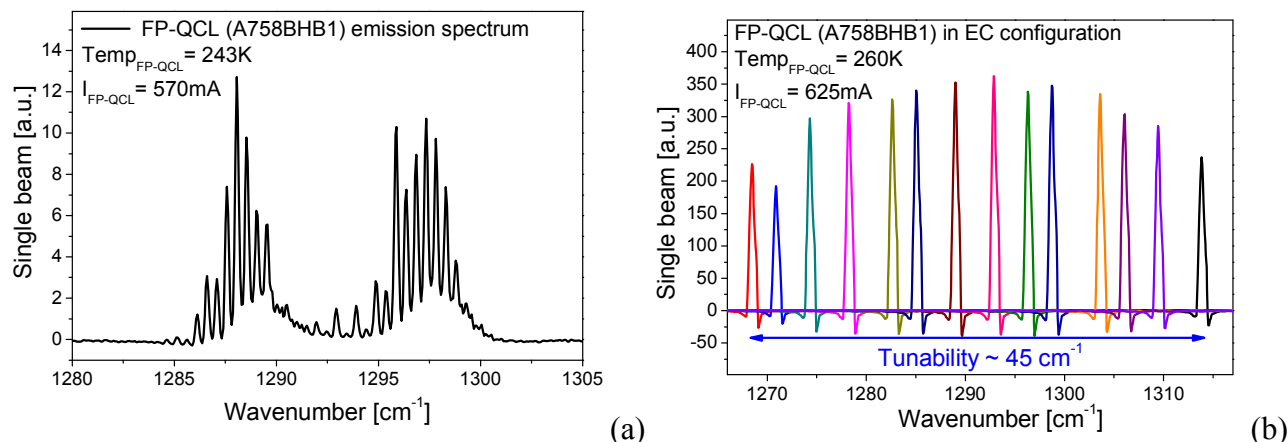


Figure 3. Multimode radiation spectrum for FP-QCL (A758BHB1) recorded by FTIR (a) and FTIR single mode spectra with the same laser implemented into EC configuration (b).

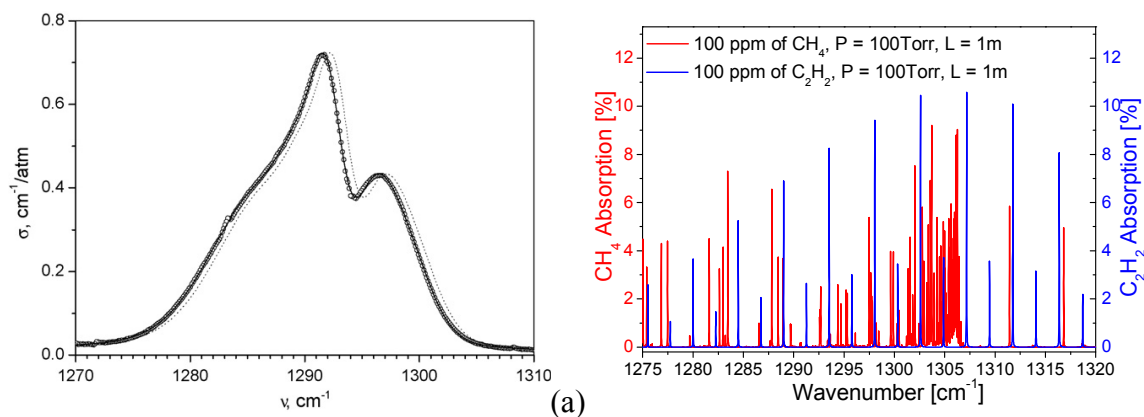


Figure 4. Spectrum of absorption cross-section σ of an analyzed uranium hexafluoride sample (circles) as well as the obtained model spectra of $^{238}\text{UF}_6$ (solid line) and $^{235}\text{UF}_6$ (dotted line) [4] (a); HITRAN simulation for 100 ppm of CH_4 and C_2H_2 concentrations within the available FP-QCL (A758BHB1) tuning range (b). The spectra were simulated at a 100 Torr pressure and 1 meter pathlength.

3. EXPERIMENTAL SETUP AND RESULTS

To perform a high resolution spectroscopic measurements a FP-QCL chip (A758BHB1 shown in Figure 3) was placed in Littrow type configured external cavity (EC) system platform providing independent control of the EC length, diffraction grating angle and laser current [7]. This EC-QCL system has been used before for sensitive detection of both small molecules (NO and N_2O) as well as complex, broadband absorbing molecules such as Freon 125 and acetone with different laser spectroscopy techniques [8,9]. A schematic configuration of the EC-QCL based system for direct absorption spectroscopy measurements of CH_4 molecule is shown in Fig. 5. A collimated EC-QCL output beam (3mm in diameter) is modulated by a mechanical chopper at ~ 4 kHz. A 20 cm long reference gas cell, filled with 0.5% of CH_4 at 120 Torr, was located between a mechanical chopper and pyroelectric detector.

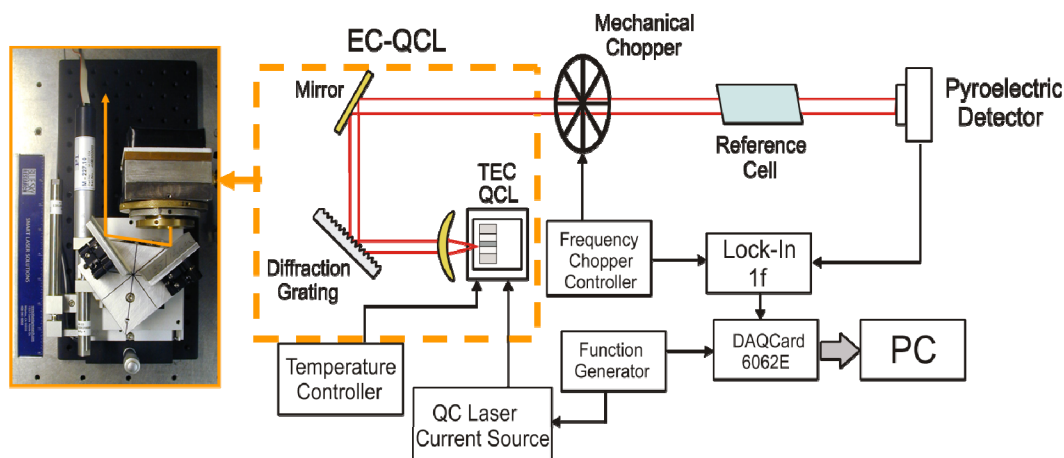


Figure 5. Schematic of an EC-QCL based LAS sensor system for CH_4 measurements.

Figure 6b depicts preliminary result of CH_4 detection. During this measurement the EC-QCL current value was set at $\sim 550\text{mA}$. The LAS measurement was acquired by performing a mode-hop-free tuning over 0.4 cm^{-1} with 1 Hz wavelength scan repetition frequency. The recorded spectrum of CH_4 absorption lines near 1303.5 cm^{-1} , was averaged 100 times and compared with HITRAN spectroscopic database shown in Fig. 6 a.

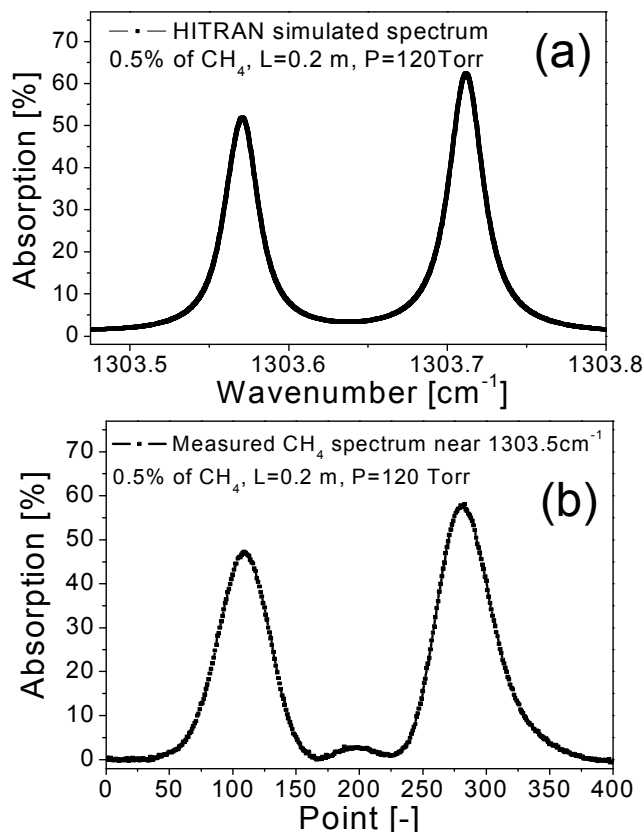


Figure 6. HITRAN simulated spectrum (a) compared with direct absorption spectroscopy for CH₄ molecule in the vicinity of 1303.5 cm⁻¹ (b).

Quartz enhanced photoacoustic spectroscopy (QEPAS) as a practical, sensitive and compact detection technique will be employed for enrichment verification measurements of UF₆ molecule. This approach to photoacoustic detection of trace gases utilizing a quartz tuning fork (QTF) as a sharply resonant acoustic transducer was first reported in 2002 [10,11]. In general, PAS technique relies on the detection of the sound waves following the heating of gas by optical radiation. The basic idea of QEPAS is to invert the more common PAS approach and accumulate the acoustic energy not in a gas-filled cell but in a sharply resonant acoustic transducer. A natural candidate for such a transducer is a low loss, piezoelectric quartz crystal. A nearly optimum, readily available transducer can be found in quartz tuning forks (QTF) intended for use in electronic clocks and watches as frequency standards. The QTFs typically resonate at 32,768 (2¹⁵) Hz in clock circuits. A typical design of the QEPAS based spectraphone and its practical module for mid-IR sensor applications is shown in Figure 7. The laser radiation is focused between the prongs of the QTF. Generally, for amplitude modulation (AM) or 2f wavelength modulation (WM) the intensity or the wavelength of the excitation beam must be modulated in such a way that the energy input into the gas is modulated at the resonant frequency of the QTF, f_0 or $f_0/2$ respectively. The modulated energy input results in a periodic expansion-contraction of the gas volume overlapping with the excitation beam. The acoustic wave at f_0 induced by absorption of the laser radiation by the gas medium causes mechanical vibrations of the QTF. Due to the piezoelectric effect in a quartz crystal, the QTF deformation leads to separation of electrical charges on its surfaces. These charges are then collected by metal electrodes deposited on the QTF, and produce measurable electrical signals even for extremely small, $<10^{-11}$ cm, displacements of the QTF prongs. The electrodes are configured in such a way that only the anti-symmetric mode of QTF vibration (prongs moving in opposite directions) is electrically active. This design results in the important QTF property of being a spatially selective microphone. The electrical signal produced by this mode of vibration is amplified by an ultra-low noise pre-amplifier

prior to a lock-in detection measurement. A gas-filled acoustic micro-resonator formed by two rigid tubes is usually added for QEPAS signal enhancement. The micro-resonator can increase the QEPAS sensitivity up to 20 times based on specific target molecular species.

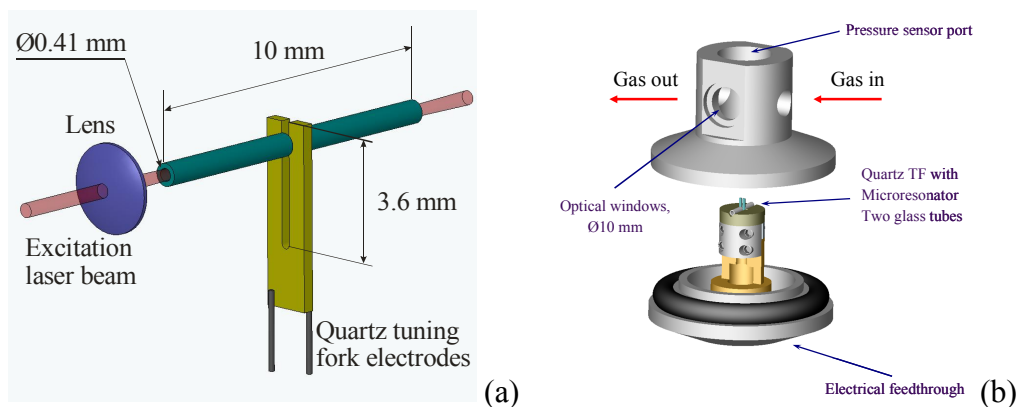


Figure 7. Design of a QEPAS based spectraphone (a) and its practical module for mid-IR sensor applications (b)

Advantages of QEPAS compared to conventional resonant photoacoustic spectroscopy include QEPAS sensor immunity to low environmental acoustic noise, a simple and rugged spectraphone, and the capability to analyze small gas samples, down to 1 mm^3 in volume. QEPAS possesses a remarkably large dynamic range of 9 orders of magnitude of the acoustic signal, its noise is limited by the fundamental Johnson thermal noise of the QTF, and long averaging times (up to 3 hours were demonstrated) can be used to improve the QEPAS signal to noise ratio. This is particularly attractive and robust technology for development of sensitive, light-weight, compact sensor systems that can be installed permanently in the IAEA audited facilities or in the form of portable systems could be easily carried and used by IAEA inspectors. QEPAS sensor technology has already been applied to detection of >14 different molecular species, both with pulsed and CW NIR and MIR semiconductor laser excitation sources.

In the future we plan to implement a high performance CW RT DFB-QCL from AdTech Optics, designed to emit radiation $\sim 1291 \text{ cm}^{-1}$ with an emitted optical power >150 mW (Figure 8). This will significantly improve sensitivity for the AM-QEPAS technique, which scales linearly with power of the laser source. In addition small size housing and room temperature operation of the AdTech QCL is beneficial in design of a compact and water cooling free sensor system.

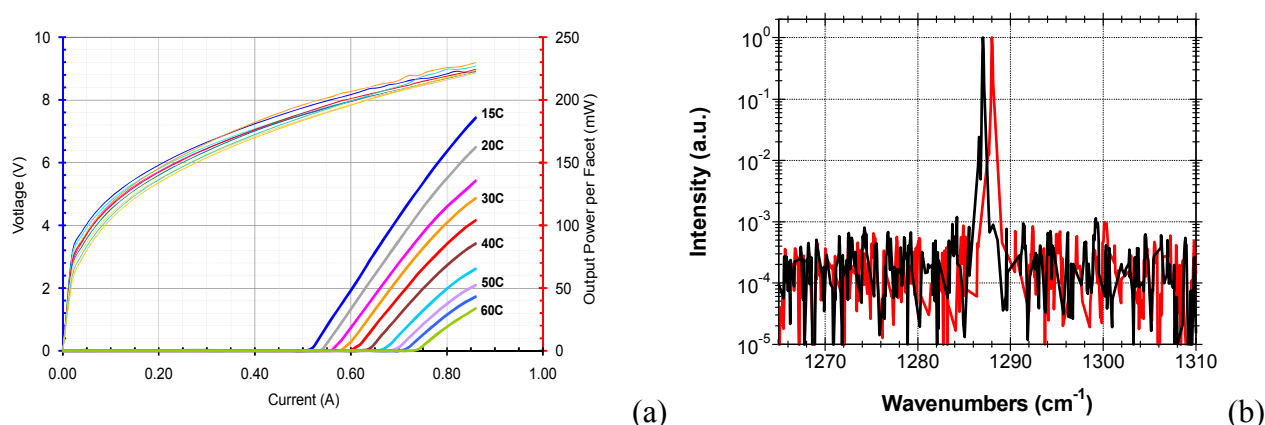


Figure 8. LIV curve (a) and emission spectra at two different currents (b) for the AdTech Optics $7.74 \mu\text{m}$ CW DFB QCL.

4. SUMMARY

An optical spectroscopic sensors based on either high performance cw TEC DFB QCL or widely tunable EC-QCL source emitting radiation at $7.74\text{ }\mu\text{m}$ (1291 cm^{-1}) have a potential for detection and verification of nuclear materials and activities, especially for the determination of ^{235}U enrichment in UF_6 gas. The single mode spectral frequency tuning range of the tested FP-QCLs, covering the $\nu_1 + \nu_3$ UF_6 combination band at $\sim 1291\text{ cm}^{-1}$, was demonstrated. A preliminary LAS measurement for two CH_4 absorption lines near 1303.5 cm^{-1} , was performed with a 0.4 cm^{-1} mode-hop-free tuning range. Quartz enhanced photoacoustic spectroscopy (QEPAS), employing an amplitude modulation (AM) technique, can be employed for the precise, sensitive, selective and fast trace gas detection of UF_6 (tested with its simulants, C_2H_2 and CH_4). For the QEPAS technique, amplitude modulation can be performed either by an on-off modulation of the QCL current or by using an additional quartz tuning fork, which when supplied with a voltage can act as a mechanical chopper at 32 kHz.

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