Mid-infrared laser based trace gas sensor technologies: recent advances and applications

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http://www.rice.edu/~laserap/

“Curiosity” Landed on Mars on August 6, 2012

Laser-Based Trace Gas Sensing Techniques

- Optimum Molecular Absorbing Transition
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (Mid-IR)
- Long Optical Pathlength
  - Multipass Absorption Gas Cell (e.g., White, Herriot, Chemin, Aera Technologies, and Circular Cylindrical Multipass Cell
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector or back scattering from topographic target): Standoff and Remote Detection
  - Fiberoptic & Wave-guide Evanescent Wave Spectroscopy
- Spectroscopic Detection Schemes
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic & Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

Other Spectroscopic Methods

- Faraday Rotation Spectroscopy (limited to paramagnetic chemical species)
- Differential Optical Dispersion Spectroscopy (DODiS)
- Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)
- Frequency Comb Spectroscopy
- Laser Induced Breakdown Spectroscopy (LIBS)

HITRAN Simulated Mid-infrared Molecular Absorption Spectra
Selection of Absorption lines in the mid-IR Spectral Range (3–5 μm)

- 2.5 μm < λ < 5 μm (4000 cm⁻¹ - 1900 cm⁻¹)
- Access to molecular fundamental rotational-vibrational states
- Atmospheric window (3.5–4.8 μm)

Applications
- Medicine
- Sensing
- Emission monitoring
- Process control
- Free-space communication
- Defense
- Homeland security

Mid-IR Source Requirements for Laser Spectroscopy

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
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<tr>
<td>Sensitivity (ppb to ppt)</td>
<td>Optimum Wavelength and Power</td>
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<tr>
<td>Selectivity (Spectral Resolution) or Specificity</td>
<td>Stable Single Mode Operation and Narrow Linewidth</td>
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<td>Multi-gas Components, Multiple Absorption Lines, and Broadband Absorbers</td>
<td>Mode Hop-Free Wavelength Stability</td>
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<td>Directionality or Cavity Mode Matching</td>
<td>Beam Quality</td>
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<tr>
<td>Rapid Data Acquisition</td>
<td>Fast Time Response Time</td>
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<tr>
<td>Room Temperature Operation</td>
<td>High Wall Plug Efficiency, No Cryogenics or Cooling Water</td>
</tr>
<tr>
<td>Field Deployable in Harsh Environments</td>
<td>Compact and Robust</td>
</tr>
</tbody>
</table>

Key Characteristics of Mid-IR QCL & ICL Sources – March 2016

- Band structure engineered devices
- Emission wavelength is determined by layer thickness – MBE or MOCVD. QCLs operate in the 3–24 μm spectral region and ICLs can cover the 3 to 5 μm spectral range.
- Narrow linewidth, tunable, and continuously variable.
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength devices
- Wide spectral tuning ranges in the mid-IR
  - 1.5 cm⁻¹ using injection current control for DFB devices
  - 10–30 cm⁻¹ using temperature control for DFB devices
  - 10–20 cm⁻¹ using current and temperature control for QCLs (DFB–DQW–HBT)
  - 52 cm⁻¹ (220 Å) using an external grating element and FP cavity
- High indium and CW powers of QCLs and ICLs at TECRT temperatures
  - Room temperature peak power of ~ 300 W with 10% wall plug efficiency for QCLs
  - ~ 1 W CW DFB ECHELON QCL, wall plug efficiency 25% at 4.6 μm
  - ~ 500 mW CW DFB ICL at TECRT on the 3 to 4 μm (water) range

A miniaturized External Cavity QCL with MEMS Technology

- Optical output power: P > 45 mW @ 1585 cm⁻¹
- SMSR > 20 dB

Methane Detection

Methane is one of the major atmospheric greenhouse gases contributing to global warming and climate change.

- Global warming potential (GWP) of 25 compared to GWP of 1 for CO₂ for a 100-year period
- Short lifetime in the atmosphere (~12 yrs) compared to CO₂ and N₂O
- Atmospheric background concentration ~1 ppm
Typical Texas Oil & Gas Production Site near Houston

The result of a sequence of four tracking injections obtained by directional drilling which creates horizontal production in the target stratum is depicted in a figure as published in Physical Today 2016. A DOE ARPA-E funded methane detection project at 3.3 nm was started in 2015 Texas located well pad sites typically measure 10-30 m with 1 m spatial resolution.

Comparison of proposed Rice CH₄ Sensor System and current commercially available CH₄ Sensor Platforms

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Rice</th>
<th>PharSys ABL-AG I</th>
<th>ABL-AG II</th>
<th>Aerodyne</th>
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</thead>
<tbody>
<tr>
<td>Opt. Path length and method</td>
<td>50 m (DLAS)</td>
<td>200 m (DLAS)</td>
<td>200 m (DLAS)</td>
<td>200 m (DLAS)</td>
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<tr>
<td>Sensitivity</td>
<td>6.3 ppm</td>
<td>1.2 ppm</td>
<td>2 ppm</td>
<td>2 ppm</td>
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<tr>
<td>Accuracy (ppm)</td>
<td>±2 ppm</td>
<td>±2 ppm</td>
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<tr>
<td>Cell Volume</td>
<td>40 L</td>
<td>20 L</td>
<td>500 L</td>
<td>400 L</td>
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<tr>
<td>Pump Size (inlet)</td>
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<td>&lt;1 Lpm</td>
<td>&lt;1 Lpm</td>
<td>&lt;1 Lpm</td>
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<tr>
<td>Cond. Methane</td>
<td>95% - 99%</td>
<td>&gt;95.99%</td>
<td>&gt;95.99%</td>
<td>&gt;95.99%</td>
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<tr>
<td>Power Consumption</td>
<td>20 W</td>
<td>100 W</td>
<td>100 W</td>
<td>100 W</td>
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<tr>
<td>Weight</td>
<td>4 kg</td>
<td>10 kg</td>
<td>15 kg</td>
<td>40 kg</td>
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<tr>
<td>Cost</td>
<td>$10,500 USD</td>
<td>$40,800 USD</td>
<td>$10,000 USD</td>
<td>$19,000 USD</td>
</tr>
</tbody>
</table>

Beer's Law: \( I_o = I_e \exp(-k \cdot L) \)

where: \( I_o \) is transmitted light intensity, \( I_e \) is incident light intensity, \( k \) is absorption coefficient, \( L \) is optical path.

Multispectroscopy Fundamentals

Spectroscopy Fundamentals

Multipass Gas Cell (MPGC):

The minimum detection limit can be improved by increasing the effective optical path without increasing the physical length.

3D Rice LSG simulation of a multipass cell

Based on RLSG custom software

(L=100mm R=10mm D=15mm)

CH₄ Absorption Line Selection

- The fundamental \( v_1 \) and \( v_2 \) CH₄ bands are located at 7.7 μm and 3.3 μm, respectively.
- A high detection sensitivity for methane measurements using quantum cascade lasers (QCLs) at 7.7 μm was previously reported.
- Compact, TEC, CW, DFIR ICLs emitting at 3-μm wavelengths became recently commercially available.
- An interference-free CH₄ absorption line located at 3081.5 cm⁻¹ was selected as the optimum target absorption line.
- The 3.3 μm CH₄ absorption line can be used at atmospheric pressure.

ICL Characterization & Performance Evaluation

Nanoplus ICL, 3.291 μm center-wavelength

Performance evaluation for a 3.291-μm CW RT ICL at different operating temperatures and injection currents. (a) ICL output power response curves; (b) Emission wavelength curves.

Current tuning rate: -0.332594 cm⁻¹/mA; Temperature tuning rate: -0.23994 cm⁻¹/C
Data Processing for CH$_4$ Detection

A 4-step algorithm for CH$_4$ detection:
- 150 spectra were averaged
- Baseline of the spectral scan was fitted and eliminated
- Linearized spectrum using fringe spacing of a germanium etalon
- Lorentzian line shape fitting to retrieve concentration information

Interference-free absorption line of CH$_4$ at 3038.5 cm$^{-1}$ obtained from laboratory air at atmospheric pressure together with a fitted baseline and a transmission signal from a germanium etalon.

Allan-Werle Deviation Analysis

An Allan-Werle deviation plot was acquired in a time period of ~1.5 hours using a certified 2 ppm CH$_4$ cylinder with a 1 Hz sampling rate.

1-s measurement precision is $\sigma = 10.53$ ppb
60-s measurement precision is $\sigma = 1.43$ ppb

Stationary Laboratory Measurements

CH$_4$ concentrations measured over a 7-day period in ambient air on the Rice University campus during May 2015.

Laboratory Stationary Measurements

Diurnal variations of CH$_4$ mixing ratio. Bottom whisker, bottom box line, top box line and top whisker indicate the 5th, 25th, 75th and 95th percentile, respectively. Line inside the boxes and continuous solid line represent the hourly median and mean of the data, respectively.

The diurnal profile of the methane concentration shows an increase in concentration during the early morning with a subsequent gradual decrease after ~8:00 am CDT to its typical background level of ~1.87 ppm in the Greater Houston area in May 2015.
Recent mobile Field Tests: December 2015

CH4 concentrations measured for a sampling period of ~10 minutes at a Clean Energy CHG O’Rourke Natural Gas Station in Houston, TX.

CH4 Sensor System Summary (2015-2016)

- A 3.291 μm CW room-temperature ICL based absorption sensor was developed for methane detection using a 54.6 m optical path length multipass gas cell.
- A two-floor mechanical design with a folded optical path resulted in a sensor system dimension of 32 x 20 x 17 cm³.
- Good electrical power management resulted in a low power consumption of the CH4 sensor system: 6 W.
- A minimum detectable Limit (MDL) of 10.5 ppb for CH4 with a 1 sec integration time was achieved.
- Laboratory measurements and mobile-mode field tests were conducted and results demonstrate the suitability of the sensor system to generate CH4 spatial distributions in a typical U.S. urban area and at an oil and gas storage facility in Houston, TX.

Portable three Line Methane Sampling System for Laboratory and Field Deployment

Motivation for mid-infrared Ethane (C2H6) Detection

- Application in medical breath analysis
  - Asthma
  - Schizophrenia
  - Lung cancer
  - Vitamin E deficiency
- Atmospheric chemistry and climate
  - Fossil fuel and biofuel consumption
  - Biomass burning
  - Vegetation/soil
  - Natural gas loss

C2H6 Detection with a 3.36 μm CW DFB Diode Laser using a novel compact Multipass Absorption Cell and Control Electronics

Improved C2H6 sensor system using novel MPGC and a 3.337 μm CW, DFB ICL

The system shown surrounded by red dual line is the detection scheme using direct absorption spectroscopy (DAS) technique, and the lower part surrounded by blue dotted line is the detection scheme using several harmonics wavelength modulation spectroscopy (WMS) technique. ICL: infrared diode laser; DI: direct injection; M: modulator; MP: probe; MPGC: multipass gain cell; DFB: distributed feedback laser.

Minimum detectable C2H6 concentration: 7.0 ppbv (1σ for 99% confidence) was obtained, which is limited by entrance slits due to saturated detector. A detection limit of 2.99 ppbv for a data acquisition time of 10 sec with the use of WMS compared with 77.7 ppbv with DAS can be realized.
Motivation for mid-infrared Formaldehyde Detection

- Atmospheric chemistry and climate
  - Important volatile organic compound (VOC) present in all regions of the atmosphere which reacts in the presence of sunlight to yield ozone.
  - Primary H$_2$CO sources are vehicle exhaust and fugitive industrial emissions.
  - Secondary H$_2$CO sources originate from the breakdown of primary VOCs via photochemical oxidation.
- Industrial Applications
  - Textile industry
  - Automobile industry
  - Adhesive resins for use in carpeting & plywood

Formaldehyde Line Selection in the 3-4 μm Spectral Region

H$_2$CO Sensor Configuration

Laser source
Nanoplus ICL, 3.6 μm
Injection current: 50 mA
Output power: 3mW

Compact multipass cell
Sentinel Inc.
7.6 cm multipass cell length
32 ml sampling volume
3.7 m effective optical length

λ-modulation scheme

Representative H$_2$CO Sensor Calibration Results

- H$_2$CO gas standard: Kin-Tek gas standard generator

H$_2$CO Detection Sensitivity

- Minimum detection concentration: 1.5 ppb with a 140 sec averaging time

Noise Limitations

- Zero air measurements: 1s sampling rate
Summary and Future Work (2014-15)

- Development of laser-based absorption sensors for H$_2$CO detection using an interband cascade laser & a compact xx m multipass absorption cell.
- A minimum detection concentration of 1.5 ppb with 140 sec averaging time was achieved.
- Future work is planned to further improve the sensor detectivity to sub-ppb concentration level by using a multipass cell with an increased effective optical path length. Preliminary results show that a minimum detection concentration of 1 ppb with 10 sec averaging time can be achieved.

Summary, Conclusions and Future Developments

- Development of robust, compact, sensitive, selective mid-IR trace gas sensor technology based on RT, CW high performance DFB IC/CL & QCLs for detection of explosives and TICs as well as environmental monitoring and medical diagnostics.
- Interband cascade and quantum cascade lasers were used in OEPAS and TD-LAS based sensor platform.
- Performance evaluation of seven target trace gas species were reported. The minimum detection limit (MDL) with a 1 sec sampling time were:
  - CO, MDL of 0.24 ppbv at ~3.36 μm, CH$_4$, MDL of 13 ppb at ~7.38 μm, NO, MDL of 2 ppb at ~7.38 μm.
- Development of Trace Gas Sensors for the monitoring of broadband absorbers acetone (C$_2$H$_4$O), propane (C$_3$H$_8$), benzene (C$_6$H$_6$).

Hydrogen Peroxide (H$_2$O$_2$)

- Strong oxidant species in the atmosphere
- Associated with the formation of acid rain and atmospheric aerosols
- Employed in the synthesis of multiple chemical products & as bleaching agent in the pulp and paper industry
- Used for decontamination and sterilization of medical and pharmaceutical facilities
- Biomarker of lung and respiratory system diseases in exhaled breath

Vapor-Phase Hydrogen Peroxide (VPHP)

- VPHP is used for:
  - Decontamination of health-care and pharmaceutical facilities
  - Sterilization of medical equipment and packing materials in the food industry
- VPHP units; gas-phase H$_2$O$_2$ generated from concentrated liquid H$_2$O$_2$ solutions
- H$_2$O$_2$ concentrations between 200-1200 ppm are produced in the gas-phase and maintained for ~10 min.
- After decontamination procedures, ambient H$_2$O$_2$ concentrations need to be monitored.

Techniques for H$_2$O$_2$ Detection

- Wet-chemistry methods based on fluorescence spectroscopy, colorimetric analysis and chemiluminescence
  - Transfer from gas to liquid phase required for subsequent analysis
  - Interference from other species and formation of sampling artifacts
- Mid-infrared laser based spectroscopy
  - Direct detection in the gas-phase
  - Real-time detection
  - High sensitivity and specificity

H$_2$O$_2$ Absorption in the mid-infrared spectral Region

![Absorbance vs Wavenumber](image)

Fundamental ν$_a$ H$_2$O$_2$ band located at ~7.5-8.3 μm
**Previous Employed Absorption Lines**

Previous mid-IR sensor systems developed for H$_2$O$_2$ detection suffer from significant interferences from other gas species, particularly N$_2$O and H$_2$O vapor.

1295.55 cm$^{-1}$: QEPAS-based sensor system (Rei. et al., APL, 2014)

**Selection of optimum Absorption Line**

- A comprehensive spectral study was conducted
- Potential interferences from H$_2$O vapor, N$_2$O, CH$_4$, and CO$_2$ were considered
- An interference-free absorption line at 1234.05 cm$^{-1}$ was selected for H$_2$O$_2$ detection

**EC-QCL Operating Characteristics**

- CW EC-QCL (Model 21080-M4F, Daylight Solutions)
- Tuning range: 1175-1300 cm$^{-1}$
- Mode-hop-free range: 1225-1285 cm$^{-1}$
- Power output: < 200 mW

**Sensor Architecture**

CW EC-QCL coupled into multipass absorption gas cell with 76 m optical path length

**Photo of H$_2$O$_2$ Sensor Configuration**

**Parameter Optimization**

- Pressure and modulation amplitude levels were optimized for improved SNR
- EC-QCL current & relative temperature: 300 mA & 0 °C
- Laser power output: ~ 66 mW
Sensor System Response

- Direct absorption signal
- WMS-2f signal

H$_2$O$_2$ at 1234 05 cm$^{-1}$

Calibration Results

- Different gas-phase H$_2$O$_2$ concentrations were generated by flowing air over aqueous solutions of different strengths
- Gas-phase concentrations were determined by fitting the direct absorption signals using the HITRAN database

Calibration curve and sensor response at H$_2$O$_2$ concentrations between 3 and 21 ppm

Sensor System Sensitivity

Allan-Werle deviation analysis

Minimum detection limit (MDL): 25 ppb @ 280-sec integration time

H$_2$O$_2$ Sensor System Summary

- Selected absorption line at 1234.05 cm$^{-1}$ effectively alleviates interference issues identified previously for H$_2$O$_2$ detection
- MDL and ability to operate with no interference from water make our sensor system suitable for the monitoring of H$_2$O$_2$ in:
  - Industrial sites to establish possible exceedances of OSHA permissible exposure levels (PELs)
  - Decontamination/sterilization locations using VHP
  - Exhaled breath as biomarker of lung-related diseases
- Further improvement of the MDL is necessary for application in other fields such as atmospheric monitoring

Broadband THz QCLs

- Multistack QC laser with four quantum well active regions

Broadband Spectrum

**Experimental setup**

- Mix a DFB QCL with a source operating by DFG (widely tunable)

![Diagram showing experimental setup](image)

**Use a Fabry-Perot as a spectroscopy tool**

- Can be used to measure the spectrum
- S/N limited by stability

![Diagram showing Fabry-Perot](image)

**Cavity enhanced optical frequency comb spectroscopy**

For an optimum build-up of pulses inside a sensing cavity resonator, three conditions must be met:

1. Sensing cavity has to support equidistant frequency eigenmodes.
   - Intensity dispersion compensation
2. Separation of the cavity eigenmodes and the separation of the frequency comb modes must be equal.
   - Matching with cavity length
3. Inter mode must be shifted to overlap with the cavity eigenfrequencies.
   - Alignment of the eigenfrequencies

![Diagram showing cavity enhanced optical frequency comb](image)

**What is an optical frequency comb?**

- Array of N independent DFGs combined
- Line-to-line frequency noise is uncorrelated

![Diagram showing optical frequency comb](image)

**Cavity design for ICL-comb source**

**HR mirrors radius of curvature calculation**

Cavity stability criterion:

- For $t_{\text{mirror}} = 30 \text{ mm}$

Specs for cavity mirrors design:

- $R_1 = R_2 = 20 \text{ mm}$
- Plane-concave
- Diameter: 8"
- Radius of curvature: 20mm

![Diagram showing cavity design for ICL-comb source](image)
Cavity design for an ICL-comb source

Cavity design for an ICL-comb source

Sensing cavity design for ICL-comb source

Specifications for cavity mirror material

- Transmittance within the 3-4 μm spectral range
- Transparency in the visible (red diode laser for pump beam alignment)
- High surface quality (for HR and AR coatings to be applied)

AR coatings:

HR coatings:

J = 3.99 mm
R = 99.98%

LabSage Optics was contacted on Jan 14, 2016 for a quotation of AR & HR coatings on sapphire optics from Meller Optics, Inc. (http://www.labsageoptics.com, www.melleroptics.com)

Schematic of CE-OFC sensor system

TARGET detection and identification of toxic industrial chemicals with strong absorption features in the 3-4 μm range.

Sensor system will offer:

- High detection sensitivity
- High spectral stability and purity
- High selectivity
- Possibility of multi-gas detection

Two sensor configurations

- Comb laser is locked to a high finesse cavity
- Cavity is locked to comb laser

Fast detector

- Use an intersubband Quantum Well Infrared Photoconductor (QWIP) detector

Is it a comb?

- Beat note measurement of the photocurrent (at 7.5GHz)
- For modes of amplitude $E_k$, the photocurrent at $\Delta \omega$

$$I(\Delta \omega) = \sum_k E_k E_{k+1} \cos(\phi_{k+1} - \phi_k)$$

QCL Comb

QWIP Detector

Spectrum

Analyze

Detector: W.C. Liu
Frequency noise of a comb

- Use a (matched) optical cavity as an optical discriminator
- Measures all the modes at once

\[ N \sqrt{N} \approx 300 \]

Uncorrelated modes would yield no broader than

\[ \sqrt{N} \alpha_i \]

F. Cappellato, G. Villares et al., Acta

Beatnote spectrum

- The very narrow width confirms the correlations between modes
  - Uncorrelated lines could not be narrower than Schawlow-Townes (100s Hz)
  - However the signal is only about 2% of the cw photocurrent

\[ \text{Beatnote Spectrum} \]

\[ \text{Frequency (Hz)} + 1.8999 \text{ GHz} \]

Summary, Conclusions and Future Developments

- Development of robust, compact, sensitive, selective mid-IR trace gas sensor technology based on RT, CW high performance DFB ICAs & QCLs for detection of explosives and TICs as well as environmental monitoring and medical diagnostics
- Interband cascade and quantum cascade lasers were used in ODEAS and TUDAS based sensor platforms
- Performance evaluation of seven target trace gas species were reported. The minimum detection limit (MDL) with a 1 sec sampling time were
  - C\(_2\)H\(_4\) MDL of 24 ppbv at \(-3.28 \mu\text{m}\)
  - CH\(_4\) MDL of 13 ppbv at \(-3.28 \mu\text{m}\)
  - N\(_2\)O MDL of 6 ppbv at \(-3.28 \mu\text{m}\)
- I-QMAS demonstration with a power enhancement factor of 240 providing a corresponding increase in detection sensitivity
- CO\(_2\) for the P(42) absorption line located at \(-4.33 \mu\text{m (2311 105 cm}^{-1})\), a MDL of 300 ppbv at 50 mbar was achieved for a 20 sec integration time
- Development of "active" I-QMAS system for CO and NO detection in the few ppt range
- Development of Trace Gas Sensors for the monitoring of broadband absorbers across CO\(_2\), propellant (C\(_2\)H\(_4\)O), propane (C\(_3\)H\(_8\)), benzene (C\(_6\)H\(_6\))
- Development of Mid-IR Electrically pumped Interband Cascade Optical Frequency Combs (OFCs) with JPL, Pasadena, CA, NRL, Washington, and the U of Bari (Italy)

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New QCL data at 1 \(\sim\) 3.3\(\mu\text{m}\)