

# **Monitoring of Hydrocarbons Using the ChemDetect Gas Analyzer**

## **CI - C9 Monitoring**

### **Initial Observations**

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## Executive Summary

Spectroscopic monitoring of the C1 - C9 hydrocarbons using a commercially available CD-GA, mid-infrared quantum cascade laser-based spectrometer. The 5.8 to 7.5  $\mu\text{m}$  spectral region is ideal for simultaneous monitoring of multiple hydrocarbon species: identifying spectral features, lack of strong spectral overlap, and a single tunable QCL solution indicate a cost-effective sensor is possible. Simulation of C7 - C9 impurity monitoring in natural gas streams suggests that these species can be monitored with 1% sensitivity while allowing simultaneous monitoring of the main C1 - C6 species.

## Overview

A number of industrial sensor opportunities require monitoring of hydrocarbons. Hydrocarbons are often designated according to the C1 - C9 series, indicating the number of carbon atoms in the molecule. For a given number of carbon atoms, there are also a variety of chemicals that are possible based on bonding. This leads to a wide variety of species that can be present in hydrocarbon monitoring.

The mid-infrared spectral region is ideal for monitoring hydrocarbons: strong spectral features abound, especially in the 3  $\mu\text{m}$  C-H stretch region and the longer wavelength skeletal vibration region. This can lead to complications, however, when multiple hydrocarbons are present at significant concentrations. Interferences between bands can complicate spectral monitoring, and outright optical saturation can occur at many wavelengths for high concentrations.

Quantum cascade lasers (QCLs) are an ideal tool for monitoring hydrocarbons. They offer high spectral resolution ( $0.2\text{ cm}^{-1}$ ) and rapid broad tuning (hundreds of  $\text{cm}^{-1}$ ) when operated in pulsed mode. This enables multiple hydrocarbons to be monitored at once, even if the spectra are rotationally resolved or broad. In order to optimize a QCL-based sensor, it is desirable to find a spectral region where multiple species can be monitored at once without significant interferences.

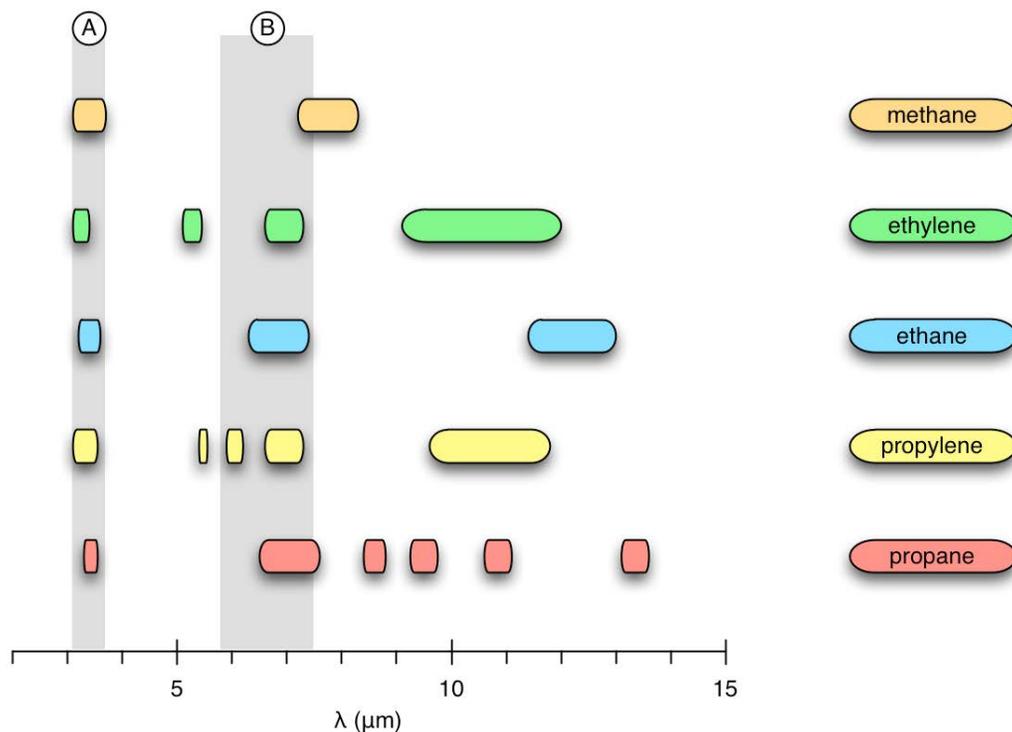


FIG. 1. Spectral ranges of dominant features for main C1 - C3 hydrocarbons. Region A, or the C-H stretch region at 3  $\mu\text{m}$ , has the greatest overlap, but also suffers from spectral congestion. Region B, from 5.8 to 7.5  $\mu\text{m}$ , has been identified as the best region for simultaneous monitoring of all species.

Figure 1 shows the main spectral features for the dominant C1 - C3 hydrocarbons. Although the C-H stretch region at 3  $\mu\text{m}$  offers strong features, they also strongly overlap, making interferences a problem. A second region between 5.8 and 7.5  $\mu\text{m}$ , however, has the potential to provide simultaneous monitoring of these species without significant interferences. This is highlighted in Fig. 2, where the actual spectra are compared.

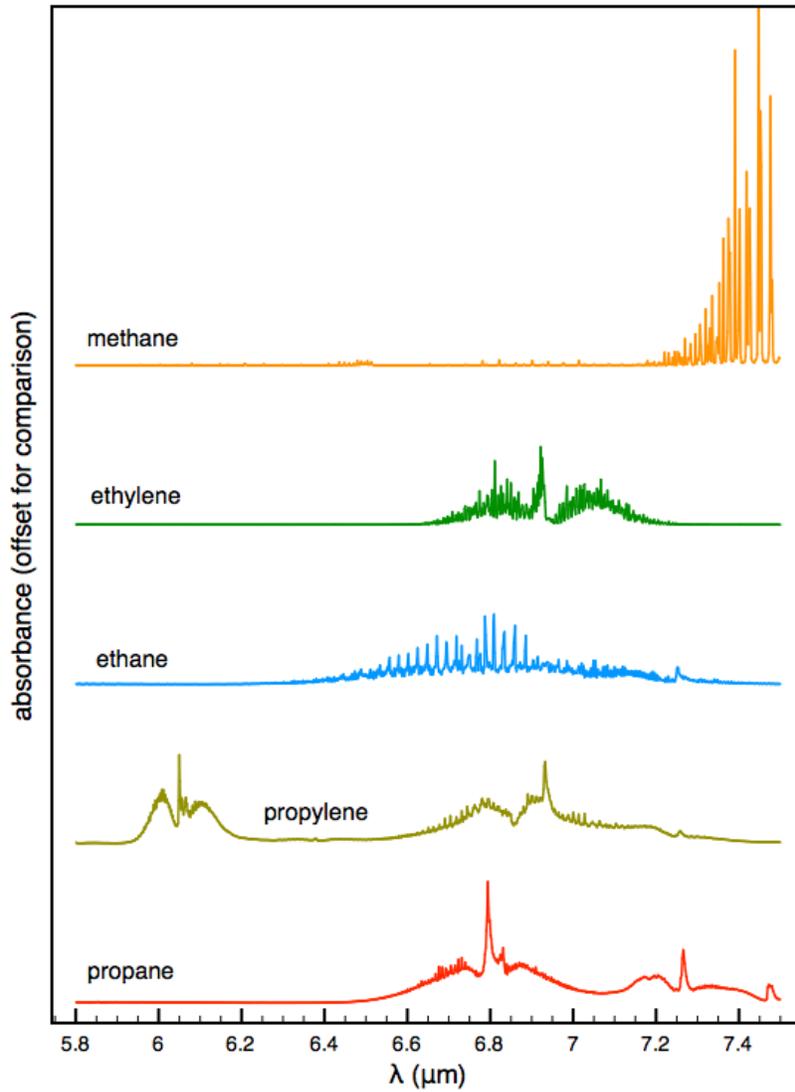


FIG. 2. Comparison of PNNL absorption spectra for the main C1 - C3 hydrocarbons in the 5.8 to 7.5  $\mu\text{m}$  spectral region. Conditions: same concentration and path length for each, 25°C, 760 torr

In addition, QCL technology has advanced to the point where a single QC device can tune over this hydrocarbon region. Figure 3 shows sample QC device gain profiles with high power and broad tuning to cover 5.8 to 7.5  $\mu\text{m}$ . A single QCL solution makes a hydrocarbon sensor cost effective and offers the highest performance characteristics.

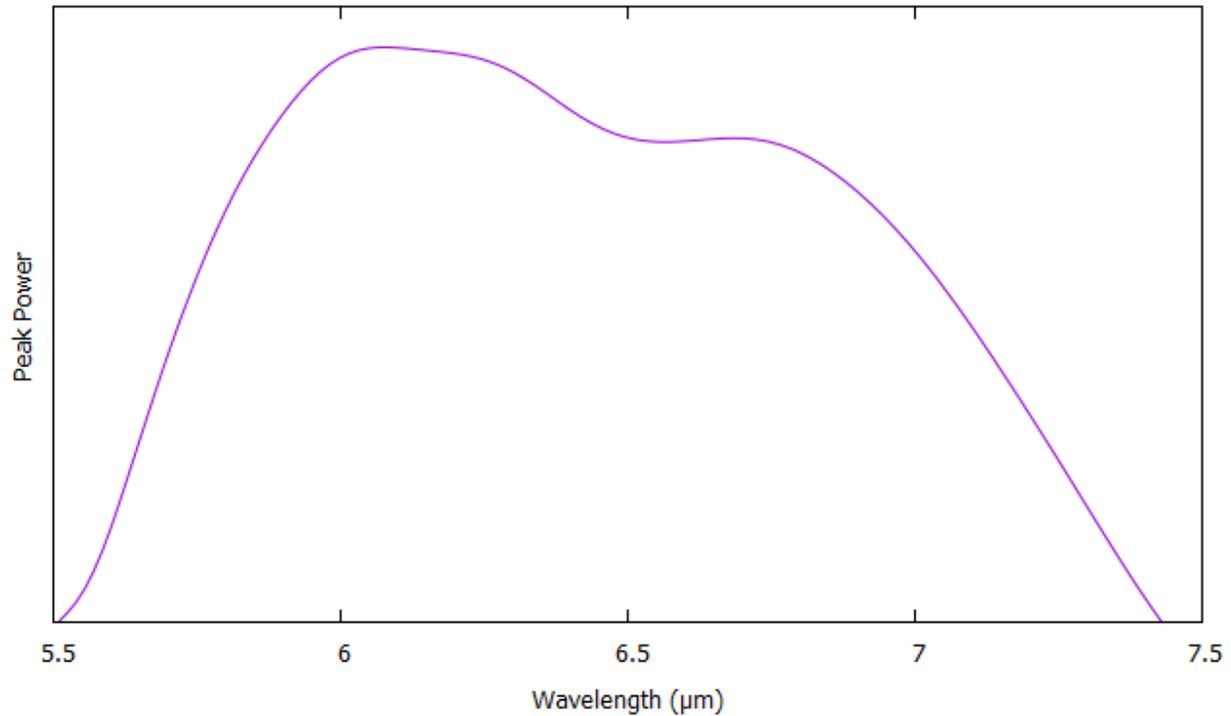


FIG. 3. Sample QC device gain profiles for different operating conditions. Gain curves indicate single tunable QCL solution from 5.8 to 7.5  $\mu\text{m}$  is possible.

## C7 Monitoring in Natural Gas

The monitoring of C7 - C9 impurities in natural gas is important in custody transfer. However, spectroscopic monitoring in relatively pure hydrocarbon streams presents challenges due to absorption saturation. Typical natural gas streams consist of up to 80% (up to 99%) methane, 10% ethane, and 10% propane. Spectroscopically, this leads to absorption levels that require shorter path lengths if monitoring is to be done in the 5.8 to 7.5  $\mu\text{m}$  region. Figure 4 shows that it is still possible to use the 5.8 to 7.5  $\mu\text{m}$  region in natural gas, but short path lengths (10 cm) are required to keep the absorptions from saturating.

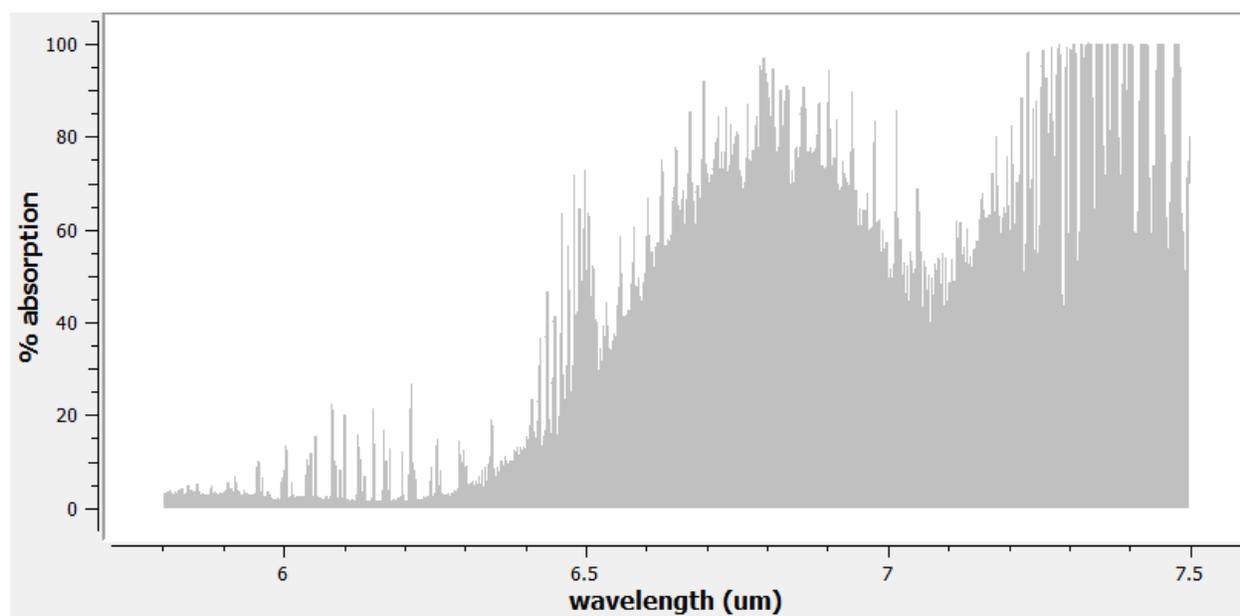


FIG. 4. Optical absorption for mixture of 80% methane, 10% ethane, and 10% propane over 10 cm at 25°C, 760 torr. Based on PNNL absorption spectra and instrument resolution of  $0.17\text{ cm}^{-1}$ .

As a quick assessment of the feasibility of monitoring C7 - C9 impurities in natural gas, a spectroscopic simulation of detection sensitivity is done for the three main C7 species: heptane, heptene, and cycloheptene. Figure 5 shows the spectral features for these species in the region of interest. The concentration range of interest for these species is up to 500 ppm. As can be seen in Fig. 4, at these levels the absorption strength is significant, suggesting that spectroscopic monitoring should be possible.

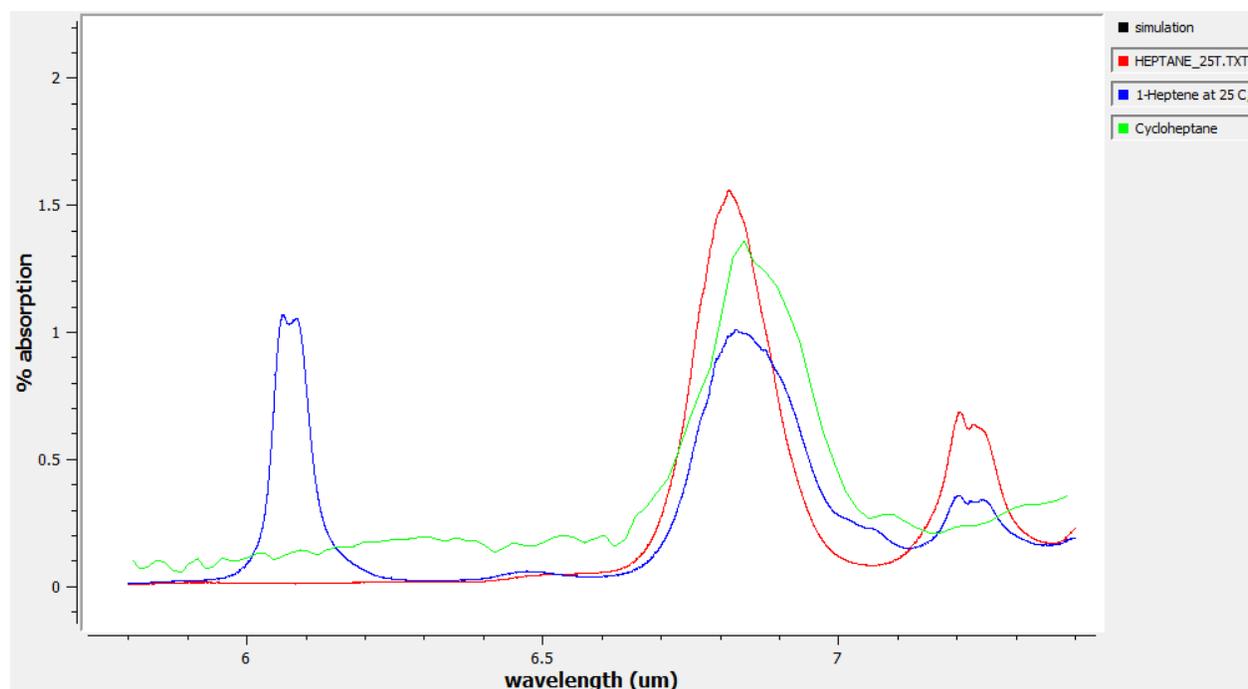


FIG. 5. Simulation of C7 species at 25°C, 760 torr, 500 ppm, and 10 cm path length. Heptane and heptene spectra from PNNL, cycloheptene from NIST Chemistry WebBook. Note that cycloheptene absorption strength is not available from spectrum and is plotted to show spectral features compared to other species.

Sensitivity simulations are carried out in the following manner: the three main hydrocarbon species are fixed at the following values: 80% methane, 10% ethane, and 10% propane. PNNL spectra are used to simulate absorption spectra for 25°C, 760 torr, and a 10 cm path length. Small fractions of the C7 species are added at 100 ppm each. The spectrum is then broadened by the QCL spectrometer resolution ( $0.17 \text{ cm}^{-1}$ ) and transmittance noise of 0.1% is added. Multiple linear-least-squares fits of the C7 species are carried out while changing the noise addition for each iteration. This allows an rms deviation in fitted concentration for the C7 species to be determined.

The simulation results are encouraging: they suggest that the C7 species can be monitored with about 10 ppm uncertainty even with the high background from the C1 - C3 species and the 10 cm path length. This translates to C7 impurity monitoring with 1% sensitivity in the unmodified

gas stream. Moreover, it should be possible to monitor the C1 - C6 species with the same measurement.

Simulations of C8 and C9 species were not carried out due to a lack of quantitative spectral information. Spectroscopic measurements would be necessary to validate the measurement of these species, although absorption strengths and sensitivity would likely be similar.

## **Conclusions**

Spectroscopic monitoring of the C1 - C9 hydrocarbons looks promising in the 5.8 to 7.5  $\mu\text{m}$  region. Multiple strong absorption features, a lack of strong overlap interferences, and a single QCL solution suggest that a high-performance, cost-effective QCL sensor is possible. Consideration of C7 monitoring in natural gas streams suggests that 1% sensitivity to C7 - C9 impurities is possible, and that simultaneous monitoring of C1 - C6 species is also possible. Further spectroscopic studies in actual conditions would be necessary to validate these simulations.