Widely-Tunable Rapid-Scanning Mid-IR Laser Spectrometer for Industrial Gas Process Stream Analysis

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Widely-Tunable Rapid-Scanning Mid-IR Laser Spectrometer for Industrial Gas Process Stream Analysis

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Abstract: We demonstrate selective detection of hydrocarbons using a widely-tunable, rapidly-swept, high-resolution spectrometer based on a mid-infrared laser source using difference-frequency generation in periodically poled lithium niobate waveguides.
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Rapid, non-intrusive sensors for small hydrocarbon molecules are needed by the petrochemical industry to monitor the concentrations of multiple species in its process streams, so that the yield of the desired end products can be optimized. We report the spectroscopic detection of methane, ethylene, and propylene using a sensor which is capable of meeting industry requirements for selectivity, sensitivity, speed, and compactness. This instrument could be used to detect a wide variety of small molecules containing carbon-hydrogen bonds.

The sensor is a laser spectrometer based on difference-frequency generation (DFG) in periodically poled lithium niobate (PPLN) waveguides. Waveguide DFG has been shown to be an effective method of generating tunable mid-infrared radiation for a variety of gas-sensing applications [1]. The tuning range of such a laser source is limited by the phase-matching properties of PPLN. Recently we have shown that broad phase-matching resonances for mid-infrared generation in waveguide DFG can be observed when the wavelengths of the interacting lasers are properly chosen [2]. This work is built upon the DFG experiments of Goldberg et al., who observed broad phase-matching resonances in bulk DFG [3]. In the present work, a tuning range of >400 cm⁻¹ is demonstrated using a new waveguide device which allows a telecommunications laser, engineered for rapid wavelength sweeps, to be used as the tuning element. The tuning speed and linearity of the swept-wavelength laser determine the instrument’s speed and spectral accuracy, and, since both lasers are narrow-linewidth, the spectral resolution is limited only by the laser linewidths and limits on the data acquisition rate. In terms of speed and resolution, this spectrometer rivals the performance of high-resolution FTIR instruments.

The mid-IR spectrometer is shown in Figure 1. This system is based on difference frequency generation (DFG) in a PPLN channel waveguide with an 18.5 mm long mixing region, utilizing a 931 nm fixed-wavelength pump laser (Sacher Lasertechnik Lynx series, ~50mW when fiber-coupled) which is mixed with a tunable, swept-wavelength signal laser tunable between 1263 nm and 1343 nm (Thorlabs/Radians Innova INTUN –T series ~6mW when fiber-coupled). The fiber-coupled outputs of the lasers are combined in a fiber-optic coupler (Canadian Instrumentation & Research Ltd., using 980-nm PM fiber), and the output fiber ferrule is butt-coupled and epoxied to the PPLN waveguide. All fibers are PM to preserve the polarization necessary for proper guiding in the waveguide and the connectors are APC to eliminate etalons. To achieve proper phase-matching, the PPLN chip is heated to 65°C and the resulting mid-IR light is focused by a ZnSe lens and filtered by a broadband mid-IR pass filter. The light is then chopped at ~4kHz, split into signal and reference beams by a ZnSe beamsplitter and detected using a pair of thermoelectrically cooled InAs detectors. The signal beam passes through a gas cell with wedged, anti-reflection coated ZnSe windows allowing differential absorption measurements. Ratiometric detection is used to eliminate etalon effects from the tunable laser, PPLN chip and other optics and to account for laser power and wavelength-dependent coupling efficiency variations. The signals from the detectors are sent to two lockin amplifiers and the resulting voltage signals are detected by a fast data acquisition (DAQ) board. The DAQ board is also used to send a sweep analog signal to the tunable laser for tuning.

The acquisition speed and accuracy of the obtained spectra are predicated on the tuning characteristics of the analog swept-wavelength laser which is, by design, highly linear and highly repeatable and can be tuned at speeds up to 100nm/s. The linearity of the scan is further improved by pre-compensating the analog waveform for any linearity variations (which can be measured by scanning the laser over a known etalon and accounting for any observed linearity errors) and using this corrected waveform when scanning the laser. A program written in LabVIEW controls the coordinated laser scanning, linearity calibration and simultaneous data acquisition. The minimum achievable linewidth for the spectrometer, determined by the convolved lineshape functions of the pump and signal lasers, is ~120 MHz. In practice, the linewidth is larger than this because of limitations imposed by the finite DAQ rate. For example, a typical measurement scanning the entire tuning range of the instrument in
~10 seconds yields an effective linewidth of ~0.01 cm⁻¹. Tradeoffs among scan range, resolution and speed can be made based on the measurement requirements. The system has a tuning range of 3046-3556 nm (3283-2812 cm⁻¹), corresponding to 510 nm (471 cm⁻¹) of mode-hop-free tuning and delivers 0.17 μW of mid-IR power with 6 mW of near-IR power launched into the waveguide. The PPLN waveguide has a device efficiency of 2.9%/W.

Figure 2 shows the relative mid-infrared power as a function of idler wave number with the pump laser fixed at 931.4 nm, and the signal laser tuned between 1263 nm and 1343 nm. Broad phase-matching is obtained with this combination of pump and signal wavelengths because the phase mismatch is, to a first-order approximation, independent of the wavelength of the laser being tuned [3]. The waveguide is engineered to center this broad resonance within the C-H stretching region near 3000 cm⁻¹.

Figures 3-5 show absorption spectra, acquired using the DFG-based spectrometer, of three hydrocarbon molecules which are of importance in petrochemical manufacturing: methane, ethylene, and propylene. The laser linewidth is narrow enough to resolve the shapes of most of the absorption lines, which are dominated by pressure broadening (1 atmosphere total pressure with N₂ as the buffer gas). Each spectrum was acquired in a single sweep. The sweep lengths for methane, ethylene, and propylene were 10, 60, and 20 seconds, respectively. Also shown, for comparison, are Fourier transform infrared (FTIR) spectra of the same gases (0.112 cm⁻¹ resolution, 1 ppm-meter, 1 atmosphere total pressure) from the Pacific Northwest National Laboratory (PNNL) database [4]. The line positions and relative line strengths measured using the laser spectrometer are in good agreement with the FTIR measurements. Clearly, the tuning range of the laser source is wide enough to capture a large number of characteristic absorption features for each molecule. Therefore, the spectrometer can be used to measure the relative concentrations of these three species in real time during hydrocarbon cracking, thus providing feedback which can be used to optimize the yield of the desired product mix.
Fig. 4. Absorption spectrum of ethylene (171 Torr, 4 cm path length), recorded using the experimental apparatus shown in Fig. 1 (lower curve), along with a scaled FTIR spectrum from Reference [4] (upper curve). The curves have been vertically displaced for clarity.

Fig. 5. Absorption spectrum of propylene (101 Torr, 4 cm path length), recorded using the experimental apparatus shown in Fig. 1 (lower curve), along with a scaled FTIR spectrum from Reference [4] (upper curve). The curves have been vertically displaced for clarity.

This spectrometer, with its ability to quickly acquire spectral data over hundreds of wave numbers in the C-H stretching region at high resolution, will enable numerous molecular species to be selectively detected in a variety of applications, including pharmaceutical manufacturing, environmental monitoring, and combustion diagnostics.

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References


