A widely tunable difference-frequency-generation laser for high-resolution spectroscopy in the 667–865 cm⁻¹ range

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ABSTRACT

Mid-infrared (MIR) laser sources are used in a number of applications such as remote sensing, air pollution monitoring, combustion diagnostics, and molecular spectroscopy. Here, we present our work on the development of a MIR laser source based on the difference frequency generation (DFG) process between an external-cavity quantum-cascade-laser tunable over 1750–1835 cm⁻¹ (pump source) and a CO₂ gas laser tunable over 921–1083 cm⁻¹ (signal source). The DFG process was realized in a nonlinear, orientation-patterned GaAs crystal, and resulted in an idler spectral range between 667–865 cm⁻¹ with a linewidth of ~2.3 MHz and an output power of up to ~31 μW. Exploiting the fine tunability of our DFG laser source, we performed high-resolution absorption measurements of ethylene (C₂H₄) and acetylene (C₂H₂).

Keywords: Difference frequency generation, mid-infrared laser sources, high-resolution spectroscopy, laser spectroscopy.

1. INTRODUCTION

The capability of resolving individual absorption features is of high importance in many applications, including molecular spectroscopy and metrology. In this context, mid-infrared (MIR) is an attractive spectral region because it contains strong, fingerprint vibrational bands of many species of interest in many applications, such as air quality monitoring and medical and combustion diagnostics. Fourier transform infrared (FTIR) spectrometry has been a gold standard technique for infrared spectroscopy applications. However, the spectral resolution of FTIR spectrometers is relatively low due to the limited scanning range of mechanical delay lines and to the poor spatial and spectral coherence of thermal light sources. Alternatively, optical frequency combs can be used as a light source for FTIR spectroscopy with high resolution and accuracy¹. Optical frequency combs provide a series of narrow linewidth teeth over a broad spectral bandwidth^{2,3}. While optical frequency combs offer high resolution and absolute frequency calibration, the spacing between comb teeth is often of the order of a few hundred MHz. This is relatively high spacing when detecting narrow absorption features. Continuous-wave (cw) lasers can overcome this issue and have been widely used for MIR spectroscopy applications. However, the longest wavelength from semiconductor diode and disk lasers is less than 5 μm⁴. Furthermore, MIR fiber lasers reach wavelengths only up to 3.5 μm⁵. Quantum cascade lasers (QCLs) cover a wide MIR range with a very good beam quality, sufficient laser linewidth, and high output power^{6,7}. However, cw-QCLs are limited to ~ 13 μm in wavelength and do not offer broad mode-hop-free tunability. In contrast, nonlinear frequency conversion based lasers, including optical parametric oscillation⁸ and difference-frequency generation (DFG)⁹, provide broad tunability and can be designed to target specific MIR regions with wide spectral bandwidth and tunability¹⁰.

In our present work, we developed a widely tunable laser based on the DFG process between an external-cavity quantum cascade laser (EC-QCL), as the pump source, and a CO₂ gas laser, as the signal source, in a nonlinear orientation-patterned (OP) GaAs crystal. The CO₂ gas laser was operated in kHz-pulsed mode, while the EC-QCL was continuously mode-hop-free tuned. This results in a quasi-cw idler emission between 666.53–865.28 cm⁻¹ with a laser linewidth of ~2.3 MHz and a spectral spacing in the MHz range. We applied our DFG laser to perform direct absorption measurements of ethylene (C₂H₄) and acetylene (C₂H₂).

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2. EXPERIMENTAL SETUP

2.1 OP-GaAs crystal

The OP-GaAs crystal used here has a length of 35 mm, a width of 20 mm, and a fan-out structure with poling periods from 183 to 203 μm . The length of the crystal ensures phase matching over the entire tuning range of the pump laser. The width of the crystal is sufficiently large to discard any efficiency drop due to non-uniform phase-matching conditions between the pump and signal laser beams. The conversion efficiency is characterized by a phase-matching bandwidth of about 20 nm corresponding to $\sim 6\text{ cm}^{-1}$. This means that there is no need to adjust the crystal position when tuning the pump within a wavelength range of 20 nm at a specific signal wavelength.

2.2 DFG laser

The experimental setup of the DFG laser is depicted in Fig. 1(a). The signal laser, CO₂ gas laser, is non-continuously tunable between 9.23 and 10.86 μm ($920.81\text{--}1083.42\text{ cm}^{-1}$). The average output power of the CO₂ gas laser varies between 0.7 and 10 W depending on the emitting laser line and the pulse repetition rate. The pump laser, EC-QCL, can be mode-hop-free tuned between 5.45 and 5.71 μm ($1749.97\text{--}1834.93\text{ cm}^{-1}$) with an output power of up to 200 mW. An optical isolator (OI) was installed after the EC-QCL to suppress any back reflections that may affect or damage the laser. The OI causes about 50%-drop in the laser power and rotates the polarization of the pump laser beam by 45° . A waveplate (WP) was installed after the OI to maintain the vertical polarization of the EC-QCL, i.e., it rotates the polarization back by -45° . As a result, the idler laser power is increased by a factor of two, compared to its value without a WP.

Figure 1. Schematic of the experimental setup of (a) the DFG laser, and (b) the absorption measurement setup with a 23-cm-length gas cell and two nitrogen-cooled HgCdTe detectors. EC-QCL: external-cavity quantum cascade laser; OI: optical isolator; WP: wave plate; CM: concave mirror; FM: flat mirror; BC: beam combiner; PM: parabolic mirror; OP-GaAs: orientation-patterned GaAs crystal; LF: long-pass filter; BS: beam splitter; D: detector.

To maximize the DFG efficiency, the beam waists of the pump and signal lasers were adjusted at the OP-GaAs crystal using two sets of concave mirrors. The OP-GaAs crystal was placed between two parabolic mirrors (PMs). The first PM was used to focus the pump and signal laser beams onto the OP-GaAs crystal after they were aligned through a beam combiner (BC). The second PM was used to collect and collimate the idler laser beam. A long-pass filter (LF), with a cut-on edge near 11.2 μm , was placed after PM₂ to filter out both the pump and signal lasers. The linewidths of the pump and signal lasers are 1.7 MHz and 1.5 MHz, respectively, as retrieved from the beat-note with a 100 kHz linewidth frequency comb¹¹. The idler laser linewidth of ~ 2.3 MHz was estimated from the convolution of the pump and signal laser spectra.

The spectrum of the EC-QCL, not shown here, includes a number of strong water absorption lines. To reduce the effect of ambient water absorption on the measurements, the DFG laser setup was placed in a sealed box purged with nitrogen. As a result, the humidity inside the laser box was reduced to 0.68%.

2.3 Absorption measurement setup

The absorption measurement setup is shown in Fig. 1(b). After the LF, the idler laser beam was split into two beams using a beam splitter. The transmitted beam was directly focused onto a nitrogen-cooled HgCdTe detector, D₁, using PM₃ and used as a reference. The reflected beam was aligned through an optical cell (gas cell) via coated-ZnSe windows and then focused onto the second nitrogen-cooled HgCdTe detector, D₂. We used a digital oscilloscope (PicoScope 5000, Pico Technology) to record detectors' signals.

2.4 Idler laser output power

We measured the idler output power using D₁ before installing the BS. Figure 2(a) shows a representative idler average power curve over the accessible wavenumber range. The data points refer to the idler power values at selected signal laser wavenumbers, while the solid black line is used as an eye-guide. Here, the signal laser was operated at a repetition rate of 2.5 kHz and a duty cycle of 30%. We set the CO₂ gas laser at specific emission lines (represented in the figure with different colors, while the pump wavelength was stepwise changed through the laser control software. Besides, when the pump laser was tuned to a specific wavelength, the OP-GaAs crystal position was adjusted to optimize the idler laser output power. Thereby, the idler wavenumber can be tuned over a broad range between 666.533 cm⁻¹ (15.003 μm) and 865.277 cm⁻¹ (11.557 μm). The maximum output power of about 31 μW was measured at 791.766 cm⁻¹. The idler output power decreases when the pulse repetition rate of the signal laser is increased to achieve reduced spectral spacing. Figure 2(b) shows an example of the nearly exponential dependency of the idler output power on the pulse repetition rate of the CO₂ gas laser.

Figure 2. (a) DFG average output power as a function of the wavenumber measured at several CO₂ gas laser lines when the EC-QCL was stepwise tuned. (b) The dependency of the idler average output power on the signal, CO₂ gas laser, pulse repetition rate.

3. SPECTROSCOPY MEASUREMENTS

3.1 Spectral spacing

The wavelength tuning of the EC-QCL (pump laser) is originated from a mechanically motorized diffraction-grating. Hence, the EC-QCL scan speed determines the number of spectral points of the DFG laser spectrum. We set the scan speed to the minimum value of 25 nm/s to increase the number of probed spectral points with respect to the pulse repetition rate of the CO₂ gas laser. Moreover, the EC-QCL scan speed can be further reduced using a piezoelectric transducer (PZT) implemented in the laser to mechanically modulate the grating. However, when the PZT modulation is applied, the maximum scan range is 1 cm⁻¹. One can also decrease the spectral spacing by increasing the pulse repetition rate of the CO₂ gas laser. Additional spectral points (reduced spectral spacing) can be obtained by repeating the measurements. The phase of the signal laser pulse train at the starting time of the EC-QCL scanning is not held constant. Hence, the DFG process between the train of CO₂ laser pulses and the EC-QCL takes place arbitrarily, in time, for repeated measurements.

Figure 3. Signals recorded on detectors D1 and D2 are shown in (a1) when the gas cell was under vacuum and (b1) when the cell was filled with test gas (C_2H_4). The inset in (a1) is a magnification showing the signals over a short time range. (a2) and (b2) illustrate the P-P amplitudes of the signals presented in (a1) and (b1), respectively. (c) P-P amplitudes of the signal recorded on D2 when the gas cell was under vacuum and compared with the signal when the cell was filled with C_2H_4 at a pressure of 15 Torr. (d) The transmission spectrum of C_2H_4 obtained from the spectra of (c) after converting the x-axis from time to wavenumber.

3.2 Data processing

Signals recorded on D_1 and D_2 were post-processed and analyzed using MATLAB software. Figures 3(a1) and (b1) show the signals recorded on detectors when the gas cell was vacuumed and when it was filled with C_2H_4 at a pressure of 15 Torr. The CO_2 laser wavenumber was set to 1046.901 cm^{-1} with a pulse repetition rate of 30 kHz, and the EC-QCL was swept around 1786.4 cm^{-1} over a wavenumber range of $\sim 8\text{ cm}^{-1}$ width. The signals in Fig. 3(a1) and (b1) were reordered when the wavelength of the EC-QCL was scanned from shorter to longer wavelength. The scan time is about 1.5 s. The inset of Fig. 3(a1) is a magnification showing the idler pulsed signals over a short-time range. The detectors used in our experiment are highly sensitive. Therefore, to avoid the effects of any fluctuations in the intensity offset, we used the peak-to-peak (P-P) amplitude of the signals to obtain the transmission spectra. Fig. 3(a2) and (b2) show the P-P amplitudes of the signals presented in Figs. 3(a1) and (b1), respectively. The sharp features, i.e., deep gaps, across the P-P spectrum of D_2 in Fig. 3(b2) are due to the absorption lines of C_2H_4 .

We used the reference signal recorded on D_1 to correct any fluctuation in the laser intensity when obtaining the transmission spectra. Figure 3 (c) shows the temporal change of the P-P amplitude of the signals recorded on D_2 when the gas cell was vacuumed and when it was filled with C_2H_4 at a pressure of 15 Torr. To analyze the signals, their starting points were synchronized to the start (zero) of the time-axis. Since the CO_2 laser wavelength was fixed during the scan measurements, the calibration of the DFG wavelength just follows the calibration of the wavelength of the EC-QCL, i.e., converting the x-axis from time to wavelength (wavenumber). When running a scan measurement, a wavelength reference TTL pulse was issued by the laser every 0.2 nm, based on an internal calibration between the wavelength and the motorized diffraction-grating. The TTL pulses' signal was recorded alongside the detectors' signals. The wavelength (wavenumber) axis was determined by linearly interpolating the wavelength reference pulse signal. We used the ethylene absorption lines' positions in the HITRAN database to correct any drift in the wavelength axis. Figure 3(d) shows the transmission spectrum of C_2H_4 at a pressure of 15 Torr, obtained from the spectra of Fig. 3(c) after converting the x-axis from time to wavenumber.

Figure 4. A comparison between simulated (top) and experimentally measured (bottom) transmission spectra of C_2H_4 over $719.5\text{--}762.5\text{ cm}^{-1}$ at a pressure of 150 Torr. The simulated spectrum is taken from the HITRAN database¹².

3.3 Absorption measurements

We performed high-resolution absorption measurements of the ν_{10} band¹³ of ethylene (C_2H_4) at a pressure of 150 Torr. Figure 4 shows the experimentally measured transmission spectrum of ethylene compared with the simulated spectrum from the HITRAN database¹². The spectrum was piecewise measured over a wavenumber range between 719.5 and 762.5 cm^{-1} . The wavenumber piece-width was between 6 and 8 cm^{-1} , with respect to the DFG phase-matching bandwidth. The wavelength of the signal laser, CO_2 gas laser, was set to $9.552\text{ }\mu\text{m}$ (1046.901 cm^{-1}) with a pulse

repetition rate of 10 kHz, while the start and end pump wavelengths were chosen to cover the target DFG spectrum pieces. The spectral spacing of the transmission spectrum was found to be mostly $< 4 \times 10^{-4} \text{ cm}^{-1}$ ($< 12 \text{ MHz}$) when the measurements were repeated five times.

We also performed absorption measurements of a narrow spectral range of acetylene (C_2H_2). Here, the CO_2 laser wavelength was set to $9.329 \text{ }\mu\text{m}$ (1071.926 cm^{-1}) with a pulse repetition rate of 10 kHz. The EC-QCL wavelength was fine-tuned around $5.5810 \text{ }\mu\text{m}$ (1791.801 cm^{-1}) using the PZT modulation. The relatively slow tuning of the EC-QCL wavelength results in a decreased spectral spacing. This is due to the increased number of CO_2 laser pulses mixed with the EC-QCL narrow spectrum and converted to DFG pulses in the OP-GaAs crystal. An example of high-resolution transmission measurements of the $2\nu_5^0 - \nu_5^1$ band¹⁴ of C_2H_2 is shown in Fig. 5(a2) and compared with the spectrum from the HITRAN database¹² shown in Fig. 5(a1).

Figure 5. A comparison between simulated (a1) and experimentally measured (a2) transmission spectra of C_2H_2 over $719.77\text{--}719.97 \text{ cm}^{-1}$ at a pressure of 0.12 Torr. The simulated spectrum is taken from the HITRAN database¹². (b1) Measured transmission spectrum (blue squares) and simulated Voigt profile (orange line) for the absorption feature near 719.792 cm^{-1} . (b2) Residuals [(measured value – simulated value) $\times 100$]. (c) A magnification of the measured absorption feature near its center; the bottom x-axis is the wavenumber shifted to 719.792 cm^{-1} , while the top x-axis is the corresponding frequency shift.

Figure 5(b1) shows the absorption feature near 719.792 cm^{-1} , which is well fitted with the Voigt line-shape profile^{15,16}. The residuals from the Voigt fitting are shown in Fig. 5(b2). Overall, the fluctuation in the transmission spectra is in the range of ± 0.007 due to the detectors' noise and etalons in the setup. To display the very dense spectral sampling of the measured spectrum, a magnification of the absorption feature near its center is shown in Fig. 5(c). Here, the wavenumber axis is shifted to 719.792 cm^{-1} . The top x-axis of Fig. 5(c) represents the frequency shift obtained from the wavenumber shift values. The spectral spacing is in a MHz scale, which is in the range of our DFG laser linewidth of $\sim 2.3 \text{ MHz}$ ($7.8 \times 10^{-5} \text{ cm}^{-1}$).

SUMMARY

We have reported the development of a widely tunable DFG-based laser source emitting in the MIR range between 666.533 and 865.277 cm^{-1} ($11.557\text{--}15.003 \text{ }\mu\text{m}$) with an idler laser linewidth of $\sim 2.3 \text{ MHz}$ and an output power of up to $\sim 31 \text{ }\mu\text{W}$. An EC-QCL and a CO_2 gas laser were used as the pump and signal lasers for the DFG process and were frequency-mixed in a nonlinear OP-GaAs crystal. The EC-QCL was continuously tuned with mode-hop-free emission, while the CO_2 gas laser was operated in kHz-pulsed mode, resulting in a quasi-cw idler emission. We applied the DFG laser system to perform direct absorption measurements of ethylene (C_2H_4) and acetylene (C_2H_2). Our measurements demonstrated the capability of the spectrometer to resolve absorption spectra with a highly dense frequency grid in the MHz range ($3.34 \times 10^{-5} \text{ cm}^{-1}$).

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