

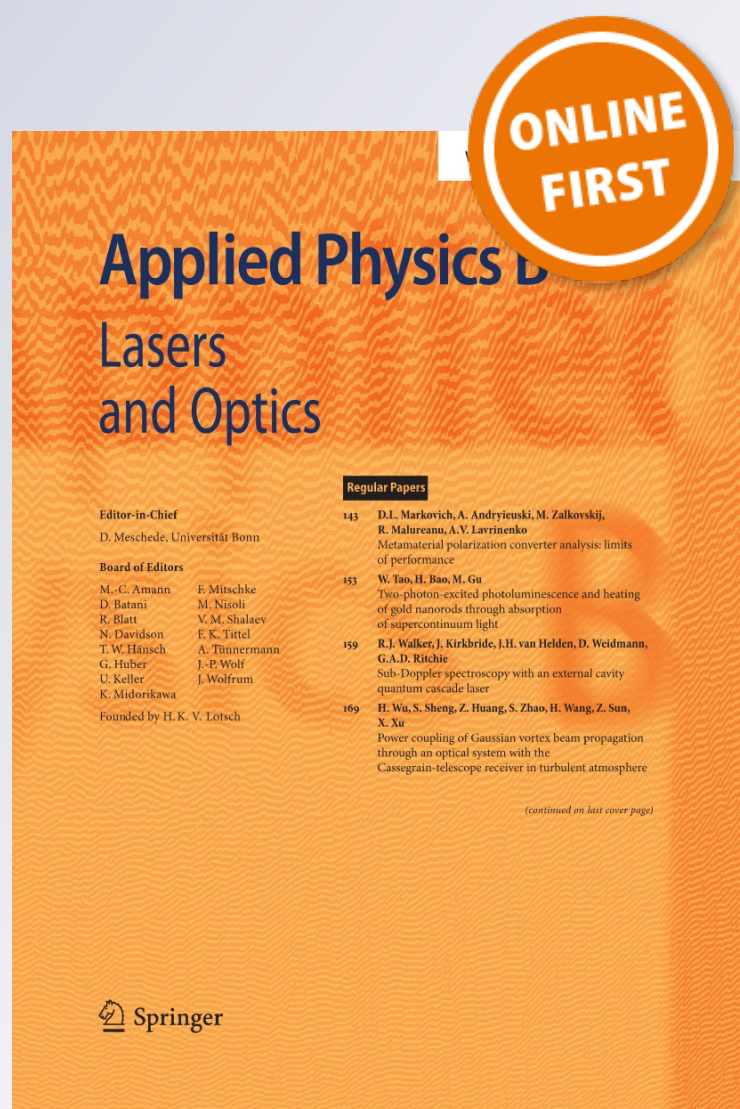
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J. Lehtinen & T. Kuusela

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Broadly tunable quantum cascade laser in cantilever-enhanced photoacoustic infrared spectroscopy of solids

J. Lehtinen · T. Kuusela

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Abstract An external cavity quantum cascade laser (EC-QCL) is applied in the photoacoustic detection of solid samples. The EC-QCL used has a broad tuning range of 676 cm^{-1} ($970\text{--}1,646\text{ cm}^{-1}$) in the mid-infrared region, which enables accurate broadband spectroscopy of large molecules. The high spectral power density of the EC-QCL is combined with an extremely sensitive optical cantilever microphone of the photoacoustic detector to achieve an ultimate sensitivity. The carbon black, polyethylene, and hair fiber samples were measured with the EC-QCL photoacoustic detection using electrical amplitude modulation to demonstrate the possibilities of the setup. The same measurements were repeated with a Fourier transform infrared (FTIR) spectrometer combined with a photoacoustic detector for a comparison. The EC-QCL photoacoustic setup yielded roughly a decade better signal-to-noise ratios than the FTIR setup with the same measurement time.

1 Introduction

The recent achievements in the field of quantum cascade lasers (QCL) have introduced vast opportunities in infrared (IR) spectroscopy. Not only are QCLs commercially available in wider range of wavelengths, but also the tuning ranges have been dramatically increased by including an external cavity (EC) [1]. In addition, multiple QCLs can be combined with the EC design to cover even broader tuning

range. Also, the prices are more reasonable nowadays. The latest designs offer a tuning range for over 600 cm^{-1} in the pulsed mode in the mid-IR region. The tuning range can be selected to cover the fingerprint region in mid-IR enabling the possibilities for material identification and accurate spectroscopy with solid materials, which has previously been limited to standard Fourier transform infrared (FTIR) spectrometers. The applications of interest in QCLs include, for example, broadband multicomponent spectroscopy and IR microscopy [2–4].

One of the most important attributes of IR spectroscopy is its ability to handle physically small samples or small features on samples. This can be done, if the IR beam is small enough: In some applications, the diameter should only be few micrometers. When using conventional FTIR device with an extended thermal source, there are optical limits for how small the focused image of the source could be. If a smaller beam size is needed, the beam must be reshaped by other methods, but it also means very high attenuation of the IR beam. In contrast, the QCL is a point source, and it can be imaged down to a very small spot without excessive losses of throughput. In practice, the spectral radiance of a QCL source can be even seven orders of magnitude higher than the FTIR source.

Quantum cascade lasers have mainly been utilized in the measurement of trace gases in photoacoustic spectroscopy (PAS) [3, 5, 6]. Also, a few research groups have made studies with solids [7–11]. However, to the best of our knowledge, this broad tuning range (676 cm^{-1}) of an EC-QCL has never been used in the photoacoustic detection of solid samples. In this paper, two ultra-sensitive technologies, laser spectroscopy and cantilever-enhanced photoacoustic detection, have been combined to challenge the current established techniques in the research field of IR spectroscopy. The carbon black, polyethylene, and hair

J. Lehtinen (✉) · T. Kuusela
Laboratory of Optics and Spectroscopy, Department of Physics
and Astronomy, University of Turku, Vesilinnantie 5, 20014
Turku, Finland
e-mail: jaaleht@utu.fi

fiber samples have been measured to demonstrate the functionality and possibilities of this setup.

2 Broadband laser spectroscopy

Although tunable laser and FTIR spectroscopies might appear very much alike when used in the mid-IR region, they have some fundamental differences. The data acquisition in a FTIR instrument induces connections between the acquisition parameters that are absent in the laser spectroscopy. The first obvious difference is in the collected wavenumber range. With the EC-QCL, the spectral points are collected independently, which allows the user to determine the collected range. Of course, the measurement time will decrease, if a smaller part of the spectrum is to be investigated. In contrast, the measurement time of a FTIR device cannot be lowered by narrowing the collected range of wavenumbers because of the simultaneous acquisition of the full spectrum. In some sources, this is called the inverse multiplex advantage [4]. Another difference lies in the optical power and resolution. In the case of EC-QCL, the spectral power density is not limited by the used resolution or the size of the laser beam, but merely limited by the line width of the laser. This leads to a great advantage when using high resolution or small sample sizes. In FTIR instruments, a blackbody radiator is used as an IR source. The optical power of the source is spread to the different wavelengths according to Planck's law of blackbody radiation. In FTIR spectroscopy, the resolution should be kept as low as possible, because when the resolution is lowered, signal-to-noise ratio (SNR) increases linearly [12]. If the SNR is to be kept constant when doubling the resolution, the measurement time has to be increased by a factor of 4. Also, the size of the aperture is limited by the used resolution: A full aperture cannot be used, if a spectrum of the highest resolutions is to be recorded. Reduction in the size of the aperture also results in a significant decrease in the optical power and SNR.

Modulation of the source output is a special requirement of the photoacoustic detection. In the case of EC-QCL, the modulation can be performed electrically by altering the current of the QCL chip, or mechanically, with an optical chopper. In each of these cases, the modulation frequency does not depend on the laser wavelength. In the FTIR instrument, the modulation frequency rises linearly when moving from low to high wavenumbers, because the signal from all wavenumbers is gathered simultaneously. In mid-IR region (approximately $400\text{--}4,000\text{ cm}^{-1}$), this means a decade difference in the modulation frequency between the extremes. Particularly in photoacoustic detection, this means that the signal comes from a different depth in the sample in different parts of the spectrum. The thermal

diffusion length is inversely proportional to the square root of modulation frequency, which results in a threefold thermal diffusion length in the lowest wavenumbers [12].

These features can also be related to the comparison of grating and FTIR spectrometers, but without the benefits of QCLs in optical power and resolution. In conclusion, the EC-QCL systems offer a more sophisticated control over the measurement parameters than the FTIR instrument along with the increased spectral power density.

3 Experimental setup

The setup consisted of a broadly tunable EC-QCL and a photoacoustic detector for solid and liquid samples. The EC-QCL was electrically amplitude modulated by altering the current of the QCL chip with the digital signal processing (DSP) unit of the photoacoustic detector. The operation and features of the EC-QCL are discussed in detail in the next section. The laser beam was guided into the photoacoustic cell with an adjustable plane mirror and a focusing mirror. The setup for the detection of the photoacoustic signal is illustrated in Fig. 1. All the components were mounted on an optical table for a stable alignment of the laser beam. A PM100D (Thorlabs, Inc.) optical power and energy meter was used in the measurement of the output power over the full tuning range of the EC-QCL. The laser output power was measured in a separate measurement, in which the power meter was placed right in the front of the EC-QCL before the plane mirror in Fig. 1. As a reference, all EC-QCL measurements were repeated with a Tensor 37 (Bruker Optics, Inc.) FTIR spectrometer using the same photoacoustic detector and measurement parameters. The measurement parameters for all measurements can be found in Table 1.

3.1 EC-QCL

The laser source used in these experiments was a Laser-Tune 610 (Block Engineering, Inc.). In this laser type, a broadband QCL chip is positioned between the collimating output and cavity lenses. The EC on the other side of the cavity lens is a modification of a Littrow configuration with back extraction (the output beam is in the opposite side). A modulating optical element acts as the tuning component. This serves to select the wavelength of the light diffracted from the grating, which couples back into the QCL chip and creates the laser output, in an ideal case, at single wavelength. In practice, however, a diffraction grating always has a certain amount of dispersion, i.e., the grating will allow a small number of laser modes (and not only a single mode) to be simultaneously amplified. In addition, the electrical chirp of each laser

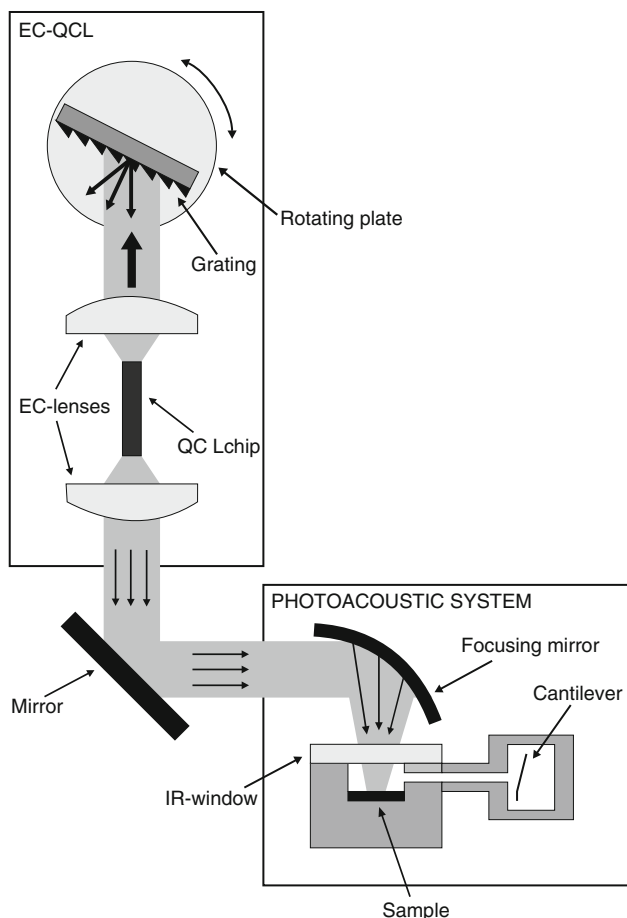


Fig. 1 EC-QCL photoacoustic setup. The operating wavelength of the EC-QCL is selected by the alignment of the grating. Adjustable mirror is used to guide the laser beam into the photoacoustic detector, whereas another mirror is used to focus the beam to the sample cell

Table 1 Measurement parameters. The calculated modulation frequency of the FTIR instrument represents an average value of the modulation frequency in the tuning range of the EC-QCL

	EC-QCL	FTIR
Resolution (cm ⁻¹)	1	1
Modulation frequency (CB, PE) (Hz)	186	182
Modulation frequency (hair) (Hz)	433	414
Measurement time (CB, PE) (min)	26	26
Measurement time (hair) (min)	53	53
Size of the IR beam/aperture (mm)	2 × 4 (elliptical)	6

The corresponding mirror velocities for the FTIR instrument are 2.2 kHz (182 Hz modulation) and 5 kHz (414 Hz modulation)

pulse gives rise to competing laser modes that will broaden the line width, especially at higher duty cycles. This effect can be seen as a significantly larger line width of the output when comparing to typical high-quality single mode laser. Typically, the line width of EC-QCL is

<1 cm⁻¹, and the maximum output power can be several tens or even over a 100 mW [1, 2].

Further, the quantum cascade gain function is high enough for laser operation only over certain range of wavelengths. Thus, if very wide tuning range is needed, also the QCL chip must be changed or several QCLs having differently centered gain curves must be integrated into the system. In the EC-QCL used in this work, two QCL chips with separate cavities were multiplexed into the beam path to achieve continuous spectral coverage. The tuning range of the laser used in our experiments was 676 cm⁻¹ (970–1,646 cm⁻¹), which is wider than any other commercially available mid-IR laser source.

The laser was run in pulsed mode, with a pulse repetition rate of 1.0 MHz and a duty cycle of 3.3 %. From the perspective of the photoacoustic detection, the pulses are very fast, and the operation of the laser can be regarded as continuous or semi-continuous. The actual modulation was performed by taking a burst of pulses. The average output power was few mWatts (the output power as a function of the wavenumber is presented in Sect. 4). The spectral line width of the output light was 1 cm⁻¹. This line width limits the maximal spectral resolution of the system. The tolerance of the wavelength setting was <0.5 cm⁻¹ and repeatability <0.1 cm⁻¹. The laser beam had an elliptical form with dimensions of 2 × 4 mm. The divergence of the beam was <8 mrad. The output beam was strongly polarized, but in the photoacoustic use, this feature was not important. The EC-QCL was used in a step mode, which means that when each time the angle of the grating is altered, a certain time is given for the laser to stabilize. The tuning of the laser could also be performed by altering the angle continuously, which would notably decrease the measurement time.

3.2 Photoacoustic detector

A PA301 (Gasera, Ltd.) photoacoustic detector for solids and liquids was used in all of the measurements. The detector featured an optical cantilever microphone, which can achieve 1–2 decades higher sensitivity when compared to the conventional condenser microphones [13]. The detector consisted of the photoacoustic cell with a focusing mirror and a DSP module for the optical microphone. The total volume of the photoacoustic cell was 8 cm³. The detector used sample cups with 10 mm of diameter, with a maximum sample height of 9 mm; 2-mm-high sample cups were used in the measurements. The photoacoustic cell was purged with helium between the measurements for an enhanced signal. The detector used a 10-μm-thick, 4 × 1 mm silicon cantilever. The position of the tip of the cantilever was measured optically with a Michelson-type

interferometer, and a DSP module was used to process the signals from the interferometer.

4 Results

First, a carbon black sample was measured with the EC-QCL PA setup described earlier. Because carbon black is used as a reference material in FTIR photoacoustic spectroscopy, its photoacoustic signal should only show features of the used equipment. In this case, that is mainly the variation in the laser output power. Figure 2 displays the measured photoacoustic spectrum of carbon black along with the measured output power of the EC-QCL. The photoacoustic signal follows the output power of the laser almost precisely. The sharp downward peaks between 1,400 and 1,580 cm^{-1} indicate a presence of water vapor in the optical path. This could be eliminated by isolating the optical path and purging it with nitrogen, but is not necessary in this study. The ripple in the spectrum around 1,000–1,300 cm^{-1} comes from the tuning of the laser and is highly repeatable. Thus, it is a feature of the laser output power and should not be confused with the noise related to a measurement. Because the ripple is highly repeatable, it appears similarly in all the measured spectra and cancels out, when a spectrum of a sample is divided with a spectrum of the reference material. The results indicate that carbon black should be used as a reference material in this setup similarly to FTIR. Carbon black has been used as a reference material also in some previous EC-QCL photoacoustic studies of hydrocarbons and polymer beads [9, 10].

A polyethylene (PE) disk (1 cm in diameter, 2 mm thick) was measured with the EC-QCL and FTIR setups to investigate the high-resolution performance of both

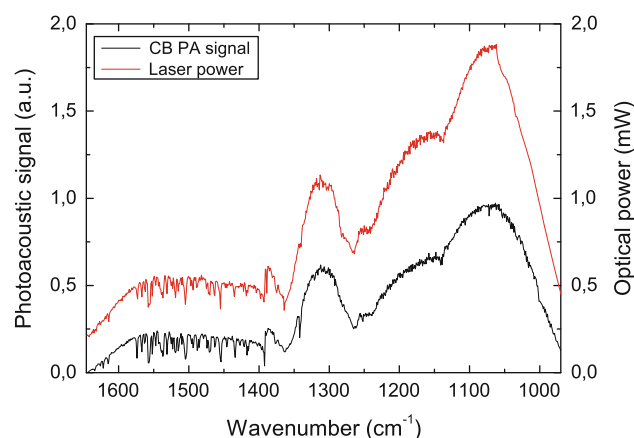


Fig. 2 The optical power of the EC-QCL measured over the whole range and the corresponding photoacoustic spectrum of a *carbon black* (CB) sample

systems with a simple polymer. The background was normalized by dividing the photoacoustic spectrum of polyethylene with the spectrum of carbon black sample in each of the cases. The intensities of the spectra were further normalized by setting the maximum of the methylene group (CH_2) deformation peak (1,460–1,475 cm^{-1}) to have a value of 1. The measured spectra are shown in the Fig. 3. Both spectra share the same features, except for slightly different peak positions and ratios between 1,400 and 1,500 cm^{-1} . The difference in peak positions is probably due to tolerance in the wavelength accuracy of the EC-QCL. If an accurate analysis of the peak positions should be performed, the wavenumber scale of the laser output should be verified with a wavelength meter. The different ratio of the peaks is explained by the sampling of the data points. Even with 1- cm^{-1} resolution, the sharp peaks in the spectra are undersampled. The data collection is different in EC-QCL and FTIR cases, and they both have completely different sources of error.

A more noticeable difference is the noise. The EC-QCL spectrum appears virtually noiseless in this view, while the FTIR spectrum shows a clear noise, especially at wavenumbers below 1,100 cm^{-1} . SNR was calculated for both cases to demonstrate the high sensitivity of the EC-QCL setup. The root-mean-square (RMS) and peak-to-peak noises were calculated from a straight and featureless part of the spectra (from 1,125 to 1,155 cm^{-1}). The calculated values for RMS and peak-to-peak noise levels as well as calculated SNRs for the methylene peak ($2 \times \text{RMS}$) are shown in Table 2. The SNR is roughly speaking one decade better in the case of EC-QCL. In measurement times, this makes even more significant difference as the noise is inversely proportional to the square root of time. The SNR

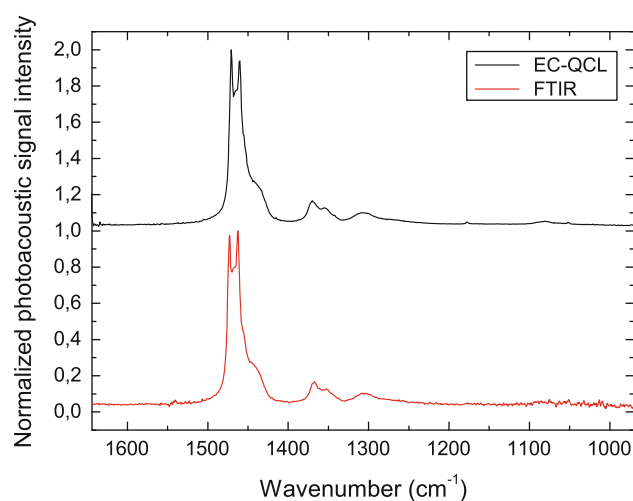


Fig. 3 A mid-IR spectrum of a polyethylene (PE) disk measured with the EC-QCL and FTIR photoacoustic setups. The EC-QCL spectrum has an offset of 1 for a better visualization of the noise level. Both spectra share the same features as expected, but with a different SNR

Table 2 Calculated values for noise and SNR for both EC-QCL and FTIR setups with a polyethylene sample

	EC-QCL	FTIR
RMS noise	4.88×10^{-4}	3.64×10^{-3}
Peak-to-peak noise	2.46×10^{-3}	1.69×10^{-2}
SNR ($2 \times$ RMS)	1,025	137

could further be improved in the case of EC-QCL by equalizing the measurement time for the particular methylene deformation peak instead of the full wavelength range of laser (inverse multiplex advantage).

A single hair fiber (8 mm in length, approximately 50 μm in diameter) was measured with the EC-QCL and FTIR setups to evaluate the performance in a case, in which a small sample has to be measured with high resolution. The situation described could be evident for example in a forensic case, where maximal amount of information should be extracted from small pieces of material. The hair sample was raised from the bottom of the sample cup with a custom-made sample holder to prevent any thermal loss in the cup material. The background was normalized in both cases with a carbon black sample, and the spectra were further normalized by their intensity. Figure 4 shows the measured photoacoustic spectra for both setups. Peaks at 1,020, 1,044, 1,081, 1,105, 1,127, 1,150, 1,175, 1,183, 1,194, 1,203, 1,213, 1,221, and 1,230 cm^{-1} can be distinguished in the EC-QCL photoacoustic spectrum of hair fiber. All the features, except for 1,105 and 1,150 cm^{-1} peaks, could also be identified in the low-resolution reference spectrum measured from a large amount of hair fibers with FTIR in a previous study [14]; 1,020, 1,044, and 1,081 cm^{-1} peaks belong to the symmetric and asymmetric S=O stretching vibrations [15, 16], and 1,127 cm^{-1} peak belongs to the cystine dioxide [16]. Peaks in 1,175–1,230 cm^{-1} can be found in the fine structure of amide III band, which is a combination of N–H and C–O bending, and C–N and C–C stretching vibrations. A more precise explanation for these vibration modes can be found in [17] and [18]. One has to keep in mind that the reference is measured from a bulk of hair and represents an average spectrum of the sample material. Hair is a very heterogeneous material, and the spectrum of a single hair fiber can differ significantly from the spectrum of the bulk. The 1,105 and 1,150 cm^{-1} peaks can also arise from a contamination at the surface of the hair fiber. For example, carbohydrates have peaks at 1,105 and 1,150 cm^{-1} [17]. The FTIR spectrum shows hardly any features as it is heavily buried under the noise. The only features that probably could be identified are the slope of the amide III band and the 1,081 cm^{-1} peak area; 1,050–1,080 cm^{-1} shows a dramatic change in the signal that might represent

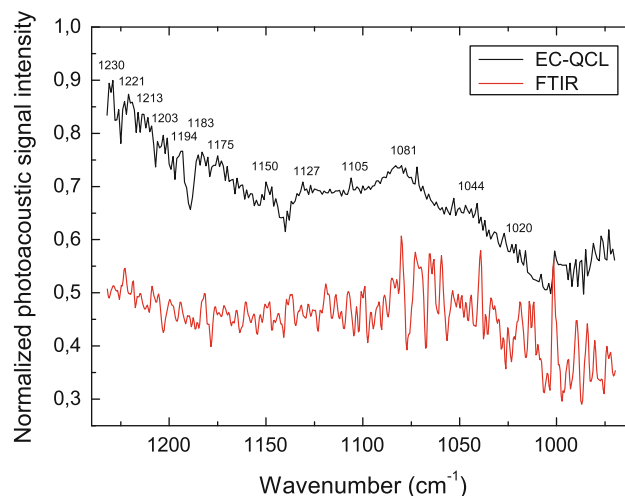


Fig. 4 A single 8-mm hair fiber measured with a high resolution using both EC-QCL and FTIR photoacoustic setups. The EC-QCL spectrum has an offset of 0.2 for a better visualization. The EC-QCL spectrum shows all the significant features of the hair sample in this wavenumber range, while the FTIR spectrum shows mainly noise

the 1,081 cm^{-1} peak. However, nothing can be said about the exact values for the peak position and intensity based on the FTIR spectrum.

Furthermore, in the FTIR measurement, a full 6-mm aperture was used. A full aperture of the FTIR instrument limits the resolution at wavenumbers above 2,222 cm^{-1} . If higher wavenumbers in the mid-IR range should be investigated using the same resolution, the size of aperture needs to be decreased, which will further significantly lower the optical power and thus SNR. Contrary to the FTIR, the beam of the EC-QCL can be narrowed down to a scale of micrometers without losing any throughput due to its point source nature.

5 Conclusion

The EC-QCL proved to be a worthy choice for a source in the mid-IR photoacoustic detection of solids with a decade better SNR than that of the FTIR. In a case of small samples, the difference is even greater, due to the considerably higher spectral radiance of the EC-QCL. In consequence of the higher spectral radiance, all the significant features and fine structure of the spectrum of the hair sample were observed in the EC-QCL spectrum, while the FTIR spectrum provided mainly noise. In addition to the higher spectral radiance and spectral power density, QCL systems are also more independent by their parameters and do not include a complicated entanglement between different settings of measurement parameters. The setup described in this study could have applications especially

in high-resolution spectroscopy of small or low-absorbing samples and in IR microscopy.

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