

Mid-infrared photoacoustic spectroscopy of solids using an external-cavity quantum-cascade laser

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We describe the use of a pulsed external-cavity quantum-cascade laser (EC-QCL) for the acquisition of mid-IR photoacoustic (PA) spectra of solids. The EC-QCL employed in this work operates from 990 to 1075 cm^{-1} (9.30–10.10 μm). A gas-microphone PA cell was used as the detector, and the signal was demodulated using a lock-in amplifier. PA EC-QCL spectra of solids display bands significantly narrower than those in corresponding PA Fourier transform infrared spectra. © 2008 Optical Society of America
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The external-cavity quantum-cascade laser (EC-QCL) has become an important radiation source in several types of mid-IR (400–4000 cm^{-1} , 2.5–25 μm) spectroscopy. While an off-the-shelf QCL can be tuned over a relatively narrow ($\sim 3\text{--}5\text{ cm}^{-1}$) range, incorporation of this device together with a grating in an EC yields tunability over intervals on the order of 100 cm^{-1} or more in width. Several research groups have constructed such laser systems in recent years [1–11], and EC-QCLs are now commercially available. A few applications of these lasers in gas-phase spectroscopy have been reported [12–16].

EC-QCLs can be designed for cw or pulsed operation. The pulsed mode is particularly amenable to time-domain studies or other experiments that intrinsically require modulated excitation. Photoacoustic (PA) spectroscopy belongs to the latter group: Modulated radiation is absorbed by a sample and converted to a thermal wave, which is detected by a suitable transducer. PA IR spectroscopy of solids and liquids has been investigated in detail using Fourier-transform IR (FT-IR) spectrometers and conventional gas-microphone PA cells in our laboratory [17] and discussed in detail by McClelland *et al.* [18,19]. The utilization of a pulsed EC-QCL in an IR PA experiment obviates the usual need for external modulation; lock-in detection at the incident (laser) frequency yields the PA signal. We have recently implemented this technique in the study of condensed-phase materials. Initial results are described in this Letter.

An ambient-temperature EC-QCL with a nominal wavelength of about 9.7 μm ($\sim 1030\text{ cm}^{-1}$), manufactured by Daylight Solutions, was employed in this work. Figure 1 shows the 9.30–10.10 μm (990–1075 cm^{-1}) tuning range of this laser, measured directly with a commercial PA detector containing carbon black powder as the absorbing sample. The solid curves depict tuning curves obtained at two laser currents, 1500 and 1650 mA. In a separate test, the laser emission was monitored using a room-temperature optical detector and a lock-in amplifier.

The result is plotted as the dashed curve in Fig. 1. The three curves in this figure closely resemble the data provided with the laser. It can also be mentioned that the widths of the laser emission lines, measured with an FT-IR spectrometer in this work, are less than 1 cm^{-1} . This is consistent with the specification provided by the manufacturer.

The EC-QCL was employed in conjunction with the PA detector and lock-in amplifier in several experiments. A schematic representation of the layout is depicted in Fig. 2; no spectrometer was used in these measurements, which consisted of series of single-wavelength observations. Figure 3 displays the dependence of the carbon black PA signal on laser pulse width. The duty cycle varied from 0.005 to 0.025% in this trial. Laser emission was at 1055 cm^{-1} and the pulse frequency was 500 Hz. Similar data were obtained at 990 and 1075 cm^{-1} and frequencies that ranged from 100 to 1250 Hz. The results clearly dem-

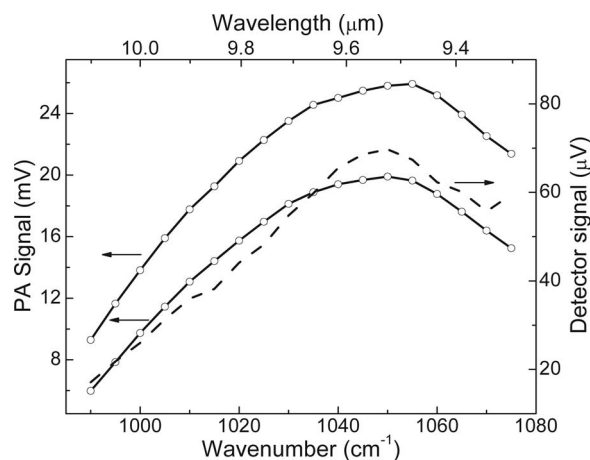


Fig. 1. Tuning range of the EC-QCL used in this work. Solid curves indicate PA signals obtained for carbon black at laser currents of 1650 mA (upper curve) and 1500 mA (lower curve). The dashed curve shows the laser output at 1650 mA measured using an optical detector. In both experiments, the pulse frequency and width were 2 kHz and 0.5 μs , respectively.

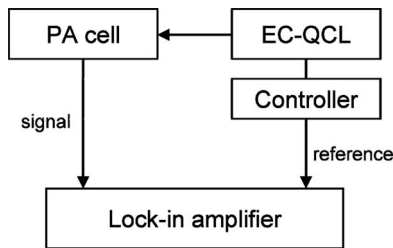


Fig. 2. Schematic diagram of experimental setup for PA spectroscopy using an EC-QCL as the mid-IR source.

onstrate the proportionality between the PA signal and the width of the laser pulse; in other words, the PA signal varies linearly with the energy in the incident beam. This scheme is qualitatively different from more familiar amplitude-modulation experiments in which a cw laser or thermal-source beam is chopped mechanically with a duty cycle of 50%. By contrast, the maximum duty cycle of the EC-QCL used in this work is 5%.

The relationship between PA signal and laser pulse frequency (f) at constant duty cycle (0.08%) is illustrated in Fig. 4 (solid curve). Monotonic diminution of the PA signal is observed for frequencies up to about 1 kHz. At higher pulse frequencies, PA cell resonances near 3 and 10 kHz interrupt this regular decrease. The 3 kHz resonance was also observed in a separate FT-IR experiment using the same PA detector (dashed curve). The response of this detector was assumed to be constant at frequencies as high as several kilohertz.

Closer examination of the EC-QCL data in the 100–1000 Hz region (Fig. 4, inset) shows that the PA signal intensity diminishes linearly when displayed in a log–log plot. The slope of the fitted line (-0.98) is consistent with the expected f^{-1} dependence for an optically opaque, thermally thin solid such as carbon black. Similar frequency dependencies are readily observed in several amplitude- and phase-modulation PA experiments. Possible fine structure due to sample absorption is not discernible in spectra acquired under these conditions.

Another perspective on the laser-frequency dependence of the PA signal is obtained through measure-

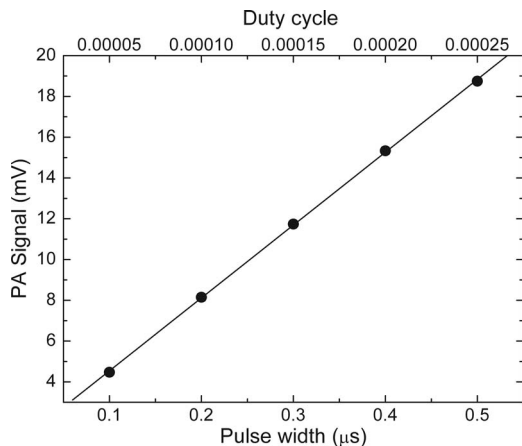


Fig. 3. Carbon black PA signal observed with the EC-QCL at 1055 cm^{-1} using a pulse frequency of 500 Hz. The laser current was 1650 mA. The line is a least-squares fit.

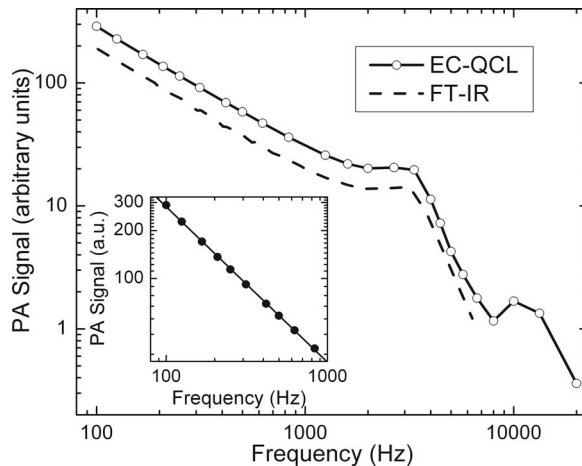


Fig. 4. Variation of the carbon black PA signal with pulse (modulation) frequency. Solid curve, EC-QCL (duty cycle, 0.08%; wavenumber, 1055 cm^{-1} ; current, 1650 mA); dashed curve, FT-IR. The maxima near 3 and 10 kHz correspond to resonance frequencies of the PA cell. Inset, EC-QCL data at frequencies up to 1000 Hz. The line is a least-squares fit and has a slope of -0.98 .

ments where the pulse width is fixed and the duty cycle varies together with f . Figure 5 presents typical results obtained at 1055 cm^{-1} using a pulse width of $0.5\ \mu\text{s}$. The above-mentioned PA cell resonances at 3 and 10 kHz are more prominent in this plot; the first resonance yields signals approximately twice as great as nearby off-resonance values. More important, the PA signal is practically independent of frequency below 1 kHz and the f^{-1} dependence mentioned above is not observed. This finding can be explained by the fact that the PA signal varies linearly with the incident energy (Fig. 3). The f^{-1} dependence of the PA signal is thus canceled by the increase in incident energy with f . Under these circumstances selection of the laser frequency is mainly a matter of convenience, provided that the pulse width is large enough to ensure viable PA in-

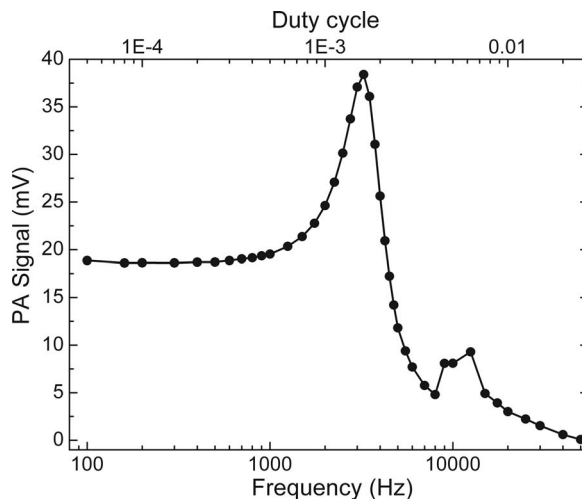


Fig. 5. Variation of the carbon black PA signal at 1055 cm^{-1} with pulse frequency and duty cycle (pulse width, $0.5\ \mu\text{s}$). Maxima are due to PA cell resonances. The laser current was 1650 mA. The line is drawn to aid the reader.

tensity. At very high frequencies, the response of the PA cell falls off and the recorded signals are reduced accordingly.

Finally, we present a result demonstrating the use of the EC-QCL for the acquisition of a PA absorption spectrum. Figure 6 compares the spectrum obtained for 75–150 μm acetyl polystyrene beads using the EC-QCL (solid curve) with a similar PA FT-IR spectrum (dashed curve) recorded at 6 cm^{-1} resolution. Both spectra were source compensated through division by carbon black spectra recorded under like conditions. The EC-QCL spectrum displays bands significantly narrower than those in the FT-IR spectrum. Individual bands are visible near 1005, 1015, 1030, 1045, and 1075 cm^{-1} in the EC-QCL curve. The breadths of the features in the FT-IR spectrum, which may indicate partial PA saturation, hinder the observation of some of these bands. For example, the 1005 cm^{-1} band cannot be identified at all in the FT-IR spectrum. The pulse (modulation) frequency was 475 Hz in both experiments; reduction or elimination of saturation in the EC-QCL spectrum can tentatively be attributed to the use of a pulsed laser. Improved band definition was also observed in EC-QCL PA spectra of several other samples.

In conclusion, this Letter describes the use of an EC-QCL for the measurement of PA IR spectra of solids. The laser used in this work operates from 990 to 1075 cm^{-1} (9.30–10.10 μm). The variation of the PA signal with pulse frequency was investigated

using a constant duty cycle or, alternatively, a fixed laser pulse width. In the former case, the magnitude of the PA signal exhibited the expected f^{-1} dependence. PA absorption spectra of solids obtained using the EC-QCL displayed bands narrower than their counterparts in PA FT-IR spectra.

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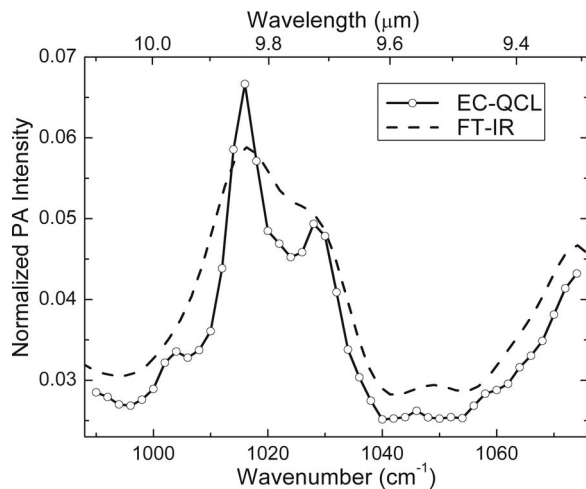


Fig. 6. PA spectra of acetyl polystyrene beads (75–150 μm). Solid curve, EC-QCL (pulse width, 0.5 μs ; current, 1650 mA); dashed curve, FT-IR (resolution, 6 cm^{-1}). The pulse (modulation) frequency was 475 Hz in both experiments.