

Dual beam photoacoustic infrared spectroscopy of solids using an external cavity quantum cascade laser

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Quantum cascade laser-based instrumentation for dual beam photoacoustic (PA) spectroscopy is described in this article. Experimental equipment includes a 4.55 μm (2141–2265 cm^{-1}) continuous wave external cavity quantum cascade laser (EC-QCL), two gas-microphone PA cells, and two lock-in amplifiers. Correction for the time and wavenumber dependence of the laser output is effected through real-time division of the PA signals derived from the sample and reference channels. Source-compensated mid-infrared absorption spectra of carbon black powder and aromatic hydrocarbon solids were obtained to confirm the reliability of the method. Absorption maxima in the EC-QCL PA spectra of hydrocarbons are better defined than those in Fourier transform infrared spectra acquired under similar conditions, enabling the detection of several previously unknown bands. [<http://dx.doi.org/10.1063/1.4727877>]

I. INTRODUCTION

The ultimate goal of any spectroscopic technique, including direct and indirect (e.g., photoacoustic (PA)) absorption methods, is to generate reproducible spectra with identifiable features for post-experiment analysis. This is possible when influences from the radiation source, detector, and the ambient environment are minimal or can be removed, either instrumentally or numerically. For example, most PA infrared spectroscopy¹ is based on single-beam measurements using broadband or tunable light sources. Experiments are usually performed under the assumption that these sources provide stable energy output so that data acquired at different times can be compared reliably. Moreover, variations of the source intensity with wavenumber must be gradual if narrow absorption bands are to be identified unambiguously. As discussed below, these considerations motivated the development of a dual-beam PA system in the present study.

External cavity quantum cascade lasers (EC-QCLs), which operate at a number of mid-infrared wavelengths in pulsed and cw modes, are now capable of providing high power (typically tens to hundreds of milliwatts for cw lasers). Many commercially available EC-QCLs can be tuned across intervals of about one to two hundred wavenumbers. An initial investigation in our laboratory demonstrated the use of a pulsed 9.7 μm (990–1075 cm^{-1}) QCL in the PA infrared spectroscopy of solids.² This previous study employed an ordinary single-beam configuration, necessitating sequential measurement of sample and reference spectra.

The current work extends this research through the utilization of a 4.55 μm (2141–2265 cm^{-1}) cw EC-QCL. Because the emission profile of the laser does not vary smoothly throughout this interval, a dual-beam arrangement was developed. Simultaneous detection of sample and reference PA signals corrects for effects caused by the time- and wavenumber-

dependent laser output, facilitating identification of weak spectral features. The dual-beam apparatus incorporates two gas-microphone PA cells and lock-in amplifiers. Many absorption bands observed with this equipment, like those in the previous work,² are narrower than the corresponding maxima in Fourier transform infrared (FT-IR) PA spectra acquired using broadband sources. This enhancement made it possible to identify a number of previously unknown transitions. PA infrared spectra of four common aromatic hydrocarbon solids were acquired with the dual-beam system in this investigation.

II. DUAL BEAM EXPERIMENTAL SETUP

Figure 1 shows a schematic representation of the dual-beam PA setup. The cw beam from a Daylight Solutions 21045-MHF 4.55 μm EC-QCL (power level ~ 70 mW) is modulated by a mechanical chopper at frequencies ranging from about 50 to 200 Hz and divided using a CaF_2 beamsplitter oriented at approximately 75° to the normal. The transmitted and reflected beams, which have nearly equal power levels, impinge on two MTEC 300 PA cells; the cell in line with the original beam ordinarily contains the sample to be investigated, while the other cell contains the reference material (carbon black powder). It should be noted that both laser beams strike the PA cell windows at normal incidence. The signals from the two PA cells are demodulated using Signal Recovery 7265 lock-in amplifiers referenced to the chopper frequency. An IEEE-488 GPIB interface digitizes the demodulated signals at a rate of 2 Hz by means of a Labview program. The PA signals are sampled 10 times and averaged at each laser wavenumber setting. The average for the sample is divided by that for the reference within the program, producing an ordinate in the ratioed sample spectrum. A complete spectrum is built up point-by-point across the laser tuning range as the QCL output is shifted by 0.5- cm^{-1} increments in step-scan mode; each spectrum contains $2 \times (2265$

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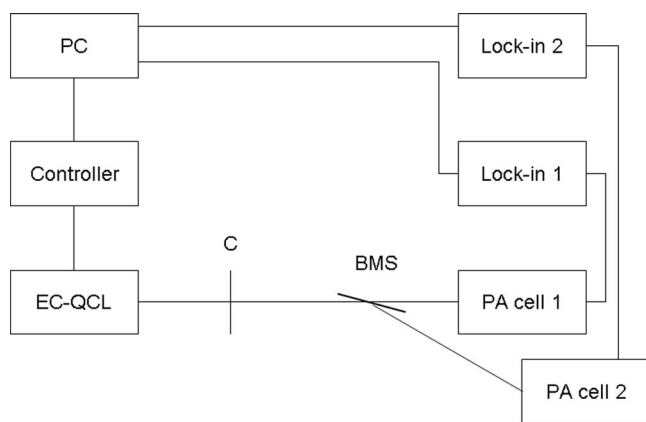


FIG. 1. Schematic representation of equipment used for dual-beam PA infrared spectroscopy. EC-QCL, $4.55\ \mu\text{m}$ cw external cavity quantum cascade laser; C, chopper; BMS, beamsplitter; PC, computer. In practice, laser radiation impinges on both PA cells at normal incidence.

$-2141) + 1 = 249$ points. Data are acquired as the laser emission is step-scanned in either direction (towards higher or lower wavenumbers). The wavenumber accuracy of the laser, as specified by the manufacturer, is $\pm 0.5\ \text{cm}^{-1}$ (about $\pm 15\ \text{GHz}$). The wavelength and current modulation capabilities of this EC-QCL, which are most relevant in high-resolution infrared spectroscopy,³ are not utilized in the present PA experiment. These modulation techniques have recently been implemented in other work.⁴

III. RESULTS

A. Source-compensated carbon black spectrum

Figure 2(a) shows PA spectra of carbon black powder obtained using the sample (lower curve) and reference (upper curve) cells in the dual beam arrangement. The narrow fringes are characteristic of the QCL output. (b) Ratio of the two curves in (a).

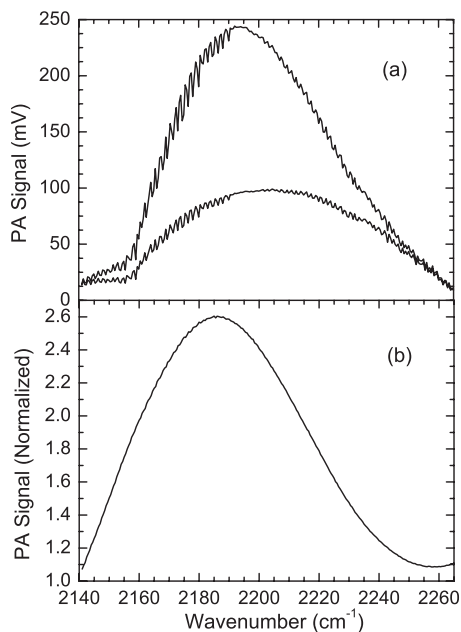


FIG. 2. (a) PA spectra of carbon black obtained at a modulation frequency of 160 Hz using the sample (lower curve) and reference (upper curve) cells in the dual beam arrangement. The narrow fringes are characteristic of the QCL output. (b) Ratio of the two curves in (a).

curve) channels in the dual-beam arrangement. This form of elemental carbon is optically opaque and thermally thin under typical conditions. Consequently PA spectra of carbon black are independent of the absorption coefficient, and can be taken as energy curves. Although the spectra from the two cells tend to converge at both ends of the laser tuning range, their amplitudes differ significantly from about 2145 to $2250\ \text{cm}^{-1}$. In addition, the maxima of the two curves occur at slightly different locations. These results suggest that the characteristic responses of the two PA cells are intrinsically different. The orientation of the beamsplitter and differences in the beam cross-sections may also affect the profiles of the spectra. Both curves display prominent fringe-like structure in the ~ 2140 – $2190\ \text{cm}^{-1}$ region with similar, less intense, structure also appearing above $2200\ \text{cm}^{-1}$. An etalon effect, caused by imperfections in the antireflection coatings, is the likely source of these fringes. The inflections near $2160\ \text{cm}^{-1}$ arise from a QCL mode hop (transition between resonator modes).

Division of the reference spectrum by the sample spectrum in Fig. 2(a) yields the nearly featureless curve in Fig. 2(b). Encouragingly, the triangle-like oscillations in the recorded spectra are virtually eliminated by this simple operation; calculation confirms that their amplitudes are reduced by about two orders of magnitude in the quotient. It is also noteworthy that the mode hop does not produce a signature in the ratioed spectrum. The curve in Fig. 2(b) thus exhibits the desirable source characteristics mentioned in the Introduction. This ratioed carbon black spectrum was used as a reference (background) to correct the hydrocarbon spectra described in the next section. A similar reference spectrum was obtained when the PA cells were exchanged, further suggesting that the profile may arise from geometrical effects. A three-point FFT smoothing filter was applied to the corrected spectra where necessary.

B. PA spectra of aromatic hydrocarbons

PA infrared spectra of pyrene and perylene, four- and five-ring aromatic hydrocarbon solids with empirical compositions $\text{C}_{16}\text{H}_{10}$ and $\text{C}_{20}\text{H}_{12}$, are shown in Fig. 3(a) and 3(b), respectively. Figure 3(a) displays three pyrene spectra. The dashed curve was recorded at a resolution of $6\ \text{cm}^{-1}$ using an FT-IR spectrometer, while the solid curves were obtained in separate dual beam EC-QCL experiments. It should be noted that the lower QCL spectrum has been shifted down by 5 per cent of full-scale intensity for clarity. The improved band definition and good reproducibility of the EC-QCL spectra are clearly evident in this figure. For example, three maxima at 2239 , 2245 and $2251\ \text{cm}^{-1}$ are clearly visible in both EC-QCL spectra; these features coalesce to form a single broad band in the FT-IR spectrum. It should be noted that the width of the FT-IR band (greater than $15\ \text{cm}^{-1}$) is minimally influenced by instrumental broadening. In like fashion, the bands at lower wavenumbers are also significantly narrower in the QCL spectra than in the FT-IR data. A similar result is observed for perylene in Fig. 3(b), where the three curves have the same significance as their counterparts in Fig. 3(a). In fact, the reproducibility of the dual-beam spectra for perylene is

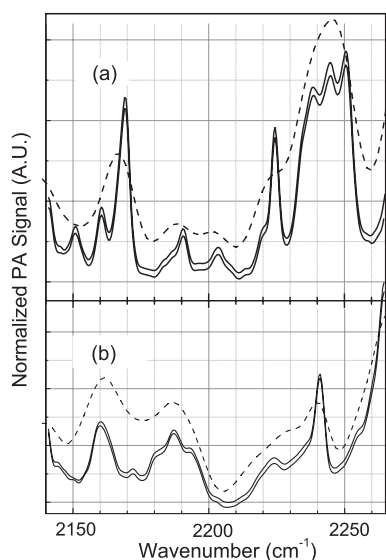


FIG. 3. PA spectra of (a) pyrene and (b) perylene. Dashed curves show FT-IR spectra recorded at a resolution of 6 cm^{-1} . Solid curves are spectra obtained using the dual beam EC-QCL system described in this article. The lower QCL spectra are shifted down by five per cent of full-scale intensity for clarity.

such that the two curves can not be distinguished from each other unless they are offset along the intensity axis, as shown.

Pentacene and tetracene (molecular formulas $\text{C}_{22}\text{H}_{14}$ and $\text{C}_{18}\text{H}_{12}$) yielded the spectra in Fig. 4(a) and 4(b), respectively. A single EC-QCL curve is plotted for the appropriate species in each part of this figure. The dual-beam PA spectra display much more detail than that in the FT-IR spectra, similar to the differences observed for pyrene and perylene in Fig. 3. Indeed, many of the absorption bands in the $2141\text{--}2265\text{ cm}^{-1}$ region for all four hydrocarbons (discussed briefly in the next section) were observed for the first time in this investigation. In addition, the high signal/noise ratios in the QCL spectra make it possible to identify both strong and weak features with confidence.

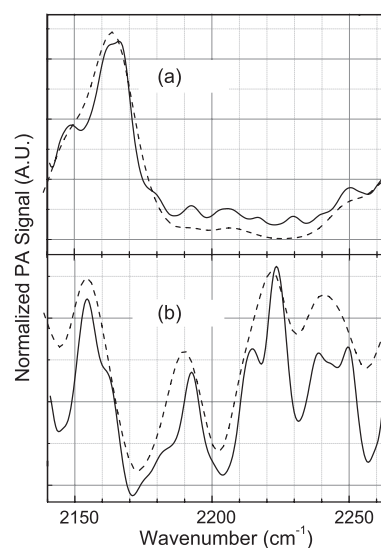


FIG. 4. PA spectra of (a) pentacene and (b) tetracene. Dashed curves show FT-IR spectra recorded at a resolution of 6 cm^{-1} . Solid lines are spectra obtained using the dual beam EC-QCL system.

C. Band positions and assignments

The locations of the observed bands in the EC-QCL and FT-IR spectra for pyrene and perylene (Fig. 3), together with potential band assignments, are listed in Table I. Corresponding data for pentacene and tetracene (Fig. 4) appear in Table II. All of the bands reported in these tables arise from combinations or overtones of the much stronger fundamental transition bands below 1500 cm^{-1} in the infrared and Raman spectra⁵ of these hydrocarbons. These combinations and overtones occur because of mechanical anharmonicities in the molecular vibrations. As might be expected, several possible assignments can be proposed for some of the bands in Tables I and II; for simplicity, only one assignment per band is given in the tables. More importantly, it should be emphasized that the dual beam EC-QCL spectra enable

TABLE I. PA infrared bands (in cm^{-1}) of pyrene and perylene observed in EC-QCL and FT-IR spectra. Columns 3 and 6 show possible assignments to combinations or overtones of bands at lower wavenumbers.⁵

Pyrene ($\text{C}_{16}\text{H}_{10}$)			Perylene ($\text{C}_{20}\text{H}_{12}$)		
EC-QCL	FT-IR	Assignment	EC-QCL	FT-IR	Assignment
2151	2151	$912 + 1241 = 2153$	2144	2145	$813 + 1332 = 2145$
2160	...	$1064 + 1096 = 2160$	2160	2160	$1040 + 1126 = 2166$
2169	2167	$963 + 1206 = 2169$	2172	...	$889 + 1288 = 2177$
2183	...	$912 + 1274 = 2186$	2180	2181	$967 + 1211 = 2178$
2187	...	$1014 + 1171 = 2185$	2187	2186	$1040 + 1149 = 2189$
2191	2189	$2 \times 1096 = 2192$	2193	2194	$813 + 1382 = 2195$
2204	2203	$963 + 1241 = 2204$	2203	...	$769 + 1439 = 2208$
2214	...	$750 + 1466 = 2216$	2224	2222	$889 + 1332 = 2221$
2220	...	$803 + 1419 = 2222$	2235	2231	$899 + 1332 = 2231$
2224	2224	$912 + 1313 = 2225$	2241	2240	$752 + 1494 = 2246$
2235	...	$1064 + 1171 = 2235$	2255	...	$967 + 1288 = 2255$
2239	...	$912 + 1324 = 2236$			
2245	2244	$1000 + 1241 = 2241$			
2251	2251	$1064 + 1185 = 2249$			

TABLE II. PA infrared bands (in cm^{-1}) of pentacene and tetracene observed in EC-QCL and FT-IR spectra. Columns 3 and 6 show possible assignments to combinations or overtones of bands at lower wavenumbers.⁵

Pentacene ($\text{C}_{22}\text{H}_{14}$)			Tetracene ($\text{C}_{18}\text{H}_{12}$)		
EC-QCL	FT-IR	Assignment	EC-QCL	FT-IR	Assignment
2149	2146	$759 + 1392 = 2151$	2155	2156	$959 + 1197 = 2156$
2163	2163	$1013 + 1051 = 2164$	2162	...	$753 + 1409 = 2162$
2166	...	$1051 + 1116 = 2167$	2175	...	$881 + 1297 = 2178$
2180	...	$959 + 1221 = 2180$	2182	...	$1061 + 1122 = 2183$
2193	2191	$771 + 1421 = 2192$	2193	2192	$784 + 1409 = 2193$
2205	2202	$908 + 1298 = 2206$	2200	...	$904 + 1297 = 2201$
2217	...	$743 + 1474 = 2217$	2215	...	$753 + 1464 = 2217$
2229	...	$2 \times 1116 = 2232$	2223	2224	$931 + 1297 = 2228$
2240	...	$743 + 1498 = 2241$	2239	...	$1043 + 1197 = 2240$
2250	2249	$908 + 1342 = 2250$	2243	2241	$836 + 1409 = 2245$
2264	...	$991 + 1272 = 2263$	2250	2248	$971 + 1280 = 2251$

identification of absorption bands which are not observable by conventional methods, thus permitting a fuller characterization of these species.

IV. DISCUSSION AND SUMMARY

This article describes a simple dual beam PA spectroscopy system based on a commercially available cw mid-infrared EC-QCL. In this setup, modulated laser radiation is arranged to fall on two gas-microphone PA cells. The signals from these cells are demodulated using lock-in amplifiers and analyzed in a Labview program. The dual beam system allows simultaneous measurement of two spectra (e.g., sample and reference), thus facilitating real-time correction for fluctuations in laser power and the variation of laser intensity with wavenumber. Relative intensities of medium and strong bands can be quantified using this methodology.

Bands in PA spectra of hydrocarbon solids acquired with the dual beam apparatus are significantly narrower than those in medium-resolution FT-IR spectra. Modulation frequencies are similar in the two experimental methods. Analogous results were observed previously in single-beam PA spectroscopy using a pulsed EC-QCL and tentatively attributed to reduced PA saturation with that system.² However, the relatively high laser powers employed in the current work and other PA experiments using a CO_2 laser⁶ tend to suggest that

this reasoning is unlikely. The resolution enhancement may instead be ascribed to motional narrowing⁷ arising from the intense laser radiation. Experiments designed to study this effect are currently in progress. The linewidth of the QCL (less than 45 MHz, or about 0.0015 cm^{-1}) could also contribute to the observed narrowing. Irrespective of cause, the reduced widths facilitated the observation of a number of previously unknown bands with the dual beam system. These bands were readily assigned to combinations and overtones of fundamental transitions at lower wavenumbers. The fundamental bands were observed in separate FT-IR experiments using broadband sources and PA detection, or alternatively by use of Raman spectroscopy. Further EC-QCL PA investigations based on the dual beam system are presently under way in our laboratory.

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