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Near-infrared broad-band cavity enhanced absorption spectroscopy using a superluminescent light emitting diode

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A fibre coupled near-infrared superluminescent light emitting diode that emits ~10 mW of radiation between 1.62 and 1.7 μm is employed in combination with a broad-band cavity enhanced spectrometer consisting of a linear optical cavity with mirrors of reflectivity ~99.98% and either a dispersive near-infrared spectrometer or a Fourier transform interferometer. Results are presented on the absorption of 1,3-butadiene, and sensitivities are achieved of \(6.1 \times 10^{-8} \text{ cm}^{-1}\) using the dispersive spectrometer in combination with phase-sensitive detection, and \(1.5 \times 10^{-8} \text{ cm}^{-1}\) using the Fourier transform interferometer (expressed as a minimum detectable absorption coefficient) over several minutes of acquisition time.

Introduction

Broad-band cavity enhanced methodologies, *i.e.* those techniques that utilise broad-band emission sources, are increasing in popularity where it is desirable either to measure several compounds simultaneously that absorb in different spectral regions or where specificity is required for target species with extended absorption features (such as relatively large molecules or surface/liquid-borne species). Several studies have been reported that combine different broad-band sources such as arc-lamps1–6 and light emitting diodes (LEDs)7–12 with dispersive and interferometric detection schemes to detect gas phase species such as iodine oxides,3 NO, compounds7,8,10,11 and solutions containing dyes (e.g. coumarin 334, brilliant blue-R, and rhodamine B and 6G)12,13 which absorb at visible wavelengths. High power supercontinuum sources have also been demonstrated in cavity enhanced spectroscopy,14,15 but these are devices that represent a major financial investment, generate a wide spectral output, usually much larger than the stop band of the high reflectivity cavity mirrors, and generally have optimised performance in the visible and near-IR (<1 μm). Only recently have results appeared utilising sources for cavity enhanced spectroscopy in the near-IR1 in an incoherent broad-band cavity enhanced absorption spectroscopy experiment (IBB-CEAS) using a Xe arc source and an FTIR spectrometer. As a consequence of the low spectral power density, mirror reflectivity and spatial coherence of the arc-lamp, and the high resolution desired in these experiments, long acquisition times (>1 h) were required in order to attain reasonable sensitivities (~10^{-6}–10^{-5} \text{ cm}^{-1} \text{ Hz}^{-1/2}).6

In this paper, we present work that utilises a fibre coupled superluminescent light emitting diode source (SLED) that has a relatively high spectral power density (~200 μW nm^{-1}) and a high spatial coherence, in the spectral range 1.6 μm < λ < 1.7 μm, where hydrocarbon molecules such as isoprene, acetone and butadiene exhibit broad, congested overtone absorptions, in contrast to the narrow linewidth absorptions of species such as CO₂ and HDO, previously studied by IBB-CEAS in the near-IR.6 Such molecules are important as markers of disease, and/or because of their toxicology.16–18 Here, results are presented on the absorption of 1,3-butadiene, a hazardous air pollutant produced on an industrial scale for the generation of synthetic rubbers and plastics, which is released from the burning of plastics and is present in cigarette smoke and vehicular exhaust: it is known to produce respiratory problems and is a human carcinogen.19 Detection schemes, making use of a dispersive monochromator with lock-in detection and a Fourier transform interferometer, are demonstrated and compared. Relatively high levels of sensitivity are achieved (~10^{-5}–10^{-7} \text{ cm}^{-1}) within a moderate measurement time (a few minutes).

Experiment and methodology

The SLED (DenseLight Semiconductors) generates ~10 mW of total output power (from the fibre) at a driving current of ~300 mA (Thorlabs current driver LDC205C), and its measured spectral output is shown in Fig. 1 (peak at 1650 nm; 3 dB bandwidth of 50 nm). The unit is temperature stabilised (Thorlabs temperature controller TED200C) within a 14 pin diode laser butterfly package and situated in an appropriate mount (Newport). A schematic of the experimental arrangement is shown in Fig. 1. The SLED fibre output is decoupled and directed to a linear optical cavity consisting of two high reflectivity mirrors (REO Inc.) and is of length ~25 cm, and is enclosed within a vacuum vessel. A diode laser operating at 1650 nm is co-aligned with the SLED to aid in the alignment of the optical cavity. The cavity is then aligned with the diode laser such that low order modes dominate the cavity transmission. The light exiting the cavity is directed towards one of two spectrometers. The first is a 0.5 m scanning monochromator (SPEX Industries) in a Czerny–Turner configuration, and the second, an FTIR device (Perkin Elmer Spectrum 100). For the former, two lenses are used to first collimate the cavity output beam and then focus the radiation into the spectrometer so as to satisfy the spectrometer’s internal optical arrangement and illuminate as much of the grating as possible. An InGaAs detector (Thorlabs DET410) is positioned behind the exit slit to record the intensity of the selected radiation component as the spectrometer scans, and is connected to a lock-in amplifier (Stanford Research) which receives a reference signal (~1 kHz) from the mechanical chopper controller in order to realise phase-sensitive
detection. For the FTIR spectrometer the collimated beam, exiting the optical cavity, is directed into the interferometer without further modification. The same detector (DET410) is used to detect the resulting interferogram; for the FTIR, the cavity signal is amplified (×10) and processed on-board. No lock-in detection is used in conjunction with the FTIR.

Samples of 1,3-butadiene (Sigma-Aldrich 99+%) are used without purification, and are diluted with air to 1 in 100 dilutions for detection in the optical cavity. Single pass (i.e. non-cavity enhanced) data are also recorded of various pressures of neat 1,3-butadiene by removing the cavity mirrors from the vacuum vessel. In general the sample pressure within the vacuum vessel is kept between 5 and 70 Torr and is monitored by a capacitance manometer (Leybold Piezovac). Single pass absorption is analysed assuming standard Beer–Lambert absorption behaviour, while that of the cavity enhanced absorption is treated according to the equation:

$$\frac{(I_0 - I)}{I} = \frac{\alpha L}{1 - R}$$

(1)

where $I$ and $I_0$ are the recorded signal with the presence and without the presence of the absorber, respectively, $\alpha$ is the absorption coefficient, $L$ is the pathlength, and $R$ is the geometric mean of the mirror reflectivity. Background spectra are acquired by pumping down the vacuum vessel, and the wavelength dependent mirror reflectivity was determined by comparing the single pass data with those of the cavity enhanced data.

**Results and discussion**

Single pass absorption spectra of 1,3-butadiene are shown in Fig. 2a,b using the SPEX and the FTIR spectrometers with the SLED as a source. The independent determination (not shown) of the wavelength calibration and the resolution of the SPEX spectrometer is achieved by measuring the transmission of the 1650 nm diode laser, and also measuring a methane spectrum, where the Q-branch of the $2v_1$ molecular overtone can be clearly recognised (@ $\lambda = 1666$ nm). By changing the exit slit width, and adjusting the lock-in time constant such that it does not limit the resolution (this can influence the resolution because the spectrometer is used in a scanning configuration), resolutions of ~1.8 cm$^{-1}$ are possible with this spectrometer. All the butadiene absorption data are in good agreement, and a clear linearity in absorption is observed as a function of 1,3-butadiene pressure (Fig. 2b inset). We note that greater noise levels are apparent at the limits of the SLED emission profile as a consequence of the lower light intensity in these regions ($\lambda < 1615$ nm and >1680 nm). The resulting absorption cross-sections derived from these data (see Fig. 2) are in reasonable agreement with other reported values determined with a diode laser (2.5 × 10$^{-20}$ cm$^2$ at 1651.52 nm). Some data are used to extract the wavelength dependent mirror reflectivity when analysing the cavity enhanced datasets, and the resulting reflectivity is then used to correct the cavity enhanced absorption of different datasets (see Fig. 3). No attempt was made to further verify the wavelength dependence of the mirror reflectivity, using, for example, another broad-band absorber with well known absorption cross-sections, but we note that with a methane sample in the cavity appropriate levels of methane absorption were observed commensurate with the reported reflectivity at 1666 nm. The broad features in the absorption profile are a result of an amalgamation of various overtones and combination bands consisting of C–H stretches as defined in ref. 22, and even using the highest resolution available with the FTIR (0.5 cm$^{-1}$) the absorption spectrum shows very little fine detail or structure.

With the optical cavity in place, the SPEX spectrometer in conjunction with the lock-in detection is configured to optimise the measurement of the broad absorption features; the combination of the dispersion, the exit slit width, and the time constant yield an approximate resolution of ~15 cm$^{-1}$. Results of single scans are shown in Fig. 3a for varying sample pressures and expressed as $(I_0 - I)/I$. The wavelength dependent mirror reflectivity ($R(\lambda)$) is also determined from a comparison of the cavity enhanced butadiene data with the cross-section measurements and is shown in Fig. 3b. The absorbance ($\alpha L$) can then be extracted and is presented in Fig. 3c.

**Fig. 1** Experimental schematic. IR radiation from the SLED is directed into the optical cavity (consisting of concave mirrors M$_1$ and M$_2$) within a vacuum chamber. For detection using the SPEX spectrometer, the IR is collimated and then focused in through the entrance slit in such a way as to fill the grating and satisfy the spectrometer’s internal optics. With the FTIR, the light is merely collimated and aligned into the interferometer. No phase-sensitive detection is used with the FTIR. A diode laser (shown) is used for cavity alignment purposes. The inset graph shows the SLED emission profile.
Fig. 2 (a) Single pass spectroscopy of neat butadiene at different pressures as acquired using the SPEX spectrometer with no lock-in detection. The resolution is estimated to be 15 cm⁻¹ for these data, controlled by the size of the exit slit. (b) Single pass spectra of neat butadiene using the FTIR for different sample pressures at a resolution of 0.5 cm⁻¹. The inset shows the height of the absorption peaks at 1625 nm and 1666 nm as a function of sample pressure, indicating a linear relationship. The main features marked A, B and C, correspond to the 0|0|0, 0|2|0 and 0|0|2 combination and overtone transitions, respectively, where |nᵢ|ₛ₀ₙᵢ|ₜᵢ⟩ represents vibrational quanta in the trans-terminal, cis-terminal and non-terminal C–H stretches. The measured cross-sections for these features are 4.25 x 10⁻²⁴ cm², 1.84 x 10⁻²⁵ cm², and 2.43 x 10⁻²⁵ cm², respectively, with an estimated 5% error.

Fig. 3 (a) Cavity enhanced data recorded using the SPEX spectrometer of 1 in 100 dilutions of butadiene at the total pressures of 6.7, 9.9 and 13.1 Torr. (b) The mirror reflectivity as a function of wavelength extracted from a different dataset to those shown (to avoid merely reporting a mathematical self-consistency in (c)). (c) The cavity enhanced spectra corrected for the changing mirror reflectivity in (b). The instrumental resolution is 15 cm⁻¹; data are acquired over about 6 min, and the best mirror reflectivity recorded here is 99.97% at 1660 nm. The lock-in time constant is 10 s.

A similar exercise was completed using the FTIR spectrometer, but optimising the on-board instrument resolution. At high resolution (~0.5 cm⁻¹) regular features can be seen in the cavity enhanced absorption, which we attribute to the possible presence of a residual etalon or to small instabilities in either the SLED output, or in the detection system (see Fig. 4). Further investigation is required to identify this noise source; however, it is not apparent in the low resolution spectra, and consistent with the SPEX data we find that an optimal resolution for accurate, but low noise reproduction of the absorption features is 16 cm⁻¹. The values of absorbance deduced for different sample pressures of butadiene as measured by the FTIR are shown in Fig. 4 (corrected for R(λ)); the 16 cm⁻¹ resolution data took 240 s of measurement time. Sequential background scans and analysis through eqn (1) results in a minimum detectable absorption coefficient of 1.5 x 10⁻⁸ cm⁻¹ for these data, which corresponds to butadiene levels of 600 ppb, assuming an average absorption cross-section of 1 x 10⁻²⁷ cm². The higher resolution scan in Fig. 4 took 14 min to acquire, and a mirror reflectivity of up to 99.98% recorded, resulting in a pathlength enhancement factor (~1/(1 - R)) of 5000.

We note immediately that the sensitivities attainable from these two spectrometers are of the same order of magnitude over a similar acquisition time, and for the same resolution. The main advantage that the FTIR provides over the scanning monochromator is one of speed (the Felgett or multiplex advantage). This can be approximated by considering the ratio of the total spectral range covered (~100 nm) to the effective step size of the monochromator (this is ~1 nm), which is ~100, and would therefore lead to an increase in S/N ratio for the FTIR of 10 (i.e. the monochromator would take 100 times longer than the FTIR to attain the same S/N ratio at every point over the spectrum). However, the ability of the phase-sensitive detection to...
mitigate noise in the scanning monochromator experiments seems to have resulted in a gain in sensitivity for that system, and this almost certainly results in the similarity of the sensitivities. A wide range of sensitivities have been reported for BB-CEAS techniques (from \( \sim 5 \times 10^{-10} \text{ cm}^{-1} \) to \( \sim 10^{-6} \text{ cm}^{-1} \) (see, for example, refs 1–8, 10, 11)), primarily because of widely different parameters, such as physical pathlength, spectral power density, mirror reflectivity, and resolution. A comparison between different studies is thus difficult, particularly as in many cases quantities, such as the spectral power density incident on the cavity, are unknown or not reported. Nevertheless, the sensitivity reported here seems appropriate compared with cw-laser based cavity methods, where the spectral power density is perhaps \( \sim 10^4 \) times higher, and better sensitivities are reported with much faster acquisition times. At higher resolution, the sensitivity can be maintained, but data acquisition takes necessarily longer. The real benefits of using BB-CEAS, and accessing the highest sensitivity achievable with a relatively simple technique, are where absorption features are broad-band and thus where resolution can be sacrificed to optimise detection performance. Clearly, this method is therefore suited to the sensitive detection of relatively large molecules in the gas phase, molecules in a liquid or solid matrix, or those upon surfaces, although it should be noted that the success of such a technique may well ultimately depend upon interfering species that absorb in the same spectral region.

**Conclusion**

BB-CEAS has been demonstrated using a convenient SLED source in the near-IR using both a scanning monochromator with lock-in detection and with an FTIR spectrometer. The FTIR exhibits a slight advantage in sensitivity, but a major advantage in convenience: the FTIR comes as a stand-alone package, which is much easier to align optically, provides near real-time visualisation of data, and is without the need for phase-sensitive detection. The experimental systems have been applied to the detection of dilute gaseous samples of 1,3-buta diene in an optical cavity with an effective pathlength enhancement factor of 3000. Without sample preconcentration, sub-ppm sensitivity levels are reported, therefore, with the techniques presented here, there is a real prospect of direct and quantitative measurements of butadiene from industrial and vehicular sources.

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**Notes and references**