



Optical fibre long period grating based selective vapour sensing of volatile organic compounds

S.M. Topliss^a, S.W. James^{a,*}, F. Davis^b, S.P.J. Higson^b, R.P. Tatam^a

^a Engineering Photonics Group, School of Engineering, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK

^b Cranfield Health, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK

ARTICLE INFO

Article history:

Received 1 May 2009

Accepted 2 October 2009

Available online 29 October 2009

Keywords:

Optical fibre sensor

Long period grating

VOC

Calixarene

ABSTRACT

The chemical sensing capabilities of an optical fibre long period grating (LPG) coated with a functional material are explored. The LPG period and coating thickness are chosen such that the mode transition region, characteristic of LPGs coated with nanostructured coatings, corresponds with the phase matching turning point, ensuring optimum sensitivity. The functional material is a calixarene, which is shown to exhibit sensitivity to the aromatic compounds toluene and benzene, while being relatively insensitive to the aliphatic hydrocarbon hexane. A nanoscale cavity in the calixarene molecule entraps the VOC molecule, thereby altering the refractive index of the coating and influencing the transmission spectrum of the LPG. A sensitivity to toluene of 231 ppmv has been achieved, based on a spectrometer resolution of 0.3 nm. This is a weak molecular interaction thereby ensuring the sensor gives a reversible response when the VOC is removed. The recovery time is of the order of 15 s.

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1. Introduction

The sensing of volatile organic compounds (VOCs) is of importance in a range of applications, for example, monitoring air quality in both indoor and outdoor environments, and for monitoring soil and water contamination [1]. VOCs can originate from fuel and petroleum products, from paints and inks, and by combustion processes, natural sources and farming [2]. There are a wide range of VOCs but the BTEX chemicals, that is benzene, toluene, ethylbenzene and xylene, are of particular interest. The ability to detect this chemical family and be able to distinguish it from the other aliphatic hydrocarbons is an important requirement for a detection system, since the aromatic hydrocarbons have a far higher toxicity. Although less toxic than benzene, the health effects arising from exposure to toluene are numerous, including respiratory problems and the abnormal development of the foetus in pregnant women, leading to birth defects [3]. The detection of BTEX compounds using SPR techniques [4] has been reported with spin coated films of calixarene onto gold coated glass substrates, obtaining increasing levels of sensitivity for xylene, butanol, hexane, toluene and benzene.

The use of fibre optic long period gratings (LPGs) coated with films of functional materials as a platform for the development of chemical sensors has been explored in recent years [11,12,17].

Changes in the refractive index or thickness of the film in response to the analyte influence the attenuation bands that are characteristic of the transmission spectrum of the LPG. The sensor described in this paper utilizes a calixarene to form the nanostructured coating, which is shown to facilitate the sensing of toluene and benzene, while being relatively insensitive to aliphatic hydrocarbons.

2. Dual resonance in long period gratings

An LPG consists of a periodic modulation of the refractive index of the core of an optical fibre [29]. The modulation of the core refractive index may be achieved in a number of ways, perhaps most often by ultraviolet (UV) irradiation [5], irradiation by CO₂ lasers [6], and electrical discharges [7]. The period of the LPG, typically in the range 100 µm to 1 mm, is such that light is coupled from the core of the fibre to a subset of symmetrical cladding modes at discrete wavelengths, creating attenuation bands within the transmission spectrum of the fibre, with the resonant wavelengths governed by the phase matching expression [8].

$$\lambda_{(x)} = \frac{(n_{\text{core}} - n_{\text{clad}(x)})\Lambda}{N} \quad (1)$$

where $\lambda_{(x)}$ represents the wavelength at which coupling occurs to the LP_{0x} mode, n_{core} is the effective refractive index of the mode propagating in the core of the fibre, $n_{\text{clad}(x)}$ is the effective index of the LP_{0x} cladding mode, Λ is the period of the LPG and N is an integer representing the order of diffraction.

* Corresponding author.

E-mail address: s.w.james@cranfield.ac.uk (S.W. James).

The efficiency of coupling to the asymmetric modes is small, and thus in general no attenuation bands corresponding to this coupling are visible in the transmission spectrum. The core and cladding modes experience differential changes in their effective indices in response to measurands such as strain, temperature and bending. Since the cladding modes' effective indices will be influenced by the optical properties of the material surrounding the cladding [9], this facilitates the formation of sensors based upon the measurement of the change in refractive index of a coating deposited onto the region of fibre containing the LPG.

Such devices show two modes of operation, differentiated by the refractive index and thickness of the coating. For films of refractive index lower than that of the cladding and of appropriate thickness (typically $>1\ \mu\text{m}$) the response is the same as that exhibited by LPGs when they are bulk-immersed in a medium of lower refractive index [10]. Here, increasing refractive index results in a blue shift of the central wavelength of the attenuation bands, which exhibit their highest sensitivity when the coating's refractive index approaches that of the cladding. This has been reported recently for the detection of toluene vapour and xylene vapour, demonstrating minimum detectable concentrations of 0.22 ppm [11] and 300 ppm, respectively [12].

For coatings of refractive index higher than that of the cladding, the LPG transmission spectrum has been shown to exhibit a strong sensitivity to the optical properties of the coating for thicknesses of order 100 nm [13]. The response is characterised by reorganisation of the cladding modes when the optical thickness of the coating is such that the lowest order cladding mode is phase matched to a mode of the waveguide formed by the coating [14]. The mode reorganisation is accompanied by a rapid increase in the effective refractive index of the cladding modes, and a concomitant change in the wavelength of the attenuation bands. The optical thickness range over which the reorganisation occurs is termed the mode transition region. These effects have been used to demonstrate sensors, with detection limits in the sub-ppm range, for the chemical compound chloroform [17]. Optimisation of the sensitivity of these devices relies on careful choice of the period of the LPG and of the thickness and refractive index of the coating and requires high resolution control over the coating thickness, which can be achieved by depositing the film using the electrostatic self assembly [15], Langmuir–Blodgett (LB) [13] and dip coating [16] techniques.

Phase matching curves generated by the solution of Eq. (1) are an important design tool for long period gratings, allowing the calculation of a complete set of discrete wavelength resonances [18]. Fig. 1 shows the phase matching curves predicted for a fibre of cut-off wavelength 670 nm. The cladding modes are numbered, corresponding to the order of each mode, and the resonant wavelengths are indicated by the intersection of the phase matching curve and a line parallel to the wavelength axis. A turning point in the phase matching curves is seen [19], making it possible to couple to the same cladding mode at two different wavelengths, producing dual-resonant bands in the transmission spectrum [20].

When the grating period is such that the phase matching turning point is accessed, a single resonant band is observed in the spectrum. As the difference between the effective indices of the core and cladding mode decreases in response to an external perturbation, as might be observed if the surrounding refractive index is increased, the phase matching curves move in the direction indicated by the arrow. The extinction ratio of this resonant band increases and its full width at half maximum broadens but the central wavelength remains fixed, until dual-resonant bands are resolved. Further increases in the effective index of the cladding mode cause the dual-resonant bands to move apart in wavelength. It has been shown that the region of onset of dual resonance gives the greatest sensitivity in terms of wavelength change with change in thickness or refractive index [21].

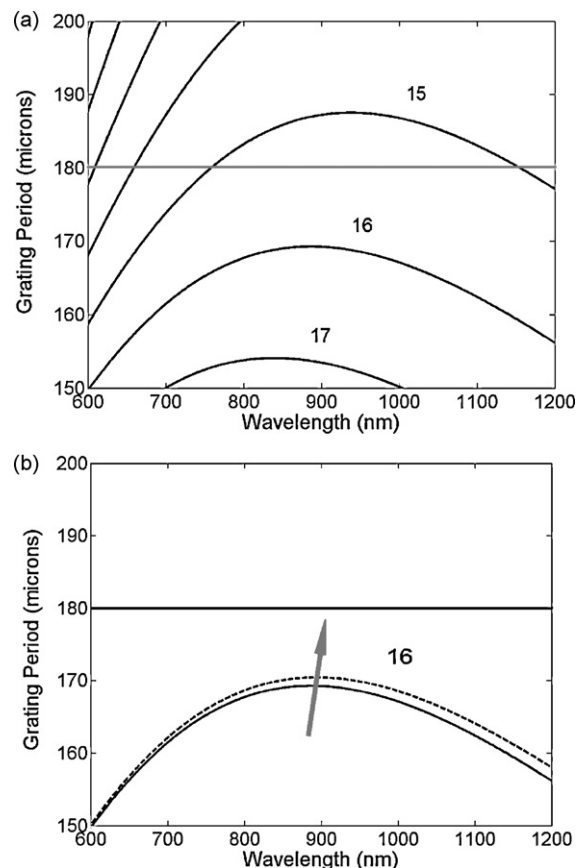


Fig. 1. (a) The relationship between the grating period and the wavelength at which coupling occurs to a set of symmetric cladding modes (LP_{015} – LP_{017}) for an optical fibre with a 670 nm cut-off wavelength. The numbers refer to the order of the cladding mode, LP_{0x} . The horizontal line indicates an LPG period of 180 μm . (b) The influence of an increase in the surrounding refractive index, analogous to the deposition of a coating onto the cladding, on the phase matching curve for LP_{016} . The arrow indicates the direction of increasing refractive index.

Thus optimum sensitivity of the coated LPG will be accessed for the period at which the phase matching turning point and the mode transition region are coincident. This effect is illustrated in the grey scale plot shown in Fig. 2. The resonant band corresponding to the LP_{015} cladding mode shows the location of the transition region, while for the LP_{016} mode the transition region and the phase matching turning point are coincident in this thickness range. The increase in sensitivity for the LP_{016} mode is evident. Plotting the data in such a way allows the relationship of the dual resonance band with respect to the mode transition region to be observed.

3. Coatings for selective sensing

Calixarene molecules are structures containing a number of phenol or resorcinol aromatic rings interconnected to form a larger ring. The calixarene used here is derived from four resorcinol aromatic rings and is referred to as calix-4-resorcarene [26]. The molecular structure is shown in Fig. 3. In three dimensions this is a bowl like structure [22] that has a cavity in the centre. The eight hydroxyl groups give the molecule a part hydrophilic nature. The hydrocarbon chains are known as pendants [23] and give the molecule hydrophobicity. These long hydrophobic chains are added to make the molecule amphiphilic, such that it is part hydrophobic and part hydrophilic, which is a requirement to allow the chemical to be deposited onto the optical fibre using the Langmuir–Blodgett technique [22].

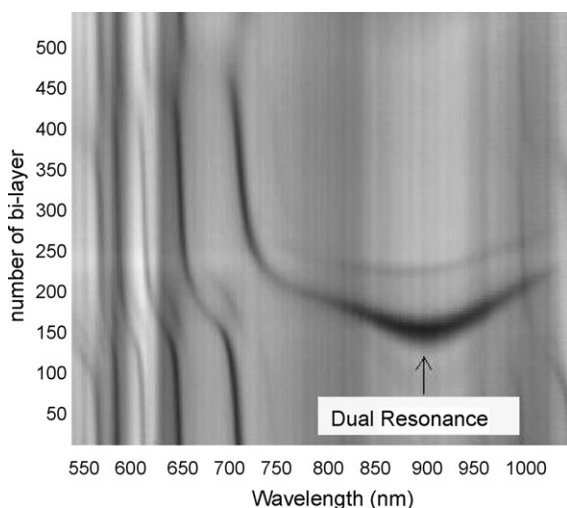


Fig. 2. Grey scale plot illustrating the response of the transmission spectrum of an LPG of period 180 μm to the deposition of a coating of calix-4-resorcarene using the LB technique. The spectra were recorded with the LPG in the air subphase. The attenuation band originating at approximately 900 nm shows the development of the dual resonance effect.

Using this technique for deposition, a coating of calixarene consists of a matrix of nanoscale cavities formed by the calixarene ring, and other voids generated with the alternate packing of the molecular layers of the coating [30]. The orientation of the film structure is such that the alkyl chains interdigitate, and the molecules align bowl to bowl [22].

The analyte molecule can penetrate into this matrix structure. The analyte molecule becomes temporarily entrapped in the hydrophobic calixarene cavity and the voids. An interaction then occurs between a host molecule, calixarene, and the analyte [1]. Weak interactions [24] occur involving the aromatic rings of the analyte and the host molecule. Since they are weak and do not involve covalent bonding, the analyte molecule is easily liberated from the cavity, and this results in a sensor whose response is reversible, an important consideration in chemical sensor development.

The size and shape of the analyte molecule determines how deeply it can penetrate the calixarene matrix, and the chemistry of the analyte and host determines the nature of the molecular interaction when the analyte is contained in the cavity. These con-

siderations lead to responses that have different levels of sensitivity to various analyte molecules.

The refractive index of the calixarene coating has been measured to be 1.47 at 632 nm using SPR [22], making it a suitable choice to exploit the LPG sensing principles based on nanostructured coatings. Upon adsorption of the analyte, the cavities and voids become filled with the analyte and the optical density and refractive index increases.

4. LPG fabrication

An LPG of period 180 μm and length 35 mm was fabricated in hydrogen loaded single mode fibre of cut-off wavelength 650 nm, SM750, via UV inscription using the point by point technique [25]. The calixarene was deposited using the Langmuir–Blodgett technique. The calixarene was dissolved in chloroform at 0.2 g/l, and spread onto a pure water subphase of one compartment of a Nima Technology Model 2410A Langmuir–Blodgett trough modified for use with fibre optic substrates [13]. The material was compressed to a surface pressure of 30 mN/m. The dipping speed for the fibre substrate was set to 10 mm/min. As the coating is deposited, the layers interdigitate giving an individual layer thickness of 1.17 nm [22]. The transmission spectrum of the fibre was monitored by coupling the output from a tungsten–halogen lamp into the fibre and connecting the distal end of the fibre to an Ocean Optics CCD spectrometer of resolution 0.3 nm. The spectrum was recorded when the LPG was above and below the water subphase. This is important, as it has been noted previously that the thickness of the coating required to access the mode transition region is dependent on the surrounding refractive index [8]. Thus for gas sensing the spectrum recorded with the LPG above the subphase was used when deciding on the optimum coating thickness.

To establish the optimum coating thickness, a thick film in excess of 1 μm was deposited. This allows the grey scale plot shown in Fig. 2 to be generated which highlights the response of the transmission spectrum to the deposition of the coating. The LPG was then cleaned and coated with 163 layers of calixarene, deposited as a Y-type LB film, corresponding to a calculated coating thickness of 190.7 nm. The number of layers was chosen to ensure that a dual-resonant attenuation band develops in the transmission spectrum of the fibre upon exposure to the analyte, indicating that the LPG is operating at the phase matching turning point.

5. Experiment

The coated LPG was placed inside a closed vessel and fixed quantities of the analyte were injected into the chamber. At room temperature and atmospheric pressure, the analyte solution vaporised inside the chamber and the response of the sensor to the vapour concentration was monitored.

The toluene solution took around 30 min to evaporate, depending upon the quantity of solution injected. Benzene on the other hand took around 10 min to evaporate. Once a steady state had been reached, the spectrum was recorded using the CCD spectrometer. Upon opening of the closed vessel, the vapour concentration was quickly released into a fume cupboard.

The sensor was also tested with hexane, an aliphatic hydrocarbon, and cyclohexane, a hydrocarbon with a fully hydrogenated ring. This allowed for comparison of the sensitivity of the device to four VOCs and the determination of the selectivity of the sensor.

6. Results and discussion

The response of the transmission spectrum to exposure to different concentrations of toluene is shown in Fig. 4. The initial

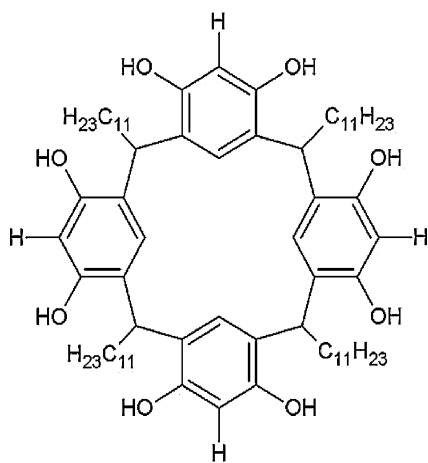


Fig. 3. Calixarene molecule, calix-4-resorcarene used for coating the optical fibre. The space encompassed by the larger ring forms the cavity into which the analyte molecule becomes entrapped.

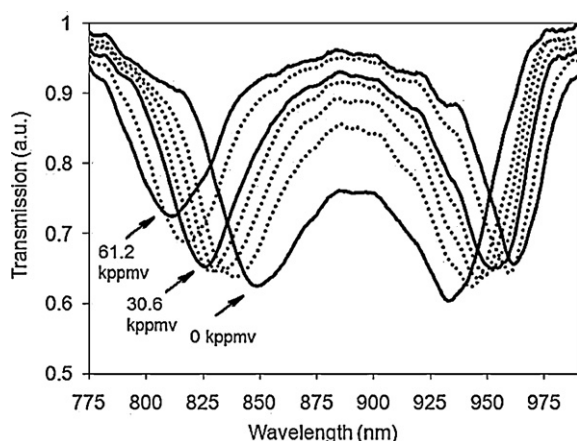


Fig. 4. Response of a long period grating of period 180 μm fabricated in SM750 fibre coated with a calixarene to toluene vapour. The sensor was characterised at concentrations of up to 61.2 kppmv. For clarity, 3 spectra, corresponding to concentrations of 0 pppmv, 30.6 kppmv and 61.2 kppmv are highlighted to indicate the trend for increasing separation of the resonant bands with increasing concentration. The dashed lines are intermediate steps of 7.65 kppmv, 15.3 kppmv, 22.95 kppmv and 45.9 kppmv.

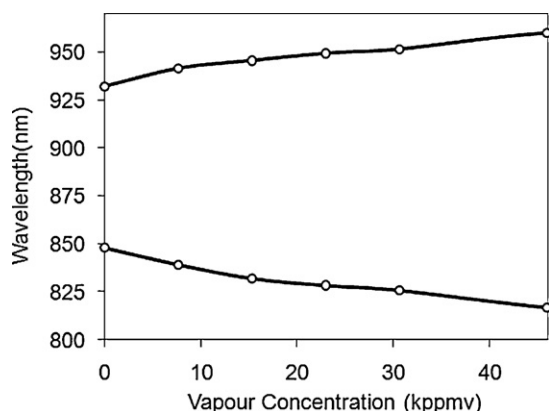


Fig. 5. Wavelength shift of the longer and shorter wavelength resonant bands to increasing toluene vapour concentration. The solid lines are a guide to the eye.

response in air (0 ppm by volume) shows two resonant bands at 850 nm and 930 nm which are resolvable. The dual-resonant bands become further resolved with increasing vapour concentrations up to 61.2 kppmv (thousand ppm by volume).

The response can be analysed by measuring the wavelength shifts of the two resonant bands, or by considering the change in amplitude at a fixed wavelength. The two resonant bands move apart in wavelength as depicted in Fig. 5. A change in wavelength of 0.7 nm per kppmv for the shorter wavelength band and 0.6 nm per kppmv for the longer wavelength band result in a differential wavelength change of 1.3 nm per kppmv. Utilizing this differential shift gives a sensitivity of 231 ppmv based on a spectrometer resolution of 0.3 nm.

The change in transmission of the LPG measured at a wavelength of 900 nm as a function of the concentration of toluene, benzene, hexane and cyclohexane has also been measured. This is shown in Fig. 6 and allows for a determination in the selectivity of the sensor. The results show that at levels up to 10 kppmv vapour concentration, the sensitivity to hexane is only 7.5% compared to toluene. For cyclohexane the sensitivity is 14.8% compared to toluene. This indicates that the sensor has a high selectivity to toluene.

Upon repeating these measurements, the responses to toluene, benzene and cyclohexane were similar with the exception of hexane. Hexane has shown a response of the same magnitude but

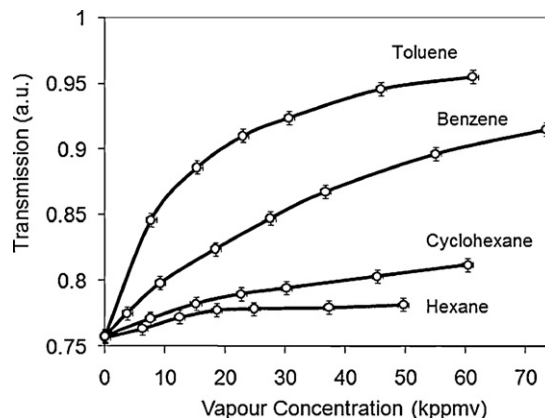


Fig. 6. Volumetric sensitivity of the sensor to the vapours toluene, benzene, hexane and cyclohexane. The transmission is monitored at 900 nm and an increase in transmission occurs which corresponds to the separation of the dual-resonant attenuation bands. The lines are a guide to the eye.

with opposite polarity. This has been reported to be due to the low refractive index of liquid hexane ($n_{\text{hexane}} = 1.37$), compared to liquid toluene ($n_{\text{toluene}} = 1.49$) [30]. However, the lesser response to benzene, which has a higher refractive index ($n_{\text{benzene}} = 1.50$) than toluene indicates that the sensing mechanism is based upon changes in the properties of the functional coating, rather than a response to the refractive index of the analyte.

Due to the response of the spectrum to exposure to the analyte at the particular wavelength of 900 nm, the amplitude monitored response for toluene tends towards saturation above 10 kppmv. This is a result of the increasing separation of the two attenuation bands that has decreasing influence on the transmission at 900 nm the further the bands separate. However, the two resonant bands continue to diverge at the higher vapour concentrations as indicated in the wavelength response in Fig. 5.

The relative sensitivities of the four organic compounds is evident from Fig. 6. The size and shape of the analyte molecule can determine how deeply the analyte can move through the calixarene matrix, and the chemistry of the host and guest determines how it becomes confined in the cavity. The calixarene cavity has an upper rim diameter of 1.32 nm [27].

Hexane has a single chain molecular structure with dimensions 1.03 nm \times 0.49 nm \times 0.4 nm [28] and it is suggested that its large size cannot enter the calixarene cavity easily. It is conjectured that the small response may be due to the analyte molecule filling voids between adjacent calixarene molecules.

Cyclohexane is a ring but being fully hydrogenated is more bulky than the aromatic ring. The cyclohexane molecule has dimensions of 0.72 nm \times 0.64 nm \times 0.49 nm [28]. The results indicate that there can be little molecular attraction between cyclohexane and the cavity.

Benzene is the smallest molecule investigated with dimensions 0.74 nm \times 0.67 nm \times 0.37 nm [28] and the progressive response shown in Fig. 6 indicates that it can penetrate deeper into the calixarene film with increasing vapour concentrations. Although there is some correlation of interaction with the solvent volatility, there is also some specific interaction with aromatic molecules since benzene interacts more strongly than cyclohexane even though they have the same boiling point.

The largest magnitude response is observed on exposure to toluene, which, with its methyl group, shows that this can cause a greater molecular attraction between host and guest, which is not evident for benzene. The results show that toluene is optimal above the other VOCs measured here for becoming confined in the cavity of the calixarene matrix.

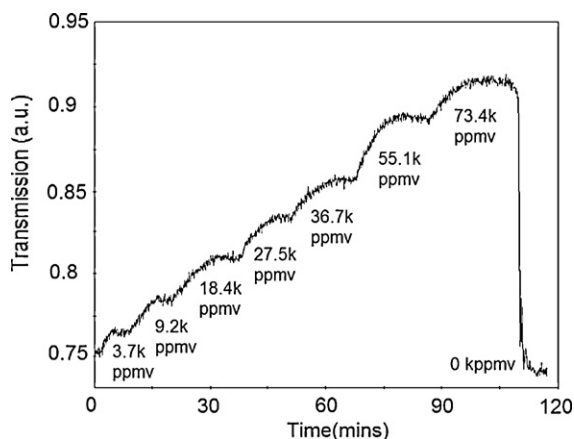


Fig. 7. shows the evaporation time and the temporal response of the sensor to benzene vapour, monitored at 900 nm.

The rise time and fall times of the sensor are shown in Fig. 7, with the transmission monitored at 900 nm. The rise time is dictated by the time required for the volatile solvent to vaporise. However, the fall time of the order of the 15 s shows the speed of response of the sensor when the analyte vapour is released.

Centred at around 900 nm, a broad spectral feature appears at the phase matching turning point which has a FWHM bandwidth in excess of 50 nm. This is shown in Fig. 4 between the wavelengths of 825 nm and 950 nm. The change of transmission of the fibre at the central wavelength of this broad spectral feature could conveniently be used to develop a low cost sensor, requiring the use of only an LED of bandwidth 50 nm and a photodiode to measure optical power, and with an appropriate reference channel to compensate for the effects of source intensity fluctuations and changes in download losses.

7. Conclusion

It has been demonstrated that, by using a fibre optic long period grating in conjunction with a functional nanostructured coating, chemical vapour sensing can be performed. Dual resonance in the spectral response of the LPG has been exploited to obtain improved sensitivity. The phase matching curves allow the grating to be designed such that the sensor operates within a desired wavelength range. Further tailoring of the grating period allows the utilization of the mode transition region to attain higher sensitivities.

Using a calixarene coating, toluene and benzene vapour sensing can be performed. Nanoscale cavities in the coating are suited to a corresponding size and shape of a particular analyte molecule. In this way, the response of the sensor is species selective. This has been demonstrated with the relative sensitivity to toluene being 13 times greater than that to hexane for the same vapour concentration. Similarly, the sensitivity to toluene is over 6 times greater than that to cyclohexane.

A broadband spectral feature resulting from the moving apart of two attenuation bands occurs in dual-resonant long period gratings. This is not due to a change in extinction ratio of the bands, but a natural result of the two bands moving apart. This feature has the potential to be utilized in conjunction with simple detection optoelectronics to implement a low cost sensor system.

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Biographies

Stephen Topliss was born in 1965, and received a BEng in Electronic Engineering from Sheffield University in 1986, and a MSc in Optoelectronic Systems and Devices from Glasgow University in 1987. For the next ten years, he worked on the technology of broadband passive optical networks, the burst mode receiver, the bit phase aligner, and interferometric intensity noise. He was involved with the award winning RACE II research project Broadband Access Facilities. From 1997, he has worked mainly on the design of backplanes and their EMC compliance, for DSLAM and aerospace applications. Since 2007, he has studied at Cranfield University for a PhD in the area of long period fibre gratings with their application to chemical sensing.

Stephen James graduated from Imperial College, London, in 1987 with a Physics Degree, and obtained his MSc in Applied Optics from the same institution in 1988. He studied for his PhD at Southampton University, before moving to Cranfield University in 1993, where he has progressed from post-doctoral research fellow to Reader. He has interest in the development and application of a broad range of optical technologies, particularly optical fibre sensors, to make measurements of physical and chemical parameters in real engineering environments. He is an author of more than 200 papers, won the National Measurement Awards Frontier Science and Measurement category in 2004 and is the Editor in Chief of Optics and Laser Technology.

Frank Davis graduated from Lancaster University (UK) in 1987 and obtained his PhD at the same institution in 1991. Following postdoctoral experience at Manchester and Sheffield universities, he then spent four years within the battery research group at Gillette UKRDL, Reading. He joined Cranfield Health, Cranfield University (UK) in August 2002. He has a wide experience of the synthesis of calixarene type materials and novel amphiphilic and surfactant molecules. Much of his research is focused

towards the incorporation of novel sensing moieties within ultra-thin films and their use to detect a wide variety of species including organic solvents and carcinogens, as well as biological species such as ascorbate. Dr Davis is the author of in excess of 90 published papers and 6 patents. He is a member of the Royal Society of Chemistry and a Chartered Chemist.

Professor Séamus Higson joined Cranfield University in 2002 as Professor of Bio- and Electroanalysis. He is the Dean of the Faculty of Health. Professor Higson's previous career spans academic departments of Chemistry, Medicine and Materials Science and this is reflected in the multi-disciplinary research interests of the group he now heads. Current research is primarily focussed towards practical implementation of electro-analytical science and analytical biochemistry for biomedical, environmental and industrial process control applications. Professor Higson's research includes the design and fabrication of microelectrode arrays for applications ranging from DNA analysis, (including genomic and proteomic applications), through to enzymatic biosensors and electro-analytical chemical sensors. Professor Higson is also author of the textbook 'Analytical Chemistry' published by the Oxford University Press.

Ralph Tatam is the Dean of the Faculty of Engineering and Aerospace at Cranfield University and heads the Engineering Photonics Group. He graduated with a BSc in Physics and Chemistry from Exeter University (UK) in 1981 and received a PhD in physics (CNA) in 1986, and a DSc (Exeter) in 2005. Following four years at the Physics Laboratory at the University of Kent he moved to Cranfield University. He has been active in optical and optical fibre based instrumentation and sensing for more than 20 years and his current research interests include optical flow measurement, speckle interferometry and optical fibre sensors. He has published more than 300 papers and has been involved with numerous national and international conferences. He won the National Measurement Awards Frontier Science and Measurement category in 2001 and 2004. He is a Fellow of the Institute of Physics (IOP) and the SPIE and was elected to the SPIE Board of Directors in 2009.