Design, development and studies on Raman-based fibre-optic distributed temperature sensor

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This article reports the development of an optical fibre-based multi-point temperature measurement system. Such sensors permit the measurement of temperature as a function of length along a single fibre with no taps or branches. This feature greatly increases the information from a single instrument and hence decreases the cost-benefit ratio. With the present setting, it is possible to measure temperature at 16 points simultaneously with a resolution of $\pm 8^\circ\text{C}$ using a 200-m-long silica fibre.

Optical fibre sensors are the subject of considerable interest for the measurement of a large number of physical parameters, including temperature, strain, pressure, rotation, etc. They offer special advantage for remote measurements in hazardous environments or in environments which suffer from severe electromagnetic interference. Sensors consisting of optical fibres can be rugged, light in weight and chemically stable.

The highest state-of-the-art in optical sensing is achieved with optical fibre distributed sensors. Such sensors permit remote measurement of spatial distribution of the physical parameter of interest, providing tremendous information with a single long fibre as an intrinsic sensor. These sensors use a one-dimensional optical radar called Optical Time Domain Reflectometer (OTDR), in one form or other, to detect externally-induced changes in backscatter signature of long optical fibres. In fact, these sensors are especially useful in a wide range of applications such as temperature monitoring of power cables (overground or underground), transmitting electrical power from power station to cities, supervision and control of high voltage transformers and motors, surveillance of dams and structures like bridges and smart structures.

In the present communication, we describe the design and development of a new class of optical fibre distributed temperature sensor system based on Raman Optical Time Domain Reflectometry (ROTR). It is capable of simultaneously measuring temperature at many points (about 20) along the length of a 200-m-long fibre. In this technique, a short laser pulse is sent along the fibre and backscattered Raman light is detected with high temporal resolution. This Raman light contains information about temperature along the fibre.

Raman-based distributed temperature sensors (DTS) are now well established as practical sensors. They have low cross-sensitivity to other parameters such as strain, pressure, cable type, etc. However, there have been no efforts to develop these sensors in our country, perhaps due to one significant drawback; the Raman scattered signal is between 20 and 30 dB weaker than the Rayleigh signal. Therefore, we have developed suitable pulsed lasers capable of providing high launch power and instrumentation for low-light level detection. This technique is clearly attractive for applications such as ‘smart skins’, as the sensor can measure variation of temperature over significant areas of the outer layer of vehicles such as aircraft, launch vehicles, etc.

ROTR is a one-dimensional optical radar which provides an echo scan of the entire length of an optical fibre at Raman stokes and anti-stokes lines. The basic arrangement of ROTR is shown in Figure 1. Briefly, a laser system is used to launch short optical pulses into a fibre via a directional coupler. As the pulse travels along the fibre, it is attenuated via several mechanisms such as Rayleigh scattering, Raman scattering, Brillouin scattering, absorption, etc. Some part of the scattered light is also guided by the fibre, back to the launching end where it is detected by a suitable detector. The resulting wave-form takes the shape of a decaying pulse, since the forward-travelling light and portion of light backscattered are both attenuated by propagation along the fibre. In ROTR, one uses a monochromator and suitable blocking filters to suppress the Rayleigh scattering.

The Raman scattered light is produced by inelastic scattering of incident light by vitreous silica glass material of the fibre, with the intensity of Raman shifted light depending upon the glass temperature. From standard

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Figure 1. Experimental arrangement of ROTR.
texts on Raman scattering, the ratio \( R \) of anti-stokes (high frequency) to stokes signal observed at equal separation (\( \Delta \nu \)) from central excitation line is given by the relationship:

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R(T) = \left( \frac{\lambda_s}{\lambda_{s-s}} \right)^d \exp \left( \frac{-hc \Delta \nu}{\kappa_B T} \right)
\]

where \( h \) is the Planck constant, \( c \) the velocity of light in vacuum, \( \kappa_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( \lambda_s \) and \( \lambda_{s-s} \) are the wavelengths of stokes and anti-stokes light being monitored. It is thus clear that the ratio on anti-stokes to stokes backscatter signal intensities can provide an absolute value of temperature of the medium irrespective of laser power, launch conditions, fibre geometry, etc.

The experimental set-up (see Figure 1) consists of a pulsed laser operating at 532 nm, a 50 : 50 optical coupler, a 200-m long silica fibre used as an intrinsic sensor, a quarter metre monochromator with blazed grating, suitable optical filters and a photomultiplier tube with S-11 cathode as detector. Since in the present setting, it is not possible to record anti-stokes and stokes signals simultaneously, the output of photodiode is used as a reference for laser power variation and is also used to correct the signal data, if required, during post-processing. The output from the detector is processed with 1 GHz/s digital storage oscilloscope (DSO) having mathematical functions like integration, averaging, ratio, etc. Alternatively, the signals are processed through a boxcar integrator having a computer interface for direct readout and processing through a computer. For demonstration of the capability of the instrument, a 200-m long fibre is wound on many spools. A length of about 25 m on each spool thus provides the flexibility for selectively heating or cooling of a section of the fibre. Barring spool no. 1 (dead zone), spools nos 2 and 4 are heated up to 70°C by keeping them in heated water bath (this protocol of selecting of

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**Figure 2.** Backscattered waveforms with wavelength tuning.

**Figure 3.** Backscattered waveforms with wavelength tuning antistokes side. (Laser at 532 nm; anti-stokes at 520 nm; background at 526 nm).
spools and number of spools is flexible). The monochromator is manually set either at stokes or at anti-stokes lines while making observations.

The following procedure is adopted to record the experimental data. The laser operating at 532 nm is typically set at 2 kHz repetition rate with nominal pulse duration of 85 ns.

In order to know the background intensity as we move towards stokes or anti-stokes lines, the monochromator is slowly tuned away from the Rayleigh line. Figure 2 shows the intensity data curves for 535 nm and 544 nm. The green solid line curve at 535 nm shows two prominent Fresnel reflection peaks arising from the front and far end of the fibre. It also implies that there is still some weak Rayleigh scatter light at 535 nm. The difference of 2 microns between two peaks also shows that the length of fibre is 200 m (in OTDR mode, 1 m = 10 ns for silica fibre). The signal at 537 nm becomes negligible (data not shown).

Now as we move to stokes peak at 544 nm (12 nm shifted for silica-based fibre), the signal intensity shown by the blue curve rises significantly (The same pattern is observed when we tune the monochromator to anti-stokes line (Figure 3)).

Having confirmed the peak intensity wavelength settings of stokes and anti-stokes lines, the stokes signal is recorded at 544 nm and stored in memory. The monochromator is then set for anti-stokes peak wavelength and the signal intensity is then recorded at room temperature. The rest of the high temperature data are then taken at this setting. The spools are now selectively heated by putting them in water bath and the series of signals (for every 10°C change) are recorded as the heated spools slowly return to room temperature. Figure 4 shows the anti-stokes signals for the fibre kept at room temperature and for the same fibre whose two spools are selectively heated to 60°C. Figure 5 shows the ratio of anti-stokes to stokes signals for a fibre which was selectively heated to 73°C in two zones taken on different days. The ratio in selected zones varies from 0.7 to 0.9 as we heat two spools to 73°C, whereas the rest of the fibre is at room temperature. It is thus clear that the instrument is capable of locating hot zones along the length of the fibre. Efforts are on to automate the entire sequence and to determine the spatial resolution.

It is observed that when the temperature of the selected zones is increased from 25 to 60°C, there is a signal change of about 16% in the anti-stokes light intensity. This corresponds to the temperature sensitivity of 0.45% per °C, which is sufficient for a ± 4°C resolution.

Commercial systems report a spatial resolution of 1 m and temperature resolution of 1°C. The spatial resolution is mainly governed by exciting laser pulse width and detector response time. Even though our detector is quite fast, the minimum laser pulse width of exciting laser in
our case is 85 ns and hence our resolution is limited to 8.5 m. On the other hand, the temperature resolution is dependent on many factors such as laser peak power, fibre Raman cross-section, light coupling factors, etc. We have not yet analysed the effect of these factors, but it has been observed that a change of 5°C results in a detectable change in anti-stokes signal and hence we consider the temperature resolution to be 5°C.


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Cobalt(II)-bis-(1,10-phenanthroline)-triphenylmethylene dye complexes and their photo-sensitization properties in nano-porous photovoltaic devices

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Bromopyrogallol-red and pyrocatechol-violet, the two triphenylmethylene-type ligands, can be readily complexed with [Co(1,10-phen)$_2$]$^{2+}$ moiety. The resulting complexes are capable of enhancing photovoltaic properties when compared with the corresponding ligands. Absorption and photocurrent action spectra suggest that a low-lying weak electronic charge transfer process, possibly a metal-to-ligand charge transfer (MLCT) process, is responsible for the enhancement of photovoltaic properties.

**Transition** metal polypyridyl complexes capable of binding onto wide band-gap semiconductors like nano-porous TiO$_2$, continuously attract much attention as potential dye material in dye-sensitized nanoporous photovoltaic devices. However, most of the work that has been carried out so far is based on ruthenium polypyridyl metal complexes, largely ignoring other transition metal centres. We have found that two types of triphenylmethylene dye material, namely bromopyrogallol-red (BPR) and pyrocatechol-violet (CatV) can be readily complexed with [Co(1,10-phen)$_2$]$^{2+}$ moiety. The resulting complexes are capable of producing enhanced photovoltaic properties when compared with the corresponding uncoordinated triphenylmethylene ligand-sensitized photovoltaic cells. The use of ligand-based dye material such as cyanidin (a flower pigment) and the two triphenylmethylene-type dyes involve ligand-centred (LC) electronic transitions. One of the major disadvantages when using such ligands is that the rapid recombination of photogenerated charge carriers, i.e. electrons and holes before their separation, results in a low quantum efficiency for the charge injection ($\eta_{inj}$). A more efficient system would be a cell sensitized through a charge-capturing mechanism, such as a metal–ligand charge transfer (MLCT) transition, where charge recombination is less probable (see Scheme 1).

Nano-porous layers of TiO$_2$ were coated on conducting tin oxide (CTO) glasses (1.5 cm × 2 cm, sheet resistance approx. 20 $\Omega$cm) by the following method. Glass plates were washed with a detergent solution, dilute NH$_4$OH and HNO$_3$ respectively. Plates were boiled with propan-2-ol and dried using hot air. The Degussa TiO$_2$ powder was dissolved in 96% ethanol and sonicated for 15 min. These glass plates were placed on a hotplate (temperature of growth 125°C) and Degussa TiO$_2$ powder solution was sprayed on 1 cm$^2$ of each CTO plate. The plates were sintered at 450°C for 20 min.

[Co(1,10-phen)$_2$]$^{2+}$ and triphenylmethylene dye complexes were prepared as follows.

CoCl$_2$·4H$_2$O (BDH Chemicals) and 1,10 phenanthroline (Aldrich Chemicals) were mixed (1 : 2 molar ratio) in 100 ml of methanol and the mixture was refluxed for 5 h under a nitrogen atmosphere. The resulting mixture was reduced to a volume of 20 ml and decanted into 200 ml of acetone. After a few minutes pink-coloured [Co(1,10-phen)$_2$]$^{2+}$ crystals were filtered out.

[Co(1,10-phen)$_2$]$^{2+}$ was dissolved in 100 ml of methanol and triphenylmethylene ligand (in methanol), i.e. BPR or CatV was added slowly over 30 min (1 : 1 molar ratio). The mixture was again refluxed for 10 h under nitrogen atmosphere. The volume of the mixture was reduced to 20 ml and decanted into a saturated, aqueous sodium

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