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Above The Italian research vessel Urania, carrying a Swedish laser radar system, which has sailed under the smoky plumes of Sicilian volcanos in Italy measuring the sulphur dioxide content

Applications of Laser Spectroscopy

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As the new millennium approaches the know how in the field of laser-matter interactions has matured to the stage of enabling several exciting real life applications. Several of these applications rely on the narrow bandwidth of tuneable lasers, which allows extreme selectivity in the interaction with free atoms and molecules. In other applications, the high spectral intensity available with pulsed as well as continuous wave (CW) lasers may saturate optical transitions or induce a variety of nonlinear effects, as for example multiphoton ionisation, thus providing the basis for highly sensitive detection schemes. In fact, single-atom or molecule detection is widely used, representing the ultimate sensitivity in analytical chemistry. In a different trend, ultrafast lasers have allowed detailed temporal monitoring of chemical reaction dynamics at femtosecond timescales (femtochemistry). In this way, significant insight into the basic steps of chemical processes has been gained. Finally, in the form of holographic techniques the coherence properties of laser light are the basis of ultrasensitive structural diagnostics applications.

In recent years, laser sources have become more rugged, easy-to-use and cheaper to allow real world applications of laser spectroscopy. Semiconductor diode lasers have become very reliable and easily accessible, and their wavelength range is extended higher and higher up into the visible region. We can mention the emerging blue diode lasers based on gallium phosphide, and frequency conversion of the output of reliable, high-power diode lasers into new wavelength regions. New laser materials, such as titanium-doped sapphire, allow all-solid-state tuneable systems with considerable power to be constructed. Diode-laser pumping of solid-state materials is making flash-lamp pumping gradually obsolete and enables compact, reliable and energy-efficient laser sources, especially when combined with current frequency conversion schemes (*eg* optical parametric amplifiers).

Laser-based analysis and diagnostics can readily be performed *in situ* and in many cases non-destructively. A variety of beam manipulation schemes are available for the irradiation of samples either directly or after preparation. The unique properties of laser radiation in terms of coherence, intensity and directionality permit remote chemical sensing, where the analytical equipment and the sample are separated by large distances, even of several kilometres. Absorption, and in particular differential absorption, can be utilised in long-path measurements, whereas elastic and inelastic backscattering as well as fluorescence can be used for range-resolved radar-like measurements (LIDAR: light detection and ranging). Laser light can also be efficiently transported in optical fibres to remotely located measurement sites. Various properties of the fibre itself influence the laser light propagating through the fibre, thus forming a basis for fibre optic sensors.

Applications of laser spectroscopy constitute a vast field, which is difficult to cover comprehensively in a review. Rather than attempting such a review, examples from a variety of fields are chosen for illustrating the power of applied laser spectroscopy.

Applications in Analytical Chemistry

Laser spectroscopy is making a major impact in many traditional fields of analytical spectroscopy. For instance, optogalvanic spectroscopy on analytical flames increases the sensitivity of absorption and emission flame spectroscopy. Extremely sensitive direct absorption measurements with CW lasers can be performed using frequency-modulation spectroscopy with a $1:10^7$ absorption sensitivity. A high sensitivity in absorption can also be achieved in intracavity experiments.

Traces of material can be detected using the REMPI (Resonance Enhanced Multi-Photon Ionisation) or RIMS (Resonance Ionisation Mass Spectroscopy) techniques, both employing pulsed, tuneable lasers. In the first method, selectively produced ions of the element are detected through the ion current, whereas the second method employs a mass spectrometer for additional selectivity.

The breadth of standard analytical-chemistry techniques can be further improved through laser spectroscopy, employed for enhanced detection sensitivity and multiplexing. Thus, laser-induced fluorescence (LIF) can be utilised for detecting the separated fractions passing the detector position in

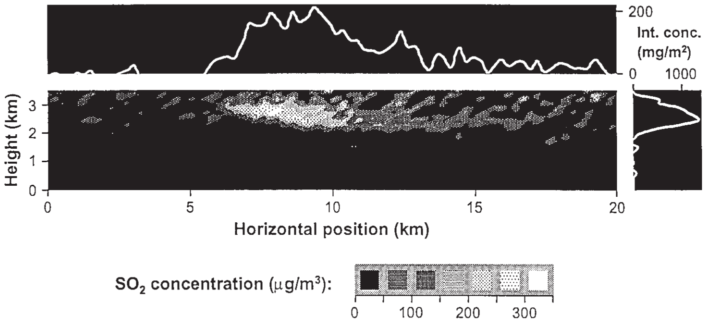

Fig 1 Left The Italian volcano Stromboli, seen from the research vessel Urania
Below The volcanic plume of Mt Etna as recorded by laser radar techniques in September1994 during a ship-borne traverse under the plume. Integrated vertical and horizontal profiles of sulphur dioxide are shown. The total flux was 44 tonnes/hour

HPLC (High Performance Liquid Chromatography) and Capillary Electrophoresis. Further, a whole section of the column can be illuminated and the fluorescence along the column can be imaged on a linear array or a CCD detector, to provide simultaneous detection of all species undergoing separation. Differences in fluorescence spectra can also be utilised for further discrimination. Fluorescence labelling can be used, detecting simultaneously chromophores with different fluorescence characteristics and binding to different positions in the DNA strand. These developments are very important, for example for the Human Genome Project.

Laser ablation which occurs upon the interaction of intense laser radiation with solid targets has provided a number of novel analytical schemes in combination with mass spectrometric or optical detection. Along these lines, there are several industrial applications, in which on-line monitoring may occur by laser-induced breakdown spectroscopy (LIBS). This technique exploits changes in the emission spectra of laser-produced plasmas depending on the stage and quality of processing. In a relevant recent application LIBS has been applied on polymer samples for the identification and separation of polymeric materials for recycling purposes.

Combustion Processes

Combustion remains the most important means of energy conversion. Laser spectroscopy provides a very powerful, non-intrusive measurement capability for the reactive and aggressive media constituted by burning or exploding combustion gases. A large number of techniques has provided new possibilities to measure the concentration of species including short-lived radicals, and also the capability of determining temperature and flow speed. The measurements have allowed a realistic interplay with the advanced kinetic computer codes that are used for modelling combustion. Important issues in combustion include NOx and soot formation, engine ignition and engine knock.

LIF has been extensively used, also in imaging configurations, to monitor the distribution of molecules such as OH, C_2, CH and CN. Using a gated and image-intensified CCD detector the full distribution can be captured using a single laser shot ($\approx 10^{-8}$s). To this end, a sheet of light is formed through the burning medium using cylindrical optics. In a similar way, recordings using transitions starting in states with a temperature-dependent population can obtain temperature distributions. Flow velocities are evaluated using Doppler shifts in the recorded signals. A further method is to mark a gas package by a laser pulse (repumping or dissociating the molecules) and then identify the package position at a later time using a second laser pulse.

CARS (Coherent Anti-Stokes Raman Scattering) is a powerful technique, especially for temperature measurements in strongly luminous media. A coherent, laser-like beam is obtained carrying the signal, making it largely immune to the background light. By single-shot CARS recordings, PDFs (Probability Density Functions) for temperature can be determined, yielding important information on statistical fluctuations in turbulent combustion. Realistic measurements on test engines, jet engines and even coal-fired power plants have been performed. Polarisation spectroscopy and DFWM (Degenerate Four-Wave Mixing) spectroscopy are further powerful techniques in combustion diagnostics.

The methods developed for combustion diagnostics are also applicable for the monitoring of other reactive media such as in plasma etching or MOCVD (Metal Organic Chemical Vapour Deposition) for semiconductor processing.

Monitoring of the Atmosphere

The atmosphere can be monitored by laser techniques employing absorption or

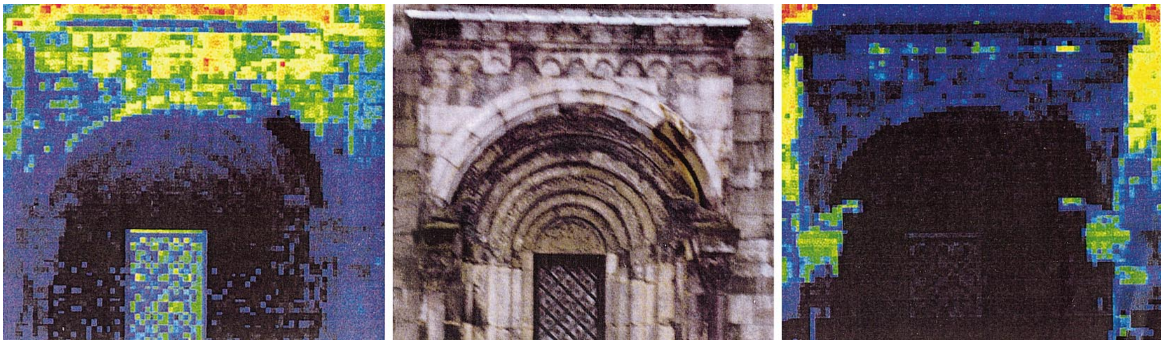

Fig 2 Fluorescence imaging of the northern gate of the Lund Cathedral. Images were recorded through pass-bands centred at 438 and 682 nanometers using a scanning laser radar system positioned about 50 meters from the gate. A normal colour photograph of the gate is shown centre

Fig 3 Above A restored area on a painting is differentiated with respect to the original and analysed by using quantitative fluorescence multispectral imaging—in visible light no difference is observed. The characterization of the image relies on a narrow hue distribution

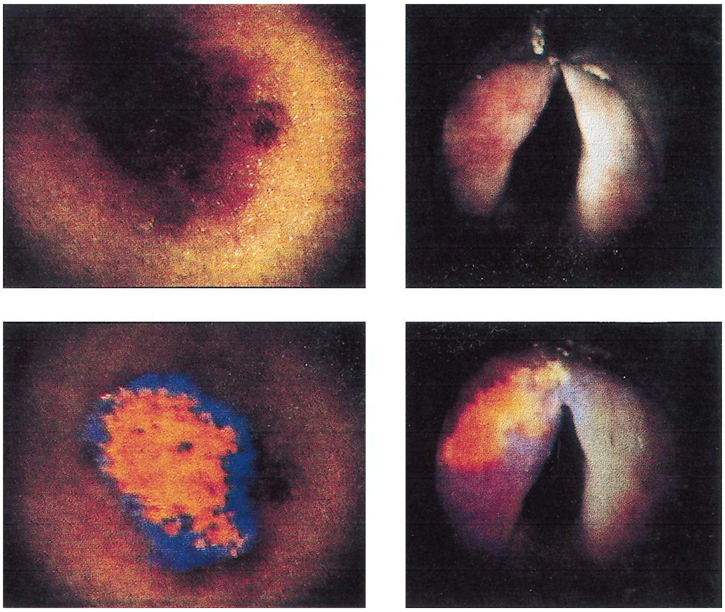

Fig 4 Right Fluorescence images and tumour diagnostics. Pixels, fulfiling a 'cancer criterion' in fluorescence are shown in false colour superimposed on a normal colour video representation of the area. **(Left)** Basal cell carcinoma, note the non-cancerous brown spot, which is benign **(Right)** A tumour on vocal cords

laser-induced fluorescence. The LIDAR, or laser radar, technique using a pulsed laser as a transmitter and an optical telescope as a receiver in a radar-like manner allows a mapping of pollution concentrations and also meteorological parameters, such as temperature, humidity and wind velocity. Lidar systems can be operated from fixed laboratories, trucks, airplanes or even spacecraft.

At atmospheric pressures LIF cannot be used for species monitoring because of a strong collisional quenching (combustion diagnostics with LIF is still feasible because of the possibility of saturating the optical transitions, leading to full fluorescence intensity even in the presence of collisional transitions). Mesospheric monitoring of meteorite-derived Li, Na, K and Ca layers using LIF lidar works well because of the low pressures.

Tropospheric pollution monitoring is most frequently performed using DIAL (Differential Absorption Lidar). Range-resolved optical transients due to elastic backscattering from aerosol particles are recorded for a laser wavelength set on a characteristic absorption line and just off it for reference, in alternating laser shots. By dividing the resulting curves, unknown atmospheric parameters are eliminated and the concentration of the particular species can be evaluated. Typical ranges for SO_2, O_3, NO_2, NO and Hg monitoring are 0.5 to 5 kilometres. The techniques are particularly valuable for urban and industrial measurements. Total fluxes from an industrial complex can be evaluated if gas concentration values as well as the wind speed at the relevant height are known. The wind speed can be determined by video correlation techniques using visible structures in the moving plume. Lidar techniques are also being used for the monitoring of gases of geophysical origin; *eg* atomic mercury from Italian geothermal fields and from mercury mines in Italy and Spain have been studied. The fluxes of sulphur dioxide from the volcanoes Mount Etna, Stromboli and Vulcano have been assessed in several campaigns with lidar on board a research vessel making traverses under the volcanic plumes. An example of results for Mount Etna is shown in *figure* 1.

Vegetation Monitoring

Ultraviolet laser pulses transmitted from a lidar system can induce fluorescence when directed into water or onto vegetation. The fluorescence collected by the receiving telescope can be analysed using an optical multichannel analyser equipped with an image intensifier, which is gated in synchronization with the return of the signal. In this way, background due to the ambient light can be suppressed. Fluorescence data from the earth surface can complement reflectance data widely collected by multi-spectral sensors installed in satellites such as LANDSAT or SPOT. Lidar systems are under development featuring effective measurement ranges mostly below one kilometre (truck, helicopter or airplane installations). Water LIF signals include a sharp OH-stretch Raman signal for water that is valuable for referencing, a broad bluish fluorescence light distribution due to distributed organic matter (DOM), and rather sharp peaks in the near IR region due to algal chlorophyll. The technique is particularly valuable for the monitoring of oil spills and algal blooms.

Land vegetation features clear chlorophyll signals (the ratio between two red peaks allows an evaluation of the chlorophyll concentration) as well as blue fluorescence due to a variety of molecules present in the leaves. Of particular interest is exploring the possibilities for early detection of forest decline prior to visible signs. By expanding the laser beam, a certain area can be illuminated, and by a fluorescence imaging system the whole scene can be captured in properly selected wavelength bands.

Cultural Heritage Preservation

During recent years lasers have also found applications in the area of cultural heritage. Fluorescence imaging is a powerful method used to detect areas in paintings which have been modified or retouched. Raman, LIF and LIBS analysis of pigments and varnish can also help reveal the authenticity of a particular painting. Intense UV pulses can be used to remove soot and dirt by ablation from the surface of icons, paintings *etc*. Also, stone statues can be cleaned using higher pulse energies. Spectroscopic imaging and LIBS can be used for the on line monitoring of the cleaning process in order to safeguard from potential damage.

Recently, the diagnostic techniques have been extended for applications also on building monuments. For this purpose, a scanning LIF lidar system can be utilised for assessment of modifications to the stone surface and the presence of algal or lichen growth. An example is given in *figure 2*, where data for the northern gate of the Lund Cathedral are shown. Generally, LIF is suitable for the non-destructive and *in situ* analysis of pigments and binding media of painted artworks. This technique can be complemented by LIBS for obtaining in depth profiles of elemental composition. A typical example is shown in *figure 3* in which quantitative fluorescence imaging of a retouched area of a painting called “La Bella” (originating from the school of Palma di Vecchio and today in a private collection) is delineated and verified by LIF and LIBS spectra. In this case, the extent and composition of the white pigments used in the restored area as well as in the original painting can be accurately determined.

Laser Spectroscopy in Medicine

The analytical-chemistry applications discussed above are of substantial interest in medical research. However, much more direct applications in medical diagnostics have emerged during recent year. Thus, tissue LIF has been extensively studied and applied for early detection of malignant tumours and for studies of atherosclerotic plaque. Tissue exhibits a natural fluorescence when excited by UV or violet light. Important natural chromophores emitting fluorescence are elastin, collagen, NADH and NAD^+. They all yield broad, but somewhat different distributions in the blue-green spectral region. However, exogenously administered agents such as porphyrins, chlorines and phtalocyanines, which are selectively retained in tumour cells, yield sharp and characteristic peaks in the dark red wavelength region, signaling the presence of cancer. An increase in the red fluorescence is frequently accompanied by a decrease in the blue-green fluorescence, and thus by a ratio formation an enhanced tumour demarcation from normal tissue can be achieved. At the same time the monitoring of a dimensionless quantity, such as a ratio, makes the data immune to changes in geometry, illumination, detection efficiency *etc*. Fibre optic probes, through which both excitation light and induced fluorescence are conducted, have been developed and utilised for studies of tumours in different organ systems. Multi-colour imaging devices have also been constructed, making the presentation of an image processed for cancer detection possible; video mixed with the normal white-light reflectance image obtained through an endoscope. Tumours detected can be treated by photo-dynamic therapy (PDT) using red laser light, which excites the administered sensitiser molecules with subsequent transfer of ground-state triplet oxygen to the toxic singlet state. A selective necrosis of tumour cells will result. Of particular interest is the introduction of diagnosis and PDT using δ-aminolevulinic acid (ALA), which is a natural molecule in the haemoglobin cycle in the human body. Prolonged sensitivity of the skin to sun radiation, which is a complication for many sensitisers, is eliminated with ALA. Examples of real-time tumour imaging are shown in *figure* 4.

Atherosclerotic plaque can be fibre-optically detected in *in vivo* transluminal monitoring in vessels. Atherosclerotic plaque is characterised by a change in the elastin/collagen balance and can be observed in time integrated or time-resolved measurements of LIF. The construction of a guidance device for the safe use of a fibre optic laser coronary angioplasty system on line would be of considerable interest. Clinical studies have demonstrated the potential of this approach.

Raman spectroscopy is also being developed for tissue diagnostics. Much sharper but weak signal features are obtained. In order to suppress competing fluorescence the laser irradiation wavelength is chosen in the near IR region. Also, direct IR reflectance spectroscopy has a diagnostic potential.

Scattering Spectroscopy

Red light penetrates tissue particularly well, a fact which is utilised to achieve PDT for tissue thickness up to a few millimetres. The weak penetration of red light also through thicker tissue layers would suggest optical mammography without using ionising radiation. However, the heavy multiple scattering in tissue leads to image blurring reducing the value strongly. However, by transmitting picosecond laser pulses through tissue and electronically detecting only the first emerging photons it is possible to reject the scattered light and retain an image with good contrast. Many different techniques working on this general principle are now being developed with the main aim of detection of breast cancer, the most common malignant tumour disease in women. Prototype systems for optical mammography are being constructed. Similar technology can also be used for oxygenation measurements in the brain, and also possibly for localising haematoma following trauma to the skull. It is also useful for spectroscopic measurements of strongly scattering liquids such as blood, for which it is of great interest to monitor the concentration of various molecules, such as urea and glucose.

Spectroscopy in strongly scattering media can also be used in non-medical applications, such as studies of light propagation in green leaves (photosynthesis) or sheets of paper (quality assessment through information of fibres *etc*).

Laser spectroscopy is finding many real-world applications. The many powerful methods allow advanced sensing, both locally and remotely. Of great importance in the process of taking the technology into everyday applications is the fast development of cheap and reliable laser sources, fibre-optical components and computers.

Further reading

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