By Sune Svanberg

Real-World Applications of Laser Spectroscopy

Snapshot: Laser spectroscopic techniques are powerful tools for monitoring real-world phenomena. A wide variety of methods for establishing spectroscopic contact with a species exist: Absorption, emission, fluorescence, Raman scattering, acousto-optic, and opto-galvanic phenomena. Extreme sensitivity and specificity characterize the methods, which can be used for *in situ* monitoring and, in some cases, for remote sensing. Combustion diagnostics and atmospheric pollution monitoring are examples of gas-phase applications, while vegetation studies and early cancer detection illustrate interactions with solids.

Laser radiation can be used for chemical sensing based on the wavelength-dependent interaction between electromagnetic radiation and matter. The narrow bandwidth of modern tunable lasers makes the interaction extremely selective, based on the complex and sharp spectral features of free atoms and molecules. Furthermore, the high spectral intensity available with pulsed, as well as CW, lasers makes saturation of the optical transition possible. Thus, individual atoms or molecules can absorb more than a million photons per second leading to extreme sensitivity. Single-atom or single-molecule detection is even possible. In a further developmental trend, ultrafast lasers provide a detailed assessment of the dynamics of chemical reactions (femtochemistry). This field offers insight into the nature of many basic chemical processes.

During the last few years, the use of laser sources for real-world applications have become practical. Semiconductor diode lasers are more reliable, easily accessible, and their range has extended higher into the visible region. Tunable crystal materials, such as titanium-doped sapphire, allow the construction of all-solid-state systems with considerable power. Diode-pumped solid-state materials have resulted in compact, reliable sources that are making flash-lamp pumping gradually obsolete.

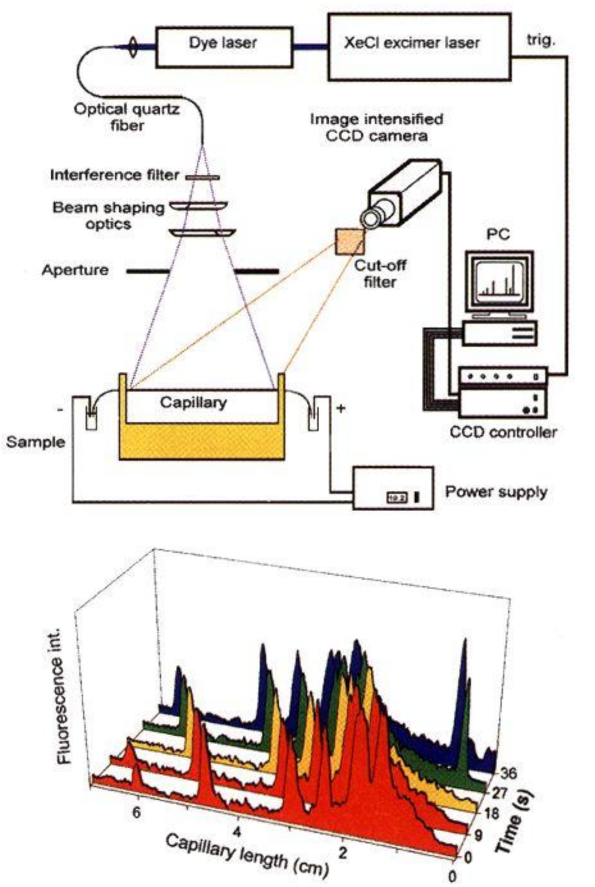

Figure 1. Experimental setup and recorded signals in a capillary electrophoresis study of the separation of components in an oligonucleotide mixture.[7]

Practical sensing can readily be performed *in situ* with laser spectroscopic techniques. In this case, laser radiation is locally brought into contact with the sample either directly or after sample preparation. Since laser light is coherent and basically only diffraction limited in terms of beam propagation, it can be used for remote sensing, where the measurement device and the sample, frequently distributed, are spatially separated. Absorption, and in particular differential absorption, can be used in long-path measurements, whereas elastic and inelastic backscattering, as well as fluorescence, can be used for range-resolved, radar-like measurements (lidar). Laser light can also be efficiently focused into optical fibers and can be transported over large distances to a number of remotely located measurement sites. Fiber optic techniques provide a link

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between truly local measurements and remote sensing. Various properties of the fiber which influence the laser light propagating through it also form the basis for fiber sensors.

Applied laser spectroscopy is a vast field that is difficult to cover comprehensively in a review. Rather than attempting such a review, this article uses examples from a variety of fields to illustrate the power of applied laser spectroscopy. General material pertaining to applied laser spectroscopy can be found in References 1-5.

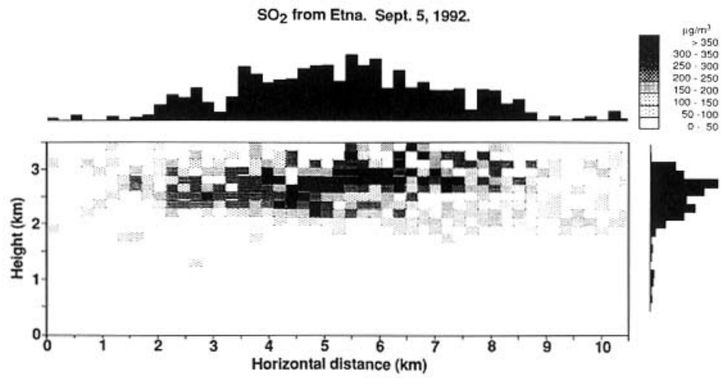

Figure 2. Lidar monitoring of the SO_2 plume from the Mt. Etna volcano obtained in vertical soundings from a shipborne lidar system. The flux is about 60 tonnes/h.[12]

Analytical chemistry

Laser spectroscopy has entered many traditional fields of analytical spectroscopy,[5,6] (*e.g.*, opto-galvanic 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. Small absorptions can also be detected in intracavity experiments.

Resonance enhanced multi-photon ionization (REMPI) or resonance ionization mass spectroscopy (RIMS) can detect small amounts of material using pulsed, tunable lasers. In the first method, selectively produced ions of the element are detected through the ion current, whereas the second method uses a mass spectrometer for added selectivity.

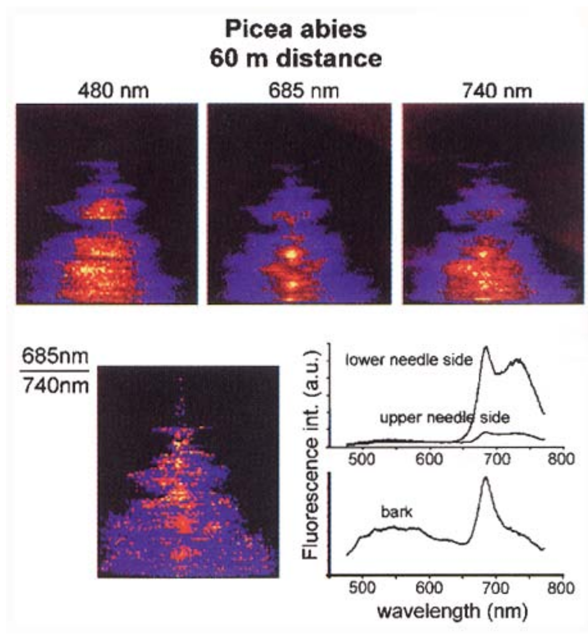

Figure 3. Simultaneous imaging of a spruce tree in three fluorescence bands using laser-induced fluorescence, where a horizontal streak of UV laser light was scanned over the tree from root to top. Selected fluorescence spectra are also included.[14]

The power of standard analytical-chemistry techniques can be further improved with laser spectroscopy. Laser-induced fluorescence (LIF) can detect the separated peaks passing the detector position in high performance liquid chromatography (HPLC) and capillary electrophoresis. In addition, a whole section of the column can be illuminated and the fluorescence along the column can be imaged on a linear array or CCD detector, providing simultaneous multi-species detection (See Fig. 1, page 17).[7] Differences in fluorescence spectra can also be used for further discrimination. Fluorescence labeling can detect simultaneously four chromophores, binding to different positions in the DNA strand and with different fluorescence characteristics.

Combustion diagnostics

Laser spectroscopy provides non-intrusive measurement capability in reactive and aggressive media, such as burning or exploding combustion gases. A host of techniques has provided new possibilities to measure the concentration of species, including short-lived radicals, and the capability to measure temperature and flow.[8] The measurements have allowed an interplay with the advanced kinetic computer codes that are used to model combustion.

LIF has been extensively used 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 ($\simeq 10^{-8}$ sec). In a similar way, temperature distributions can be obtained by recordings using transitions starting in states with a temperature-dependent population. Flow velocities are evaluated using Doppler shifts in the recorded signals.

Coherent anti-Stokes Raman scattering (CARS) is a powerful technique, especially for temperature measurements in realistic, strongly luminous media. A coherent, laser-like beam carries the signal making it largely immune to background light. By single-shot CARS recordings, probability density functions (PDFs) for temperature can be determined that yield important information on statistical fluctuations in turbulent combustion. Polarization spectroscopy and degenerate four-wave mixing (DFWM) spectroscopy are other powerful techniques in combustion diagnostics, which aim at an improved understanding of pollution and soot formation as well as engine ignition and knock.

The methods developed for combustion diagnostics are also applicable for monitoring other reactive media such as those used in plasma etching or metal organic chemical vapor deposition (MOCVD) for semiconductor processing.[9]

Atmospheric remote sensing

The atmosphere can be monitored by laser techniques using absorption and laser-induced fluorescence.[10] The light detection and ranging (LIDAR) technique which uses a pulsed laser as a transmitter and an optical telescope as a receiver in a radar-like manner allows for three-dimensional mapping of pollution concentrations and also meteorological parameters, such as temperature, humidity, and wind velocity.

At atmospheric pressures LIF cannot be used for species monitoring because of a strong quenching. Combustion diagnostics with LIF are still feasible because the optical transitions can be saturated even in the presence of collisional transitions. Mesospheric monitoring of meteorite-derived Li, Na, K, and Ca layers using LIF lidar is still possible because of low pressures, and powerful applications related to the use of laser guide-stars have emerged. Tropospheric pollution monitoring is most frequently performed using differential absorption lidar (DIAL).[11] Range-resolved optical transients resulting from elastic backscattering of 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 0.5-5 km. The techniques are particularly valuable for urban and industrial monitoring. Total fluxes from an industrial complex can be evaluated in near-real time. Lidar techniques have also been used for monitoring gases of geophysical origin, such as emissions from geothermal fields and active volcanoes (See Fig. 2).[12]

Hydrospheric and vegetation remote monitoring

If an ultraviolet pulsed laser beam from a lidar system is directed onto a water surface or vegetation, fluorescence is induced and can be collected and analyzed at the site of the lidar system.[10, 13] Fluorescence data from the Earth's surface can complement reflectance data widely collected by multi-spectral sensors installed in satellites such as LANDSAT or SPOT. LIF lidar is under development and can presently only be used in test experiments at kilometer ranges (truck, helicopter, or airplane installations). Water laser-induced signals include a sharp OH-stretch Raman signal 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 (685 and 740 nm) due to chlorophyll. The technique is particularly valuable for monitoring oil spills and algal blooms.

Land vegetation fluorescence features clear chlorophyll signals (the ratio between the two peaks allows an evaluation of the chlorophyll concentration) as well as a blue distribution due to a variety of molecules present in the leaves.[13] Recently, a considerable effort has been devoted to assessing the possibilities of early detection of forest decline in the fluorescence signals (*i.e.*, the European LASFLEUR project). 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 (See Fig. 3).[14]

Medical fluorescence diagnostics

Laser spectroscopy has an impact on medical research through its use in various analytical-chemistry techniques. However, more direct applications in medical diagnostics have emerged during the last few years. Thus, tissue LIF has been extensively studied and applied for early detection of malignant tumors and for studies of atherosclerotic plaque.[15, 16] 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 or phthalocyanines, which are selectively retained in tumor cells, yield sharp and characteristic peaks in the dark red wavelength region, signaling the presence of cancer. An increase in red fluorescence is frequently accompanied by a decrease in blue-green fluorescence. Using the ratio the tumor can be differentiated from normal tissue. In addition, monitoring a dimensionless quantity makes the data immune to changes in geometry, illumination, and detection efficiency. Fiber optic probes, through which both excitation light and induced fluorescence are conducted, have been developed and used for construction of a spectral library for tumors in different organ systems. Multi-color imaging devices have also been constructed making the presentation of an image processed for cancer detection possible. This image is video mixed with the normal white-light reflectance image obtained through an endoscope. Tumors detected can be treated by photodynamic therapy (PDT) using red laser light, which excites the administered sensitizer molecules with subsequent transfer of ground-state triplet oxygen to the toxic singlet state. A selective necrosis of tumor cells results.

Fiber optics can detect atherosclerotic plaque in *in vivo* transluminal monitoring in vessels. A change in the elastin/collagen balance characterizes atherosclerotic plaque and can be observed in time-integrated or time-resolved LIF measurements. A guidance device for the safe use of a fiber optic laser coronary angioplasty system would be of considerable interest.

Raman spectroscopy is also being tested for tissue diagnostics. Much sharper, but weak signal features, are obtained. To suppress competing fluorescence, the laser irradition wavelength is chosen in the near-IR region.

Scattering spectroscopy in turbid media

Red light penetrates tissue particularly well due to the reduced hemoglobin absorption. This is used to achieve PDT over tissue thicknesses of a few millimeters. The weak penetration of red light also through thicker tissue layers would suggest optical mammography without ionizing radiation. However, the heavy multiple scattering in tissue leads to image blurring, reducing the value of this technique. 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 addressing this general principle are now being pursued for breast cancer detection.[17] Prototype systems for optical mammography are under development. Similar technology can also be used for oxygenation measurements in the brain, and also possibly for localizing hematoma, following trauma to the skull. An example of gated viewing detection of a breast cancer tumor (in vitro) is shown in Figure 4, in which a pulsed near-IR diode laser and time-correlated single-photon counting were used.[18]

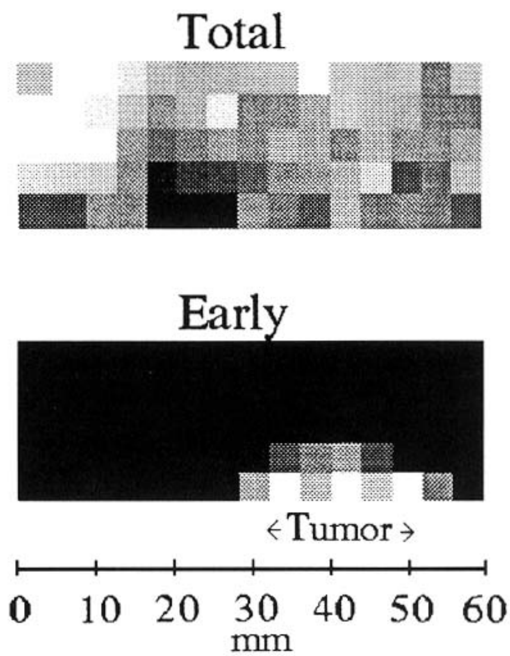

Figure 4. Transillumination imaging of a ductal cancer in a mastectomy specimen. By gated viewing of the early arriving photons only the tumor emerges. No contrast is obtained if all transmitted light is accepted. A pulsed near-IR diode laser and time-correlated single-photon counting were used.[18]

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

Conclusions

Applied laser spectroscopy is a rapidly evolving field, where new applications appear all the time. The methods can be expected to make their way into everyday applications at an increased rate with the fast development of cheap and reliable laser sources, fiber optic components, and computers.

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