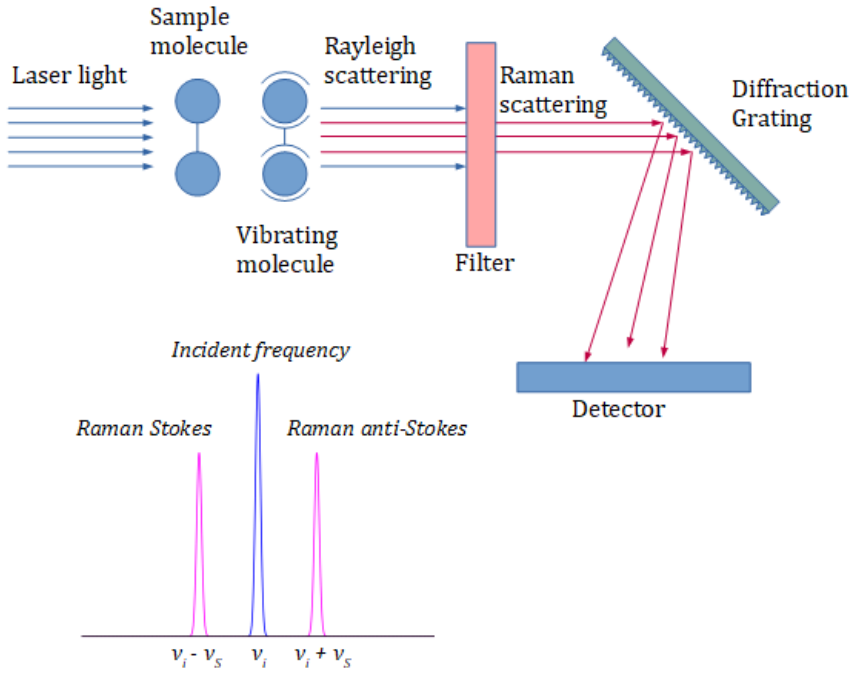
Spectroscopy and Lasers

Spectroscopy is a class of analysis methods meant for chemical species identification and concentration measurement, based on the detection of emission spectra, if properly irradiated by a light source. Fluorescence-based spectroscopy is one of the oldest spectroscopic techniques, related to electron-photon interactions and relying on the absorption of high energy photons and subsequent emission of lower-energy longer-wavelength fluorescence photons, with the energy difference associated to vibrational phonons. Due to the unique level structure of the different chemical species, the emitted photons represent unambiguous fingerprints of their presence. From the amount of collected fluorescent radiation, concentration evaluation is straightforward.



Concept diagram of Raman scattering

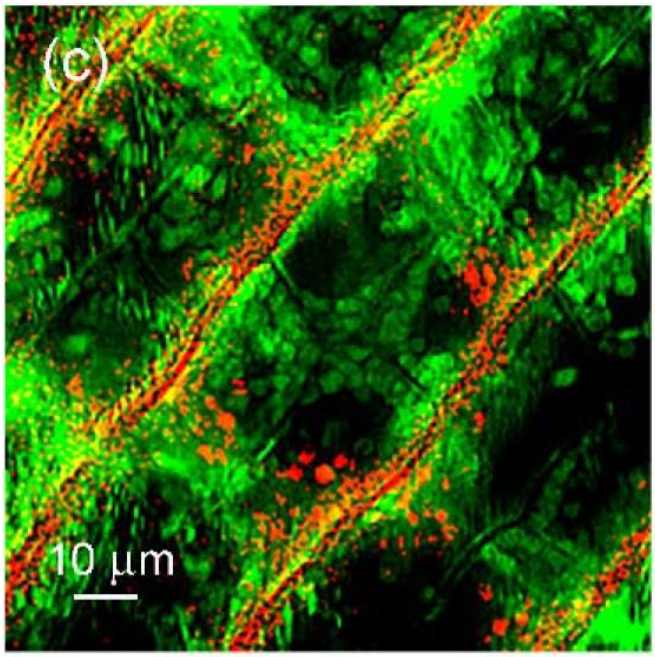
Even though fluorescence molecular response can be in principle excited by simple incoherent light sources, such as UV lamps, as attested by the evidence that spectroscopic techniques are way older than laser invention in the 60's, the development of coherent light sources remarkably improved performance of existing spectroscopic techniques and enabled new concepts based on nonlinear processes with unprecedented high resolutions and sensitivities. Lasers are light sources which potentially emit high-intensity radiation over a very narrow wavelength range. Nowadays, lasers cover most of the spectrum

from near-UV down to mid infrared radiation. Different physical concepts for octave-spanning tunable laser sources have been investigated and developed up to the breakthrough of industrial grade commercially available robust and reliable devices, providing high intensities over extremely narrow bandwidths, and allowing to resolve spectral features less than 1-MHz wide, while the highest-resolution grating spectrometers based on broadband incoherent sources could achieve resolutions only hundreds-of-time lower. Atomic lines as narrow as a few Hz out of a transition frequency of 100s of THz could readily be observed nowadays with laser spectroscopy.

On the other hand, lasers might operate in pulsed regimes, exploiting 100s-of-nanometers-wide bandwidths to achieve pulse durations down to few femtoseconds, including only a few cycles of electromagnetic radiation in the visible or near infrared spectral window. Apart from enabling time-gated spectroscopy with unprecedented time resolutions, ultrashort laser pulse durations can easily achieve several GW/cm^2 peak intensities, at which most nonlinear effects takes place, enabling very high resolution and sensitivity techniques, such as multi-photon absorption spectroscopy or the different flavors of Raman-based spectroscopy.

Two photon absorption (TPA), for instance, due to its intrinsically nonlinear nature, allows to achieve much higher resolution and contrast with respect to linear fluorescence excitation, by employing laser sources with double the wavelength and half the photon energy. In addition, the operation in a lower photon energy longer wavelength regime has the remarkable advantage of reduced photo-toxicity and higher pulse energies available from existing laser technologies for femtosecond pulse generation.

Raman-based spectroscopy, on the other hand, is a completely different nonlinear technique, relying on the frequency shift experienced by laser radiation incident on a molecule related to its rotational and vibrational modes. Not being related to electronic transitions, the Raman shift is relative with respect to the irradiating wavelength and therefore laser source tunability is not required, unless coherent excitation is pursued. Being a nonlinear process, ultrashort pulse generation is usually required. On the other hand, being the Raman gain generally higher than TPA cross sections, cheaper and simpler picosecond lasers could be efficiently employed in incoherent Raman spectroscopy, while practical TPA set-ups usually require < 300 fs pulse durations. In addition, being Raman spectroscopy spectral resolution related to the laser source bandwidth, the narrower bandwidths of picosecond lasers represent a remarkable advantage with respect to their femtosecond counterparts. For pulsed laser sources, spectral bandwidths and pulse durations are related by a Fourier-transform relationship, descending from the time-energy Heisenberg uncertainty principle. More precisely, the minimum spectral bandwidth is inversely proportional to the pulse duration. The shorter the pulse duration, the larger the bandwidth for a given temporal pulse profile. For instance, for pulse duration of ~1 ps at the wavelength of ~1 μm, the minimum FWHM spectral bandwidth is ~1 nm. For pulses ten times longer at the same wavelength (~10 ps), the minimum spectral bandwidth is 10 times narrower (~0.1 nm).



Overlay of SRS image targeting the cellulose at 2890 cm-1 in red and the TPEF in green of an 'Elodea' aquatic plant. Courtesy of IFN-CNR, Dipartimento di Fisica, Politecnico di Milano and Center for Nano Science and Technology @ Polimi, Istituto Italiano di Tecnologia

Since the spectral resolution in Raman spectroscopy is related to the spectral bandwidth of the illuminating source, 10-ps-long pulses would potentially provide better spectral resolution than 1-ps-long pulses. On the other hand, longer pulses provide lower peak power for a given average power and repetition rate, and therefore lower signal and worse S/N ratio.

An optimal pulse duration of few picosecond is generally accepted for usual set-ups as a good trade-off between the different requirements. Moreover, it is important to remark that the FWHM spectral bandwidth above mentioned is a minimal value. It is not uncommon for practical lasers to emit pulses with broader spectrum than the narrowest (transform-limited) theoretical profile, as a consequence of residual uncompensated linear or non-linear phase shift.

Generally speaking, ultrafast fiber lasers, while usually representing more compact and rugged technological solutions with respect to the solid-state counterparts, are likely to be more affected by poorer spectral properties, especially if linear and nonlinear effects are not carefully managed. Poorer spectral profile, if not a critical issue for a number of different industrial applications, might be a remarkable drawback for Raman spectroscopy.

Bright Solutions' narrowband picosecond laser

Bright Solutions' NPS laser platform is a new ultrafast picosecond laser series, especially tailored for spectroscopic applications, by combining compactness and ruggedness of fiber laser technology with spectral purity of the DPSS design.

According to the number and the features of the proprietary amplification stages, it is possible to achieve several power levels at 1064.3nm and its harmonics.

For more information about Bright Solutions' NPS lasers, please visit the Bright Solutions' website or write us to sales@brightsolutions.it.