

An XTRA Laser Source for Raman Spectroscopy: Towards Process Control

Once considered an exotic, difficult-to-handle technique, Raman spectroscopy has become an established routine in chemical and material science. Even the pharmaceutical industry has taken advantage of Raman scattering, from the discovery and high-throughput screening phase of new drugs to process development and quality control. At the 2002 Pittcon exhibition, Munich-based diode laser manufacturer TOPTICA Photonics AG presented a new laser source tailor-made for dispersive Raman spectroscopy and Raman microscopy.

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Related Products

TOPTICA Photonics AG XTRA

1 Scattering the Raman Way

When light interacts with a molecule, the most likely reaction is – nothing. The incident light is scattered and leaves the molecule at exactly the same wavelength, an effect known as Rayleigh scattering. It exists, however, a one-in-a-million possibility of inelastic scattering: A photon strikes a molecule, or a crystal lattice, and experiences a distinct energy shift. The effect, now known as Raman scattering, was discovered in 1928 [1] by Chandrasekhar Venkata Raman (1888-1970), at that time professor of physics at Calcutta University, India. It forms the basis of Raman spectroscopy.

There are two scenarios related to Raman scattering. In the first, a photon strikes a molecule and induces a vibration (or a phonon, in the case of a crystal lattice). The light quantum is re-emitted instantaneously, but at a longer wavelength, as part of its original energy has been transferred to the excited vibrational state of the molecule (Figure 1). This scenario is labelled Stokes Raman scattering. If, on the other hand, the molecule is already in a vibrational state, the photon can take up part of the energy and leave the molecule at a shorter wavelength, an effect referred to as Anti-Stokes Raman scattering.

Dispersive Raman spectroscopy mostly makes use of Stokes Raman scattering of monochromatic laser light. The scattered light is dispersed and filtered in order to eliminate the contribution of Rayleigh scattered light. Subsequent analysis by wavelength yields qualitative and quantitative information on the composition of the illuminated sample: The energy shift between incident and emitted light is determined by, and unique to, the molecular vibration that has been excited (e.g. a C-H stretch, or a CH₂ bend). Each vibrational peak or band, therefore, originates from a specific chemical bond and can be employed to determine the chemical structure and dynamics of the analyte.

The transition of Raman spectroscopy from a time-consuming, experts-only method to a standard analytical technique was propelled by several technological advances in the fields of optics and electronics. The key factor is the light source: The low-pressure mercury vapor lamp of the days of yore has been replaced by Argon and Krypton ion lasers, frequency doubled solid state lasers or, most recently, diode lasers. Optical fiber probes for remote monitoring applications have become available. Furthermore, volume holographic instruments greatly facilitate measurements: Notch filters efficiently eliminate the contribution of Rayleigh scattered light, which would otherwise dominate the spectrum. Holographic gratings serve to disperse the Raman scattered light on the detector. Here, modern multichannel detectors, e.g. CCD detectors, allow to sample the entire dispersed spectrum simultaneously.

2 Getting the Light right

The intensity of the Raman signal is linearly proportional to the intensity of the incident laser light and inversely proportional to the fourth power of the laser wavelength ($S_{\text{Raman}} \propto 1/\lambda^4$). While this at first sight looks like a compelling argument to utilize short wavelengths, visible or UV light has the inherent disadvantage of inducing fluorescence in many organic compounds. As the fluorescence signal is many orders of magnitude higher than the Raman signal, a weak fluorescence background suffices to obscure a Raman spectrum completely. In practice, short wavelengths are used for known "non-fluorescing" samples, such as inorganic pigments or catalysts. However, for the investigation of new or unknown petrochemicals, pharmaceuticals or biomaterials, where fluorescence may occur, one generally prefers infrared lasers. The XTRA wavelength of 785 nm accommodates this demand and, in addition, matches the spectral sensitivity of silicon-based CCD detectors: At this excitation wavelength, a full spectrum up to relative wavenumbers of 3500 cm^{-1} can be read using off-the-shelf CCD detectors.

However, selecting the proper wavelength is not the only requirement in Raman spectroscopy. Applications in industrial process control demand an extreme long-term wavelength stability during continuous operation of the laser. In addition, a high output power is needed in order to achieve a good signal to noise ratio of the measurements. Finally, many tasks require high spatial resolution. Thus, a laser with a diffraction-limited, transversal single mode beam had to be developed.

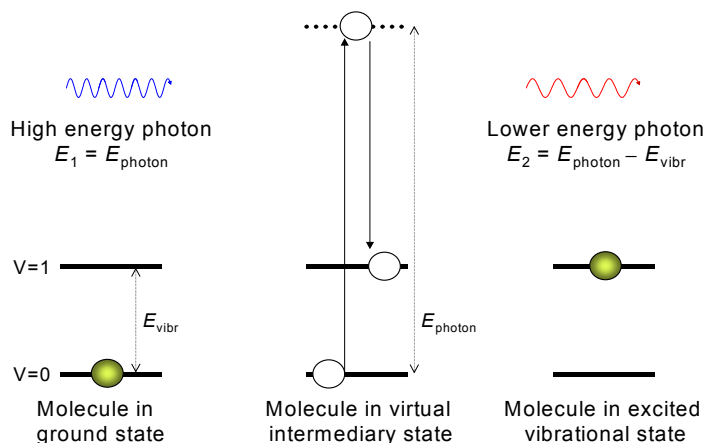


Figure 1 Principle of the Raman effect. The process is sketched from left to right. A photon is scattered by a ground state molecule (1). The molecule is transferred, via a virtual intermediate state (2), to a resonant vibrational state (3). It retains part of the original photon energy. The photon travels on at a reduced energy $E_2 < E_1$.

A new wavelength stabilized tapered laser source by German diode laser manufacturer TOPTICA Photonics AG now sets another milestone in Raman laser technology. The compact device dubbed XTRA (Figure 2) was presented at the 2002 Pittcon exhibition in New Orleans, Louisiana. The XTRA features a near-infrared grating-stabilized diode laser system with a GaAs-based high power semiconductor chip, sophisticated thermal management and a microprocessor-driven laser stabilization controller.



Figure 2 The XTRA laser system was designed to meet the most demanding requirements in Raman spectroscopy and Raman microscopy. The compact device features a grating-stabilized semiconductor chip, yielding high output power and excellent wavelength stability.

3 The XTRA Laser

The XTRA system features a laser head with integrated control electronics and an external power supply. The separate power supply minimizes the impact of heat and electronic radiation on the laser head. A high-quality optical isolator is integrated in the laser head to avoid unwanted optical feedback of the beam due to back-reflections. The grating-stabilized external cavity design results in an extremely narrow spectral bandwidth of < 10 MHz. The excellent beam profile (transversal single mode beam, TEM₀₀) allows focussing the laser to micrometer spots, making the XTRA system particularly attractive for applications in Raman microscopy.

In order to minimize the wavelength drift during operation, a new microprocessor-driven laser stabilization controller was developed: Even though an external cavity diode laser “behaves” most of the time, showing very little intensity fluctuations, particular combinations of parameters (minor temperature or current drifts, or ageing of the diode) can still lead to longitudinal mode hops. Before a mode hop occurs, mode competition causes fluctuations in intensity and frequency, which is intolerable in sensitive spectroscopic applications.

Engineers at TOPTICA Photonics AG therefore designed a “coherence quality” stabilization – an active control loop restraining the laser to longitudinal single-mode emission. Thus, a frequency drift of less than < 3 GHz (0.1 cm⁻¹) over a 100 hour period can be achieved. The tapered semiconductor chip has an output power of > 300 mW, and the background of amplified spontaneous emission (ASE) is suppressed by more than 50 dB (Figure 3).

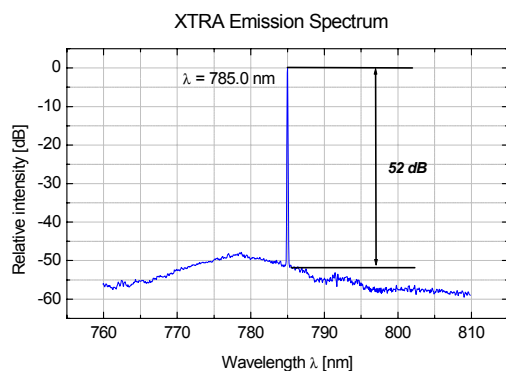


Figure 3 The optical spectrum of the XTRA shows one distinct peak at the adjusted wavelength of 785 nm. The background of amplified spontaneous emission is suppressed by more than 50 dB.

Apart from the standard wavelength of 785 nm, a larger choice of wavelengths will be available in the future. Presently a 730 nm laser for medical applications is being developed.

As many applications require coupling of the laser light to a remote probe head, TOPTICA Photonics AG

also manufactures a fiber-coupled version of the device. An output power of > 200 mW is obtained after a polarization preserving single-mode fiber, which forms a perfect Gaussian beam ($M^2 = 1.0$). Alternatively, multi-mode fibers can be employed.

The laser parameters can be controlled by a standard PC via an integrated RS232 interface. High-sensitivity environmental and industrial measurement tasks can thus be performed rapidly, even via remote operation. The XTRA therefore provides a rugged, reliable instrument, well-suited to a wide variety of applications.

4 Multi-wells and Forensic Fibers

Raman techniques stand the test in biological, pharmaceutical or chemical investigations which require non-contact measurements and real-time data analysis. For most applications, no laborious extraction or preparation of the sample is needed. In addition, the method is well-suited to aqueous solutions, because water only produces a weak Raman signal.

The overt benefits have led to the adoption of Raman spectroscopy by the pharmaceutical industry. Near-IR laser light supports basically all stages of drug development, from screening of multi-well plates to process optimization and quality control. An interesting aspect of drug development is that most active pharmaceuticals are polymorphic, i.e. there exists more than one crystalline form. The polymorphs often differ in their physical and/or chemical characteristics (stability, dissolution rates etc.). Raman spectroscopy helps to investigate the properties of the individual polymorphs [2], as each form displays its own specific Raman spectrum.

Materials science is another important candidate for Raman techniques (Figure 4). Applications include identification of compounds in mixtures of synthetics, quality control during recycling of synthetics, chemical analysis of strongly corrosive liquids and the surveillance of chemical processes, e.g. the curing of glue.

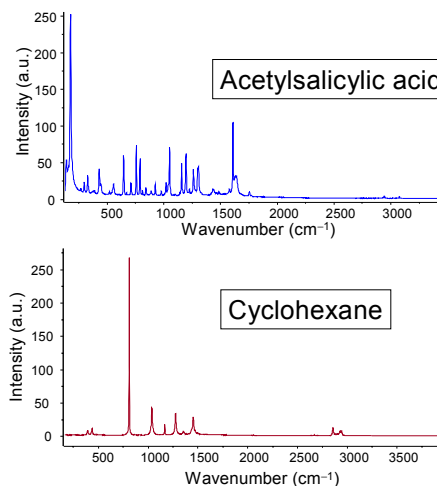


Figure 4 Raman spectra of acetylsalicylic acid (top) and cyclohexane (bottom).

Due to its excellent beam profile and small focus size, the XTRA appears particularly well-suited to applications which require spatial resolutions on the micron scale, like Micro-Raman spectroscopy, or Raman microscopy, of solid state surfaces. Confocal Raman microscopy combines a Raman spectrometer with a confocal microscope to analyze spectra within a clear-cut volume element. The attainable resolution is given by the diffraction limit of the laser beam. The XTRA, which can be focussed down to 1 μm , presents an ideal device for a non-destructive chemical analysis of samples on a micron scale.

Raman microscopy is not only able to distinguish between chemical compounds but can also image their local distribution. The method can be applied to insulating, semiconducting or metallic probes, to single- and polycrystalline substances or thin films. The microscopic analysis of semiconductor surfaces, for instance, yields insights about the stoichiometric composition, crystal structure or dotation of the sample. An investigation of the surface morphology of thin films of particular metal oxides may improve our understanding of the mechanisms of high temperature superconductance. In mineralogy, Raman techniques allow to identify both structure and mineral inclusions of a probe.

However, Raman microscopy has also gained ground outside fundamental science. It is employed for the determination of microstructures in quality evaluations of ceramic layers or optical coatings. The list of possible objects to be scrutinized further includes test tubes for drugs, fibers and inks in forensic medicine, precious stones and archaeological artifacts.

With stone-age objects, for instance, not only the kind of rock, but often also its origin can be determined.

Recently, even medical applications of Raman microscopy have been proposed. Scientists from Dortmund and Erlangen, Germany, utilized Raman scattering for the detection of tooth decay. Infected regions within the dentin beneath the surface of the tooth, which are hard to detect by traditional means, could be located by spectroscopic techniques [3]. Dutch and American researchers have developed a technique to identify in vivo the chemical composition of intraocular lenses, determining components such as polymethylmethacrylate (PMMA), acrylic and silicone [4].

Some 75 years after its discovery, the Raman effect has found its way into most diverse applications, and it looks like the end of this development is nowhere near. With a stable and powerful, easy-to-operate laser source at hand, Raman's future is indeed looking bright.

5 References

- [1] C. V. Raman and K. S. Krishnan, Nature 121, 1928, 501.
- [2] R. Geiger, VDI-Berichte Nr. 1667, 2002, 81.
- [3] K. Kincade, Laser Focus World, 07/1998, 83.
- [4] S.C. Hennink, Biophotonics International, 12/2001, 28.