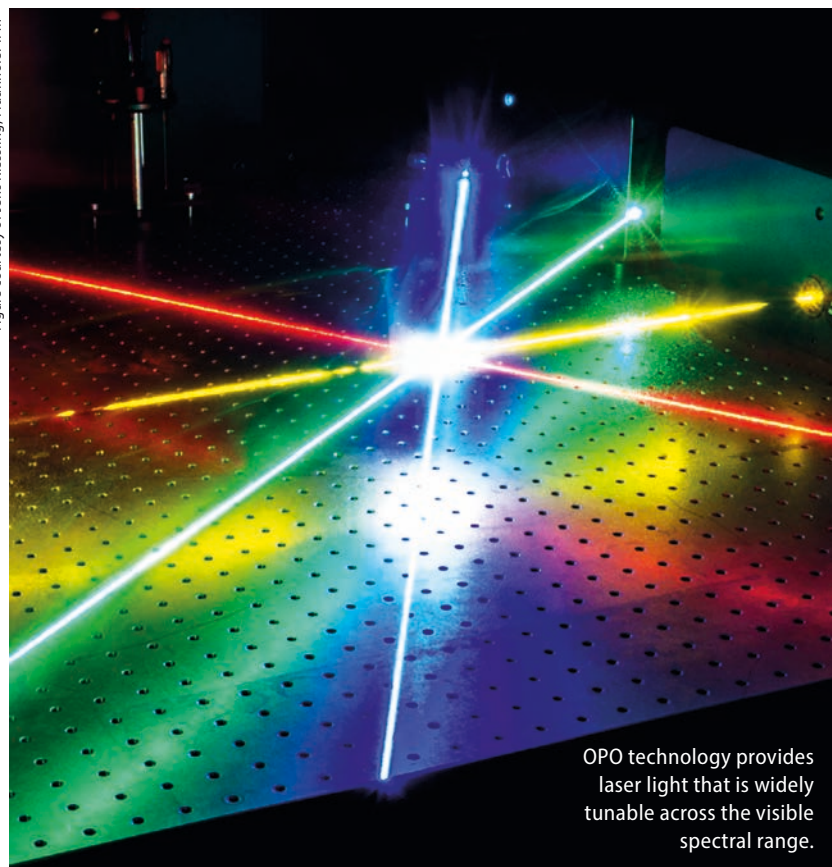# Spectroscopy at the tip

Novel tunable lasers enable excitation-tunable tip-enhanced Raman spectroscopy.

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Figure courtesy of Jens Kiessling, Fraunhofer IPM

OPO technology provides laser light that is widely tunable across the visible spectral range.

Photonics research undertakes considerable efforts to continuously refine nanoimaging techniques driven by the desire to characterize electronic and vibronic properties of new materials with nanometer resolution. Tip-enhanced Raman spectroscopy (TERS) is an approach that has been well recognized and relies on strongly localized enhancement of Raman scattering of laser light at the point of a near atomically sharp tip. However, not least due to the lack of sources delivering laser light tunable throughout the visible spectral range, the vast majority of TERS experiments so far has been limited to single excitation wavelengths. A recent study demonstrates excitation-dependent hyperspectral imaging, exemplified on carbon nanotubes by implementing a tunable continuous-wave optical parametric oscillator into a TERS set-up. We take a closer look at the laser technology behind the experiment and illustrate the vast potential of the method.

Flexible tunability

Optical parametric oscillators (OPOs) might be considered as light sources that deliver coherent radiation very similar to lasers – but with two main differences [1]: First, the OPO principle relies on a process referred to as parametric amplification in a so-called nonlinear optical material rather than on stimulated emission in a laser gain medium. Second, OPOs require a coherent source of radiation as a pump source, unlike lasers, which might be pumped with either incoherent light sources or sources other than light.

In practice, the OPO concept has been experimentally demonstrated more than half a century ago [2], but the progress in development and commercialization of turn-key devices has been stalled substantially by several technical obstacles [3]. Simply speaking, these obstacles have been easier to overcome at the high peak powers of pulsed devices, so that tunable OPOs operating in pulsed mode have become readily available from a variety of suppliers. Recently, there have been comparable advances in continuous-wave (cw) OPO technology [3], which have spurred the development of commercial systems.

This progress has been mainly driven by the increasing availability of cost-effective high performance cw pump lasers and by the advent and increasingly sophisticated design of new nonlinear crystals. As to pump lasers, the operation of cw OPOs puts stringent requirements on potential light sources in terms of preferential single mode operation, noise characteristics, beam quality, and beam pointing stability. Depending on power requirements of the end-user, either high performance diode pumped solid state (DPSS) lasers (for lower powers) or fiber laser based solutions (for higher powers) are typically utilized. As to nonlinear materials and novel crystal design techniques, it should be noted that the emergence of so-called quasi-phase-matched nonlinear materials like periodically poled Lithium Niobate (whose crystal structure alters with a certain periodicity) has been of great utility for the design of practical optical parametric devices.

Practical design considerations

While OPO technology appears to be ideally suited for generating tunable cw laser light across arbitrary wavelength ranges, one must keep in mind that the OPO process itself will always generate output at wavelengths that are longer than those used for pum-

ping. Consequently, OPO devices operating across the visible spectral range do either require UV pump sources, or, alternatively, need to employ additional frequency conversion stages. As of today, only the latter approach has been proven to be technically practicable and operationally stable in commercial turn-key systems.

For illustration, the essential building blocks of a tunable cw OPO [4], designed to cover the visible range, are shown in **Fig. 1**. In essence, the operational principle relies on a cascaded sequence of nonlinear optical processes within two cavities, referred to as OPO and SHG cavity, respectively. As outlined above, pump laser photons are first split into pairs of photons of lower energy (signal and idler). The particular OPO scheme employed is commonly referred to as singly resonant OPO cavity design: For a certain operational wavelength of the entire system, the cavity is operated "on resonance" at either a particular signal wavelength or a particular idler wavelength. Thereby, a precisely moveable stack of periodically poled 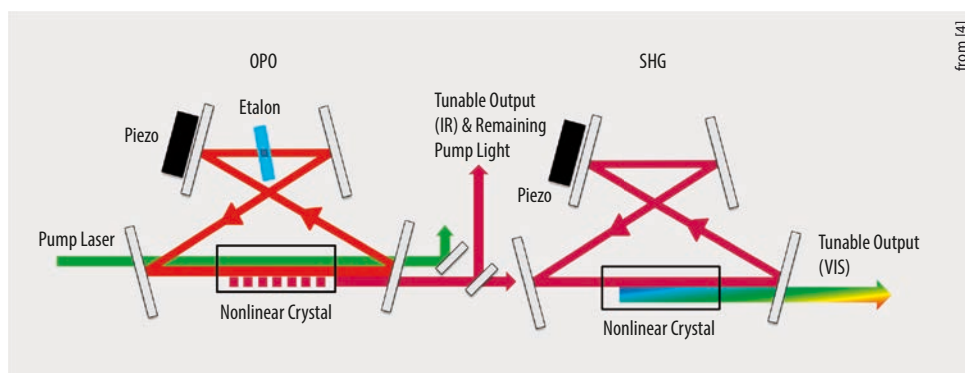nonlinear crystals allows for broad wavelength coverage. At a particular wavelength selection, a crystal layer with a suitable poling is automatically selected and its poling period fine-adjusted through a temperature control loop. At the same time, the effective OPO cavity length is actively stabilized to a multiple integer of the selected operational wavelength. While circulating one of the generated (signal or idler) waves resonantly inside the OPO cavity, its counterpart can be extracted for wavelength conversion into the visible spectral range by another nonlinear process. As illustrated in **Fig. 1**, this wavelength conversion takes place in a second, separate cavity by frequency doubling of the primary OPO cavity output, a process widely known as second harmonic generation (SHG). Though this configuration is technically practicable and provides favorable operational stability, it should be mentioned that alternative designs, like intra-cavity frequency doubling, have been successfully demonstrated in the lab.
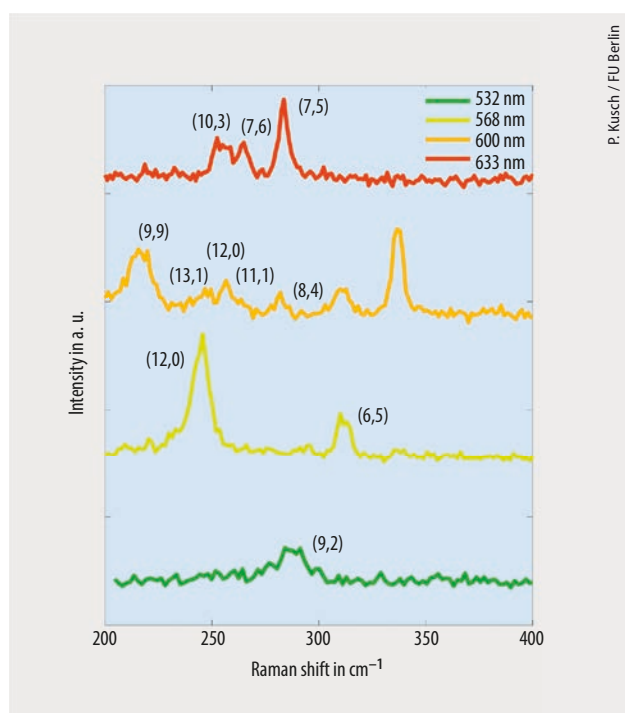

from [4]

Fig. 1 In a first step, a 532 nm laser pumps a nonlinear crystal to generate signal and idler photons (the range 900 – 1300 nm). Wavelength selection and subsequent second harmonic generation (SHG) converts either signal or idler photons into the visible range of the spectrum (450 – 650 nm). The green arrow depicts the pump laser beam, dark red and light red arrows depict the signal respectively the idler beam (arbitrary assignment).

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Fig. 2 Resonance Raman scattering spectra of a mixture of single-wall carbon nanotubes (CNTs) in ethanol solution (concentration of 1 g/l). The spectra are recorded for excitation wavelengths of 633 nm, 600 nm, 568 nm, and 532 nm (from top to bottom). The peak captions indicate the peak assignment to signals of CNTs of a particular chirality (n,m).
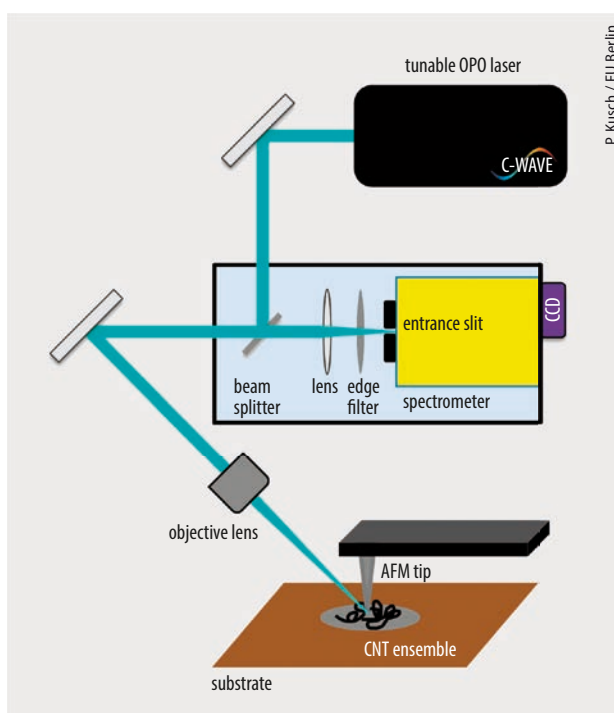

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Fig. 3 A fully tunable OPO laser is guided through a beam splitter and focused onto the tip of an atomic force microscope probe. Spectra are recorded by guiding the tip-enhanced Raman scattered light of the sample into a grating spectrometer.
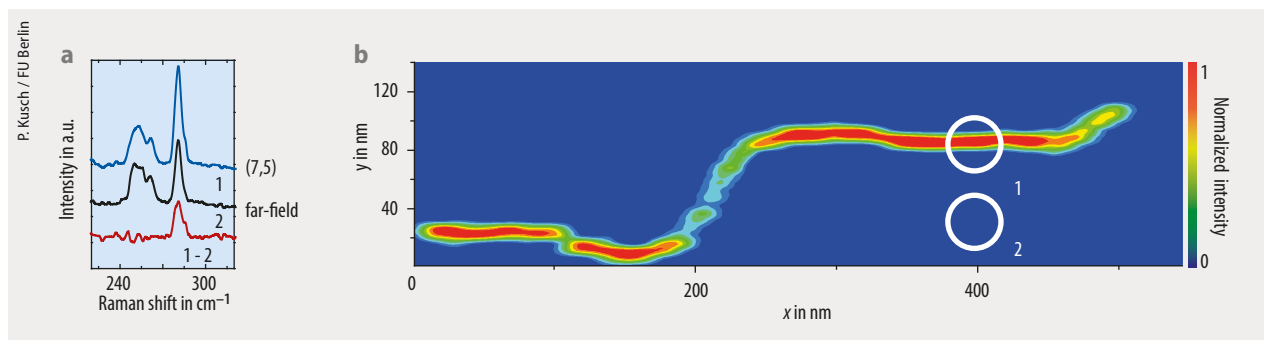
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Fig. 4 (a) Composed (blue line), far-field (black line) and tip-enhanced Raman spectra (red line) of the radial breathing modes of several carbon nanotube species. The tip-enhanced Raman spectrum can be unambiguously assigned to a nanotube of (7,5) chirality. (b) Nanoimage of the (7,5) carbon nanotube, obtained by plotting the tip enhanced RBM intensity as a function of tip position.

Raman Spectroscopy of Carbon Nanotubes

How does widely tunable laser light, as can be provided by the sources described above, advance nanoimaging techniques? To answer this question, carbon nanotubes (CNTs) have been selected as a test bed for proof-of-principle of a novel experimental approach based on tip-enhanced Raman scattering (TERS) [5]. To bridge the gap to this real-world application, we first briefly recall that a carbon nanotube is essentially a strip of a graphene (a one-atom-thick sheet of carbon), rolled up into a cylinder along a so-called chiral vector with two indices (n, m). It is this chiral vector that com-

pletely determines the CNT microscopic structure, i. e. its tube diameter and the chiral angle along the tube axis. Raman scattering has been well established as one of the main techniques to identify the chiral vectors of CNTs experimentally [6]. Thereby, so-called radial breathing modes (RBMs), that correspond to collective movements of carbon atoms in the radial direction, serve as fingerprints of particular (n, m) configurations in the Raman spectrum.

It is essential to note that the usual CNT Raman scattering signals are typically very weak and therefore of little practical relevance. However, the Raman scattering efficiency is significantly enlarged if the laser en-

ergy matches the energy of optically allowed electronic transition – an enhancement process referred to as resonance Raman scattering. In other words, for a particular laser excitation wavelength, the observed Raman signals (RMBs, respectively) from a mixture of CNTs will derive only from those CNTs that are in electronic resonance with the laser excitation (**Fig. 2**). Note that the Raman data, recorded for a mixture of CNTs in solution, is to be perceived as a compositional analysis but does not contain any spatial information whatsoever.

Excitation-Tunable Tip-Enhanced Raman Spectroscopy

The three main components of a TERS set-up are a laser light source for excitation, an atomic force microscope equipped with a carefully selected sharp metallic tip, and a Raman spectrometer recording the inelastically scattered radiation (**Fig. 3**). In essence, the physical principle behind TERS relies on so-called localized surface plasmons that are excited by the laser light in the microscope tip. These plasmons generate a strongly localized electromagnetic field, which not only enhances the incoming and Raman scattered radiation by orders of magnitude but also ensures a highly localized excitation of the sample under study. Thus, by recording tip-enhanced Raman spectra intensities as a function of the tip position, TERS allows for nanoimaging with a spatial resolution below 10 nm.

Fig. 4 illustrates the sequence of events and results of a TERS experiment carried out at a single laser
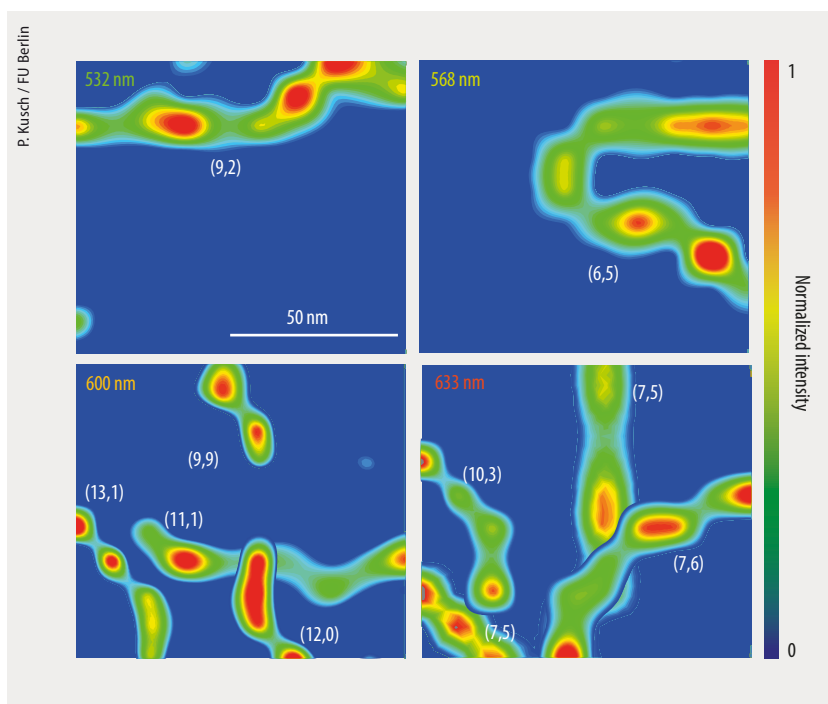

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Fig. 5 Nanoimages of carbon nanotubes recorded with four different excitation wavelengths. The different tube species are labeled by their chiral indices in the nanoimages.

excitation wavelength (633 nm) on a film of a CNT mixture. In a first step, a so-called composed Raman spectrum is recorded by placing the microscope tip at a particular (*x*, *y*) position in close proximity to the CNT film. The resulting composed Raman spectrum encompasses the RBM peaks of several CNTs (all of them in electronic resonance to the excitation wavelength). In a second step, the microscope tip is retracted, and the so-called far field spectrum is recorded without the tip-enhanced Raman contribution to the signal. By subtracting the far-field spectrum from the composed spectrum, the pure tip-enhanced Raman spectrum is obtained. Eventually, from that spectrum, the tube species underneath the tip position can be unambiguously identified (**Fig. 4a**). For a spatial image of the particular CNT, the outlined procedure is repeated: The tip position is scanned step-wise over the sample surface, and at each point the intensity of the pure tip-enhanced Raman peak is determined (**Fig. 4b**). As can be clearly perceived, the CNT is around 800 nm long and bent in a step-like shape.

The full beauty of the experimental approach unfolds realizing that the imaging capability of the set-up is no longer limited to a subset of CNTs that happen to be in electronic resonance to a particular excitation wavelength – as has been the case for the vast majority of TERS experiments. On contrary, following the lines above, the examination of the sample under study can be in principle performed for a quasi-continuum of wavelengths that is covered by the tunable laser light source. In the present example, this allows unprecedented access to a broad variety of CNT species (**Fig. 5**). This hyperspectral principle of nanoimaging is the basis of the excitation-tunable tip-enhanced Raman spectroscopy (e-TERS) [5]. By using four different excitation wavelengths, it was possible to identify and image a total of nine different CNT species within one and the same sample area (**Fig. 5**). The e-TERS nanoimages visualize, for the first time, the shape and orientation of different CNT species in spatially overlapping arrangements – and they are no longer limited to an observation window that is dictated by a narrow band of electronic transitions that fall to be in resonance with a single excitation wavelength.

Outlook

To conclude, the experimental demonstration of excitation-tunable tip-enhanced Raman spectroscopy comes in tandem with the availability of novel tunable laser light sources based on OPO technology. From the general laser technology point-of-view, the performance characteristics of OPOs make them competitive alternatives to conventional lasers and related technologies for the generation of widely tunable cw radiation. From the experimental methodology point-of-view, we expect e-TERS to open new experimental horizons for studying the electronic and vibronic properties of matter on the nanometer scale.

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