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Adaptation of a commercial Raman spectrometer for multiline and broadband laser operation

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A commercial single laser line Raman spectrometer is modified to accommodate multiline and tunable dye lasers, thus combining the high sensitivity of such single monochromator systems with broadband operation. Such instruments rely on high-throughput interference filters that perform both beam alignment and Rayleigh filtering. Our set-up handles this dual task with two independent elements: a beam splitter and a long

pass filter. Filter rotation shifts the transmission passband, effectively expanding the range of operation. Operation is demonstrated on single-walled carbon nanotubes, for which the set-up was optimized. As the set-up operates with standard optical elements it can be customized for specific needs with relative ease.

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1 Introduction Raman spectroscopy is a widespread and important tool in various fields of science from biology to physics. Commercial Raman spectrometers are usually equipped with a built-in laser and a set-up optimized for this single laser line, resulting in stable operation but inherently narrow-band characteristics. The electronic, optical, and vibrational characterization of certain materials, such as single-wall carbon nanotubes (SWCNTs) [1] requires measurements with a large number of laser lines [2] or with a tunable laser system [3, 4].

Raman spectroscopy relies on the efficient suppression of “stray light” photons with wavelengths close to that of the exciting laser (e.g. from Rayleigh scattering) which dominate over the Raman signal by several orders of magnitude. Operation down to Raman shifts of 100 cm^{-1} is made possible in modern spectrometers with the use of interference Rayleigh filters (often referred to as notch filters) with a throughput exceeding 80% for the passband, this is significantly higher than for a classical subtractive double monochromator system. Although interference filters are manufactured for the most common laser lines only, rotation extends the range of filter operation. Thus, the narrow-band constraint could be circumvented to allow broadband operation. In most spectrometers, the interference

filter has a dual role: it reflects the laser light to the sample and it functions as a Rayleigh filter. Filter rotation changes the optical path that can be corrected for with tedious and time consuming readjustment, effectively nullifying the advantage of the higher sensitivity.

In particular for the radial breathing mode (RBM) of SWCNTs, the presence of the low energy ($\geq 100\text{--}150\text{ cm}^{-1}$) [5] Raman modes and the narrow (FWHM $\sim 30\text{ meV}$) optical transition energies [3] pose several challenges to the instrumentation. A proper energy dependent Raman measurement requires a broadband spectrometer with efficient stray light rejection.

We previously described the modification of a commercial Raman spectrometer, based on replacing the built-in interference filter with a beam splitter and a separate interference filter [6]. The two functions of the filter are performed independently with no observable influence on the direction of the transmitted light. Herein, we present the operation of the instrument with a multiline laser excitation source, discuss the behaviour of the filter passband for the *S* and *P* polarizations¹ under rotation, and analyse

¹ The *S* and *P* refer to polarizations which are perpendicular and parallel to the plane of incidence, respectively.

the versatility of such a set-up with prospectus research applications.

2 Spectrometer set-up A high sensitivity, confocal single monochromator Raman system with an interference Rayleigh filter – such as described in the previous section – can be modified to enable broadband measurements with multiple laser lines or a tunable laser, which we demonstrate for a LabRAM commercial spectrometer (Horiba Jobin-Yvon Inc.) as an example. The key step in achieving the broadband operation was replacing the built-in interference filter, which acts as a beam splitter and a Rayleigh filter at the same time, with a combination of a simple beam splitter and a separate interference filter. We have to emphasize that the use of optical elements, which are non-specific to the spectrometer allows economic implementation for most spectrometer designs and is only limited by the space constraint of the set-ups. The present improvement could be easily adapted to the so-called direct mode of triple axis spectrometers, thus allowing operation down to 100 cm^{-1} with a large sensitivity.

The set-up for the modified LabRAM spectrometer is shown in Fig. 1. A multiline Ar/Kr laser (Coherent Inc., Innova C70C-Spectrum) and a dye laser (Coherent Inc., CR-590) pumped by a 532 nm 5 W solid state laser (Coherent Inc., Verdi G5) serve as excitation light sources. The former operates at multiple, well defined wavelengths while the latter allows fully tunable application. In our case, the dye laser is operated in the 545–580 nm, 580–610 nm, and

610–660 nm wavelength ranges with three dyes: Rhodamin 110, Rhodamin 6G, and DCM Special, respectively.

The spurious fluorescent background of the laser output is filtered with short pass (“3rd Millennium filters” for 580 and 610 nm from Omega Optical Inc.) and band pass (“RazorEdge” for 458, 488, 515, 532, 568, 633, and 647 nm from Semrock Inc.) filters. The light is directed toward the sample with a broadband beam splitter plate (Edmund Optics Inc., NT47-240) with 30% reflection and 70% transmission. For both excitation sources a single, long pass interference edge filter (“RazorEdge” for 458, 488, 515, 532, 568, 633, and 647 nm from Semrock Inc.) performs stray light rejection. The use of a short pass filter for laser clean-up and long pass filters for Rayleigh photon suppression limits operation for the Stokes Raman range. Our studies focused on the Stokes processes, thus we utilized long pass filters for Rayleigh filtering. As the set-up can be easily modified, studying anti-Stokes scattering would be possible with a combination of band pass or long pass and short pass filters for laser clean-up and Rayleigh suppression, respectively.

Although our studies focused only on the VIS range, modification is not limited to it as the LabRAM spectrometer is usable in the UV-NIR range as specified by the producer. In principle, the range of excitation wavelengths is only limited by the optics used. Provided that the laser source, the appropriate beam splitter, laser clean-up, and long pass filters, and detectors are available, the studied wavelengths can be extended further to the UV and NIR range, as well.

The long pass filter has a double function in the original spectrometer: it mirrors the laser excitation to the sample and acts as a Rayleigh filter, quenching the stray light. In our construction, these two tasks are performed independently by a beam splitter and a long pass filter, respectively. The broadband beam splitter plate has 30% reflection and 70% transmission, thus only a small fraction of the Raman light is lost. The application of an anti-reflective coating to the back side of the plate prohibited the emergence of higher order reflections and standing waves (whose effect is known as ghosts) within the plate. The beam splitter plate is mounted on a finely adjustable two-axis holder (Thorlabs Inc., VM1) with a homemade mounting. The fine adjustment is required for proper light alignment with the spectrometer and to maximize the Raman signal.

Increasing the incidence angle of the light changes the range of filter operation of the interference filters without the misalignment of the light. Thus, filter rotation enables broadband operation. In Fig. 2., we show the behaviour of a 633-nm long pass filter at different incidence angles. The edge of transmission blue shifts upon rotation with respect to normal incidence. However, the shift is smaller for the *S* than for the *P* polarization; i.e. the shift is larger for the horizontally polarized light when the filter is rotated around a vertical axis, which is more practical. For 1 inch apertures short and long pass filters rotation angles up to 30° were used, yielding a blue shift of about 10%; the 0.5 inch aperture of the band pass filters limited the blue shift to about 5%. The width

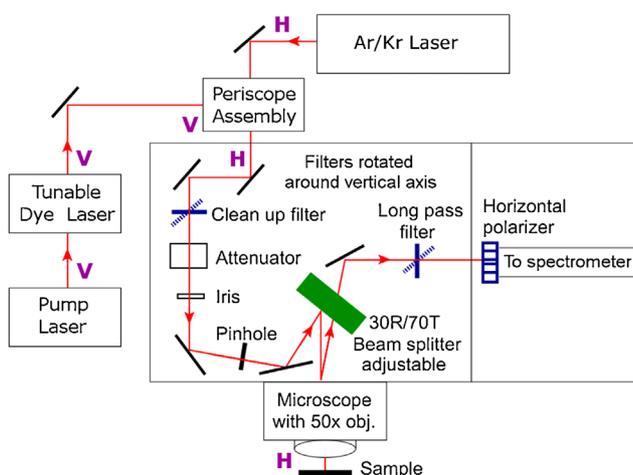


Figure 1 (online colour at: www.pss-b.com) Schematic diagram of the broadband configuration of the LabRAM spectrometer. Excitation is provided by a multiline Ar/Kr laser and a tunable dye laser. V and H denote vertical and horizontal polarizations, respectively. The laser light is aligned with the spectrometer using the periscope element, which also rotates the polarization to horizontal, if needed. The laser outputs are cleaned with a filter. The beam splitter is placed in the position of the notch filtering beam splitter in the original set-up. The unwanted vertical polarization is filtered with a polarizer.

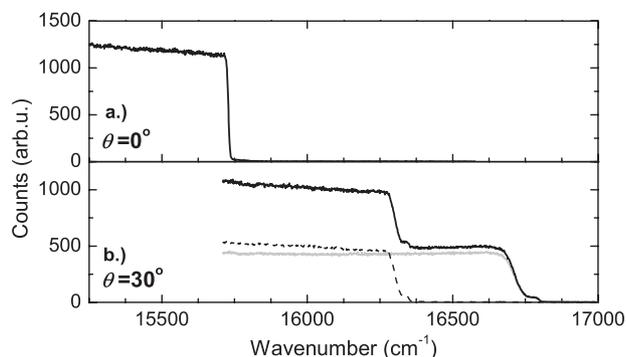


Figure 2 Transmittance of the 633 nm long pass filter using unpolarized white light; (a) at normal incidence and (b) rotated by 30°. When polarization filters are used, the two parts of the double step feature (solid black line) are separated according to the *S*- and *P*-polarization (dashed black and solid gray lines, respectively). Note the broadening of the transition width upon rotation.

of the filter transition edge also broadens for larger incidence angles. This is defined as the maximum difference between the laser wavelength at which the attenuation exceeds optical density 6 and the filter edge-wavelength at the 50% transmission point. For the 30° incidence, a fivefold increase in the transition width is observed when compared to the normal incidence, allowing operation down to 70–140 cm^{-1} .

For SWCNTs, the Raman light is polarized preferentially along the polarization of the excitation, this is due to a phenomenon called the antenna effect [7, 8]. We also verified that the LabRAM spectrometer itself is not polarization-sensitive in contrast to an older triple monochromator system. Therefore a horizontally polarized laser excitation is preferred which explains the polarizations used in our design. The less shifted *S* (in our construction vertically) polarized stray light is removed with a polarization filter before the spectrometer input.

The present set-up was constructed as a tool for the swift characterization of CNT ensembles. As it requires the best obtainable signal-to-noise ratio for a large domain of excitation wavelengths, it is optimized to exploit the aforementioned antenna effect. Given the stable and high power lines of a multi line laser, the instrument can be used to perform polarization dependent measurements at multiple excitation wavelengths, such as a depolarization study of CNTs [9, 10]. Although the detector has no polarization preference, we opt to keep the polarization of the detector's polarizer fixed as the vertical rotation of the filters is preferred. By introducing an adjustable lambda-half plate, we can freely set the polarization angle of the excitation compared to the horizontal polarizer. However, the lambda-half plate should be placed before the beam splitter, as placing the lambda-half plate between the beam splitter and microscope would not only influence the polarization of the excitation beam but the backscattered beam as well. An ideal position for this wave plate would be next to the pinhole, as

the attenuated beam would not harm the plate and would only rotate the excitation beam polarization.

3 Test measurements Test measurements of the broadband set-up were carried out with the tunable dye laser on a HiPCO SWCNT sample (Carbon Nanotechnologies Inc., Houston, TX), suspended in a 2 wt.% solution of SDBS and water using sonication.

We focused on the RBM Raman range located below 400 cm^{-1} , which is commonly studied to characterize the diameter distribution in SWCNTs [11]. Carbon-tetrachloride was used for Raman shift correction and Raman intensity normalization such as in Ref. [3] to correct for instrumental uncertainties such as a slight misalignment of the scattered light upon dye exchange. The suspended HiPCO sample was placed in a glass cuvette under the objective of the built-in microscope (Olympus LMPlan 50x/0.50, inf./0/NN26.5, $\sim 1 \times 1 \mu\text{m}^2$ spot size) and the CCl_4 reference sample was placed into the macro cuvette holder. The LabRAM spectrometer allows changing between a macro and micro mode with a mirror resulting in stable and robust spectral shift calibration and intensity normalization as there is no need for further adjustments or for sample exchange.

Laser excitation energies between 1.92 eV (648 nm) and 2.27 eV (545 nm) were covered with an energy resolution of about 12 meV ($\sim 100 \text{cm}^{-1}$). The spectrometer was operated with a 600 grooves per millimetre grating and a liquid nitrogen cooled CCD with 1024 pixels along the spectral direction. This configuration yields a $\sim 1.3 \text{cm}^{-1}$ Raman shift resolution and $\sim 1800 \text{cm}^{-1}$ spectral range for 600 nm (both are wavelength dependent). Typical laser powers of 1–5 mW were used with no observable heating effects, due to the liquid nature of both samples.

In total, 9 h were required to complete the energy dependent Raman experiments with the 29 laser lines including 2 laser dye exchanges. A typical measurement cycle of 8 min consisted of changing the dye laser wavelength, rotating of the laser clean-up and the long pass filters to the appropriate positions, shifting the spectrometer grating, nulling the spectrometer and acquisition of the spectra for the sample and the reference with an acceptable signal to noise ratio of about 300. Additional time is needed for the filter exchange (a few minutes) and to change the laser dye and realign the beam (about 1 h). We note that once the dye laser is set and the light path is properly aligned with the spectrometer, no further realignment is required when the wavelength is changed, even though the filters are rotated and the optical path is only minutely modified. Measurements of a similar scale such as published previously using a triple monochromator spectrometer [12] last for about 2 weeks, mainly due to the approximately 50 times smaller S/N ratio and the need for a spectrometer realignment upon wavelength change.

Figure 3 shows the 2D contour plot of the Raman map, compiled from spectra such as shown in Fig. 3A with a home-made software. The normalized Raman intensity is displayed on a logarithmic scale. A good agreement is observed between

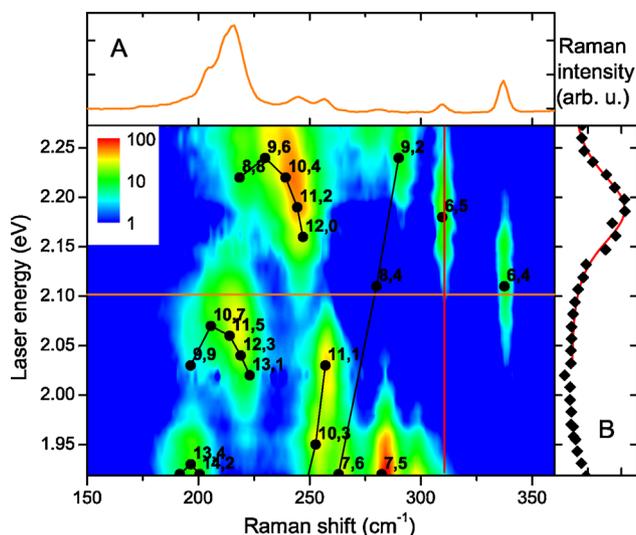


Figure 3 (online colour at: www.pss-b.com) Main plot: Raman map for the RBM range of a HiPCO/SDBS suspension measured with the broadband Raman set-up. Logarithmic scale shows the Raman intensity normalized to the maximum observed intensity. Full circles denote data published in Ref. [3]. Inset A: A spectrum of the Raman map (horizontal line) at 592 nm (2.1 eV). Inset B: Energy cross section of the Raman map (vertical line). The black diamonds correspond to the cross section at 310 cm^{-1} Raman shift, solid curve refers to a resonance Raman fit.

our data and the measurements in Ref. [3], whose resonance transition energies and Raman shifts are shown for the different SWCNT chiral indexes, (n , m), with full circles. We do not observe the (8,4) SWCNT in our measurement, due to the low intensity of the resonant Raman process [13]. Points corresponding to the same SWCNT families, i.e. when $2n + m$ is constant [11], are connected by solid lines.

Vertical, i.e. energy cross section of the Raman map (Fig. 3B) were obtained by averaging around a given Raman shift with no further corrections and were fitted with curves corresponding to the resonance Raman theory [3, 12]. These yield transition energies and quasiparticle scattering rates in good agreement with typical literature values, especially considering that the different solvent environment slightly modifies the Raman transition energies [3]. The result is remarkably smooth in comparison with similar data published in Refs. [3, 4, 14]. This is due to the robust and reproducible measurement of the reference sample and possibility of measuring Raman spectra at different wavelengths without spectrometer readjustment in between. The agreement shows the utility of the broadband arrangement with a clear advantage over previous results in terms of acquisition time.

4 Conclusions In conclusion, we presented the broadband modification of a high sensitivity commercial Raman spectrometer. The improvement allows the use of both multiline and tunable dye lasers. The spectrometer performance is demonstrated on SWCNTs where such broadband measurements are inevitable to obtain meaningful insight into vibrational and electronic properties.

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