Renishaw inVia Raman spectrometer in lab F19 – notes for training sessions

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The following notes were written for training new users. Training sessions should be tailored to the user - their content should depend on the prior experience and on the kind of measurements to be done. New users are very welcome to study this document but reading it does not replace a training session.

1. Brief overview of (vibrational) Raman spectroscopy.
   - what is Raman scattering: inelastic scattering of radiation, where the difference between photon energies equals to a transition between energy levels (in this case: vibrational energy levels/phonons)
   - in vibrational Raman spectroscopy, vibrational modes (in molecules or solids) are excited or de-excited (relaxed) during the scattering
   - a Raman spectrum shows the intensity of analysed light (measured in counts or in counts/time) plotted as a function of energy shift, called *Raman shift* (normally expressed as wavenumber, which is proportional to photon energy)
   - typical uses: getting information about sample composition (compounds and their phases), defects in the sample (esp. in graphitic materials), structural features of the material (e.g. MoS_2 or graphene film thickness, CNT diameter, graphite/graphene edge orientation)

2. Renishaw inVia Raman spectrometer.
   - produced around 2006, price ca. 140 kGBP, so use it with care
   - main components of the system (spectrometer, microscope, 2 lasers, computer) – show the light path inside the spectrometer
   - the incident laser beam is, to a good approximation, linearly polarized
   - optional accessories (e.g. microscope objectives, cooling stage, fibre optic probe)
   - the instrument can be used both for collecting Raman spectra and photoluminescence (fluorescence) spectra
   - use of the log book – make an entry when starting every session
   - basic precautions:
     - keep all areas clean and tidy
     - don't lean on the spectrometer and don't apply any larger force to it
     - don't apply any force on the lasers, turn them on/ff gently (to avoid misalignment)
     - be extra careful when the main enclosure is open, don't touch the internal components (except changing the lenses – see later)
   - turning on:
     - first, the equipment (spectrometer, stage controller, laser(s), computer), then the software (WiRE 3.4)
     - the lasers will produce a stable beam only after some time from turning them on (as they will heat up) – for the 785 laser this is 30 min, while for the 488/514 laser this is 5 min. Hence, for very important or accurate measurements it is better to wait and then calibrate and start recording spectra.
     - however, if you are not going to use a laser for a long time, turn it on only when you need it (especially the 488/514 argon laser, which has a short service life)
   - the lasers are potentially hazardous (class 3B) but they have an interlock system – they are turned off when any of the spectrometer enclosures is open AND the shutter is open at the same time
   - turning off:
     - turn off the software, then the equipment (laser(s), spectrometer, stage)
     - the correct way to turn off the 488/514 laser is to turn the key on the remote to 0, wait for the cooling fan to stop and then turn the power switch off (on the laser housing) – this is to cool down the laser
     - turn off the computer
   - logbook entry – make sure it has all details and you listed any problems encountered
   - in case of equipment problems or malfunctions, email Dr Chris Howard (c.howard@ucl.ac.uk) or Szymon Bartuś (s.bartus.16@ucl.ac.uk)

- short guide – printed copies in F19, PDF on the PC, PDF on Wiki – consult it if you didn't recently use the instrument
- the spectrometer manual (called inVia User Guide) is on the computer (WiRE -> Help) and on the group Wiki – very comprehensive
- doing maintenance (e.g. laser alignment, lens cleaning) or changing settings permanently or doing something significantly different than what was covered in the training – ask first (Szymon or Chris)

3. Sample handling.
- a risk assessment (RA) must be filed and approved on RiskNET for handing of all harmful samples (the RA can be for the whole experiment, not just for handing near the spectrometer)
- harmful samples should ideally be sealed for the measurements and must be sealed for transport to/out of the lab and for storage
- if handling a harmful powder sample is unavoidable, do it on the sample prep table on the left of spectrometer; after measurements put the powder sample back in a vial or dispose of it appropriately (and use any PPE required)
- use aluminium foil (or paper towel at least) to protect the table from the spills if handling powders; dispose it to the yellow bin afterwards
- clean up any spills immediately – you can use paper towels (with water or IPA if needed) – dispose them to the yellow bin
- you should especially avoid spills in the microscope enclosure (as most people use it without gloves)
- if the sample requires handling in gloves, take them off before touching anything else, especially the computer keyboard and mouse; dispose all gloves to the yellow bins (the cleaners don't like lab gloves in the general waste, even if they are clean)
- sample storage: preferably in other labs, but for short term storage you can use the shelf (as long as the sample is safe to store there, sealed and labelled with contents and owner's name)

4. Spectrometer configurations (laser + grating).
- this spectrometer can currently use 3 laser wavelengths: 488 nm - blue, 514 nm – green (Ar laser) and 785 nm – infrared (diode laser)
- for the 488 and 514 nm laser there is also a choice of diffraction grating: 1200 lines/mm grating or 2400 lines/mm grating
- choosing a laser: in general, the Raman peak intensity and, occasionally, peak position (Raman shift) can vary for different lasers, but we often don't know how
- choosing a grating: 2400 grating gives higher spectral resolution, but for the 785 nm laser only 1200 is available
- hence, by default, for Raman spectra I would choose the 514 nm laser (because it's popular in the literature) and 2400 line/mm grating (because it gives better spectral resolution)
- changing lenses:
    - follow the message on the screen
    - if you aren't sure if the lenses are correct, then choose another configuration in the software (without changing lenses) and then go back to the one you want
    - close the laser shutter (in the software or with a black button) – if you don't do it, the interlock will switch all lasers off
    - unlock and open the enclosure gently
    - handle all lenses with great care
    - don't touch any other components
    - hide all previous lenses in the cases immediately
    - if lenses are dirty, report it and we will clean them
    - close and lock the enclosure gently
- notes about photoluminescence/fluorescence:
    - obviously, the laser photon energy needs to be higher than the transition you want to excite (e.g. band gap)
    - laser energies: 488 nm – 2.5 eV, 514 nm – 2.4 eV, 785 nm – 1.6 eV

- energy range in the spectrum is limited by the angle range of the diffraction grating: 1200 grating: > ca. 0.9 eV, 2400 grating: > ca. 1.7 eV
- filter artefacts: when 514 nm laser is used, the edge filter leaves ripples in the region of 1.5-1.9 eV, but when 488 nm laser is used, no ripples are visible (see the white lightbulb spectra)
- alias peaks: if spectrum below 1.3 eV needs to be recorded, a long pass filter needs to be used - we have a 700 nm filter, which blocks all light with energy above 1.77 eV (wavelength < 700 nm) – normally attached with Blu Tack to the "A" lens holder

5. Recording spectra.

- calibrate the spectrometer using the autocalibration function at the beginning of each session and after changing configuration (laser/grating/lenses)
- placing the sample on the stage, adjusting the stage
- video preview *vs* the eyepieces – both can be used, video more convenient
- moving the sample and focusing – manually and with motorized stage
- microscope objectives – it's better to start with a small magnification
- higher magnifications have short working distances and it's easy to hit the objective with your sample – be careful
- Sample Review toolbar:
  - choose the same microscope objective magn. – otherwise your scale bar will be wrong
  - illumination: lightbulb power, A aperture
  - F aperture – can be used for focusing on your sample
  - if the enclosure is closed, you can check how does the laser spot look like (start with a small power, e.g. 0.1 %)
  - laser power and beam focus

- setting up a measurement from scratch:
  - choose *Spectral acquisition* dialog (New Measurement button -> Spectral acquisition or Measurement -> New -> Spectral acquisition)
  - Range: static vs extended scans (start with extended if you are not sure), note: use other units for fluorescence/photoluminescence
  - Acquisition: adjust by trial and error, but start with a low power (e.g. 0.1 %) to avoid sample damage
  - File: you can use this to automatically save the files
- to record the spectrum: press Run button
- to abort: press Abort button
- modifying the settings – use the Setup Measurement button
- note about cosmic ray peaks – very characteristic, usually 1 pixel wide (to check if a peak is from a cosmic ray, record again)

- saving the files:
  - make a folder with your full name
  - saving a spectrum: Save Measurement button
  - alternatively, save your spectra automatically using the Spectral acquisition -> File dialog
  - .wxd - Renishaw proprietary format – open it with WiRE, contains all measurement parameters (so no need for long file names)
  - other formats – you can e.g. use the WiRE Batch File Converter to convert .wxd to other formats
  - images from the microscope – you need to save them separately (images are not included in .wxd files)
  - how to save an image: choose Live Video -> Snap -> Single or press the Snap video button and then right click to save
  - no Internet connection in this computer – use a USB drive
  - copy files from this computer instead of removing them (the files will be your backup copy and also a source of measurement settings you can use later)

6. Mapping (optional).
- (to be added later)

7. Troubleshooting.
- poor signal/noise ratio or weak signal
  - check focus
  - try collection from a different region
  - try longer recording time
  - try larger laser power (you should be careful with using large power because your sample can overheat)
  - try more accumulations (recording the spectrum multiple times and averaging it)
  - try higher magnification objective
  - try a different laser wavelength (Raman scattering intensity is much larger when the energy of incident light is close to an energy of transition between electronic energy levels in the substance you are analysing, e.g. a band gap in a semiconductor - this is called resonance Raman scattering)
  - if your sample is a single crystal - try different sample orientations (the incident light is polarized)
  - additional tips for how to improve the signal/noise ratio are in the inVia User Guide: Application notes -> General instrument use notes -> Optimise data collection
- signal too strong (e.g. peak tops are cut off)
  - reduce power and/or reduce recording time
- laser burns the sample
  - try smaller power
  - try defocusing the laser beam (beam focus slider)
  - try lower magnification objective
  - try a different laser
- fluorescence (visible as raising background)
  - your sample might be fluorescent itself
  - your sample container, substrate or something else under the microscope might be fluorescent
  - record a control spectrum of an empty sample container or substrate without sample – this is always a good practice and will show you which spectral features come from your sample and which don't
  - the fibreboard plank we use in the lab is fluorescent, so covering it with Al foil is recommended
  - example of a good substrate: Si wafers, including Si wafers with thermal SiO_2 layer (no fluorescence, but strong Raman peak at 520 cm^{-1})
  - example of a good airtight containers: fused silica (a.k.a. quartz glass) cells or capillaries
  - using a different laser wavelength might also help
  - if your sample is a single crystal, changing the orientation might increase the Raman peak intensity
- no spectrum visible
  - try different laser powers – it might be that your value is either too low or too high
  - make sure that the microscope is focused
  - make sure that you have the correct lens set
  - make sure that the laser you want to use is on and chosen in the software
- other problems: check the inVia User Guide or contact us

8. Further reading.
- see e.g. our group Wiki for resources about Raman spectroscopy of nanomaterials