Experiment 8

Raman spectroscopy

8.1 Introduction

Light interacting with matter can be reflected, absorbed, or scattered. Absorption happens when the energy of the incoming photon matches the difference in the energies of two quantum levels of the system. In Raman spectroscopy these quantum levels are vibrational (and sometimes, rotational) molecular modes. After absorbing the incident photon, the system can also emit a photon, resulting in scattering. When the wavelength of the emitted photon is the same as the incident wavelength, the process is called Rayleigh scattering, but it is also possible for the system to relax into a state different from the initial one, thus producing an emitted photon of a different wavelength. In this case of inelastic scattering, longer wavelengths correspond to photons shifted to lower energies compared to the incident photons, the so-called Stokes shift, and shorter wavelengths (emitted energies higher than incident energies) correspond to the anti-Stokes shift. The observed shifts are a direct measure of the vibrational (and sometimes, rotational) frequencies in the material which depend on the chemical bond structure and molecular symmetry. In this way, Raman spectroscopy provides a “fingerprint” to identify materials.

The history of the discovery of Raman scattering is fascinating, and involves a number of very human and not just purely scientific aspects: prejudice, nationalist pride, public relations management. Chandrashekhara Venkata Raman reported the effect in 1928 via a telegram to *Nature*, and a press conference to the newspapers on February 28, 1928, both rather unusual at the time. He then successfully lobbied for a Nobel prize, and solicited the support of A.Sommerfeld, N.Bohr and E.Rutherford. He was awarded the prize in 1930, an unusually short time after the discovery, reflecting a universal recognition of the importance of the technique. Today in India, February 28 is celebrated as a National Science Day. *The Quantum Indians*, a 2013 film by Raja Choudhury is recommended viewing.

8.2 The apparatus

Fig. 8.1 shows a schematic diagram of the Raman spectrometer. The light source is a 632.8-nm (red) He-Ne laser, and a number of lenses and mirrors are used to route the incident beam to the sample and to collect the scattered light onto a narrow-slit entry point of the spectrometer. The lenses are built into the frame of the apparatus and require a minimum of adjustment, but the role of the filters needs to be well understood. Filter F_1 is a band-pass filter with peak transmission close to the 632.8-nm wavelength of the laser; filter F_2 is a notch filter greatly suppressing the 632.8-nm line. When both filters are in place, the incident light is purely the main, 632.8-nm line of the He-Ne laser, and the scattered light is at wavelengths that are *not* 632.8-nm. This combination allows for the detection of only those wavelengths that are different from the incident laser light and thus represent the Raman-shifted wavelengths.

The diffraction grating can be rotated by a micrometer screw, and its reading corresponds approximately to the wavelength at the center of the camera view. For precise measurements, the spectrometer needs to be calibrated, for every position of the grating. He-Ne laser output is strongly dominated by the the main 632.8-nm line, but a number of much weaker He plasma lines are also present; this is helpful to obtain the precise calibration of the spectrometer in the region of interest, since these wavelengths are well known. It is best to rotate the grating to a position somewhere in the 654–660 nm, as this places the main line just outside the view of the camera. Even the residual shoulder intensity is quite strong, and the use of the filter F_2 is essential. However, for calibration purposes filter F_1 should be removed. This allows the

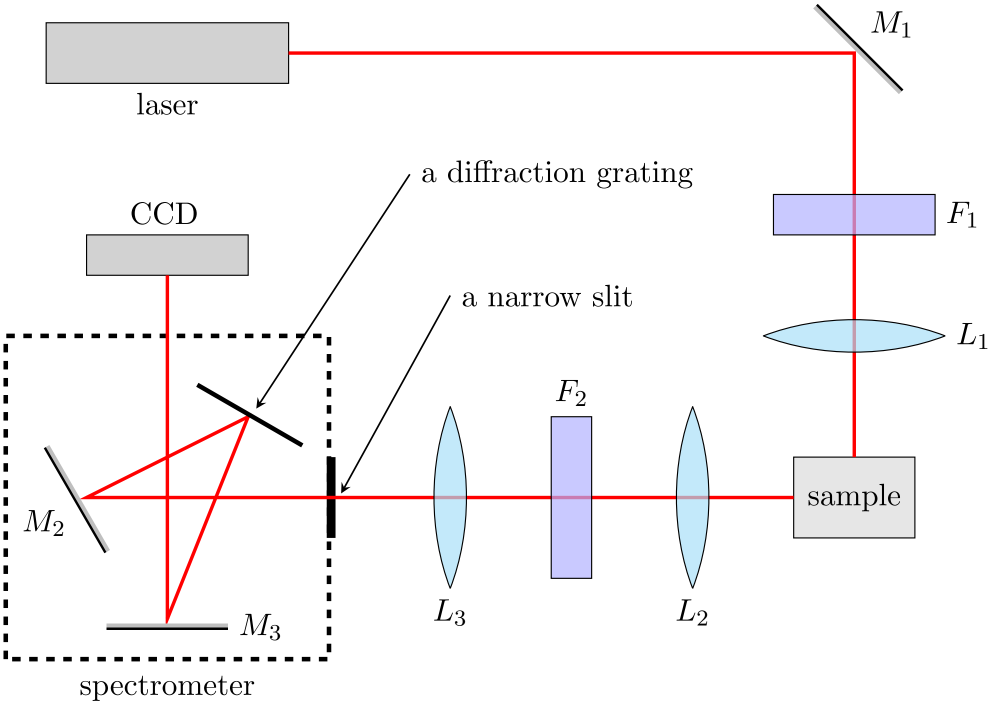
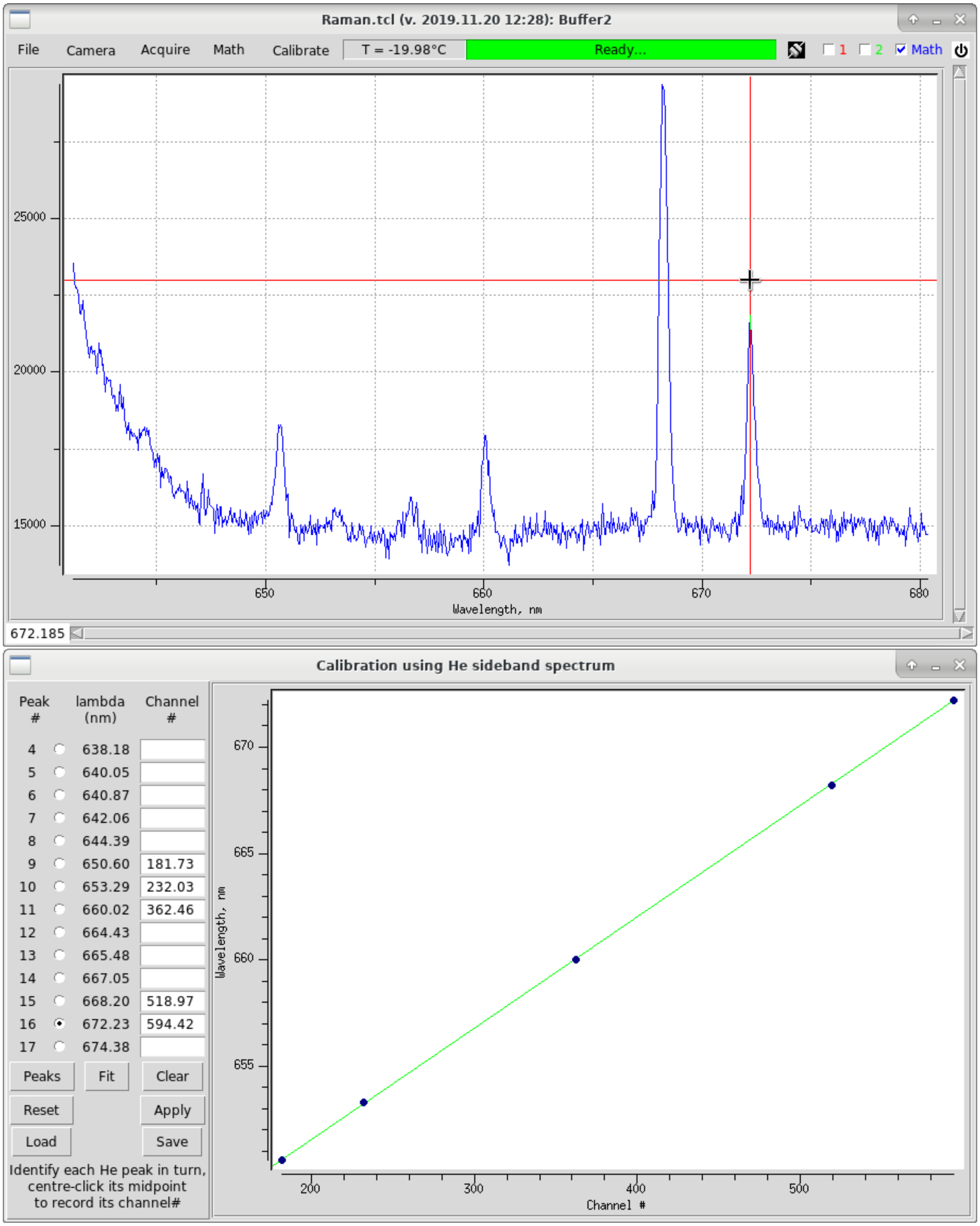


Figure 8.1: Schematic diagram of the Raman spectrometer. A 632.8-nm (red) He-Ne laser beam is directed at a sample and the scattered light passes through a narrow (50-nm) slit onto a diffraction grating before being detected by a CCD camera. A micrometer (not shown) can adjust the angle of the diffraction grating, shifting the window of detectable wavelengths. Filter F_1 is a band-pass filter with peak transmission close to the 632.8-nm wavelength used; while filter F_2 is a notch filter greatly suppressing the 632.8-nm line. This combination allows for the detection of only those scattered wavelengths that are different from the incident, purely 632.8-nm laser light. When the plasma lines from the He-Ne laser need to be detected during the calibration stage, filter F_1 must be removed. Tikz figure by C.Wilson.

plasma lines to be transmitted to the sample. Using a small metallic mirror (at grazing incidence) as the sample allows these wavelengths to be captured and used for calibration. Fig. 8.2 shows the result of a 60-second data acquisition and the resulting calibration table, as obtained using the `Raman.tcl` control script. A 60-sec dark spectrum (with the spectrometer entry slit blocked) has been subtracted. A linear fit to the calibration dataset was performed and applied, as evidenced by the x-axis labelled in nm (prior to calibration the axis reads in pixels). A remnant of the strong main line, off to the left of the observed region, is visible as a “shoulder” at 640–645 nm. The calibration data set can be saved, and if the micrometer position has not changed, loaded into the software and re-applied. The CCD is kept at -20°C to reduce noise.

Solid samples are mounted using a small amount of silicone grease on the removable steel holders. A careful adjustment of the position of the spot where the laser light grazes the surface of the solid sample is required, so that the weak scattered light is focused precisely on the narrow slit of the spectrometer, and then the notch filter F_2 placed back in the path. Liquid samples fill a cuvette, with most of the laser light passing through the liquid, and the scattered light collected at right angle to the direction of the laser beam; alignment is less critical in this case. Fig. 8.3 shows the spectrum of a liquid sample of toluene, acquired for 240 s for both the raw and the dark (with entry slit blocked) spectra. The raw spectrum is difficult to distinguish from the background of the dark spectrum, but the point-by-point difference reveals a number of weak lines.



Peak #		lambda (nm)	Channel #
4	○	638.18	
5	○	640.05	
6	○	640.87	
7	○	642.06	
8	○	644.39	
9	○	650.60	181.73
10	○	653.29	232.03
11	○	660.02	362.46
12	○	664.43	
13	○	665.48	
14	○	667.05	
15	○	668.20	518.97
16	●	672.23	594.42
17	○	674.38	

Identify each He peak in turn, centre-click its midpoint to record its channel#

Figure 8.2: He plasma lines are used to obtain the calibration of the CCD camera.

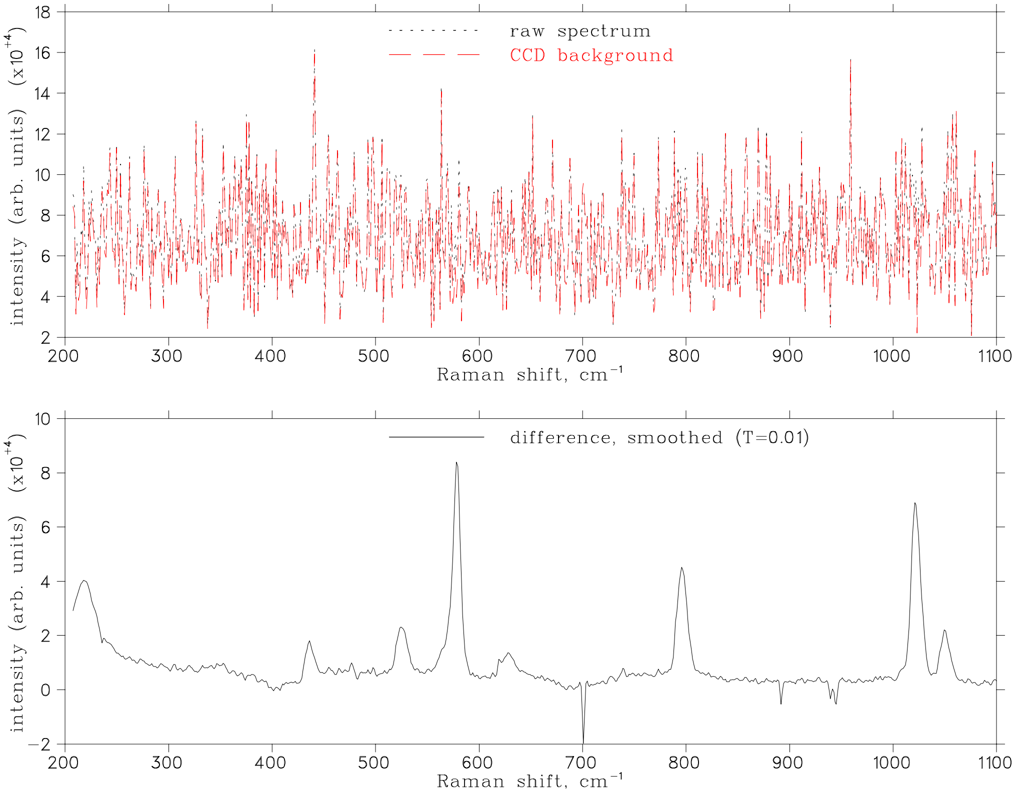


Figure 8.3: Raman spectrum of toluene.

8.3 Measurement checklist

Review this manual, and the reference materials provided, to develop your own checklist before coming to the lab. Be sure to include it in your lab report, and comment on how well it worked. Perform the spectrometer calibration using He plasma lines, then obtain spectra from several solid and liquid samples provided. Explain unusual features (*e.g.*, a sharp negative line near 700 cm^{-1} in Fig. 8.3).

References

Note that some of the links below require the class password for access.

- C.V. Raman, A new radiation. *Indian Journal of Physics*, **2**:387–398, 1928.
- *The Quantum Indians*, a film by Raja Choudhury. 2013. `https://www.youtube.com/watch?v=7z9NUV_YrOo`, accessed 2021-03-08.
- Hecht, Eugene. Optics, 4th ed. Pearson Education Inc., San Francisco, 2002.
- Legacy product support from Diffraction Limited (formerly SBIG - Santa Barbara Instrumentation Group), makers of the CCD camera. `https://diffractionlimited.com/legacy-product-support/`
- Kestrel Spec software by Catalina Scientific: `https://www.catalinasci.com/kestrelspec.cfm`. A Mac version of an older manual: `https://www.physics.brocku.ca/Courses/3P91/References/Raman/KesST6m.pdf`. A self-explanatory tcl/tk interface by Phil Boseglav offers a a more streamlined package, highly suitable for this experiment.