Raman Scattering Lab Status

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1 What is Raman Scattering?

Raman scattering is the inelastic scattering of light from vibrational or other excitations in a sample. Raman differs from fluorescence in that Raman occurs over a very short timescale, and is a coherent process over virtual states. By contrast, in fluorescence, the intermediate excited state of the sample is“really there”. This means that while fluorescence emissions have a definite color, Raman scattered light is shifted from and tied to the incoming laser frequency. The Raman shift, measured from the incoming frequency, corresponds to how much energy has been deposited in the sample, and one sees peaks in the Raman spectrum corresponding to favored excitations of the sample. For visible light, the momentum difference between the incident and scattered light corresponds to very small wavevectors (of excitations in solids). So in solids it's a good approximation to treat the momentum transfer in Raman scattering as zero.

In a Raman experiment, you will see excitations when the $\langle \mathbf{OUT}|$ (scattered) and $|\mathbf{IN}\rangle$ (incident) polarizations of the photon field match (transform like) the symmetry of the excitation in the sample. Sort of like how, for a polarizer, you'll see light on the other side when the incident electric field has a component in the transmission direction. So given a molecular or crystal structure, you can predict which excitations you ought to see, depending on how you select the polarization of the incoming and outgoing light.

Hence to see an understandable Raman spectrum, you need to pre-filter your incoming light (use a gas laser filtered for plasma lines), define the incoming polarization, select the outgoing polarization, and filter for color (energy). Using symmetry tables, you can predict which phonons (in solids) or vibrational/rotational modes (in liquids and gases) you are allowed by symmetry to see. You need a dark room, a quiet detector, and a rejection filter for your excitation, because as a higher-order process, Raman scattering is much weaker than Rayleigh scattering. Otherwise, it isn't very difficult to see the effect.

A successful denumeration of the observed modes then tells you stuff about the bonds and the phonons. Further refinements of the technique can tell you about electron-phonon and electron-electron interactions. Add temperature dependence and you can often pick up evidence of structural and electronic phase transitions for much less than the cost of a neutron scattering or X-ray spectrometer. From the larger philosophical perspective, Raman scattering presents an accessible exploration of the consequences of symmetry in quantum mechanics.

2 The Apparatus

Right now, we've got a research-grade single-grating Czerny-Turner (slit-mirror-grating-mirror-out) spectrometer (JY HR-640) which I've fixed up so that the grating moves as it should. We have two usable low-dark-current CCDs. One is a long-term loan from Arlin Crotts and the other is my own astrophotography camera. Arlin's loaner is a true research camera with much lower noise and dark current, but it requires liquid nitrogen to cool the CCD. We also have a couple of other second-hand liquid-cooled CCDs that can be made to work with a little patience. But anyhow, two are working reliably with enough software to make data analysis straightforward. We have three large (11cm square) gratings: two of them have a pitch of 2400 grooves/mm and one has a pitch of 1200 grooves/mm. In addition we have smaller gratings (7 cm square) with pitches of 600 grooves/mm and 150 grooves/mm. The spectral coverage of the spectrometer with the 1200 groove/mm grating installed, with 5000 $\AA$ as the wavelength sent to the center of the CCD, is about 1000 cm^{-1}, which is more than enough to see many phonons in a single exposure, and the intrinsic (slit-independent) resolution of the grating/camera combinations is excellent (with the 1200 groove/mm grating, .2cm^{-1} per pixel for the astro camera and 1.2cm^{-1} per pixel for the loaner).

External to the spectrometer we have enough unused optics laying about to make a good excitation/input train, and I have a low power multiline argon laser (good to see the shift-to-laser pinning and distinguish fluorescence) as well as some solid state lasers that will probably do the trick.

3 Status

As of August, 2011, I've familiarized myself with the software enough to start taking measurements. The spectrometer has been aligned with both the 1200 groove/mm and the 2400 groove/mm gratings, using lines from a mercury vapor lamp and from the argon laser, and I've begun to calibrate and look for Raman spectra in some well-known systems like crystalline silicon. These procedures are pretty close to what the undergraduates will have to do to get started.

For an example of how calibration of the spectrometer enhances the lab experience, consider my own most recent calibration. The two figures below are representative exposures of the CCD to a multiline source (in this case, an argon laser, but a mercury vapor lamp would do as well), the second with the same source, but less well-filtered than the first, and with a longer exposure time. The following thinking about this data is meant to represent the habits of imaginative reckoning and rechecking that we are trying to develop.

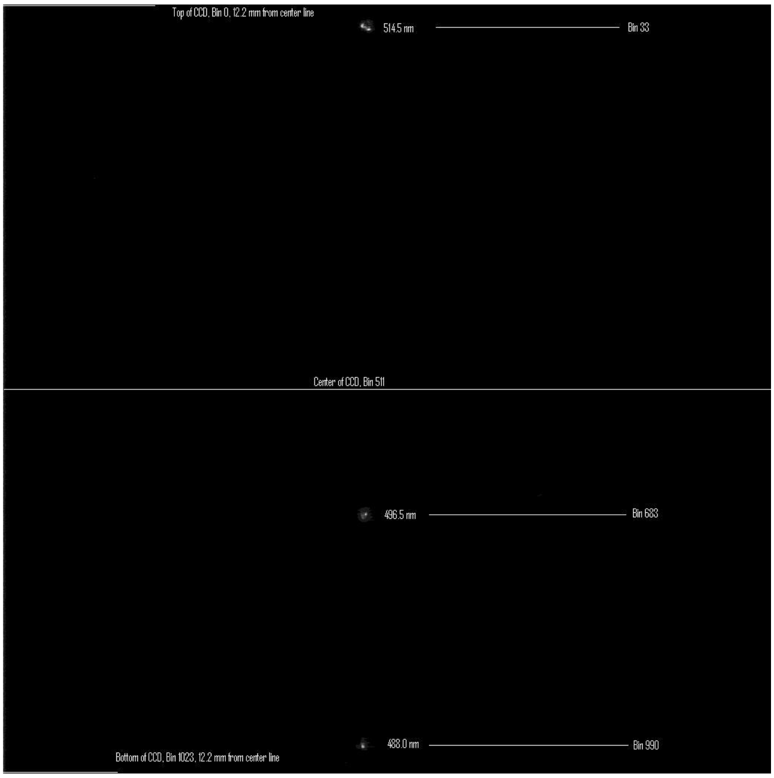

Figure 1: First multiline calibration image.

> With the grating set at a nominal central wavelength of 5018 $\mathring{A}$, the first picture shows three fairly tightly constrained spots of light from the laser. The lower spot is 4880 $\mathring{A}$, and the upper spot is 5145 $\mathring{A}$ (the students could know this by actually looking at the diffraction spots on a piece of white paper light held inside the spectrometer). From the known wavelengths of these lines, their positions on the CCD chip, and the size of the chip, one calculates the measured dispersion for the spectrum.
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> In this case, the calculated linear dispersion is a touch low (11.62 $\mathring{A}$/mm), compared to what one expects to see by doing the standard calculation and using the dimensions of the chip and the nominal focal length of the spectrometer (11.78 $\mathring{A}$/mm). Yet the experimental dispersion accurately predicts the position of the third expected line (4965 $\mathring{A}$), and when the collimation irises are opened to allow more light in and the exposure time is lengthened, the same dispersion predicts the position of a new spot that's expected to

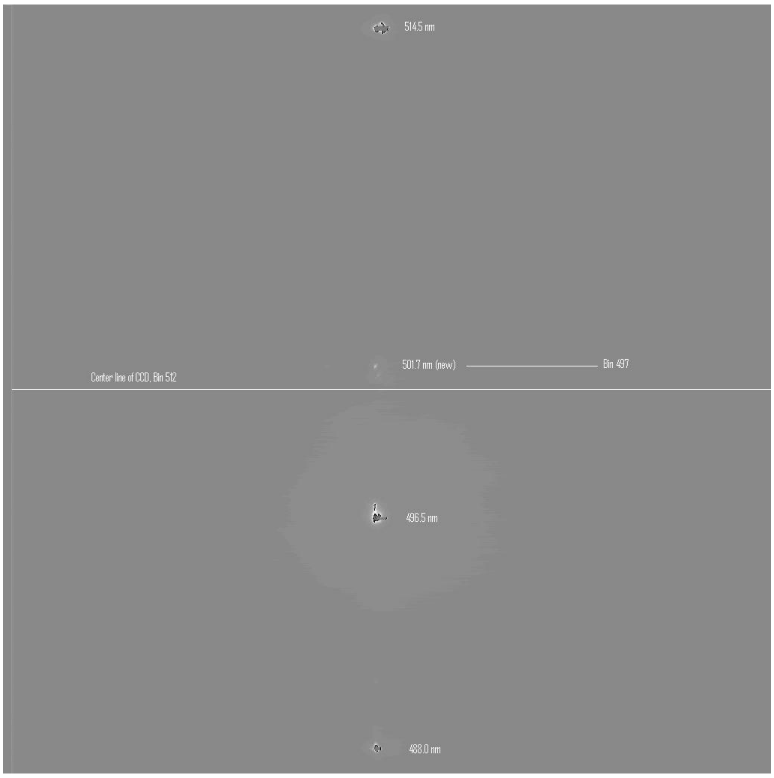

Figure 2: Second multiline calibration image. The beam is less filtered, so more lines are present. The lines from the first figure have saturated and leaked into adjoining pixels because of the longer exposure time.

contaminate the input (just about 5017 $\mathring{A}$, second picture). So the measured dispersion is believable.

An examination of the formula for the expected dispersion reveals the source of the discrepancy: the dispersion ought to vary inversely with the focal length of the setup, and the ratio of the measured dispersion to the manufacturer's quoted dispersion is about 63/64. For a 640 mm focal length, the CCD chip is about a centimeter too close, and should be placed a bit farther back from the last mirror. This would allow the diffraction fan to spread out just a bit more, leading to the nominal dispersion–but would the focus (and hence the resolution) suffer? In fact, the focus as it stands is not as perfect as it could be: the 5145 $\mathring{A}$ spot in the first picture is decidedly blurrier than the 4880 $\mathring{A}$ spot. In addition to moving the CCD, some tilting of the last, focusing mirror may be necessary.

That is how modern spectroscopy experiments start. With this apparatus, and some guidance, the students will have the opportunity to do it for themselves.

4 What we still need for Undergraduate Raman

So all of the really difficult stuff (spectrometer, gratings, detectors, lasers, software) is out of the way. Here's what's still required for a good lab experience:

- I still have to track down notch filters or nice sharp long-pass filters for the laser lines so the Raman signal won't be swamped by Rayleigh scattering. We'd like to use lower-power diode lasers, and unfortunately the filters we have around are suited to the lines of the argon laser, which are too different for them to be of use. Good edge filters are expensive–on the order of \$ 1000 each, and good notches are about \$ 1700. To establish a Raman shift requires at least two separate excitations, so we'd need \$ 2000 for edge filters. At least one notch filter would enable the students to compare Stokes/anti-Stokes intensities and so take the phonon temperature of their samples.

- To look at selection rules, you need to reliably control the laser polarization. Because of the upper limits on our laser power, we need to do this without throwing too much power away. There are several alternatives here, with educational benefit inversely proportional to price. Newport sells a polarization rotator for \$ 3150. That would be easiest to use, because it works simply for any wavelength. Alternatively, we could get at least two wave plates, for \$ 407 each from Thorlabs. Then again, we could make rotating polarization using what's at hand one of the experimental tasks, for the price of prisms (maybe \$ 750).

- Delicate things need sturdy, steady table space. An optical table would be best, though new ones can be expensive. I have seen several suitable second-hand ones for around $ 2000. Alternatively, we might get away with laying a steel plate over a regular tabletop, and using magnetic mounts. But these are bulky and tend to stick together at inopportune moments, preventing some experimental arrangements involving short-focal-length lenses.

- Raman signals tend to be faint, and lasers need to be screened. So a ceiling-mounted blackout curtain, sized for the experiment, is essential if the experiment is to share a room with others. Newport and their ilk sell really expensive laser curtains for like $ 5000. We could probably make our own for less than $ 500 (ten feet of ceiling track and 130 square feet of heavy suede, held up with some strong magnets). I requested a quote from a maker of hospital curtains (Kentek) but haven't heard back yet.
- To see Raman, one must focus the image of the laser spot on the spectrometer entrance slit, while sending the specular reflection from the sample off-axis. It's good to be able to see the laser spot when you are trying to do this. I've modified an internal flip mirror in the spectrometer so it can send an image of the slit through a port in the side. It's safer for the students to have this image go to a cheap camera and thence to a viewing screen (so they can't accidentally flash themselves right in the eye while adjusting things). A tiny security camera and the associated mounting/focusing tubes will run about $ 300. As for the screen, I picked a working color security monitor out of Columbia's bin of discarded electronics about two months ago.
- And finally, we'd need a new computer (approximately $ 1000 from the likes of Dell) to dedicate to the newer astro camera (which uses a newer USB than the current machine supports). It would also be a good place to do data analysis.