

# Laboratory work in Raman spectroscopy

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**Place:** KTH-Electrum Kista. Elevator B, level 2, meet the “lab ass” 5 minutes before the lab work starts.

**Tasks:**

- 1) Measure a spectrum from a nano structured TiO<sub>2</sub> electrode used in solar cells. Determine if it is rutile or anatase? Rutile and anatase are two different crystal structures of TiO<sub>2</sub> with different phonon spectra.
- 2) Measure a “dye sensitized” TiO<sub>2</sub> electrode. Are there any new peaks in the spectra? Use reference spectra and a molecular model to identify which peak belongs to which vibration.
- 3) Measure on Si and Ge. How many peaks do you see? What is their origin? Compare energies for Si and Ge and discuss differences.

**Preparation:** Read Jewett and Serway, chapter 43 molecular vibrations  
Hook&Hall chapter 2 lattice vibrations and phonons  
Reference spectra and molecular models will be provided on-site by the assistant.

## Introduction

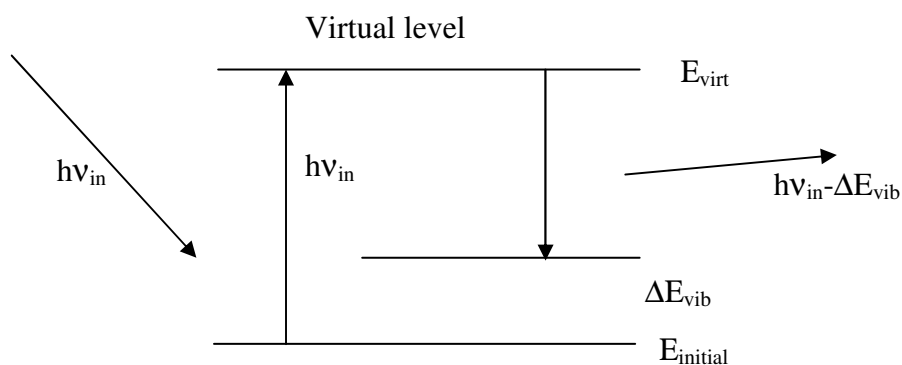
Atoms vibrate. In a molecule each bond stretch or bend. In a periodic lattice structure the atoms vibrate collectively in lattice vibrations called phonons. Each vibration is associated with an energy that depends on the masses of the vibrating atoms and the force constant of the bond between them. In lattice vibrations the atomic distance also plays a role. Knowing the vibrational frequencies identifies the bonds present in a sample, and one can extract the composition, molecular structure and/or bond geometry (often more info is needed, but we leave that out here).

To measure the vibrational energy one can use several different methods that all are based on sending a particle (electron or photon) on the crystal or the molecule to excite vibrations. The vibrational energy, or rather the difference between the initial and final vibrational level ( $\Delta E_{\text{vib}}$ ), is taken from the probing particle that leaves the surface with the initial energy minus the vibrational energy ( $E_{\text{in}} - \Delta E_{\text{vib}}$ ) or is completely absorbed.

In HREELS (high resolution electron energy loss spectroscopy) electrons are sent on the surface with typical energies at 5-10 eV. They can excite vibrations with that whole energy range, but the excitation cross section depends on the initial electron energy. This method requires vacuum.

In IRAS (infra red absorption spectroscopy) a sample is illuminated by an IR beam. Excitation of vibrations occurs with a very high probability when the IR energy matches the vibrational energy ( $\Delta E_{\text{vib}}$ ), so these photons will be absorbed. From comparison of the IR spectra before and after absorption the vibrational energies can be identified as dips in the spectra.

A third method, the one we use here, is called Raman spectroscopy. In this case a laser beam with well defined photon energy ( $h\nu_{\text{in}}$ ) is sent to a sample. Even though the photon energy does not match any vibrational transitions they can be absorbed and excite the molecule (or solid) into a virtual state from where it falls back into a vibrationally excited state. The “falling” from the virtual state to the excited state corresponds to an energy transition with an energy  $E_{\text{virt}} - \Delta E_{\text{vib}}$ , which is sent out as a photon. The out going photon energy is the in coming photon energy minus the vibrational excitation energy. Note that the vibrational energy can be either a molecular vibration or a lattice vibration (phonon).



The spectrum of photons leaving the surface contains a strong signal from the elastically scattered laser light and a set of peaks shifted away from the elastic peak by vibrational energies. A spectrum may contain one or several peaks depending on the number of possible vibrations in the sample, each peak corresponding to one vibrational mode. All peaks do not come out with the same intensity. This depends on the number of vibrations with the same energy (for example in hydro carbon molecule there are several H-C bonds that vibrate), and their respective excitation cross section (the probability of exciting a vibration). There are so-called selection rules that relate the absorption probability to the relation between bond

direction, photon polarization direction, scattering angle, surface normal and photon energy, and also the electronic properties of the sample surface. This is not always a simple relation, but will be briefly explained by your assistant in case you are interested.

### **Equipment:**

The Raman system contains a laser for excitation; the light is guided through a fiber to a “superhead” from where it is focused by a lens on to the sample. The sample is placed on an adjustable table, it is very important to put the sample at the focal distance to get good intensity. The light scattered from the surface is collected by the lens and guided back through the superhead and directed to another fiber to the spectrograph, where the light beam falls on a grating that diffracts different wave lengths in different directions. The diffracted light is detected by a CCD camera. Remember that the system is expensive and is not covered by insurance, so take it easy, please. Your assistant will describe the system in detail before you start, and there are manuals on-site.

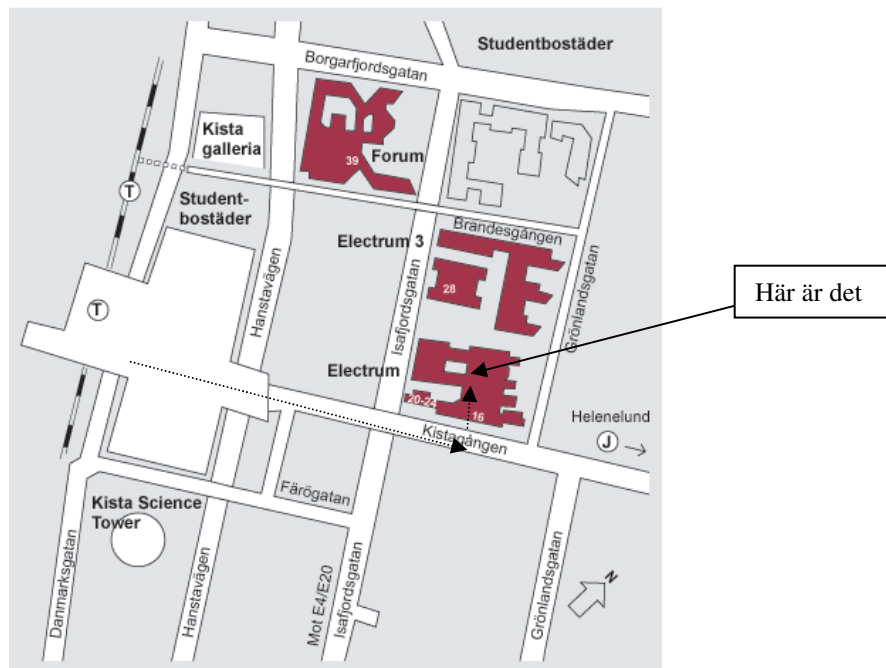
**Safety:** The laser you use is dangerous, not for skin or clothes, but for the eyes. Follow the instructions carefully and whatever you do; think first and ask your lab mates if they are ready. Do not open the laser shutter until all adjustments are properly done. Close the door to the Raman cabinet and put the blanket. Failure to do so will not prevent you from passing the lab, but from seeing properly for the rest of your life. Be careful.

### **Taking spectra:**

- 1) Start the spectrograph and the detector
- 2) Put the sample in the glass container on the adjustable table.
- 3) Start video mode, switch on white light source and adjust the sample height until you get a sharp image. It is very sensitive so if you move the table or cabinet after adjustment you may lose focus.
- 4) When the focus is fine. Switch off light source, close the knob on the superhead. Switch off video. Switch on the laser and open the laser shutter.
- 5) Close the cabinet and put the blanket.
- 6) Now you are ready for measuring a Raman spectrum. There are a few parameters to choose; grating, slit width, time and “central energy” of the window. To change grating the spectrograph rotates a grating holder and adjusts some mirrors inside the gray box. It may sound strange, but it’s normal. Don’t change grating several times. Now you can start a “quick scan” to find regions with peaks. Try to figure out which energy region you should choose. If you have problems your assistant can probably help you.
- 7) When the quick scan is done. Time to measure a real spectrum. Set measurement parameters by clicking the right icon (we will show you which one). Select start energy, end energy, time. Save and leave. Click the pig to start a spectrum. It will take a few minutes to record a full spectrum. Save it in your folder, voila it’s done. You can load several spectra in the window and compare.
- 8) Change sample and start over again.
- 9) Data bases are available on the internet, but we have selected and printed the most relevant references for you.

## To get to us

The laboration takes place in Electrum close to Kista C (see map below). In Electrum, we will meet at the elevator B level 2..



### By subway

Number 11 Kungsträdgården - Akalla (takes about ca 20 minutes from the city center). Station Kista

### Commuter train

Södertälje - Märsta. Station Helenelund. Time about 15 minutes from the city center and 15 min walking to Kista.

### Computer train

Get on the train, log on to internet and email yourself to Kista at [people@kista.se/labroom3171](mailto:people@kista.se/labroom3171)

### By car

From Stockholm. E4 north to Uppsala. Take the Kistaexit (road 279). Take the first exit to Kista Centrum.

### Parking

Parking is difficult in Kista, you can try Isafjordsgatan or the parking garage in i Kista Centrum.

### Busses

- 155 Brommaplan - Kista - Akalla
- 178 Mörby station - Bergshamra -Helenelund - Kista
- 179 Vällingby - Spånga - Tensta - Kista
- 514 Vällingby - Spånga - Kista - Sollentuna
- 517 Spånga - Hjulsta - Kista
- 518 Vällingby - Backlura - Barkarby - Kista
- 537 Kista - Upplands Väsby
- 549 Brunna - Kista
- 554 Upplands Bro- Kista
- 627 Kista - Sollentuna - Täby - Arninge