

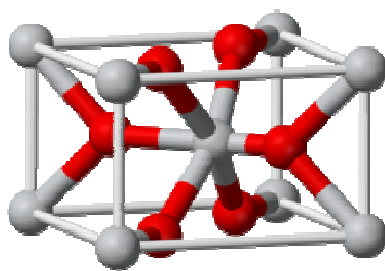
# Laboratory work in Raman spectroscopy

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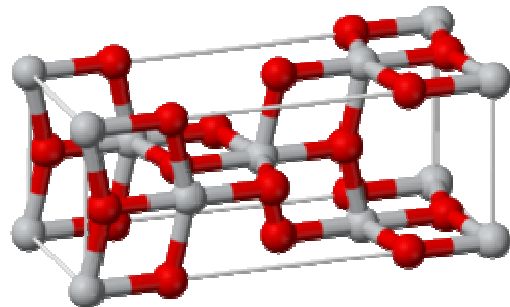
**Place:** KTH-Electrum Kista. Elevator B, level 2, meet the “lab-ass” 5 minutes before the lab work starts.

**Tasks:** 1) Nano structured  $\text{TiO}_2$  is used as electrode in solar cells. Your task is to determine if a powder sample of it is rutile or anatase or both? And determine the relative amount of each structure in the sample.

Note: Rutile and anatase are two different crystal structures of  $\text{TiO}_2$  with different phonon spectra. Measure reference spectra from single crystals (one rutile and one anatase) provided by the lab-ass.

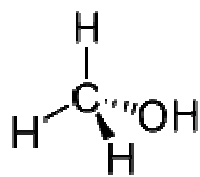


Rutile

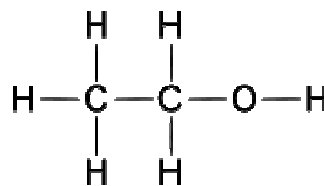


Anatase

2) Identify vibrational energies for methanol and ethanol and relate the different peaks to possible vibrations using molecular models as those presented below.



Methanol



Ethanol

**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 ass.

## Introduction

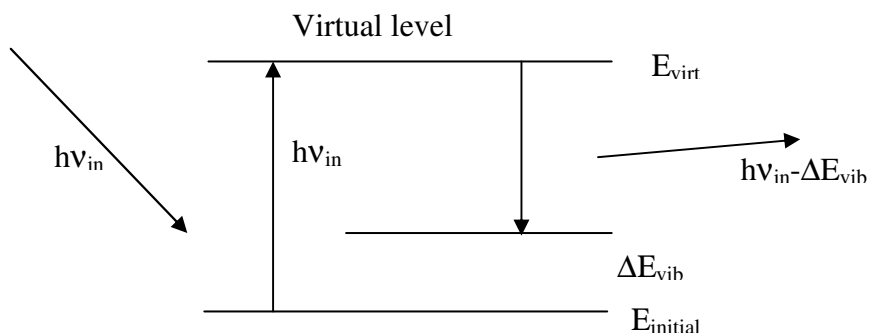
Atoms vibrate. In a molecule each bond can stretch and bend. In a periodic lattice structure the atoms vibrate collectively in lattice vibrations called phonons. Each vibration is associated with an energy that depends on the masses of the vibrating atoms and the force constants of the bonds between them. In lattice vibrations the atomic distances also play 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). Often it is enough to measure a reference spectrum from a known substance and use it as a finger print to identify its presence in other unknown substances.

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 5-10 eV. They can excite vibrations within that whole energy range, but the excitation cross section depends on the initial electron energy. This method requires vacuum since electrons will collide with gas molecules several times and will not reach the detector.

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 incoming 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 hydrocarbon 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 an optical “superhead” from where it is focused by a lens on 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 Raman cabinet using a 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) Start the software and let the detector cool to -70 °C.

While cooling

- 3) Put the sample on the adjustable table.
- 4) Start video mode in the software, switch on white light source connected to the superhead you use and adjust the sample height until you get a sharp image. It is very sensitive so if you move the table after adjustment you may lose focus.
- 5) When the focus is fine. Switch off light source, close the knob on the superhead. Switch off video. Put the curtain. Switch on the laser and open the laser shutter.

If the detector is cold then go to 6, else wait.

- 6) Now you are ready for measuring a Raman spectrum. There are a few parameters to choose; grating, slit width and “central energy” of the window.

A good choice of grating is 1200 lines/mm. 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.

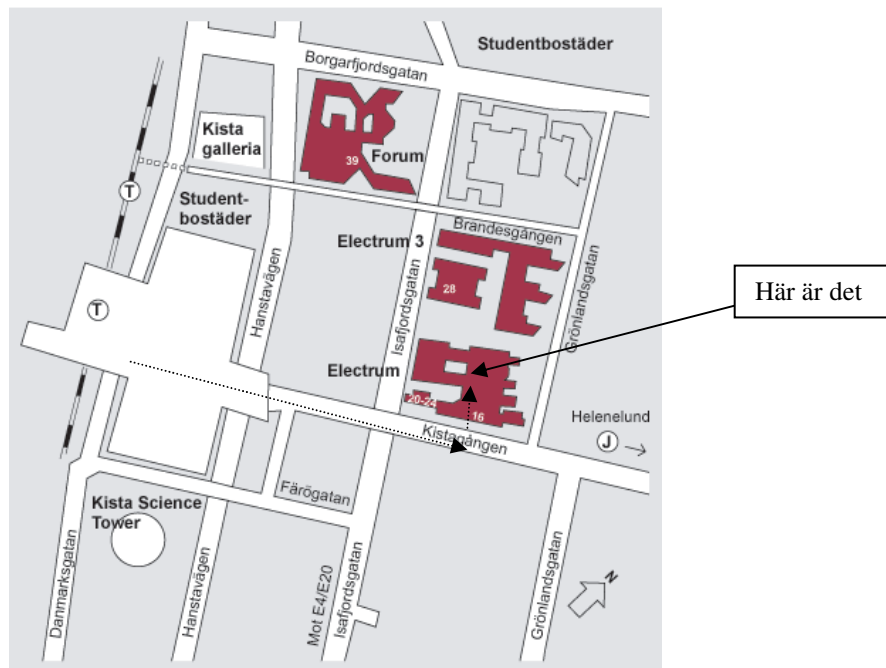
The slit will reduce the intensity on the detector. It can also influence the resolution, but in our case this is not a very strong effect. Choose 100 μm for a start. It can be adjusted later if necessary.

The central energy is the middle of the window on the screen. The width of the window is determined by the grating.

- 7) Now you can start “quick scan” to find regions with peaks. Look for the interesting energy regions on internet before going to the lab. If you have problems your assistant can probably help you. Verify that the strongest “expected peaks” are there. Perhaps you need to switch off the lights during measurement. Check if the light has any effect.
- 8) 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.
- 9) Change sample and start over again. **Don't forget the laser shutter!!**

## 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