# Lab Manual:
# RAMAN SPECTROSCOPY

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# TABLE OF CONTENT

## LIST OF SIMBOLS

$v_L$ Laser frequency

$v_{1,2}$ frequency associated to the transition (1 → 2 or 2→1) between two different vibrational levels [1]

$\mu$ Molecular dipole moment

$\alpha$ Molecular polarizability

$n_i$ Number of molecules in the vibrational state of energy $E_i$ (Boltzmann factor)[2]

$I$ Intensity

$Q$ Normal coordinate of vibration

[1] given two levels of energy E1 and E2, E2>E1, we can define $v_{1,2}$

$$v_{1,2} = \frac{(E_2 - E_1)}{h}$$

[2] given a molecular state *i* characterized by the energy $E_i$

$$n_i \propto e^{\frac{-E_i}{KT}}$$

# Introduction

Vibrational spectroscopy, Raman and infrared, are based on the interaction of electromagnetic radiation with matter. Experiments are usually non-destructive, and the samples can be reused for other investigations. The aim of both Raman spectroscopy and Infrared spectroscopy experiments is to probe the molecular vibrations, probing the transition between the ground state and the excited vibrational states. The transitions are observed as bands in the vibrational spectrum. Each molecule has a specific set of vibrational bands, which are defined by their frequencies, shapes, and intensities. By analyzing these properties, it is possible to get information about the local coordination of the atoms in your material.

The frequency of a transition ($\sim$50-4000 cm$^{-1}$)[1] directly depends on the reduced mass of the vibrating unit. Therefore, smaller reduced masses give rise to higher frequencies.

Depending on the nature of the molecular vibration, the transition may be Raman, and/or infrared active. Those techniques should therefore be used complementary, because some bands that are infrared inactive can be Raman active and *vice versa*. The physical principle behind Raman and infrared spectroscopy is very different though. Raman spectroscopy is a scattering technique where the intensity of the bands is proportional to the concentration and to the scattering cross-section of the vibrating units. Infrared spectroscopy is an absorbance technique where the intensity of the bands is proportional to the concentration and to the absorption coefficient of the vibrating units. Typically, the time needed to record a spectrum is of the order of seconds to tens of minutes. However, to increase the signal-to-noise ratio, several accumulations are customary.

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[1]Note that the frequency range is here expressed in cm$^{-1}$ (wavenumber). This is a typical unit used in Raman and Infrared spectroscopy. In question #1 you can find the formula to convert frequencies to wavenumber.

# Short theory about Raman and infrared spectroscopy

This chapter is devoted to give a short introduction to Raman and infrared spectroscopy. Extensive descriptions can be found in many textbooks, see *e.g.* references [1-5].

## Raman scattering

Raman Scattering, first observed by Raman in 1928[6], describes the inelastic scattering of the light by matter. When a photon (with not enough energy to excite electronic transitions) interacts with a molecule, it can be scattered both elastically (Rayleigh scattering) and inelastically. The inelastic scattered part is called Raman scattering, and is commonly due to photons that couple to molecular vibrations or phonons in the material. In the inelastic scattering the photons can undergo to a loos of energy (Stokes scattering) or a gain of energy (anti-Stokes scattering). The energy gained of loosed by the photon is the energy between the ground state and the first exited vibrational level of the molecule. It is important to notice that the dominant phenomenon is the Rayleigh scattering, and only a small amount of light is scattered inelastically.

The Raman effect can be easily described using the classic approach, considering the electromagnetic field (characterized by a frequency $v_L$) as a perturbation that induced in the molecule a dipole moment $\mu_i = \alpha E$.

The polarizability ($\alpha$) depends on the coordinates of the atoms in the molecule, which varies whit the time at the molecular vibrational frequency $v_{1,2}$ ($\ll v_L$). If the vibrational amplitude is small the polarizability can be expanded at the first order:

$$\alpha(t) = \alpha^0 + \left(\frac{\partial \alpha}{\partial Q}\right)_{t=0} Q(t)$$

Considering the particular case of a diatomic molecule we obtain:

$$\mu_i = E^0 \left\{ \alpha^0 cos(2\pi v_L t) + \left(\frac{\partial \alpha}{\partial Q}\right)\frac{Q}{2}\left[cos\big(2\pi(v_L + v_{1,2})t\big) + cos\big(2\pi(v_L - v_{1,2})t\big)\right]\right\}$$

The first term in the equation describes the elastic scattering, while the others terms describe the inelastic scattering.

For a complete description of the phenomena a quantum approach is necessary. In the quantum description the vibrational energy of the molecule is quantized, and the interaction with the light is described using the perturbation theory.

The incoming photon excites the molecule to a virtual state, which decay to a lower energy state. As described in figure 1.a, the Stokes scattering involve a transition from the ground state (1) and a successive transition to an exited level (2), while the anti-Stokes involve a first transition from an excited state to the virtual level. Because at room temperature the number of molecules in the ground state is higher than the number of molecules in the excited state, the Stokes scattering has an higher probability than the anti-Stokes scattering (fig 1.b).
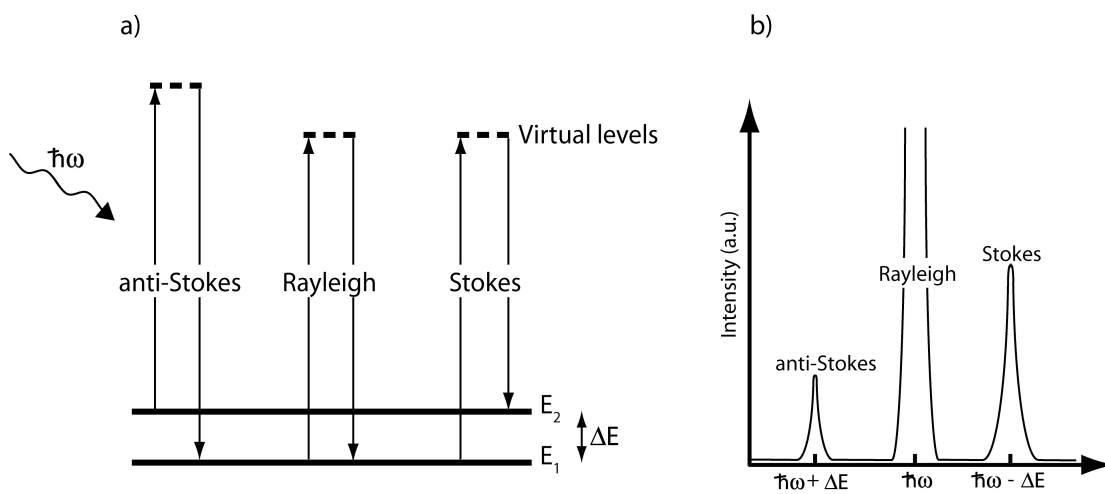


**Figure 1. a) schematic picture of the Raman process in a two-level system, and b) the resulting Raman spectrum.**

Using the quantum approach the intensity of scattered light can be estimated as:

$$I_{Stokes} \propto \frac{(v_L - v_{1,2})^4}{v_{1,2}} \left(\frac{\partial \alpha}{\partial Q}\right)^2 n_1 \quad ; \quad I_{anti-Stokes} \propto \frac{(v_L + v_{1,2})^4}{v_{1,2}} \left(\frac{\partial \alpha}{\partial Q}\right)^2 n_2$$

Two important results come directly from those expressions; first, Raman scattering only takes place if

$$\frac{\partial \alpha}{\partial Q} \neq 0$$

Moreover, the Stokes scattered light is more intense that the anti-Stokes, because of the Boltzmann factor ($n_1 > n_2$).

## Raman spectroscopy

In a Raman spectroscopy experiment, the sample is irradiated with monochromatic light; the light frequency has to be chosen in order to avoid the excitation of electronic levels.

The scattered light is detected, in order to collect the vibrational spectra of the sample. As described in the previous section, the frequencies of the light scattered by a molecule with $m$ Raman active vibrations (with characteristic frequencies $\{v_1, v_m\}$) will be

$$v_{scatt,i} = v_L \pm v_i \qquad i \in (1, m)$$

Because of the stronger intensity of the Stokes lines respect to the anti-Stokes, usually only the light at energy lower than the laser energy is collected.

Therefore, the Raman spectrum is composed by several bands, related to the different vibrations that characterize the molecule.

Raman spectroscopy allows studying only those vibrations that modulates the polarizability of the molecule under investigation ($\frac{\partial \alpha}{\partial Q} \neq 0$). For this reason complementary techniques are important in order to characterize the vibrational spectrumof a molecule.

## Infrared spectroscopy

Infrared spectroscopy takes advantage from the absorption phenomena. In this case, the photon excites a direct transition between the ground state and one of the higher vibration states of the molecule. Photons can only be absorbed if their frequency exactly matches the frequency of a particular molecular vibration in the material. A schematic illustration of the principle behind IR spectroscopy is reported in Fig. 2.
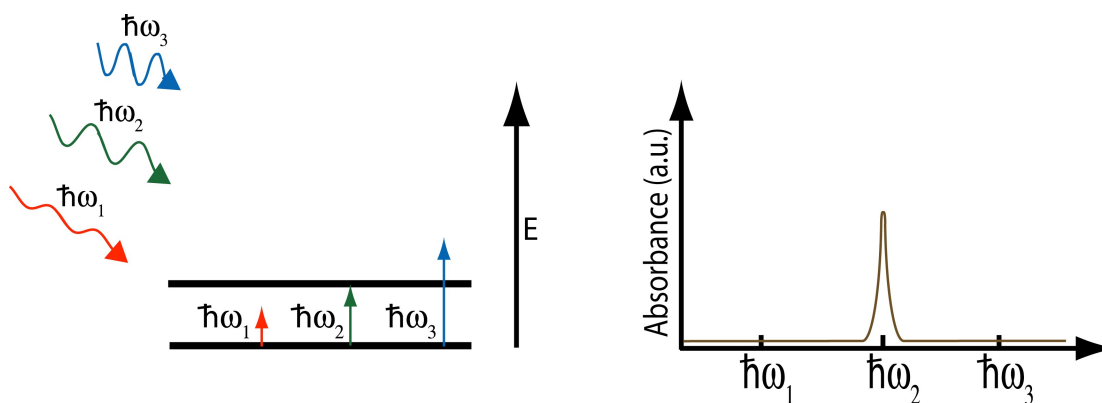


**Figure 2 The principle of infrared absorption. a) Photons with energies $h\omega_1$, $h\omega_2$, and $h\omega_3$ hit a two-level system. Only $h\omega_2$ has the same energy as the difference between the two vibrational states, and is therefore absorbed. b) The resulting infrared absorbance spectrum.**

Measuring the intensity of the *non-absorbed* light at different frequencies, it is possible to determine the spectrum (IR-spectrum) of the molecule.

The first difference between Raman and infrared is in the light source used in the two different techniques. While Raman spectroscopy requires a monochromatic light with frequency higher than the characteristic vibrational frequencies, Infrared spectroscopy requires polychromatic light with frequencies in the infrared region (~50-4000 cm$^{-1}$).

Moreover the selection rule of the Infrared absorption is different than the one for the Raman scattering. For IR absorption a molecular vibration can be observed only if it modulates the dipole moment:

$$\frac{\partial \mu}{\partial Q} \neq 0$$

This means, for example, that diatomic homonuclear molecules do not give rise to any bands in the IR spectra since those do not have a dipole moment.

# Vibrational modes

This chapter has the aim to introduce briefly some knowledge about vibrational modes. More information can be found in the references[1,3,5,7].

A molecule containing *n* atoms has 3*n* degrees of freedom; considering that *6* of this configuration describe pure translation and *3* pure rotations (non-linear molecules), there are *3n-6 (3n-5* for linear molecules*)* motions (vibrations) that change the relative position of the atoms. In each vibration the atoms carry out a harmonic motion.

Vibrations are usually divided in symmetric and ant symmetric. Moreover, different kind of vibration can occur: stretching (vibration in the same direction of a bond), bending (oscillation that implies a change of angle between two bonds), rocking (oscillation that implies a change of angle between a group of atoms), wagging (change in angle of the plane of a group of atoms), twisting (change in angle of the planes of two groups of atoms).

## Classic Harmonic oscillator

The simplest possible model that can be considered to describe the molecular vibration is the harmonic oscillator. For a diatomic molecule composed of two atoms of mass $m_1$ and $m_2$ the classical frequency is given by

$$v = \frac{1}{2\pi}\sqrt{K(\frac{1}{m_1} + \frac{1}{m_2})}$$

where K represent the force constant of the bond of the two atoms.

More generically, the N atoms of a molecule can be considered to oscillate with small amplitude around the equilibrium position. The equations of the motion are therefore

$$m_i \frac{\partial^2 q_i}{\partial t} = -\sum_{j=1}^{3N} K_{ij} q_j$$

Where $q_i$ represent the displacement from the equilibrium position. Several numerical methods can be used to solve this set of equation.

In general, approximation can be done to roughly evaluate the vibration of a specific group of atoms in the molecule. For example, because hydrogen is usually lighter than all the other elements, the stretching frequencies of bond as C-H, O-H etc. are really higher compared to other stretching frequencies (C-O, for example). Therefore vibration that involve hydrogen atoms are almost independent from the rest of the molecule.

# Experimental

Vibrational spectroscopy is a powerful tool in order to investigate a material at the molecular level. The interaction of the incident light with matter might occur by light scattering, as in the case of Raman experiment, or by light absorption, transmission or reflection, as is the case in an IR experiment. The method that best applies to a certain material highly depends on the properties of the sample, such as optical transparency, smoothness, amount of impurities, chemical composition *etc*.

A troublesome case is the luminescence arising from ionic impurities present in (unfortunately) many samples. If the luminescence is too strong, the Raman signal could be as bad as swamped, and your spectrum is practically useless! There is however a way to overcome this problem, and that is to increase the wavelength of the incident light. Approaching the infrared limit ($\lambda \approx 1064$ nm), luminescent excitations are usually minimized.

In this experimental project some different samples are provided to you, which you should investigate by applying Raman spectroscopy. You should really find out as much as you can about these materials before you start your experiments.

Be aware of the fact that some chemicals could be harmful, hence do not inhale any amount.

## Materials and experiments

The materials at your disposal for this lab are listed in the table below.

| | Planar structure | Liquid/solid |
|---|---|---|
| Methanol<br><br>$CH_3OH$ | H<br>\|<br>H — C — O — H<br>\|<br>H | L |
| Ethanol<br><br>$C_2H_5OH$ | H  H<br>\|  \|<br>H — C — C — O — H<br>\|  \|<br>H  H | L |
| Isopropyl alcohol<br><br>(2-propanol)<br><br>$C_3H_7OH$ | H  H  H<br>\|  \|  \|<br>H — C — C — C — O — H<br>\|  \|  \|<br>H  H  H | L |
| 1-pentanol<br><br>$C_5H_{11}OH$ | H  H  H  H  H<br>\|  \|  \|  \|  \|<br>H — C — C — C — C — C — O — H<br>\|  \|  \|  \|  \|<br>H  H  H  H  H | L |
| 2-propanone<br><br>(acetone)<br><br>$C_3H_6O$ | H  O  H<br>\|  \|\|  \|<br>H — C — C — C — H<br>\|      \|<br>H      H | L |
| Dimethyl carbonate<br><br>(DMC)<br><br>$C_3H_6O_3$ | H      O      H<br>\|      \|\|      \|<br>H — C — O — C — O — C — H<br>\|          \|<br>H          H | L |
| Ethylene carbonate<br><br>(EC)<br><br>$C_3H_4O_3$ | O<br>\|\|<br>C<br>O      O<br>\  /<br>H — C — C — H<br>\|  \|<br>H  H | S |
| Toluene<br><br>$C_7H_8$ | H<br>\|<br>H — C — H<br>\|<br>H      C      H<br>\  //  \\  /<br>C      C<br>\|\|      \|\|<br>C      C<br>H /  \\  //  \ H<br>C<br>\|<br>H | L |

The first 4 elements are alcohols, while acetone is a ketone, dimethyl carbonate and ethylene carbonate are carbonate esters, and finally toluene is an aromatic hydrocarbon. Moreover, you have two EC/DMC mixtures (50:50 and unknown).

Those molecules are composed only by Hydrogen, Carbon and Oxygen. Therefore, they present really similar bonds (and spectra). Frequencies relate to those bonds and Tables with the characteristic frequencies of those molecule can be find on reference [3],[9].

The aim of this lab is to obtain the Raman spectra of the different molecules and assign each peak to the corresponding vibrational mode, both by using tabulated values and comparing the different spectra. Moreover, you should discuss the differences among the spectra of the different molecules and the different bonds (frequencies, shapes and intensities).

As last part of the exercise, you should analyze the two mixtures of DMC/EC and determine the concentration of the unknown mixture.

Now, in order to be able to perform the experiment in the lab you should prepare yourself on the following issues:

a. Search in the literature for vibrational spectra/Raman spectra of the different molecules

b. Answer to the questions you find at the end of this manual.

c. Think about the differences among the different compounds. Some of them show similar structures, so you can expect similar spectra. The following questions should prepare you and help you discussing your results.

- Which molecules have O-H bonds? Where in the spectra (at which frequencies) do you expect to find the O-H vibrations? Same question about the C-O bond.

- Which molecules show the C-H bond? Which differences do you expect in the C-H band among the different alcohols? Same question about the C-C bond.

- You can observe both the single and the double CO bond. Using the theory of the simple harmonic oscillator, what do you expect to see in the spectra $(v_{C=O}/v_{C-O} =?)$?

- Which differences do you expect in the spectra of DMC/EC?

- Which differences do you expect in the spectra of EC (solid) and the spectra of the EC contained in the mixtures (liquid)?

# Laser safety

Concerning laser safety there is a really important rule: **do not look directly into the laser beam or a reflection of the laser beam at any time for one simple reason: it will damage your eyes**. The reason why laser light is so dangerous is that it is very well focused and since it is monochromatic all photons will be focused on the exact same spot of the eye. This might burn some of the cells in the eye and thus cause blindness. The laboratory is equipped with laser protection glasses, these should be worn at all times when aligning and running the measurements. In addition, avoid wearing reflecting object (such as rings, belts, etc.).

All the samples that you will analyze are sealed in glass vials; do not open the vials. Whether the vials seem to be broken or not sealed properly, avoid contact with the samples and contact the lab's responsible.

# References.

[1].  N.B. Colthup, L.H. Daly, and S.E. Wiberley. *Introduction to infrared and Raman spectroscopy*, Academic Press Inc., 3$^{rd}$ edition, 1990.

[2] Practical Raman Spectroscopy. Gardiner and Graves (Eds.) Springer-Verlag Berlin Heidelberg 1989(chapter 3)

[3] P. Larkin, *Infrared and Raman Spectroscopy; Principles and Spectral Interpretation,* Elsevier, 2011

[4] D. A. Long. *Raman Spectroscopy*, McGraw-Hill, 1977.

[5] A. Fadini, and F.-M. Schnepel. *Vibrational Spectroscopy, Methods and applications*,  John Wiley & Sons, 1989. (chapter 2)

[6] C. V. Raman and K. S. Krishnan, Nature **121**, 501 (1928).

[7] A. D. Boardman, D. E. O'connor, and P. A. Young, *Symmetry and its Applications in  Science*, McGraw-Hill, 1973.

[8] Kazuo Nakamoto, *Infrared and Raman spectra of Inorganic and Coordination compounds, Part A*, Wiley pubbl., 6$^{th}$ edition.

[9] Ernö Pretsch, Philippe Buhlmann, Martin Badertscher, *Structure determination of organic compounds – table of spectral data*

# Questions to answer before the laboratory work

1) Light can be described using both wavelength and frequency ($\lambda v = c$). The wavelength is expressed in meter (nm or µm) while frequency is expressed in Hz [GHz]. However, other units are often used instead of frequency. Those units are cm$^{-1}$ (wavenumber, $\tilde{v}$) and eV (energy associated to the single photon, E). The conversion can be done using the relations

$$\tilde{v} = \left(\frac{k}{2\pi}\right) = \frac{1}{\lambda} \quad E = hv = \frac{h}{\lambda}$$

Therefore, the conversion factors from µm to GHz, cm$^{-1}$ and eV are

$$v(GHz) = \frac{3}{\lambda(\mu m)} 10^5 \quad \tilde{v}(cm^{-1}) = \frac{1}{\lambda(\mu m)} 10^4 \quad E(eV) = \frac{1.24}{\lambda(\mu m)}$$

Express the following intervals in GHz, cm$^{-1}$ and eV

| Xray | UV | visible | Near IR | mid IR | Far IR | THz radiation |
|------|------|---------|---------|--------|--------|---------------|
| 0.01-10 nm | 10-400 nm | 400-700 nm | 0.75-1.4 µm | 1.4-15 µm | 15-1000 µm | 0.1-1 mm |

2) During your Raman experiment you will use a 532 nm Laser source. If you have molecular vibrations at 2000, 3000 and 3500 cm$^{-1}$, which frequencies you will see in the corresponding Raman spectra (note: the Raman spectra is composed by the scattered light!)?

3) Harmonic oscillator can be used to understand molecular vibration. Using

$$v = \frac{1}{2\pi} \sqrt{K(\frac{1}{m_1} + \frac{1}{m_2})}$$

Calculate the vibrational frequencies for the following bond:

C-H (K=4.9 N/cm)

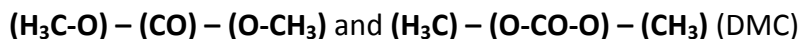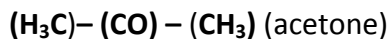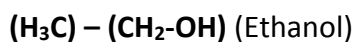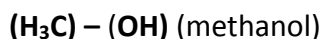N-H (K=6.4 N/cm)

O-H (K=7.2 N/cm)

C-O (K=5.1 N/cm)

C-C (K=4.4 N/cm)

4) Derive the expressions for the in-phase (symmetrical) and out-of-phase (anti symmetrical) vibrational stretching mode for the two following linear molecules

$$M - M - M$$

$$M_1 - M_2 - M_1$$

Note: in both case you have two harmonic oscillators with the same force constant. you have to impose same frequency and amplitude (they only differ in the phase shift)

Using those formula, try to figure out the vibrational frequency related to the following configuration ($K_{C-O} \sim 5.1\ N/cm$ ; $K_{C-C} \sim 4.4\ N/cm$)

**(H₃C) – (OH)** (methanol)

**(H₃C) – (CH₂-OH)** (Ethanol)

**(H₃C)– (CO) – (CH₃)** (acetone)

**(H₃C-O) – (CO) – (O-CH₃)** and **(H₃C) – (O-CO-O) – (CH₃)** (DMC)

note: you have to consider the groups of atoms in the brackets as single unit which mass is equal to the sum of the masses of the atoms. Be careful that in both acetone and DMC the center unit is actually (C=O), and therefor only the carbon atom in bonded to the neighbor carbons. After the experiment you can compare those rough values with the experimental ones.