An Introduction to Raman Spectroscopy

Gabriel Henrique Lopes Gomes Alves Nunes

Orientador: Professor Leandro Malard Moreira

Departamento de Física
Universidade Federal de Minas Gerais

February 2016
First Revision in March 2017
Second Revision in November 2017

Agradecimentos

À minha família, pelo amor e pelas oportunidades oferecidas.

Ao Professor Leandro, pela oportunidade, paciência e disponibilidade durante todo o Estudo Orientado.

Ao LabNS, pela disponibilidade da estrutura física para o experimento.

À Universidade Federal de Minas Gerais e ao Departamento de Física, pelo excelente curso de Graduação em Física.

Resumo

As aplicações da Espectroscopia Raman são vastas na Física, Química, Geologia e em outras áreas, uma vez que é possível caracterizar diferentes materiais através de seus espectros vibracionais. Esse é um método eficiente e não destrutivo, logo útil não apenas em um laboratório, mas também para alguns problemas cotidianos. Neste estudo, parte da teoria clássica da Espectroscopia Raman deve ser desenvolvida de modo que possa ser aplicada a um caso específico em um exemplo experimental. Ao fim deste estudo, todas as ideias básicas por trás da técnica da Espectroscopia Raman serão abordadas.

Abstract

Raman Spectroscopy applications are vast in Physics, Chemistry, Geology and in other areas, because it is possible to characterize different materials through their vibrational spectra. It is an efficient and non-destructive method, hence not only useful inside a laboratory, but also for some real-world problems. In this study, some of the classical Raman Spectroscopy theory shall be develop so it can be applied to a specific case on an experimental example. By the end of this study, one will have covered all the basic ideas behind the Raman Spectroscopy technique.

Contents

List of Figures

List of Tables

1 Introduction

Raman Spectroscopy applications are vast in Physics, Chemistry, Geology and in other areas, because it is possible to characterize different materials through their vibrational spectra in which information is specific to each chemical bond or molecule [6]. Its efficiency and current literature allow a quick identification of molecules through a non-destructive method [3]. Hence, some of its applications may go far from the laboratory, including some techniques to investigate works of art or historical documents, and even some in-development techniques to diagnose diseases such as the Alzheimer's disease through simple clinical methods.

Raman Spectroscopy consists of the illumination of a sample using a monochromatic light source and the subsequent analysis of the scattered light. Due to its interaction with matter, an incident light beam can polarize the molecules, which, by its turn, emits light with energy larger or smaller than the incident light. By analysing the scattered light, it is possible to assign to each band on a Raman spectrum a mode of vibration and to deduce the symmetry of each mode [2].

In this introductory study on Raman Spectroscopy, some of its classical theory shall be developed, while some of its quantum theory shall be briefly discussed. Also, some Experimental Results shall be shown and discussed.

By the end of this study, one shall have covered all the basic ideas behind the Raman Spectroscopy technique.

2 Classical Theory

2.1 Normal Modes of Vibration

The Classical Raman Spectroscopy can be seen as the scattering of light due to its interaction with matter. It is useful to model the sample as a coupled oscillators, since atoms are connected to each other and can vibrate around its equilibrium point. In this description, one can see the atoms as masses and the elastic forces between them as springs. The theory developed in this subsection can be found in the textbook *Classical Dynamics of Particles and Systems*, by Stephen T. Thornton and Jerry B. Marion [4].

From Classical Mechanics, it is easier to describe the motion if the coordinates are not coupled, which means one shall use normal coordinates to describe the coupled oscillator, maybe instead of rectangular coordinates. Furthermore, it is possible to vary with time only one of the normal coordinates by applying specific initial conditions, which means only one of the normal modes of vibration of the system has been excited, a method that allows the study of each one of them separately.

For a matter of simplicity, this introductory text will deal with some of the theory of two coupled harmonic oscillators, which is easily generalized to a more complex n-atoms system.

Two Coupled Harmonic Oscillators

Considering just a two-atoms system, such as a molecule, one could have a model just like the one below, on Figure 1. The coordinates are measured from the position of equilibrium of the respective atom.

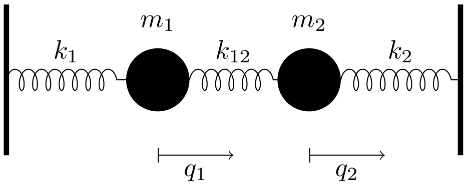


Figure 1: A coupled oscillator

It is important to observe that the motion of this particular system occurs in one dimension, what could represent the atomic link between a Carbon and a Chloride in a Carbon tetrachloride molecule, if one suppresses the translational and the rotational motions of the molecule.

Considering a displacement of q_1 and q_2 for m_1 and m_2, respectively, and considering $m_1 = m_2 = M$ and $k_1 = k_2 = \kappa$, the equations of motion are:

$$\begin{cases} M\ddot{q}_1 + (\kappa + k_{12})q_1 - k_{12}q_2 = 0 \\ M\ddot{q}_2 + (\kappa + k_{12})q_2 - k_{12}q_1 = 0, \end{cases}$$

where the coordinates are coupled. The expected solution for the oscillatory system is:

$$\begin{cases} q_1(t) = A_1 e^{i\omega t} \\ q_2(t) = A_2 e^{i\omega t}, \end{cases}$$

where ω is the frequency to be determined and the amplitudes A_1 and A_2 may be complex, which implies the existence of a magnitude and a phase, therefore the two necessary arbitrary constants.

Solving for ω:

$$\omega = \sqrt{\frac{\kappa + k_{12} \pm k_{12}}{M}},$$

which implies the existence of two characteristic frequencies:

$$\omega_1 = \sqrt{\frac{\kappa + 2k_{12}}{M}}, \quad \omega_2 = \sqrt{\frac{\kappa}{M}}$$

Finally, the general solution can be written as:

$$\begin{cases} q_1(t) = A_1^+ e^{i\omega_1 t} + A_1^- e^{-i\omega_1 t} + A_2^+ e^{i\omega_2 t} + A_2^- e^{-i\omega_2 t} \\ q_2(t) = -A_1^+ e^{i\omega_1 t} - A_1^- e^{-i\omega_1 t} + A_2^+ e^{i\omega_2 t} + A_2^- e^{-i\omega_2 t}, \end{cases}$$

a complicated solution obtained from a coupled coordinates system.

If one tries the following pair of coordinates:

$$\begin{cases} \eta_1 \equiv q_1 - q_2 \\ \eta_2 \equiv q_1 + q_2, \end{cases}$$

the equations of motion can be written as:

$$\begin{cases} M\ddot{\eta}_1 + (\kappa + 2k_{12})\eta_1 = 0 \\ M\ddot{\eta}_2 + \kappa\eta_2 = 0, \end{cases}$$

where the coordinates are uncoupled. The expected solution for the oscillatory system is, then:

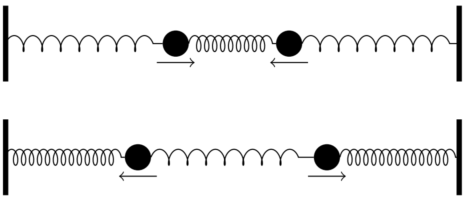
$$\begin{cases} \eta_1(t) = \mathcal{A}_1^+ e^{i\omega_1 t} + \mathcal{A}_1^- e^{-i\omega_1 t} \\ \eta_2(t) = \mathcal{A}_2^+ e^{i\omega_2 t} + \mathcal{A}_2^- e^{-i\omega_2 t}, \end{cases}$$

where ω_1 and ω_2 are the same as previously obtained.

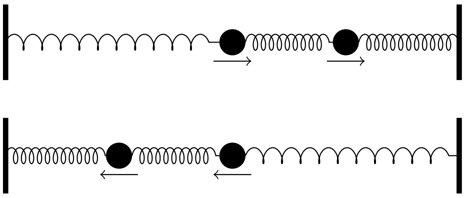
The coordinates η_1 and η_2 are the normal coordinates of the system, $\eta_1 \cdot \eta_2 = 0$, from which it is possible to excite just one of the normal modes by imposing special initial conditions.

If one lets $q_1(0) = -q_2(0)$ and $\dot{q}_1(0) = -\dot{q}_2(0)$, then $\eta_2(0) = 0$ and $\dot{\eta}_2(0) = 0$, which implies $\mathcal{A}_2^+ = \mathcal{A}_2^- = 0$. Thus, $\eta_2(t) \equiv 0$ for all t. This result means the particles oscillate always out of phase and with frequency ω_1, the anti-symmetrical mode of oscillation, Figure 2a.

Another possibility would be to let $q_1(0) = q_2(0)$ and $\dot{q_1}(0) = \dot{q_2}(0)$, which leads to $\eta_1(t) \equiv 0$. Thus, the particles oscillate in phase and with frequency ω_2, the symmetrical mode of oscillation, Figure 2b. The general motion of the system is a linear combination of those modes.



(a) Anti-symmetrical mode
($\omega = \omega_1$)



(b) Symmetrical mode
($\omega = \omega_2$)

Figure 2: Characteristic frequencies and respective modes of oscillation

Finally, if one holds m_1 or m_2 still, the resulting frequency for the oscillation of the other mass would be $\omega_0 = \sqrt{(\kappa + k_{12})/M}$, since the oscillators are identical if there is no coupling. However, in the presence of coupling, this common frequency is separated into the two characteristic frequencies previously described, one higher and the other lower than the common uncoupled frequency. Hence, $\omega_1 > \omega_0 > \omega_2$, as schematically depicted on Figure 3.

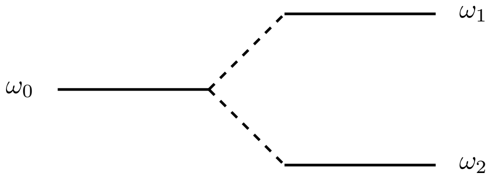


Figure 3: Separation of the common frequency due to coupling

2.2 Interaction of Light with Matter

Dielectric materials are those in which charges are attached to specific atoms or molecules. Those charges cannot freely move as charges on a conductor material can, but their slight displacements, specially when combined, account for the material's properties.

One can distort the charge distribution of a dielectric material by applying an electric field to it, resulting either on a stretch or a rotation of the atom or molecule. The theory developed in this subsection can be found in the textbook *Introduction to Electrodynamics*, by David J. Griffiths [5]. Here, only the distortion caused on a molecular level and on neutral molecules is discussed.

Induced Dipoles

A neutral molecule inside an electric field $\mathbf{E}$ is influenced by it because of the opposite charges carried by the nuclei and by the electrons. While the nuclei are displaced in the direction of the field, the electrons are displaced in the opposite way. For isotropic molecules, the result is an equilibrium between the force done by the electric field and the force done by internal attractive forces, which leaves the molecule polarized with a slight dipole moment $\mathbf{P} = \alpha\mathbf{E}$ in the same direction of the electric field $\mathbf{E}$, where α is the atomic polarizability.

Due to possible asymmetries not all molecules are isotropic, hence the response to the electric field may vary with the direction. Therefore, if the external electric field is not too strong, the general linear relation between $\mathbf{E}$ and $\mathbf{P}$ from a macroscopic point of view, no matter how asymmetric a molecule can be, is given by the Taylor series in $\mathbf{E}$:

$$\mathbf{P} = \sum_j \epsilon_o \chi_{ij}^{(1)} \mathbf{E}_j x^i + \sum_{j,k} \epsilon_o \chi_{ijk}^{(2)} \mathbf{E}_j \mathbf{E}_k x^i + \cdots ,$$

where ϵ_o is the permittivity of vacuum, $\chi_{ijk\ldots}^{(\mathcal{O})}$ is the polarizability tensor of the molecule, x^i is each of the coordinates, summed over the index i using the Einstein notation, and $\mathbf{E}_m(t) = \mathbf{E}_m^0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$ is the external electric field. Here, $\mathbf{k}$ and ω are the wave vector and the angular frequency of the electric field, and $\mathbf{r}$ is the separation vector from the source point to the field point.

This equation can be approximated to:

$$\mathbf{P} = \sum_j \epsilon_o \chi_{ij}^{(1)} \mathbf{E}_j x^i, \tag{1}$$

where $\chi_{ij}^{(1)}$ is the linear susceptibility, if one does not consider effects of higher orders. The equation can also be written in the matrix form:

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \epsilon_o \begin{pmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{xz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

2.3 Classical Raman and Selection Rules

Classical Raman

Due to the atomic vibrations inside the molecule, the matrix elements of $\chi_{ij}^{(1)}$ can be expanded in Taylor series as a function of the generalized coordinate of a given vibrational mode q_l [1]:

$$\chi_{ij}^{(1)} = (\chi_{ij})_0 + \sum_l \left(\frac{\partial \chi_{ij}}{\partial q_l}\right)_0 q_l + \mathcal{O}^{(2)}, \tag{2}$$

where $q_l(t) = q_l^0 \cos(\mathbf{q} \cdot \mathbf{r} - \omega_0 t) \cdot \hat{e}$, in which the dot product only appears in a solid medium, where plane waves can propagate, and where $(\chi_{ij})_0$ is the value of the linear susceptibility in the equilibrium configuration, and $\mathbf{q}$ and ω_0 are the wave vector and the frequency of the scattered light. Keeping only terms up to the first order, one has:

$$\mathbf{P} = \mathbf{P}_{rayleigh} + \mathbf{P}_{raman},$$

where $\mathbf{P}_{rayleigh}$ oscillates with the same frequency as the incident electric field and $\mathbf{P}_{raman}$ is due to the resulting scattering caused by the oscillation of the molecule's atoms.

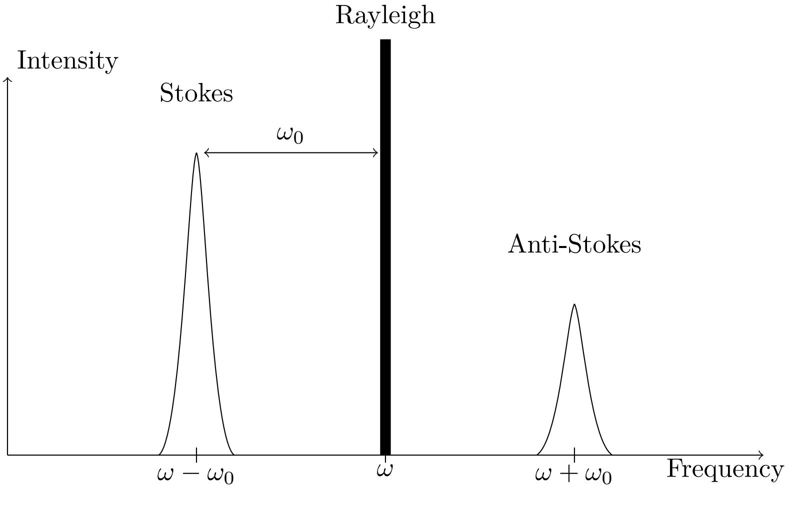


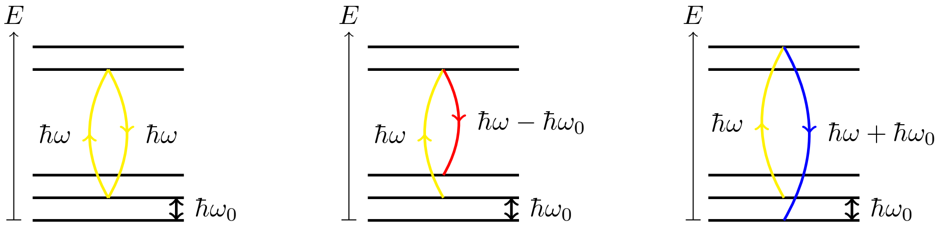
Figure 4: Schematic representation of a Raman Spectrum

Assuming the incident light electric field is given by $\mathbf{E}_m(t) = \mathbf{E}_m^0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$ and using the trigonometrical relation of cosines to expand Equation 1, one has:

$$\mathbf{P}_{raman} = \frac{1}{2}\epsilon_o \sum_{j,l} \left(\frac{\partial \chi_{ij}}{\partial q_l}\right)_0 q_l^0 \mathbf{E}_j^0 \times \{\cos[(\mathbf{k}+\mathbf{q}) \cdot \mathbf{r} - (\omega + \omega_0)t] + \cos[(\mathbf{k}-\mathbf{q}) \cdot \mathbf{r} - (\omega - \omega_0)t]\} x^i,$$

where the first cosine term has a higher frequency and the second one has a lower frequency than the incident electric field. The wave with higher frequency, with wave vector $\mathbf{k_S} = (\mathbf{k}+\mathbf{q})$ and frequency $\omega_S = \omega + \omega_0$, is called the Anti-Stokes component of the Raman scattering and the lower frequency scattered wave, with wave vector $\mathbf{k_{AS}} = (\mathbf{k}-\mathbf{q})$ and frequency $\omega_{AS} = \omega - \omega_0$, is called the Stokes component [1]. Figure 4 depicts a Raman spectrum for an incident light of frequency ω.

Another approach to describe the components of the Raman scattering is by using energy diagrams for electron transitions, but interpreting energy levels as vibrational levels, which is derived from the quantum mechanical description of the Raman phenomenon [2]. If one considers an incident light of frequency ω, the energy diagrams shown on Figure 5 depict the loss of energy on the Stokes component and the gain of energy on the Anti-Stokes component in respect to the Rayleigh scattering.



(a) Rayleigh (b) Stokes (c) Anti-Stokes

Figure 5: Energy diagrams for electron transitions between vibrational levels

The energy approach emphasizes the inelastic character of the Raman scattering.

Raman Selection Rules

The Raman selection rules allow one to determine whether a Raman shift, the appearance of the Stokes and the Anti-Stokes components, will occur and what result to expect. As previously described, the Raman shift can be found by deriving the polarizability vector of the molecule, which shows a Raman effect only if [1]:

$$\left(\frac{\partial \chi_{ij}}{\partial q_l}\right)_0 \neq 0$$

This result means that a Raman shift occurs only if the tensor χ varies in respect to a normal coordinate during the vibration. By using Group Theory or Quantum Mechanics [7] it is possible to identify Raman-active vibrations and rotations and to set up character tables, from which Raman-active modes can be found for a specific symmetry group of a molecule.

The conservation of energy and momentum are also Raman selection rules [1]. The scattered wave frequency, ω_s, must respect $\omega_s = \omega \pm \omega_0$, where ω is the frequency of the incident light and ω_0 is the Raman shift, and its wave vector, $\mathbf{k_s}$, must respect $\mathbf{k_s} = \mathbf{k} \pm \mathbf{q}$, where $\mathbf{k}$ is the wave vector of the incident light and $\mathbf{q}$ is the measurement of the molecule distortion defined by a generalized coordinate of a given vibrational mode.

2.4 Depolarization Ratio and Rules for Solutions

Depolarization Ratio

The incident light used on Raman Spectroscopy is usually sourced by a laser, which can guarantee the wavelength of the light is precise, so the Rayleigh component is well determined. Because of the source, the light is also plane polarized, what enables the study of the polarization dependence of the Raman scattering [9].

This phenomenon, called depolarization, can be studied by measuring the intensity of the scattered light in two polarization directions, one parallel, $I_{\parallel}$, and the other perpendicular, $I_{\perp}$, to the polarization plane of the incident light. The depolarization ration is then given by [2]:

$$\rho = \frac{I_{\perp}}{I_{\parallel}} \tag{3}$$

If a vibration belongs to the totally symmetric irreducible representation given by the Character Tables, the polarization plane is not rotated and $\rho = 0$, which means the vibration is polarized. If the vibration is asymmetric, the polarization plane is rotated and $\rho = 0.75$, which means the vibration is depolarized. This result is useful for the assignment of the spectral bands on a Raman spectrum, in which each band is associated with a vibrational mode.

Depolarization Rules for Solutions

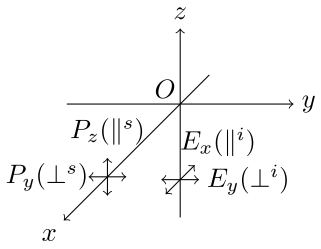


Figure 6: Reference system for depolarization

If one considers a molecule on the origin of the coordinate system and an incident light that propagates in the z direction and that interacts with the molecule, the light scattered at $\frac{\pi}{2}$ radians propagates in the x direction, as depicted on Figure 6. Hence, the scattered light has electric field components in the z and the y directions and the matrix elements of the transition dipole moment responsible for the emission of electric field can be approximated by [2]:

$$\begin{cases} P_y = \chi_{yy}\mathbf{E}_y \\ P_z = \chi_{zy}\mathbf{E}_y, \end{cases}$$

if the incident light is polarized in the y direction.

For n free molecules in the vibrational ground state, which means it is not yet excited, one may use the approximation of an ideal gas. In this model, the intensity of the scattered light is not given by $(\chi_{yy})^2$, but by $< (\chi_{yy})^2 >$, the mean value of all orientations of the n free molecules. Therefore, the depolarization ratio changes to [2]:

$$\rho\left(\frac{\pi}{2};\perp\right) = \frac{I(\frac{\pi}{2};\|^s,\perp^i)}{I(\frac{\pi}{2};\|^s,\|^i)} = \frac{3\gamma^2}{45\alpha^2 + 4\gamma^2}, \tag{4}$$

where I are the intensities and α and γ are the isotropic invariant quantities:

- mean polarizability
$$\alpha = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz})$$
- anisotropy
$$\begin{aligned}\gamma^2 =& \frac{1}{2}(|\chi_{xx} - \chi_{yy}|^2 + |\chi_{yy} - \chi_{zz}|^2 + |\chi_{zz} - \chi_{xx}|^2)\\ &+ \frac{3}{4}(|\chi_{xy} + \chi_{yx}|^2 + |\chi_{xz} + \chi_{zx}|^2 + |\chi_{yz} + \chi_{zy}|^2)\end{aligned}$$

For a detailed development of the calculation used to derive the equations for α and γ, see [6]. For another example of application of these tensor invariants in resonant Raman scattering, see [8].

3 Experiment

3.1 Experimental Setup

The basic experimental assembly to produce a Raman Spectrum of a sample consists of a spectrometer to capture and analyse the scattered light and a source of light to illuminate the sample [2]. A spectrometer receives light through a small slit, but since one cannot guarantee the light beam inside to be collimated, a collimator lens must be introduced between the slit and the diffraction grating, which is responsible for splitting and diffracting the scattered light from the sample to be captured by the detector, usually a charge-coupled device (CCD).

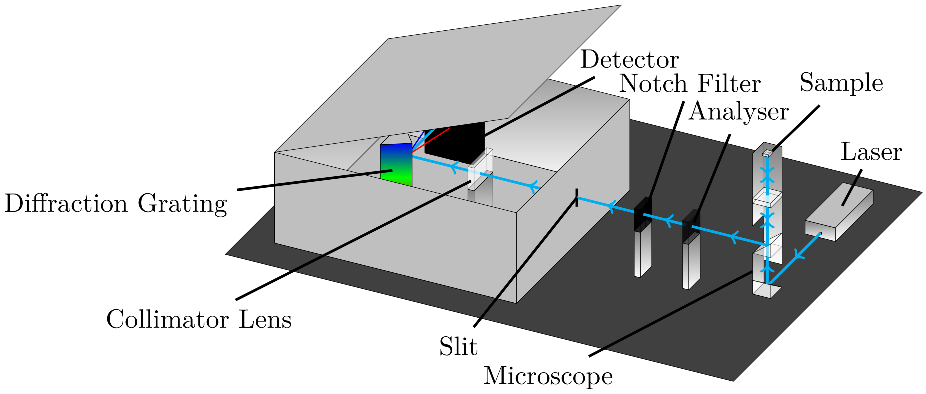


Figure 7: A schematic representation of the experimental setup used

In the following experiment, for which the setup is schematically depicted on Figure 7, it was used an intense laser beam to excite the sample, what made a notch filter necessary to prevent the light from the laser beam, which is much more intense than the relatively weak Raman signal from the sample, from suppressing it. A notch filter is wavelength-specific, only blocking the laser line while allowing long and shorter wavelengths to pass, what enables the study of both Stokes and Anti-Stokes Raman scattering simultaneously [2].

Other additions to the experimental setup were an analyser and a microscope. The analyser lets only electromagnetic waves parallel or perpendicular to its optical axis to pass, which enables the study of depolarization [2], while the microscope is responsible for focusing the laser beam over the sample. As represented on Figure 7, only the reflected scattered light from the sample is collected.

The chosen sample was a solution of Carbon tetrachloride, CCl_4, a tetrahedral molecule, better suited for an introductory text [9] because of the necessity to deal with mean values, instead of only the tensor multiplication, since each molecule may have a different orientation at a given time. This approach leads to an overall study of the classical Raman theory, covering not only solids, but also solutions.

3.2 Results

For this experiment, the scattered light from the Carbon tetrachloride solution was scanned six times and the results were summed up to produce a more reliable and intense Raman spectrum, as can be seen on Figure 9 and Figure 8. Since the spectrometer's intensity was not calibrated, the vertical axis' scales were omitted and the intensities on a spectrum can't be directly compared to the intensities on the other one.

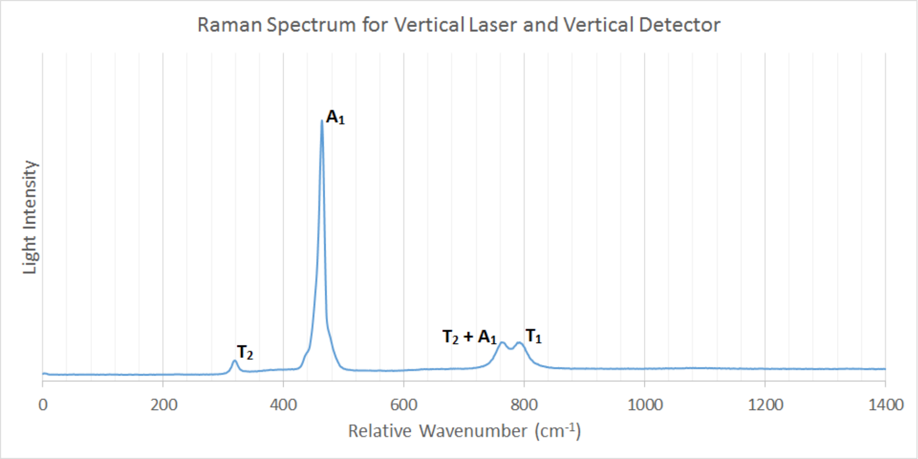


Figure 8: Raman Spectrum for vertical laser and vertical detector

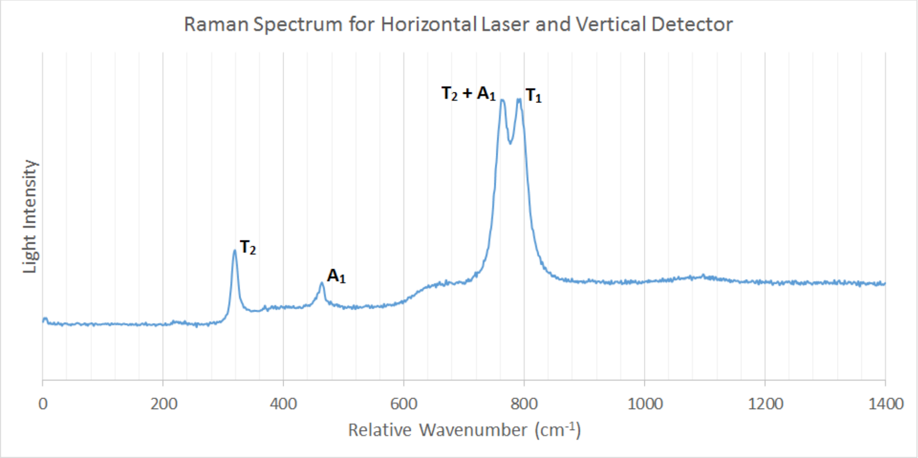


Figure 9: Raman Spectrum for horizontal laser and vertical detector

Since the Carbon tetrachloride is a tetrahedral molecule, it belongs to the point group T_d and one may expect to find the Raman active vibrational modes given by A_1, E, T_1 and T_2. In this experiment, the vibrational mode E was not detected. Furthermore, a combination mode given by $T_2 + A_1$ is also expected.

3.3 Discussion

The Raman spectrum in which both the detector and the polarized scattered laser were vertical, as shown on Figure 8, and the one in which the detector was vertical and the polarized scattered laser was horizontal, as shown on Figure 9, were achieved by the correct use of the Analyser.

If one wants to determine the depolarization ratio for each band, given by Equation 3, the first try could be the multiplication of the incident electric field vector by the square of the matrix representation of the polarizability tensor and by the transposed vector that represents the spacial configuration of the Analyser. For the T_d group of tetrahedral samples, the tensors are [10]:

A_1			$T_2(x)$			$T_2(y)$			$T_2(z)$		
a	·	·	·	·	·	·	·	d	·	d	·
·	a	·	·	·	d	·	·	·	d	·	·
·	·	a	·	d	·	d	·	·	·	·	·

Table 1: Raman tensors for the point group T_d

As detailed in the Appendix A, the depolarization ratio for the symmetric mode of vibration given by the matrix A_1 results in $\rho = 0$. This result agrees with the experiment, in which the A_1 mode of vibration fades away from Figure 8 to Figure 9, as the Analyser is rotated of $\frac{\pi}{2}$. Unfortunately, because the Carbon tetrachloride sample is a solution, the same approach leads to wrong results for the anti-symmetric mode of vibration given by the matrices T_2.

Hence, the most effective way to determine the depolarization ratio in this case is by using the previously derived depolarization ratio formula based on the approximation of an ideal gas, Equation 4, as detailed in the Appendix B.

The band at 450 cm^{-1} is assigned to the totally symmetric A_1 mode because its signal almost completely vanishes when the analyser is configured to be perpendicular to the scattered laser. The depolarization ratio for this mode is of 0.006 [2] and the molecule does not change its shape, which means the asymmetric polarization tensor does not act.

The bands at 313 cm^{-1} and at 780 cm^{-1} show the expected depolarization ratio of 0.75 for asymmetric modes. The first one is assigned to the T_2 mode and the second one to the T_1 mode. Since the band at 762 cm^{-1} is approximately the sum of the bands assigned to T_2 and A_1, it is assigned to a combination mode given by $T_2 + A_1$. This assignment is due to the fact that combination and second order modes usually appear at energies about the values obtained by the addition or multiplication of fundamental modes [9].

Finally, the proximity of the T_1 and the $T_2 + A_1$ bands results on a Fermi resonance. The consequences of this phenomenon are the increase of the T_1 and the decrease of the $T_2 + A_1$ energies and the decrease of the T_1 and the increase of the $T_2 + A_1$ intensities, what leaves them with almost the same intensity.

4 Conclusion

The Raman Spectroscopy is a very useful technique inside and outside the laboratory and its current development stage allows one to quickly make use of its benefits to study the vibrational properties of molecules in various scenarios.

In this introductory text all the basic ideas behind the Raman Spectroscopy were approached, since its theory to its application to the Carbon tetrachloride example. It is important to emphasize the demonstrated difference in the theory for the case in which the sample is a solid to that in which it is a solution, what makes the approximation of an ideal gas necessary.

5 Appendix A: Tensor multiplication

Consider an incident light described by the following electric field vector:

$$\mathbf{E}_i = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

Also, consider two possible Analyser configurations, one parallel to $\mathbf{E}_i$, $\mathbf{R}_{\parallel}$, and other perpendicular to it, $\mathbf{R}_{\perp}$:

$$\mathbf{R}_{\parallel} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad \mathbf{R}_{\perp} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

To determine the depolarization ratio given by Equation 3, one would take the Raman tensors for the sample's point group, say the T_d group for the Carbon tetrachloride from Table 1, and compute as follows.

For the symmetric mode of vibration, given by the matrix A_1:

$$I_{\parallel} = \mathbf{E}_i A_1^2 \mathbf{R}_{\parallel}^T = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}^2 \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} = a^2$$

$$I_{\perp} = \mathbf{E}_i A_1^2 \mathbf{R}_{\perp}^T = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}^2 \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} = 0$$

Therefore,

$$\rho = \frac{I_{\perp}}{I_{\parallel}} = \frac{0}{a^2} = 0$$

This result agrees with the experiment, in which the A_1 mode of vibration fades away as the Analyser is rotated of $\frac{\pi}{2}$.

For the anti-symmetric mode of vibration, given by the matrices T_2:

$$T_2^2(x) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}^2 = d^2 \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$T_2^2(y) = \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}^2 = d^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$T_2^2(z) = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}^2 = d^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{E}_i T_2^2(x)\mathbf{R}_\parallel^T = d^2 \begin{pmatrix}1\\0\\0\end{pmatrix} \begin{pmatrix}0 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{pmatrix} \begin{pmatrix}1 & 0 & 0\end{pmatrix} = 0$$

$$\mathbf{E}_i T_2^2(y)\mathbf{R}_\parallel^T = d^2 \begin{pmatrix}1\\0\\0\end{pmatrix} \begin{pmatrix}1 & 0 & 0\\0 & 0 & 0\\0 & 0 & 1\end{pmatrix} \begin{pmatrix}1 & 0 & 0\end{pmatrix} = d^2$$

$$\mathbf{E}_i T_2^2(z)\mathbf{R}_\parallel^T = d^2 \begin{pmatrix}1\\0\\0\end{pmatrix} \begin{pmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 0\end{pmatrix} \begin{pmatrix}1 & 0 & 0\end{pmatrix} = d^2$$

$$I_\parallel = \mathbf{E}_i T_2^2(x)\mathbf{R}_\parallel^T + \mathbf{E}_i T_2^2(y)\mathbf{R}_\parallel^T + \mathbf{E}_i T_2^2(z)\mathbf{R}_\parallel^T = 2d^2$$

$$\mathbf{E}_i T_2^2(x)\mathbf{R}_\perp^T = d^2 \begin{pmatrix}1\\0\\0\end{pmatrix} \begin{pmatrix}0 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{pmatrix} \begin{pmatrix}0 & 1 & 0\end{pmatrix} = 0$$

$$\mathbf{E}_i T_2^2(y)\mathbf{R}_\perp^T = d^2 \begin{pmatrix}1\\0\\0\end{pmatrix} \begin{pmatrix}1 & 0 & 0\\0 & 0 & 0\\0 & 0 & 1\end{pmatrix} \begin{pmatrix}0 & 1 & 0\end{pmatrix} = 0$$

$$\mathbf{E}_i T_2^2(z)\mathbf{R}_\perp^T = d^2 \begin{pmatrix}1\\0\\0\end{pmatrix} \begin{pmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 0\end{pmatrix} \begin{pmatrix}0 & 1 & 0\end{pmatrix} = 0$$

$$I_\perp = \mathbf{E}_i T_2^2(x)\mathbf{R}_\perp^T + \mathbf{E}_i T_2^2(y)\mathbf{R}_\perp^T + \mathbf{E}_i T_2^2(z)\mathbf{R}_\perp^T = 0$$

Therefore,

$$\rho = \frac{I_\perp}{I_\parallel} = \frac{0}{2d^2} = 0$$

This result doesn't agree with the experiment, because the T_2 mode of vibration doesn't fade away as the Analyser is rotated of $\frac{\pi}{2}$.

6 Appendix B: Tensor invariants

To determine the depolarization ratio, one could use Equation 4 instead of Equation 3 and the Tensor multiplication method discussed in the Appendix A. In fact, the following method is the only one to achieve the correct results between those two if the sample being studied is not in the solid state.

Consider the T_d group for the Carbon tetrachloride from Table 1.

For the symmetric mode of vibration, given by the matrix A_1:

$$\alpha = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}) = \frac{1}{3}(3a) = a$$

$$\begin{aligned}\gamma^2 &= \frac{1}{2}(|\chi_{xx} - \chi_{yy}|^2 + |\chi_{yy} - \chi_{zz}|^2 + |\chi_{zz} - \chi_{xx}|^2) \\ &+ \frac{3}{4}(|\chi_{xy} + \chi_{yx}|^2 + |\chi_{xz} + \chi_{zx}|^2 + |\chi_{yz} + \chi_{zy}|^2) = \\ &= \frac{1}{2}(0) + \frac{3}{4}(0) = 0\end{aligned}$$

Therefore, from Equation 4:

$$\rho = \frac{3\gamma^2}{45\alpha^2 + 4\gamma^2} = \frac{0}{45a^2} = 0$$

As expected, this result agrees with the experiment, in which the A_1 mode of vibration fades away as the Analyser is rotated of $\frac{\pi}{2}$.

For the anti-symmetric mode of vibration, given by the matrices T_2:

$$\alpha = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}) = \frac{1}{3}(0) = 0$$

$$\begin{aligned}\gamma^2 &= \frac{1}{2}(|\chi_{xx} - \chi_{yy}|^2 + |\chi_{yy} - \chi_{zz}|^2 + |\chi_{zz} - \chi_{xx}|^2) \\ &+ \frac{3}{4}(|\chi_{xy} + \chi_{yx}|^2 + |\chi_{xz} + \chi_{zx}|^2 + |\chi_{yz} + \chi_{zy}|^2) = \\ &= \frac{1}{2}(0) + \frac{3}{4}(4d^2 + 4d^2 + 4d^2) = 9d^2\end{aligned}$$

Therefore, from Equation 4:

$$\rho = \frac{3\gamma^2}{45\alpha^2 + 4\gamma^2} = \frac{3(9d^2)}{4(9d^2)} = \frac{3}{4} = 75\%$$

As expected, this result also agrees with the experiment, in which the T_2 mode of vibration doesn't fade away as the Analyser is rotated of $\frac{\pi}{2}$. Furthermore, one obtains the expected value for an asymmetric, or depolarized, vibration, which is $\rho = 0.75$ as previously discussed.

References

[1] Leandro Malard Moreira *Raman Spectroscopy of Graphene: Probing Phonons, Electrons and Electron-Phonon Interactions*, Departamento de Física, Universidade Federal de Minas Gerais, Brazil, 2009. 11, 12

[2] Matti Hotokka, *Molecular Spectroscopy, Advanced Course*, Department of Physical Chemistry, Abo Akademi University, Finland, 2014. 6, 12, 13, 14, 15, 17

[3] Wikipedia, Raman spectroscopy. As of February 2016. 6

[4] Stephen T. Thornton and Jerry B. Marion, *Classical Dynamics of Particles and Systems*, 5th edition, 2004. 7

[5] David J. Griffiths, *Introduction to Electrodynamics*, 4th edition, 1942. 10

[6] Robert P. Lucht, *Applied Laser Spectroscopy*, CRC Press, 2014. 6, 14

[7] M.S. Dresselhaus, G. Dresselhaus and A. Jorio, *Group Theory, Application to the Physics of Condensed Matter*, 2008. 12

[8] S. Reich, *Tensor invariants in resonant Raman scattering on carbon nanotubes*, Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 14

[9] David Tuschel, *Practical Group Theory and Raman Spectroscopy, Part II: Application of Polarization*, Molecular Spectroscopy Workbench, Spectroscopy, 2014. 13, 15, 17

[10] M. I. Aroyo, J. M. Perez-Mato, D. Orobengoa, E. Tasci, G. de la Flor, A. Kirov, *Crystallography online: Bilbao Crystallographic Server*, Bulg. Chem. Commun., 43(2) 183-197, 2011. As of February 2016. 17