Vibrational Spectroscopy.

1. Vibrational spectroscopy[1]

Vibrational spectroscopy comprises two different techniques that can give complementary information on the different vibrational states in a molecule or a material, namely infrared spectroscopy and Raman scattering spectroscopy. Infrared spectroscopy is very similar to absorption spectroscopy, but now using infrared light with an energy equal to the transitions between vibrational energy levels. In contrast, Raman spectroscopy relies upon the inelastic scattering of photons, meaning that there is both an exchange of energy and a change in the direction of the light propagation. Raman scattering involves vibrational energy being gained or lost by a molecule as the incident photons from a laser are shifted to lower, respectively higher energy.

In 1928, Sir Chandreskhra Venkata Raman discovered the phenomenon of Raman spectroscopy, even though at that time the instrumentation was very basic. Sir Raman used sunlight as the source and a telescope as the collector, the detector was his eyes. That such a weak phenomenon as Raman scattering was detected in this manner is remarkable. He was awarded the Nobel Prize in Physics in 1930 for his discovery. The effect had been predicted theoretically by Adolf Smekal in 1923.

Early research was concentrated on the development of better excitation sources, consisting first of various lamps and later of lasers. Lasers are indeed ideal to measure Raman scattering, given that they allow to accurately determine the lost or gained energy of the system (given that the laser energy is exactly known).

2. Vibrations of a diatomic molecule

Let us now first consider the vibrations of a diatomic molecule, in which two atoms are connected by a chemical bond, which represents a very easy and intuitive interpretation of molecular vibrations to understand Raman spectroscopy. Figure 1 presents such a diatomic molecule, with two atoms with mases m_1 and m_2 and distances r_1 and r_2 from the center of gravity. The masses are connected by a chemical bond, which is defined by a spring with a spring constant K. Thus, $r_1 + r_2$ represents the equilibrium distance between the two masses and assume that x_1 and x_2 are the displacements of atoms 1 and 3, respectively, from their equilibrium positions.
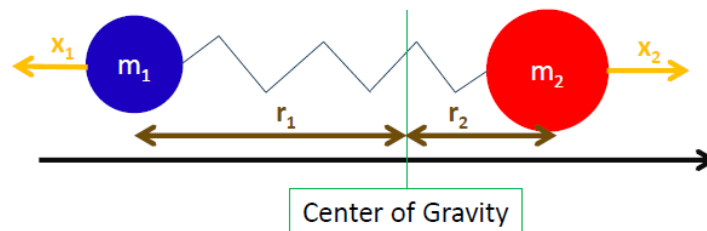

Figure 1: schematic representation of a diatomic molecule.

The conservation of the center of gravity requires the relationships:

$$m_1 r_1 = m_2 r_2 \qquad \text{(Eq. 1)}$$
$$m_1 (r_1 + x_1) = m_2 (r_2 + x_2) \qquad \text{(Eq. 2)}$$

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[1] Chapter based on the book of J. R. Ferraro, Introductory Raman spectroscopy – Chapter1: Basic Theory (2003)

Combining these two equations, we obtain:

$$x_1 = \left(\frac{m_2}{m_1}\right)x_2 \qquad \text{(Eq. 3)}$$

In the classical treatment, the bond is regarded as a spring that obeys Hooke's law, where the restoring force, f is given by:

$$f = -K(x_1 + x_2) \qquad \text{(Eq. 4)}$$

The minus sign indicates that the directions of the force and the displacements are opposite to each other. Combining this with equation 3 we obtain:

$$f = -K\left(\frac{m_1 + m_2}{m_1}\right)x_2 = -K\left(\frac{m_1 + m_2}{m_2}\right)x_1 \qquad \text{(Eq. 5)}$$

Newton's equation of motion is written for each atom as:

$$f = ma \qquad \text{(Eq. 6)}$$

$$m_2 \frac{d^2 x_2}{dt^2} = -K\left(\frac{m_1 + m_2}{m_1}\right)x_2 \qquad \text{(Eq. 7)}$$

$$m_1 \frac{d^2 x_1}{dt^2} = -K\left(\frac{m_1 + m_2}{m_2}\right)x_1 \qquad \text{(Eq. 8)}$$

By multiplying the left and right parts by the inverse of the term between brackets we obtain:

$$\frac{m_1 m_2}{m_1 + m_2}\left(\frac{d^2 x_1}{dt^2} + \frac{d^2 x_2}{dt^2}\right) = -K(x_1 + x_2) \qquad \text{(Eq. 9)}$$

Introducing the reduced mass μ and the reduced displacement q, equation 9 can be written as a simple differential equation of which the solution is known:

$$\mu\left(\frac{d^2 q}{dt^2}\right) = -Kq \qquad \text{(Eq. 10)}$$

$$q = q_0 \sin(2\pi\nu_0 t + \varphi) \qquad \text{(Eq. 11)}$$

Where q_0 is the maximum displacement and φ is the phase constant, which depends on the initial conditions. The frequency ν_0 is the classical vibrational frequency and is related to the strength of the spring and the reduced mass of the two atoms, through the following equation:

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \qquad \text{(Eq. 12)}$$

Let us now calculate the total energy o the system: $E = T + V$ with T the kinetic energy and V the potential energy. The kinetic energy is given by:

$$T = \frac{1}{2}m_1\left(\frac{dx_1}{dt}\right)^2 + \frac{1}{2}m_2\left(\frac{dx_2}{dt}\right)^2 \qquad \text{(Eq. 13)}$$

$$T = \frac{1}{2}\mu\left(\frac{dq}{dt}\right)^2 = 2\mu\pi^2 v_0^2 q_0^2 \cos^2(2\pi v_0 t + \varphi) \qquad \text{(Eq. 14)}$$

The potential energy is given by:

$$dV = -fdq = Kqdq \qquad \text{(Eq. 15)}$$

$$V = \frac{1}{2}Kq^2 = \frac{1}{2}Kq_0^2 \sin^2(2\pi v_0 t + \varphi) \qquad \text{(Eq. 16)}$$

$$V = \frac{1}{2}Kq^2 = 2\mu\pi^2 v_0^2 q_0^2 \sin^2(2\pi v_0 t + \varphi) \qquad \text{(Eq. 17)}$$

The total energy is thus a constant and equals $E = 2\mu\pi^2 v_0^2 q_0^2$.

Figure 2 shows the plot of the potential energy as a function of q. This is a parabolic potential, with $E = T$ at $q = 0$ and $E = V$ at $q = \pm q_0$. Such a vibration is called an harmonic oscillator.
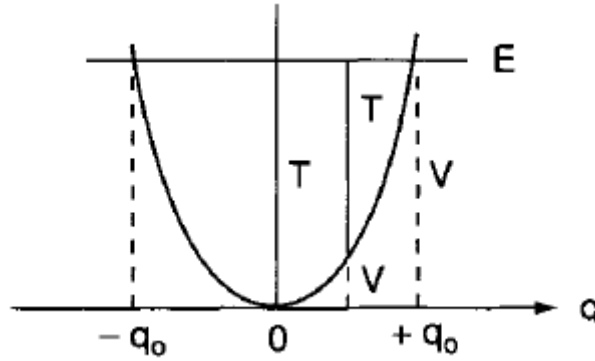

Figure 2: Potential energy for an harmonic oscillator.

In quantum mechanics, the vibration of a diatomic molecule can be treated as a motion of a single particle having mass μ whose potential energy is expressed by equation 17. The Schrödinger equation for such a system is written as:

$$\frac{d^2\psi}{dq^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{1}{2}Kq^2\right)\psi = 0 \qquad \text{(Eq. 18)}$$

When solving this equation, assuming ψ to be finite and continuous, the eigenvalues are

$$E_\varsigma = hv(\varsigma + \frac{1}{2}) \qquad \text{(Eq. 19)}$$

With v the frequency of vibration given as in equation 12 (thus the quantum-mechanical and classical frequency are the same) and ς the vibrational quantum number which can have values of 0,1,2,3,…. The corresponding eigenfunctions are:

$$\psi_\varsigma = \frac{\left(\frac{\alpha}{\pi}\right)^{1/4}}{\sqrt{2^v \varsigma!}} e^{-\frac{\alpha q^2}{2}} H_\varsigma(\sqrt{\alpha}q) \qquad \text{(Eq. 20)}$$

Where $\alpha = 2\pi\sqrt{\mu K/h} = \frac{4\pi^2\mu v}{h}$ and $H_\varsigma(\sqrt{\alpha}q)$ is a Hermite polynomial of the ςth degree. Thus the eigenvalues and corresponding eigenfunctions are:

$$\varsigma = 0, \quad E_0 = \frac{1}{2}h\nu, \qquad \psi_0 = \left(\frac{\alpha}{\pi}\right)^4 e^{-\frac{\alpha q^2}{2}}$$

$$\varsigma = 1, \quad E_1 = \frac{3}{2}h\nu, \qquad \psi_1 = \left(\frac{\alpha}{\pi}\right)^4 e^{-\frac{\alpha q^2}{2}} q 2^{\frac{1}{2}}$$

(Eq. 21)

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Figure 3 presents the quantum-mechanical wavefunctions ψ within the classical potential. As mentioned above, the quantum-mechanical frequency is exactly the same as the classical frequency. However, several differences should be noted between the two treatments. First, classically, E is zero when q is zero. Quantum-mechanically however, the lowest energy state ($\varsigma = 0$) has energy $\frac{1}{2}h\nu$ (also called the zero point energy). The latter results from the Heisenberg uncertainty principle: according to this principle, quantum systems constantly fluctuate in their lowest energy state and therefore even at the lowest temperature, atoms and molecules retain some vibrational motion, and thus a finite value for the zero-point energy. Secondly, in classical mechanics, the energy of such an harmonic oscillator can change continuously, while in quantum mechanics the energy can only change in units of $h\nu$. Thirdly, the vibration is confined within the parabola presented in Figure 3, since the kinetic energy T becomes negative outside the parabola, but in quantum mechanics there remains a certain probability of finding q outside the parabola.
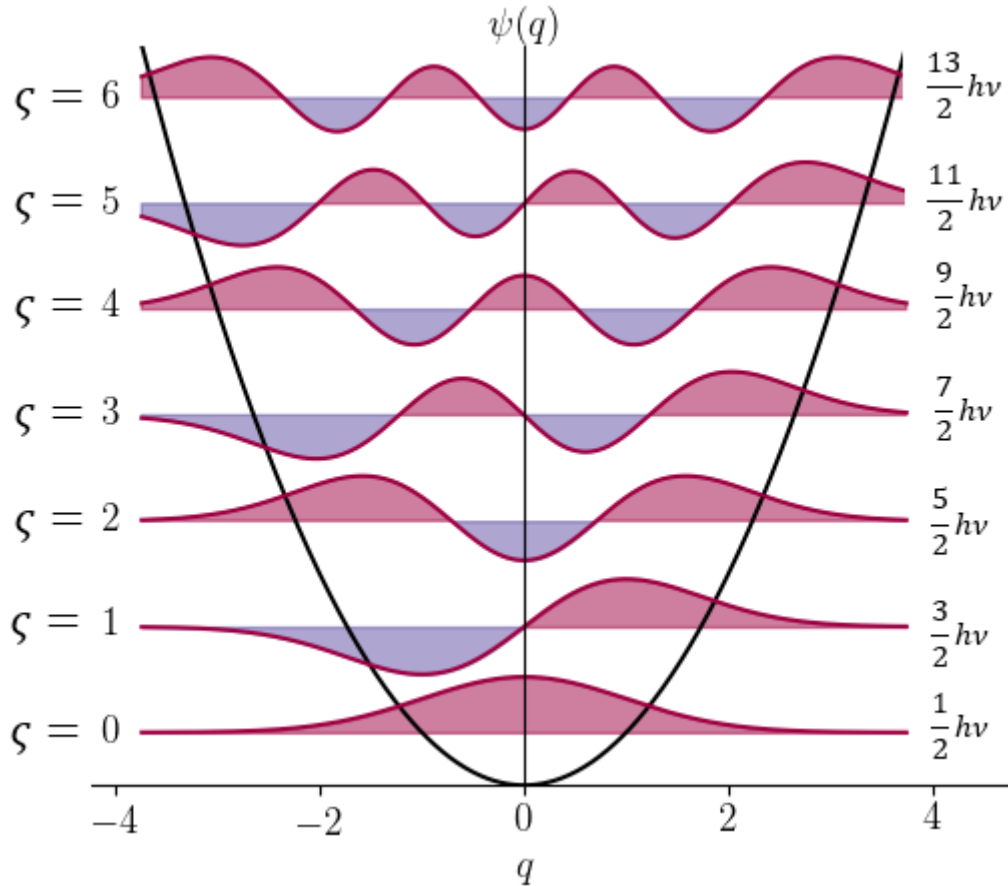

Figure 3: the quantum-mechanical wavefunctions in comparison to the classical potential (black line)

In the case of an harmonic oscillator, the separation between the different quantum states is the same: namely $h\nu$. However, in an actual molecule, this is not the case, and the potential energy is not given as a parabola but by the so-called Morse potential shown in Figure 4.

$$V = D_e(1 - e^{-\beta q})^2$$

(Eq. 22)

Where D_e is the dissociation energy and β is a measure of the curvature of the bottom of the potential well. If the Schrödinger equation is solved with this Mores potential, the eigenvalues are slightly different:

$$E_\varsigma = hc\omega_e \left(\varsigma + \frac{1}{2}\right) - hc\chi_e\omega_e \left(\varsigma + \frac{1}{2}\right)^2 + \cdots \qquad \text{(Eq. 23)}$$

Where ω_e is the wavenumber corrected for the anharmonicity of the potential and $\chi_e\omega_e$ indicates the magnitude of anharmonicity. Equation 23 then shows that the energy levels are no longer equidistant, and the separation decreases with increasing quantum number ς, as presented in Figure 4.
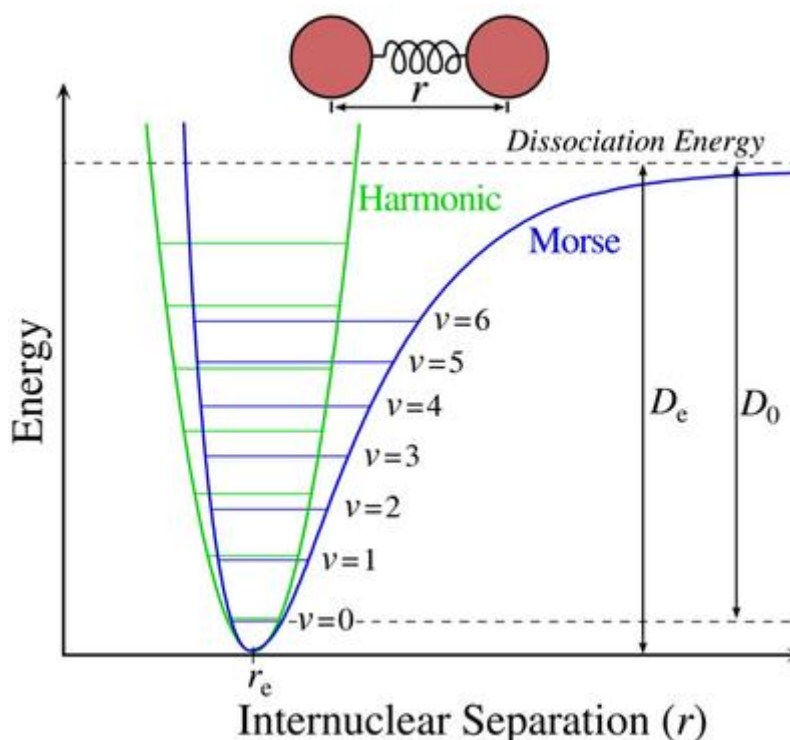

Figure 4: the quantum-mechanical wavefunctions within the Morse potential.[2] D_e and D_0 represent the theoretical and spectroscopic dissociation energies, respectively

According to quantum mechanics, only those transitions involving the change of one vibrational quantum (i.e. $\Delta\varsigma = \pm 1$) are allowed for the pure harmonic oscillator. If the vibration is anharmonic, also transitions involving $\Delta\varsigma = \pm 2,3$ are weakly allowed, yielding overtones in the Raman spectra. Among many $\Delta\varsigma = \pm 1$ transitions, that of $\varsigma = 0 \rightarrow 1$ (fundamental) appears most strongly in both IR and Raman spectra, which is expected from the Boltzmann distribution giving the population ratio of the vibrational states.

$$\frac{P_{\varsigma=1}}{P_{\varsigma=0}} = e^{-\Delta E/kT} \qquad \text{(Eq. 24)}$$

Where ΔE is the energy difference between the two states, and $kT \cong 25$ meV $\cong 208$ cm^{-1}. Typical vibrational quantums correspond to values of a few 100 cm^{-1} up to 5000 cm^{-1}. For example for the diatomic hydrogen molecule (H_2), $v = 4160$ cm^{-1} yielding a population ratio of 2.19×10^{-9}. Therefore, almost all molecules are in the quantum mechanical ground state.

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[2] Figure from: https://chemistry.stackexchange.com/questions/150844/how-is-kinetic-energy-accounted-for-when-describing-diatomic-bonds-with-a-morse

3. Origin of Raman and IR spectra

Vibrational transitions can be observed in both IR and Raman spectra. In the former, we measure absorption of infrared light by the sample as a function of frequency. The principle is therefore exactly the same as UV-vis-NIR absorption spectroscopy, where the law of lamber Beer governs the spectra, yet using infrared light which matches the transitions between vibrational states. Raman is intrinsically very different from IR. In Raman spectroscopy, an intense laser beam with frequency (ν_L) much larger than the vibrational energy (e.g. in the UV-visible region) irradiates the sample after which the scattered light is observed. This scattered light consists of two types: Rayleigh scattering which has the same frequency as the incident beam and the other, called Raman scattering scatters the light at frequencies $\nu_L \pm \nu$, where ν is the vibrational frequency of the molecule. The $\nu_L + \nu$ scattering is called anti-Stokes scattering and the $\nu_L - \nu$ frequencies are called Stokes scattering. Thus, in Raman, we measure the vibrational frequency as a shift from the incident laser frequency. Thus, in contrast to IR spectra, Raman spectra are measured in the UV-visible region where the excitation as well as Raman lines appear. Figure 5 presents a schematic of IR absorption, Rayleigh and Raman scattering. Note that in the case of Raman scattering, the laser energy in principle does not need to correspond to an electronic transition, the scattering takes place for any laser energy. We will see further, that when matching the laser energy to an electronic transition, resonant Raman scattering occurs where the Raman signal can be enhanced with several orders of magnitude.
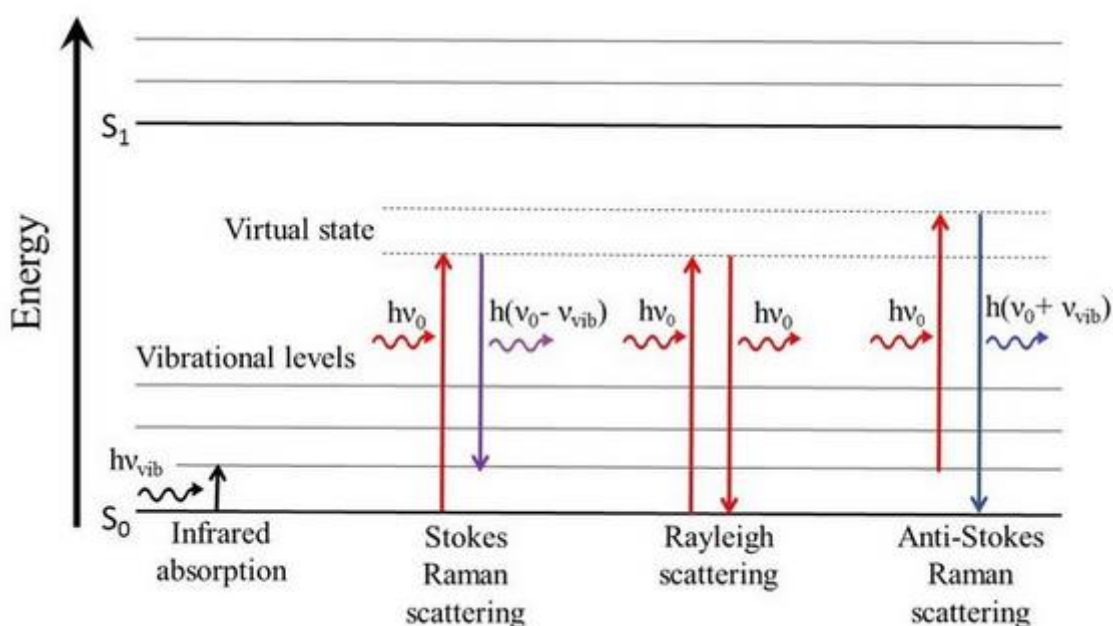

Figure 5: Principle of infrared absorption spectroscopy, Rayleigh scattering and Stokes and Anti-Stokes Raman scattering

Classically, Raman scattering can be explained as follows. The electric field strength of the electromagnetic wave (in this case a laser beam) fluctuates with time as follows:

$$E = E_0 cos(2\pi\nu_L t) \hspace{3cm} \text{(Eq. 25)}$$

Where E_0 is the amplitude of the laser and ν_L is the frequency of the laser. If a molecule, e.g. a diatomic molecule, is irradiated with this light, an electric dipole moment P is induced:

$$P = \alpha E = \alpha E_0 cos(2\pi\nu_L t) \hspace{3cm} \text{(Eq. 26)}$$

With α the polarizability of the molecule. While in absorption spectroscopy we assumed the nuclei of the molecule to be fixed, at a finite temperature the molecule can vibrate with a frequency v_m. The nuclear displacement q can then be described as:

$$q = q_0 cos(2\pi v_m t) \qquad \text{(Eq. 27)}$$

With q_0 the vibrational amplitude. This vibration will also influence the polarizability. For small amplitude vibrations, α is a linear function of q. Thus, we can write

$$\alpha = \alpha_0 + (\frac{\delta\alpha}{\delta q})_{q=0} q_0 + \cdots \qquad \text{(Eq. 28)}$$

Here, α_0 is the polarizability at the equilibrium position and $(\frac{\delta\alpha}{\delta q})_{q=0}$ is the rate of change of α with respect to the change in q, evaluated at the equilibrium position. Combining now equations 26-28 we get

$$P = \alpha_0 E_0 cos(2\pi v_L t) + (\frac{\delta\alpha}{\delta q})_{q=0} q_0 cos(2\pi v_m t)E_0 cos(2\pi v_L t) \qquad \text{(Eq. 29)}$$

And thus:

$$P = \alpha_0 E_0 cos(2\pi v_L t) + \frac{1}{2}(\frac{\delta\alpha}{\delta q})_{q=0} q_0 E_0 [cos(2\pi(v_L + v_m)t) + cos(2\pi(v_L - v_m)t)) \qquad \text{(Eq. 30)}$$

The first term then represents an oscillating dipole that radiates light of frequency v_L (Raileigh scattering), while the second term corresponds to Anti-Stokes Raman scattering at frequency $v_L + v_m$ and the last term corresponds to Stokes Raman scattering at a frequency $v_L - v_m$. Note that the above equation also shows that if $(\frac{\delta\alpha}{\delta q})_{q=0} = 0$ the vibration is not Raman active. Namely, to be Raman active, the rate of change of polarizability with the vibration must not be zero.

The above 'classical' equation however does not take into account the different population levels of the ground and vibrational states. Therefore, anti-stokes Raman scattering will always be much weaker than stokes Raman scattering, because for stokes scattering one starts from a lower vibrational state and ends up in a higher vibrational state, whereas the opposite is true for anti-stokes Raman scattering (see Figure 5). A second thing which cannot be explained by the above equation is Resonant Raman scattering which occurs when the laser energy is chosen so that it matches an electronic excited state. In that case, the Raman signal can be enhanced by several orders of magnitude. To explain this, a quantum-mechanical derivation is needed (see further).

4. Selection rules for infrared and Raman spectra.

Since the origin of IR and Raman are markedly different, their selection rules are also very different. According to quantum mechanics, a vibration is **IR active** if the **dipole moment is changed** during the vibration, whereas it is **Raman active**, if **the polarizability is changed** during the vibration.
The IR activity of small molecules can be determined by inspecting the normal modes of the vibration, and how they change the dipole moments of a molecule. Obviously, the vibration of a homopolar diatomic molecule cannot be IR active, because there is no dipole moment, whereas for a heteropolar diatomic molecule the stretching vibration of the chemical bond is IR active, as it changes the dipole moment between the two atoms (distance between the two charges is changed). For a H_2O molecule, the dipole moment is changed during each normal vibration, thus all the vibrations are IR active (see Figure 6a). On the other hand, for a CO_2 molecule not all modes are IR active, see Figure 6b. In general, symmetric vibrations typically do not cause a change in dipole moment, and are therefore IR inactive.
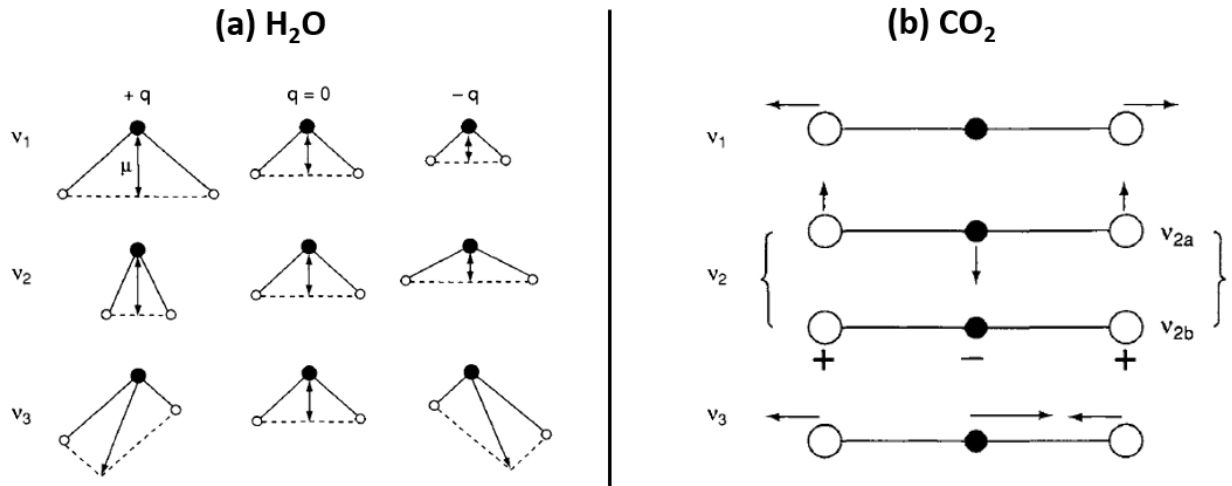
(a) H₂O   **(b) CO₂**

Figure 6: (a) Normal modes of (a) H_2O and (b) CO_2. For H_2O, each mode changes the dipole moment of the molecule and is thus IR active, while for CO_2 the first vibrational mode is not IR active, while mode 2-3 are IR active.

For Raman, one needs to see a change in polarizability. It is important to note that this polarizability α is in fact a tensor, since both the polarization and the electric field are vectors consisting of three components in the x, y and z directions. Thus, equation 26 must be written as

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \qquad \text{(Eq. 31)}$$

In normal Raman scattering, the polarizability tensor is symmetric: thus $\alpha_{xy} = \alpha_{yx}$, $\alpha_{xz} = \alpha_{zx}$ and $\alpha_{zy} = \alpha_{yz}$. According to quantum mechanics, the vibration is Raman-active if one of these components of the polarizability tensor is changed during the vibration.

Unlike the change of the dipole moment which is required for a mode to be IR active, it is not so straightforward to see when the polarizability tensor would change. However, let us consider a few examples.

Consider a linear molecule such as CO_2. Their electron clouds have an elongated like shape with circular cross-sections, such as an America football. In these molecules, the electrons are more polarizable (have a larger α) along the chemical bond than in the direction perpendicular to it. If we would plot α from the center of gravity in all directions, we end up with a three-dimensional surface. Conventionally however, $1/\sqrt{\alpha}$ is plotted to yield the polarizability ellipsoid which is presented in Figure 7. In terms of this polarizability ellipsoid, a vibration is Raman active if the size, shape or orientation of this ellipsoid changes during the normal vibration. In the case of CO_2 and the first vibrational mode, the size of the ellipsoid is changing and thus this mode is Raman active. On the other hand, although the size of the ellipsoid is also changing for the third vibration, the ellipsoids at two extreme displacement +q and -q are exactly the same in this case. Thus, the vibration is not Raman active. The difference between these two is shown in Figure 7b. Indeed, since the Raman activity is determined by the slope of the polarizability near the equilibrium position (i.e. $\left(\frac{\delta\alpha}{\delta q}\right)_{q=0}$), the third vibration is not Raman active. Similarly, for the second vibration (bottom line in Figure 7a), the shape of the ellipsoid changes but similarly for +q and -q displacements, thus again it is not Raman active.
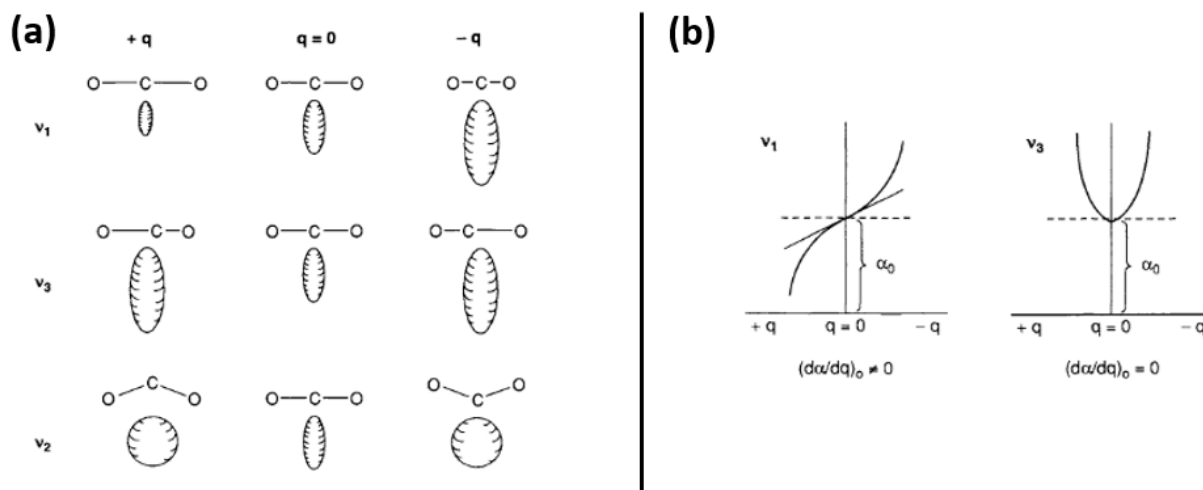
Figure 7: (a) polarizability ellipsoid for the CO_2 molecule. **(b)** difference between the first and the third vibrations in the CO_2 molecule.

Similarly we can discuss the normal modes of the H_2O molecule (see Figure 8). This shows that all modes are Raman active. Its v_1 vibration is Raman active, similar as the v_1 for CO_2. The v_2 vibration is also Raman active, because the shape of the ellipsoid is different for +q and -q displacements. Finally, the v_3 vibration is Raman active because the orientation of the ellipsoid is changing during the vibration. This activity occurs because an off diagonal element (in this case α_{yz}) is changing.
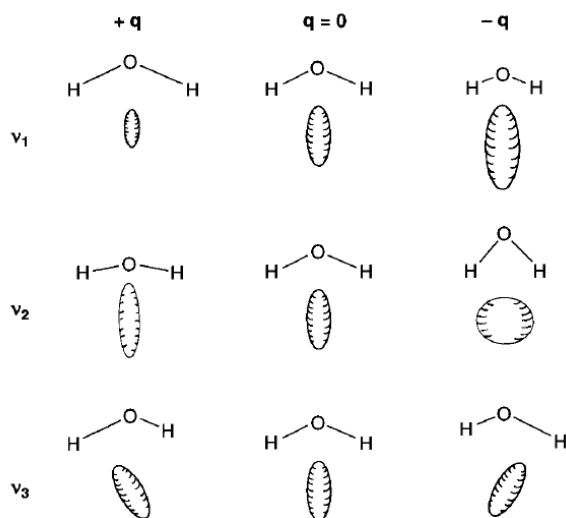

Figure 8: polarizability ellipsoid for the H_2O molecule.

Important to remember: in CO_2 the symmetric vibration is Raman active but not IR active, whereas those that are antisymmetric with respect to the center of symmetry are IR active but not Raman active. This condition is called the **mutual exclusion principle** and holds for any molecules having a center of symmetry. Therefore, Raman and IR spectroscopy can be considered perfectly complementary techniques to study the Raman modes of various molecules. Clearly, it will very quickly become complex for larger molecules to disentangle the Raman or IR active vibrational modes.

The question could then be asked, when to use Raman and when to use IR spectroscopy, or should both be used to study a material. Below a few positive and negative points are discussed:

- Most importantly, Raman and IR are complementary techniques. In most cases (in particular for centrosymmetric molecules) the mutual exclusion principle holds. For more complex modes however, they can be either both inactive, or both active.
- Some vibrations are inherently weak in IR and strong in Raman spectra. For example, the stretching vibrations of triple and double C-C bonds. In general, vibrations are strong in Raman if the bond is covalent (how easily the electrons move to change the polarizability), and strong in IR if the bond is ionic (O-H, N-H). For example, the ratio of triple, double and single C-C bonds in Raman spectra is about 3:2:1, since in general the Raman intensity increases as the slope of the changing polarizability at the equilibrium position becomes steeper.
- Resonant Raman spectroscopy provides an additional advantage to selectively enhance some vibrations, e.g. those of a chromophore group.
- In aqueous solutions, Raman is typically preferred, as the IR modes of H2O are very strong and therefore any other vibrations are hard to detect.
- The disadvantage of Raman spectroscopy, is that a single-frequency laser source is required, which should (in the case of resonant Raman spectroscopy) be tuneable to one of the electronic transitions of the system.
- Another disadvantage of Resonant Raman spectroscopy is that even if the Raman modes are strongly enhanced, when exciting a sample strong fluorescence backgrounds will make those Raman modes hard to detect.

Finally it should be noted that vibrational (both IR and Raman) spectroscopy is applicable to the solid state as well as to the gaseous state and in solution.

5. Resonant Raman spectroscopy.

As previously stated, resonant Raman scattering occurs when the sample is irradiated with an exciting line whose energy corresponds to that of an electronic transition, e.g. of a particular chromophoric group in a molecule. Under these conditions, the intensities of the Raman bands originating in this chromophore are selectively enhanced by a factor of 10^3 to 10^5. This selectivity is important not only for identifying vibrations of this particular chromophore in a complex spectrum, but also for locating its electronic transitions in an absorption spectrum.

Theoretically, the intensity of a Raman band observed at a particular frequency is given by:

$$I_{mn} \sim I_0 (v_L - v_{mn})^4 \sum_{\rho\sigma} |(\alpha_{\rho\sigma})_{mn}|^2 \qquad \text{(Eq. 32)}$$

Here, m and n denote the initial and final states, respectively, of the electronic ground state. I_0 is the intensity of the incident laser beam of frequency v_L. The term $(v_L - v_{mn})^4$ expresses the scattering term of light. Finally, $(\alpha_{\rho\sigma})_{mn}$ represents the change in polarizability caused by the transition, and ρ and σ are the x,y,z components of the polarizability tensor. The latter term can be rewritten as:

$$(\alpha_{\rho\sigma})_{mn} = \frac{1}{h} \sum_e \left(\frac{M_{me}M_{en}}{v_{em} - v_L + i\Gamma} + \frac{M_{me}M_{en}}{v_{en} + v_L + i\Gamma} \right) \qquad \text{(Eq. 33)}$$

Where e is the electronic excited state involved in the Raman scattering, v_{em} and v_{en} are the frequencies corresponding to the energy differences between the states subscribed and M_{me} etc. are the electronic transitions moments, such as

$$M_{me} = \int \Psi_m^* \mu_\sigma \Psi_e d\tau = \langle \Psi_m | \mu_\sigma | \Psi_e \rangle \qquad \text{(Eq. 34)}$$

Where Ψ_m and Ψ_e are the total wavefunctions of the m and e state, respectively, and μ_σ is the σ component of the electric dipole moment. Γ is the band width of the electronic state, and the term $i\Gamma$ represents the damping constant (line broadening of the Raman line).

From equation 33, it can be clearly seen that if the laser approaches the electronic transition energy ($\nu_{em} - \nu_L$) becomes zero, hence this term, the so-called resonance term, becomes so large that the intensity of this Raman band increases enormously. This phenomenon is called **resonance Raman scattering**.

6. Instrumentation.

6.1 IR spectroscopy: the dispersive monochromator
A first manner to measure IR spectroscopy, is similar as regular UV-VIS absorption spectroscopy. An IR source is send to the sample after which a monochromator is used to detect the absorbed IR light as a function of wavelength. A reference arm is included, together with a chopper wheel to perform the experiment with phase-sensitive detection. Although this is a very easy manner to detect IR absorption, the spectral resolution of the IR spectrometer is determined by the grating monochromator and is thus diffraction limited (and can be quite large for IR light with respect to UV-vis-NIR light). As vibrational damping factors are typically very small and thus line widths are also very narrow, this technique has its limitations to provide sufficient resolution for IR absorption.
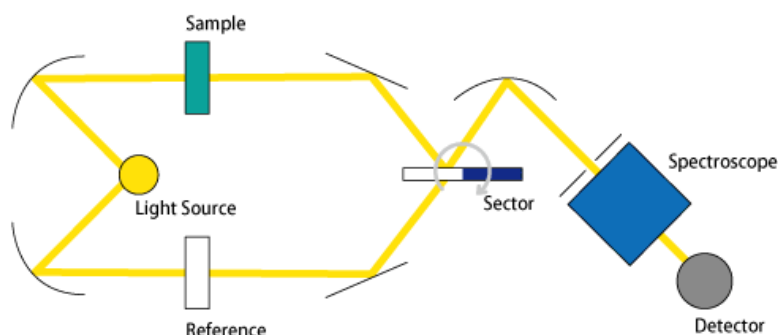

Figure 9: Example of a grating monochromator separating the spectral components in IR absorption[3]

6.2 IR spectroscopy: the fourier-transform technique
The more frequently used technique for IR spectroscopy is FT-IR, or fourier-transform IR spectroscopy, which makes use of a Michelson interferometer (see Figure 11). In this case, IR light is split up by a beam splitter and send either to a fixed mirror or a moving mirror. After returning to the beam splitter, constructive or destructive interference will occur for the different IR wavelengths, depending on the difference in pathlength between the fixed and moving mirror. If this distance is proportional to an even times the wavelength, the waves will add constructively. Therefore, the interferometer selects only one wavelength that is added constructively and is send to the sample. The resolution is now determined by how accurately the mirror can be moved, and no longer by the diffraction limit. A spectrum, called an interferogram, is measured as a function of the moving mirror position. Afterwards a fourier transformation yields the absorption spectrum.

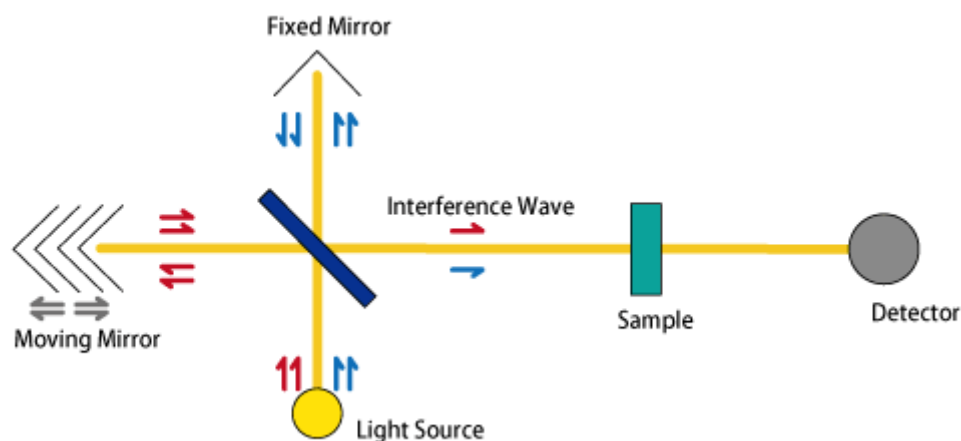[3] https://www.jasco-global.com/principle/principles-of-infrared-spectroscopy-2-history-of-ir-spectrometers/

Figure 10: Example of a FT-IR spectrometer[4]

6.3 <u>Raman spectroscopy</u>

In Raman spectroscopy, a laser excites the sample after which the scattered light is detected either in 90° degree configuration or back-scattering configuration. To have ultimate spectral resolution, while blocking any unwanted light from e.g. the much stronger Raileigh scattering, typically 3 spectrometers are put in series with each other as presented in Figure 12.
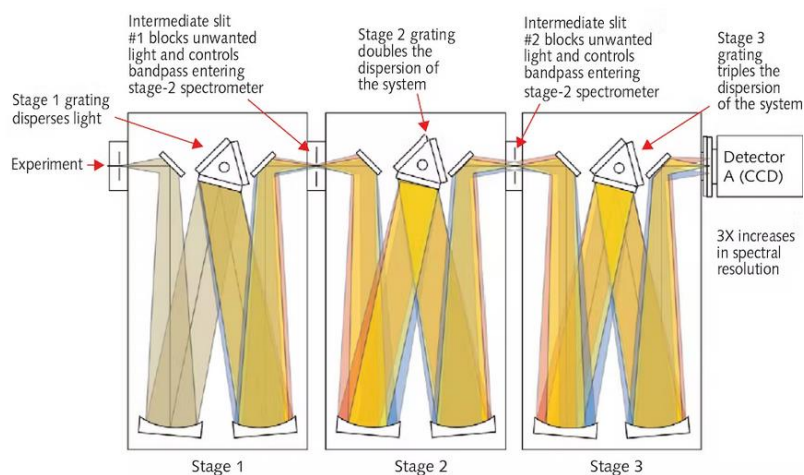

Figure 11: Example of a triple grating Raman spectrometer[5]

7. Surface-enhanced Raman spectroscopy.[6]

When performing spectroscopy on individual nano-objects, the Raman intensity is often very small. Therefore, techniques have been developed to enhance the Raman intensity of such nano-objects. They are referred to as surface-enhanced Raman spectroscopy (SERS), tip-enhanced Raman spectroscopy (TERS) or plasmon-enhanced Raman spectroscopy (PERS). Each of these techniques, would not exist without the particular optical properties of metals (with silver, Ag, and gold, Au, as the mostly used metals). Before discussing the technique, let us first look at the optical properties of bulk metals such as Ag and Au.

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[4] https://www.jasco-global.com/principle/principles-of-infrared-spectroscopy-2-history-of-ir-spectrometers/

[5] https://www.laserfocusworld.com/test-measurement/article/14203430/efficient-raman-spectroscopy-for-materials-science

[6] This part is based on the book: S. Schlücker et al, Surface enhanced Raman Spectroscopy: Analytical, biophysical and Life Science Applications, WILEY-VCH Verlag, Weinheim 2011

7.1: bulk metals

The optical properties of bulk materials are characterized by their dielectric function $\varepsilon(\lambda)$, with λ the wavelength of the light. The dielectric function of a bulk material is related to the refractive index of a material through: $n(\lambda) = \sqrt{\varepsilon(\lambda)}$. Both the refractive index and the dielectric function depend on the wavelength of light. In geometric optics, when discussing lenses and prisms etc, one considers the refractive index and the dielectric function as positive real numbers ($n, \varepsilon \geq 1$). This is related to the theory of relativity, where it is shown that information cannot travel faster than the speed of light in vacuum. However, this does not mean the refractive index cannot be less than one, since the refractive index measures the phase velocity of light, which does not carry information. This phase velocity is the rate at which e.g. the crest of a wavelength (i.e. the point at which the electric field is maximum) propagates in any medium, and is given as $v = \lambda/T$ with T the time period. This can e.g. occur close to resonance frequencies. For example, water has a refractive index of 0.99999974 for X-ray radiation at a photon energy of 30keV.[7]

The fact that the refractive index should be real is a large approximation. For most materials, the dielectric constant at a given wavelength will be a complex number ($\underline{n} = n + i\kappa$): where the real part, n, is the refractive index that indicates the phase velocity, and the imaginary part, κ, is the extinction or absorption coefficient, and indicates the amount of attenuation when the electromagnetic wave propagates through the material. This is often neglected in lens physics and geometric optics, but can of course not be neglected in metals, which are clearly not transparent materials. The optical properties of materials are of course governed by their electronic structure.

Figure 13 shows the dielectric functions of Ag and Au with their real and imaginary parts throughout the UV-vis-NIR wavelength range. Figure 13 is showing analytical interpolations for a collection of experimental results for $\varepsilon(\lambda)$ obtained with different techniques. The main characteristics of the real and imaginary parts of the bulk $\varepsilon(\lambda)$ for both metals can be summarized as follows:

- The real part for most of the visible range, is both large (in magnitude) and negative. This negative sign is crucial for the SERS experiments. Ignoring the much smaller imaginary parts momentarily, the real parts follow (at long wavelengths) one of the simplest models for the dielectric function of a metal, namely the Drude model, which predicts a $-\lambda^2$ dependence, more precise:

$$\varepsilon(\lambda) = \varepsilon_\infty \left(1 - \frac{\lambda^2}{\lambda_p^2} \right) \qquad \text{(Eq. 39)}$$

  With λ_p the so-called plasma frequency of the metal, which is proportional to the square root of the density of free electrons in it. Figure 13 shows that both Ag and Au have very similar electronic densities, since the real parts of their dielectric functions are not too different from each other.

- Real bulk materials are not transparent, and that is where the imaginary part comes into play. Even though the imaginary parts are much smaller than the real parts for most of the visible range, their effects are important and in fact crucial for SERS. As mentioned above, the imaginary part is related to the extinction coefficient thus to the absorption of the material. From Figure 13 it can be seen that the imaginary parts of Au and Ag are very different. For Au, electronic transitions in its band structure, so-called interband electronic transitions result in the two 'bumps' observed below 600nm. At longer wavelengths, the imaginary parts line up, demonstrating that in view of electromagnetic response both materials will respond very similarly (since both real and imaginary parts are very similar). Experimentally, one material can be preferred over the other for specific chemical reasons, but as far as their electromagnetic response they can be considered the same in this wavelength range.

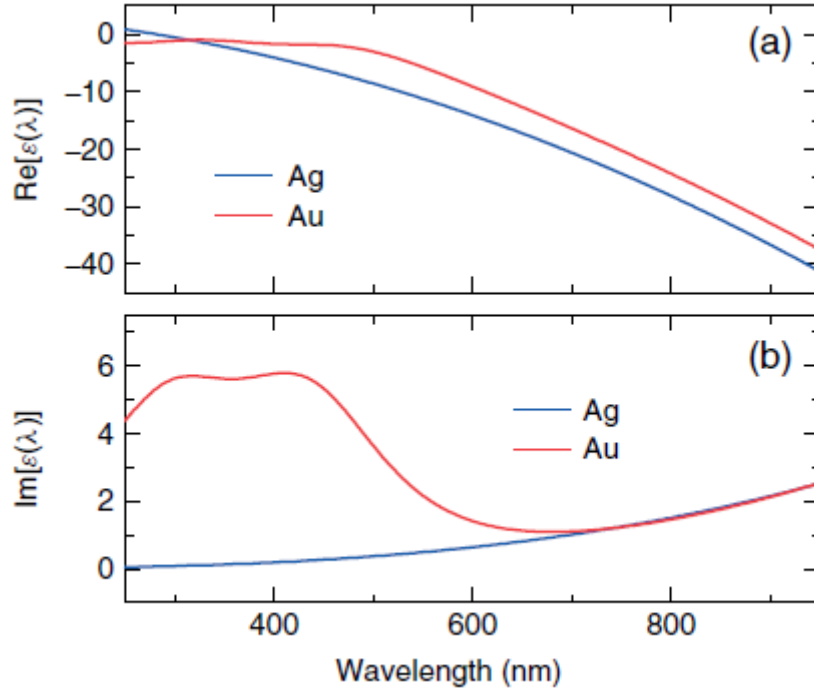[7] https://henke.lbl.gov/optical_constants/

Figure 12: Real and imaginary parts of the dielectric function for the two must used materials in SERS. Note the different vertical scales and signs for the Real and Imaginary parts.

7.2: Planar surfaces

Let us now consider planar surfaces of Ag or Au. When sending light with a specific wavelength from medium 1 to such a planar surface, the normal reflectance R (in the direction perpendicular to the surface) arises as a natural consequence of matching the boundary conditions of the light fields left and right of the interface (see Figure 14a). These boundary conditions require that the components of the electric field parallel to the surface are equal, as well as the perpendicular components of the displacement vector $\boldsymbol{D} = \varepsilon(\lambda)\boldsymbol{E}$, or in other words:

$$E_i^{\parallel} = E_t^{\parallel} \text{ and } \varepsilon_1(\lambda)E_i^{\perp} = \varepsilon_2(\lambda)E_t^{\perp} \tag{Eq. 40}$$

The normal reflectance R is then given by:

$$R = \left|\frac{n_2 - n_1}{n_1 + n_2}\right|^2 \tag{Eq. 41}$$

With $n_i = \sqrt{\varepsilon_i(\lambda)}$ the refractive index of the medium 1 or 2, with medium 2 the metal. When looking at the reflectivity in Figure 14b it can be seen that the reflectivity of Ag is very high throughout the visible range, while for gold the reflectivity below 600nm is quite low (50%). This is the reason of the yellowish color of flat gold, whereas silver is used as a mirror in the visible. On the other hand, gold can be used as a much better mirror for NIR applications.
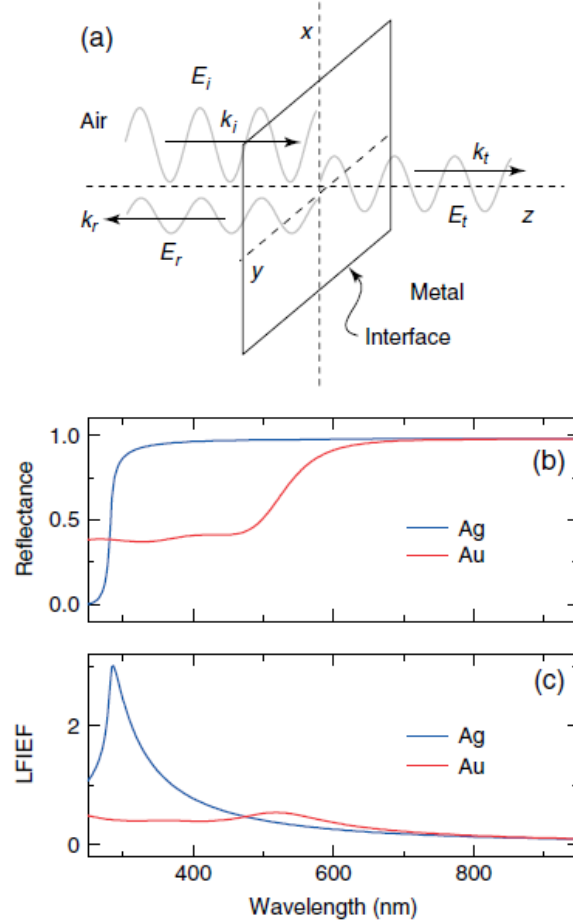
Figure 13: (a) schematics of an incoming electric field of light on an interface with a metal, resulting in transmitted and reflected waves. (b) reflectance and (c) local field intensity enhancement factor (LIFEF) at the surface of the metal.

The most important and interesting aspect, is what happens at the surface of the Au or Ag planar surface, also referred to as the Local Field intensity Enhancement Factor (LIFEF). Or in other words, at the surface the intensity of the electromagnetic field will be enhanced with respect to the intensity if the metal would not be there, which is described by the LIFEF. This local field intensity is described by the square of the electric field amplitude at a particular position and thus the LIFEF is described as:

$$\text{LIFEF}(\boldsymbol{r}) = \frac{|E(\boldsymbol{r})|^2}{|E_0(\boldsymbol{r})|^2} \qquad \text{(Eq. 42)}$$

The LIFEF is thus a dimensionless parameter expressing the change in the electric field intensity at the surface. If the LIFEF is larger than one the optical field is enhanced, if it is smaller than one it is quenched. Obviously, the LIFEF will also depend on the wavelength of light, as shown in Figure 14c. For normal incidence, and immediately at the flat surface the LIFEF corresponds to:

$$\text{LIFEF} = \left| \frac{4n_1}{n_1 + n_2} \right|^2 \qquad \text{(Eq. 42)}$$

And thus the LIFEF depends on the dielectric properties of the material. Note also in Figure 13 that a high reflectivity corresponds to a low LIFEF. Indeed a 100% reflective metal will create a field on the surface that cancels exactly the incoming one ($E_i + E_r = 0$) thus cancelling also the transmitted field ($E_t = 0$). Therefore a low LIFEF, achieved by the condition $E_i \approx -E_r$, yields a high reflectivity.

From figure 14 we could conclude that only in terms of wavelengths below 400nm, Raman spectroscopy would benefit from bringing the molecules under investigation in the proximity of a Ag surface, as then the local field is enhanced by a factor of 2, or in other words, the Raman intensity will be enhanced by the same factor. From this, we could thus conclude that metals do not bring much to win for Raman spectroscopy, however everything becomes much more interesting when considering particular shapes of these metals.

7.3: a metallic sphere (3D) or cylinder (2D)

When we want to know what happens to the electromagnetic field around a spherical or cylindrical particle, one would need to solve Maxwell's equations with the appropriate boundary conditions. This can however be very challenging. Analytical solutions for some shapes and simple geometries exist, which are useful to underpin the basic concepts and ideas. Figure 15 shows such an analytical solution for a cylinder, when the light is propagating as shown in panel Figure 15a, for Ag and Au cylinders with a radius much smaller than the wavelength of light. The external field induces an induced dipole within he metal, and a LIFEF at point A for Ag or Au at very different wavelengths and with very different magnitudes. Assume now that you have a molecule, that is resonant at about 320 nm, one could use this LIFEF to enhance the already resonant Raman signal by more than a factor of 450, by just bringing the molecule under investigation to point A. Similarly, one could use Au nanorods to enhance the signal of molecules that are resonant in the range of 500-600nm.
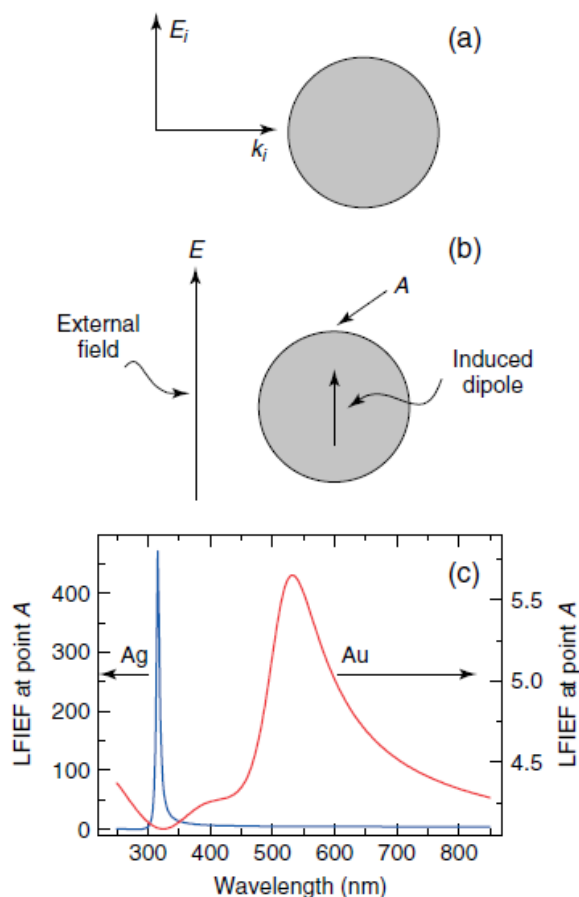

Figure 14: (a) a cylindrical metallic object that is irradiated by an electromagnetic wave coming from the side. (b) when the object is small with respect of the wavelength (~10-20nm), one can analytical solve the Maxwell equations, yielding the LIFEFs as shown in panel (c) for both gold (left axis) and Ag (right axis) obtained at point A indicated in panel (b).

The exact solution of a 2D cylinder with dielectric function $\varepsilon(\lambda)$ can be calculated, considering the superposition of the external electric field with the induced dipole centered at the origin, as shown in Figure

15. For points outside of the cylinder, the electric field looks like the superposition of this dipole, and this induced dipole is proportional to:

$$p \propto \frac{\varepsilon(\lambda) - \varepsilon_M}{\varepsilon(\lambda) + \varepsilon_M}$$

(Eq. 43)

With ε_M the (non-absorbing) medium in which the nanorod is embedded. Looking at the denominator, the interesting part to get a high LIFEF is when the real part of $\varepsilon(\lambda)$ approaches $-\varepsilon_M$. In that case, the magnitude of p will only depend on the small imaginary part of $\varepsilon(\lambda)$, and this will show as a resonance, called the dipolar localized surface plasmon (LSP) resonance of the cylinder. The fact that metals have negative real parts makes them ideal to satisfy these resonance conditions in many solutions and environments ε_M.

Objects with other shapes, will have other resonance conditions. For example, analytical results for a metallic Au or Ag sphere are shown in Figure 16, where the induced dipole in point A now corresponds to:

$$p \propto \frac{\varepsilon(\lambda) - \varepsilon_M}{\varepsilon(\lambda) + 2\varepsilon_M}$$

(Eq. 44)

Where the factor 2 in the denominator stems from the fact that here a 3D problem needs to be solved, instead of a 2D problem in the case of the cylinder.
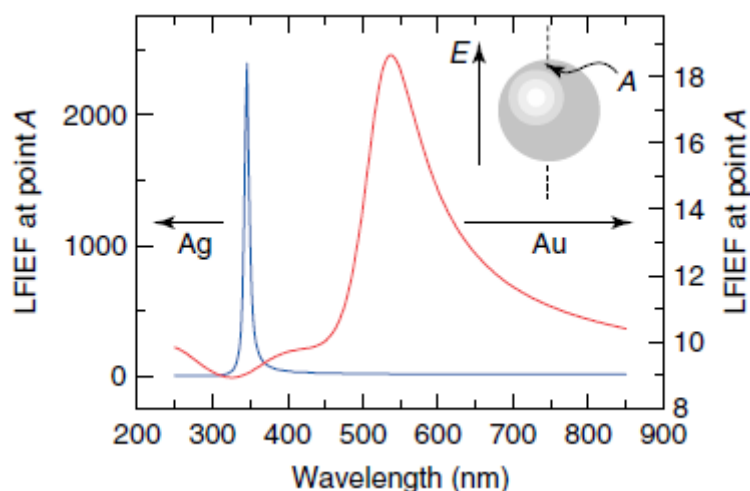

Figure 15: LIFEF for spheres of either Au or Ag.

As such, it can be shown that extremely high LIFEFs can be found depending on the size and shape of the metallic particles, where more examples will be shown in the class. Most important to remember is that in particular cases, enhancements of more than a factor of 1000 can occur, yielding therefore ideal conditions to measure Raman spectroscopy (and also other spectroscopy like fluorescence or IR absorption) of individual nano-objects. In the remaining of this chapter, I will discuss two possibilities to tune the LIFEF by wavelength and intensity.

7.4: tuning the LIFEF by combining two metallic spheres.

Figure 17 presents the details of how the LIFEF can be tuned in wavelength when combining the LIFEFs of two metallic spherical particles, and changing the distance between the two particles. By playing with the shape, size and position of the particles, as well as the polarization of the incoming laser light, one can thus obtain giant enhancement factors up to 5 orders of magnitude.
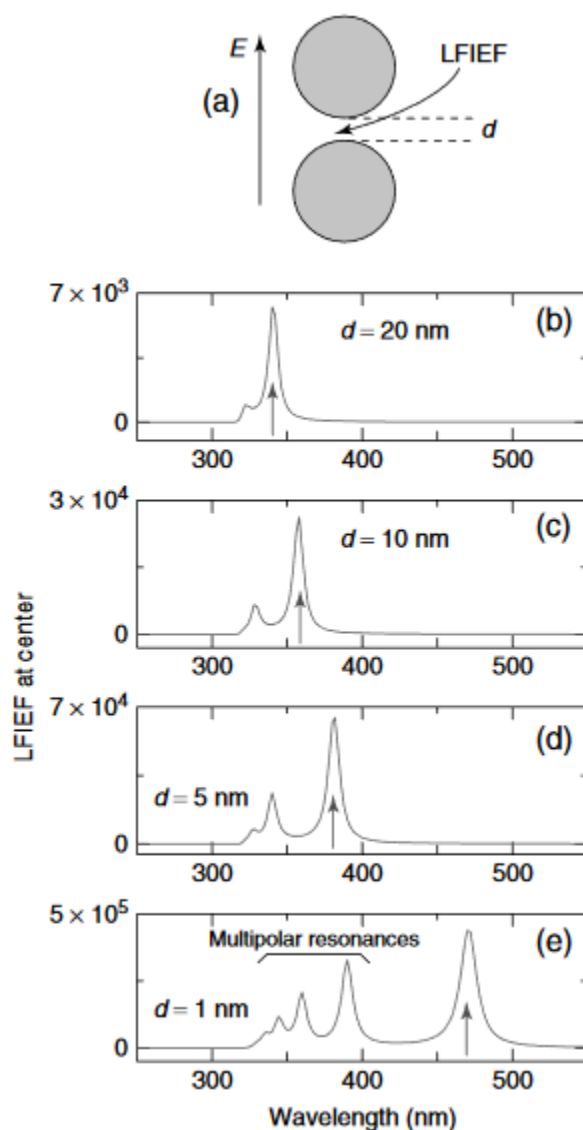
Figure 16: LIFEF for two spheres. By playing with the distance between the two spheres, other wavelengths can be targeted.

7.5 Tip-enhanced spectroscopy

The positioning of the particles at the exact position of molecule is of course not very easy to do, therefore tip-enhanced Raman spectroscopy has been developed. In this instrumentation, an AFM tip with a particular shape such that its LSP is resonant with the exciting laser beam is used as the method to induce the LIFEF. This allows not only to have a high LIFEF, but also to confine this LIFEF in a very small spatial spot in the sample. The AFM tip can then be scanned over the sample and when the tip approaches the molecule of interest, it can enhance its Raman spectrum through the obtained LIFEF. The main advantage of using this technique is that it provides a way to perform optical imaging with a spatial resolution of at least a factor of 10 below the diffraction limit, also referred to as super-resolution imaging.

In recent years, a lot of progress is made by designing specific AFM tips with different shapes to make them resonant at different wavelengths. Examples of these results will be shown during the class.