

5. Spectroscopy

Introduction to Spectroscopy

Spectroscopy is the scientific study and measurement of the interaction between matter and electromagnetic radiation. It involves the analysis of how different substances absorb, emit, or scatter electromagnetic radiation at various wavelengths, which provides information about the composition, structure, and properties of substances. Different spectroscopic techniques are used to examine different regions of the electromagnetic spectrum. For example,

- ▶ Atomic spectra (X-ray)
- ▶ Electronic spectra (UV/Vis)
- ▶ Vibrational spectra (Infrared and Raman)
- ▶ Rotational spectra (Microwave)

We will primarily focus on the study of vibrational spectroscopy techniques in this course.

Basic Definitions

In the realm of quantum mechanics, wave-particle duality suggests that both light and matter can exhibit dual behaviours, behaving as either particles or waves. For example, light can be described as photons or as electromagnetic waves. The Planck-Einstein relation relates the energy (E) of a photon of light to its frequency (ν):

$$E = h\nu$$

where h is the Planck's constant. This equation can also be expressed in terms of the wavelength λ or the wavenumber $\tilde{\nu}$:

$$E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu}$$

where

$$\lambda = \frac{c}{v}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

and c is the speed of light. The unit of ν is Hz (1/s), λ is m and $\tilde{\lambda}$ is m^{-1} . In vibrational spectroscopy, the more common unit of $\tilde{\lambda}$ is cm^{-1} .

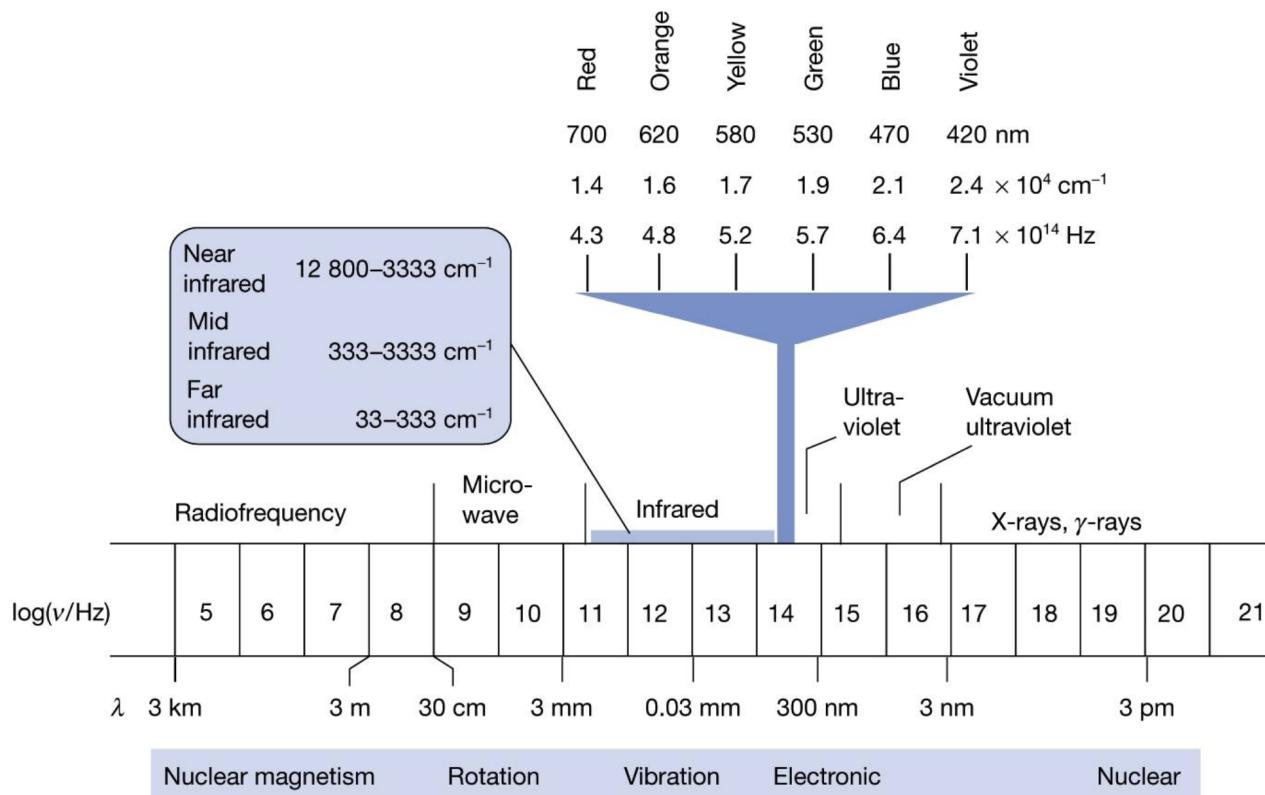
Interactions of Light and Matter

The interaction of light with matter involves the exchange of energy between the two. In some situations, matter can emit energy in the form of light and transition from an excited state to a lower energy state. Matter can also absorb energy from incident light of specific wavelengths, which results in an increase in their energy state. However, for absorption or emission to occur, the energy of the incident light must be precisely equal to the energy difference between two allowed energy states within the atom or molecule. This is the necessary condition for such energy exchanges and iterates the principle of spectroscopy, which is frequency-matching resonance.

Vibrational spectroscopy is based on the exactly parallel principle, where the frequency of absorbed radiation exactly matches the vibrational frequency of a functional group in a molecule. Molecules have various types of vibrational motions, where atoms within the molecule move in specific ways. These vibrations involve stretching, bending, and twisting of chemical bonds. Each type of vibration occurs at a specific frequency, which corresponds to a particular energy level.

The electromagnetic radiation emitted/absorbed by the sample can be expressed compactly in an electromagnetic spectrum: when incident radiation matches the energy levels associated with molecular vibrations, the molecules can absorb specific frequencies of light, leading to characteristic absorption bands in the spectrum. Therefore, characterising the wavelengths of the electromagnetic radiations provides information about the functional groups present in the sample.

Moreover, from the full electromagnetic spectrum:



The frequencies of molecular vibrations are in the mid-infrared region ($4000 - 400 \text{ cm}^{-1}$), making infrared (IR) spectroscopy particularly useful for characterising molecular vibrations.

Molecular Vibrations

To fully comprehend infrared spectroscopy, it is imperative to first understand the fundamental principles underlying molecular vibrations.

Harmonic Oscillator

The harmonic oscillator model depicts the vibrational motions of a particle in a potential energy well that resembles a harmonic oscillator potential in classical mechanics. Essentially, when a bond vibrates, they behave like springs, and can be described as harmonic oscillators. From Hooke's law:

$$F = -kx$$

where F is the force, k is the force (spring) constant and x is the displacement. The potential energy V stored in vibration is therefore:

$$V = \int -F dx = \int kx dx = \frac{1}{2} kx^2$$

Also, from Newton's second law:

$$F = ma = m \frac{d^2 x}{dt^2} = -kx$$

where m is the mass of the particle. For a simple harmonic motion, the displacement can be describe as a sinusoidal wave:

$$x = A \sin(\omega t + \phi)$$

Substitute this into Newton's second law:

$$m \frac{d^2 x}{dt^2} = -m\omega^2 A \sin(\omega t + \phi) = -m\omega^2 x = -kx$$

$$\therefore \omega = \sqrt{\frac{k}{m}}$$

where ω is the angular velocity. Therefore, the frequency of the vibration ν can be obtained:

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

For this problem, the boundary condition states there is no infinitely large compressions or extensions. The oscillator will not be found with infinite displacements. This restricts the allowed energies the particle can possess and is given by:

$$E = \left(v + \frac{1}{2}\right) h\nu = \left(v + \frac{1}{2}\right) \hbar\omega, \quad v = 0, 1, 2, \dots$$

where v is the quantum number. As a result, vibrational energy is quantised, and the separation between adjacent energy levels is:

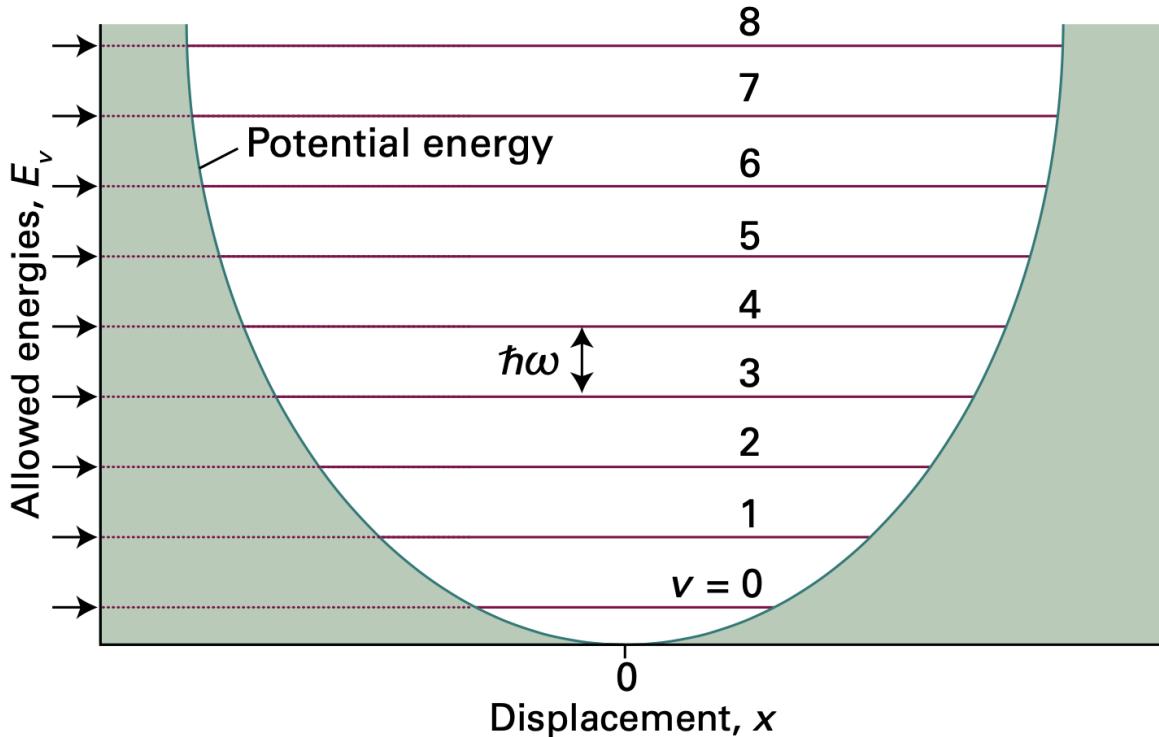
$$\Delta E = h\nu = \hbar\omega$$

It is therefore possible to link this energy level difference to the energy carried by a photon. Upon obtaining ΔE from the IR spectrum, k can be calculated.

Furthermore, when $v = 0$, the oscillator has a zero-point energy:

$$E_0 = \frac{1}{2} h\nu = \frac{1}{2} \hbar\omega$$

Graphically, the energy levels:



Now, substitute the potential into Schrödinger's equation to solve for the wavefunctions:

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} + \left(\frac{2\mu}{\hbar^2}\right) \left(E - \frac{1}{2}kx^2\right)\psi = 0$$

The wavefunction is then given by:

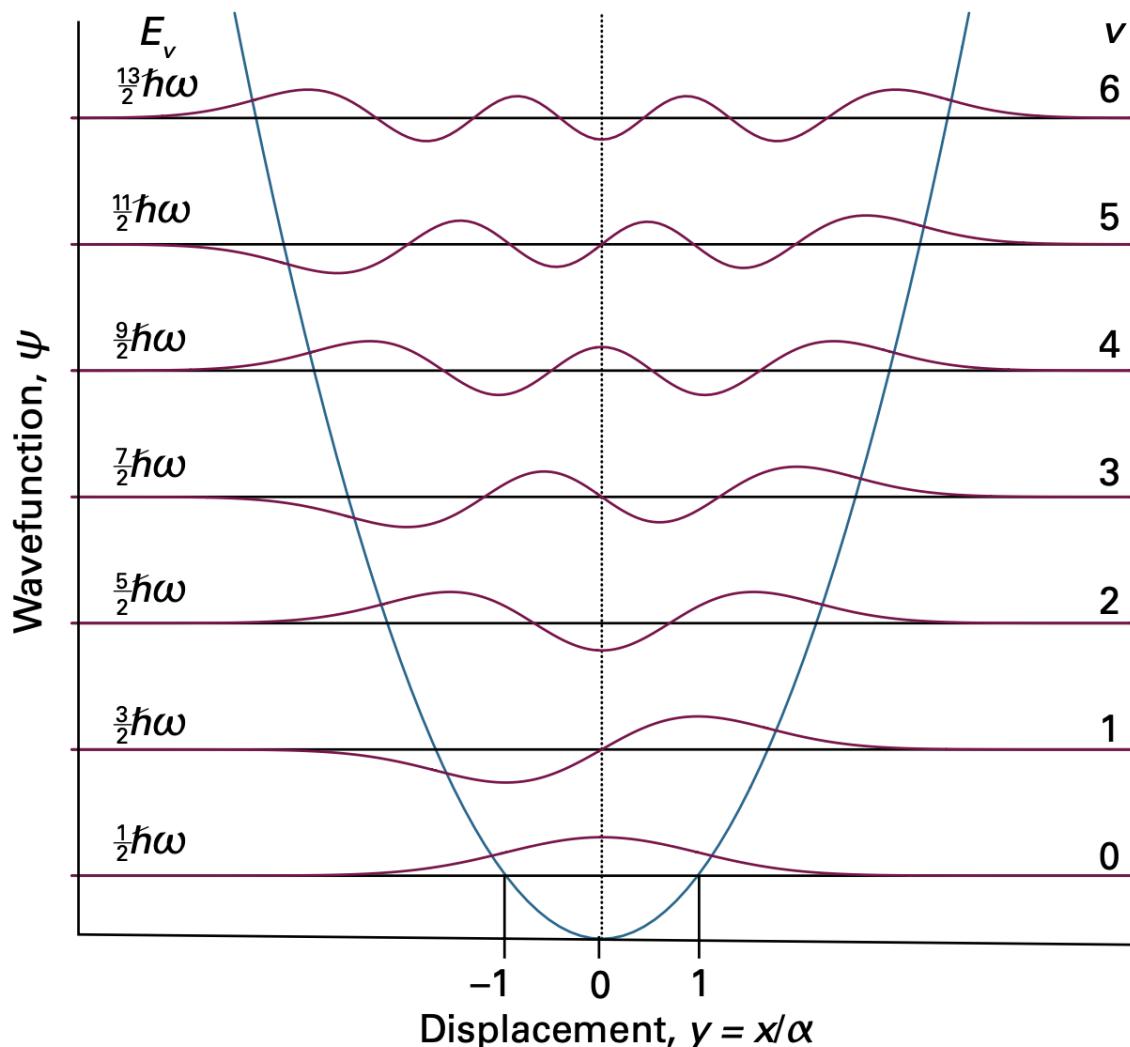
$$\psi = H_v(\xi) e^{\xi^2/2}$$

where H_v is Hermite's polynomial of order v:

v	H_v
0	1
1	ξ
2	$4\xi^2 - 2$

and ξ is the dimensionless displacement given by:

$$\xi = \frac{x}{\alpha}; \quad \alpha^4 = \frac{\hbar^2}{km}$$



Since ξ is dependent on km , the wavefunction decays more rapidly for larger masses and stiffer springs. As energy separation is also dependent on k and m , stiffer bond and smaller mass increases energy separation.

However, energy transitions induced by external perturbations (such as emission/absorption of photons) are limited by the selection rule, which states that a transition between two energy levels is only allowed if the change in the quantum number, Δv , is equal to ± 1 . In other words, the allowed transitions occur between energy levels that differ by a single quantum number.

Vibrations of Diatomic Molecules

When two atoms are present, the same expression for energy levels can still be used by replacing the mass m with the reduced mass μ :

$$E = \left(v + \frac{1}{2} \right) h\nu$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where

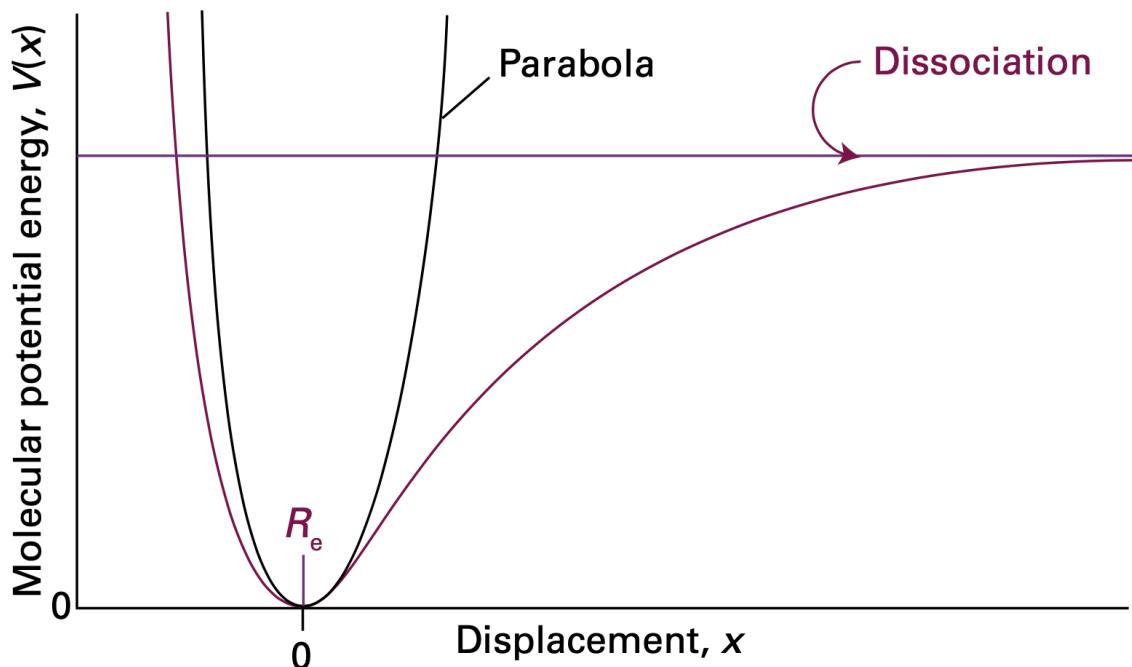
$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \rightarrow \mu = \frac{m_1 m_2}{m_1 + m_2}$$

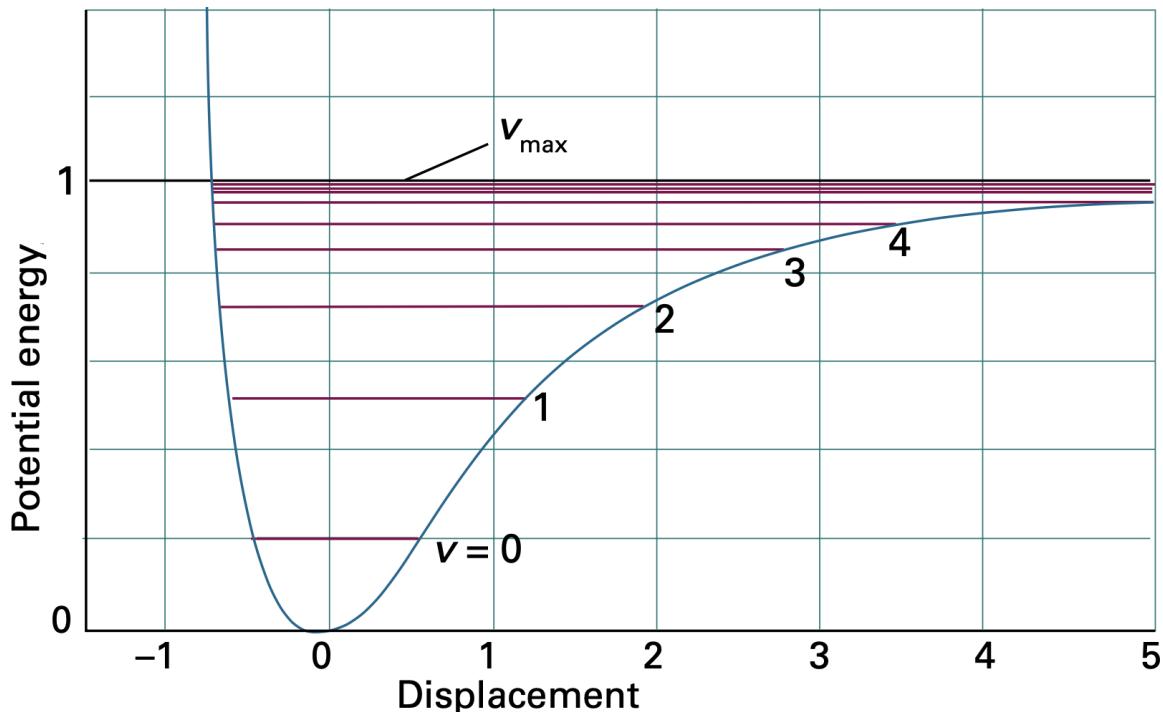
m_n is the mass of particle n . The energy spacing is:

$$\Delta E = h\nu = \hbar\omega$$

Again, this energy level difference can be related to the energy carried by a photon. Upon obtaining ΔE from the IR spectrum, the force constant of the bond k can be calculated.

Another point worth noting is that, in the harmonic oscillator model, the energy spacing between adjacent energy levels was equal, which was dependent on mass and bond stiffness. However, for real molecules, this only works fine for small displacements as bonds in real molecules do not obey Hooke's law exactly. At large displacements, the bond "breaks" and force constant k decreases. Energy separation consequently decreases. The molecular potential is now said to be anharmonic:

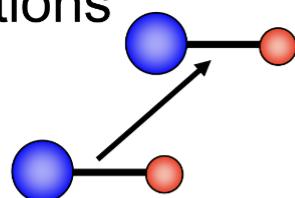




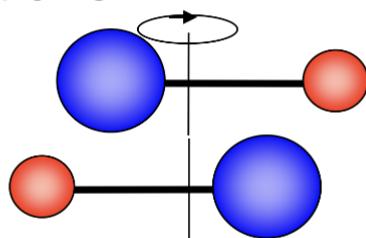
Vibrations of Polyatomic Molecules

Each molecule has three types of motion: translational, rotational and vibrational:

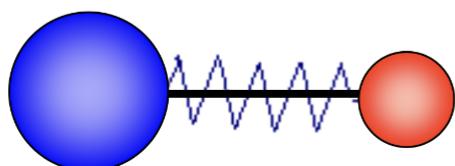
Translations



Rotations

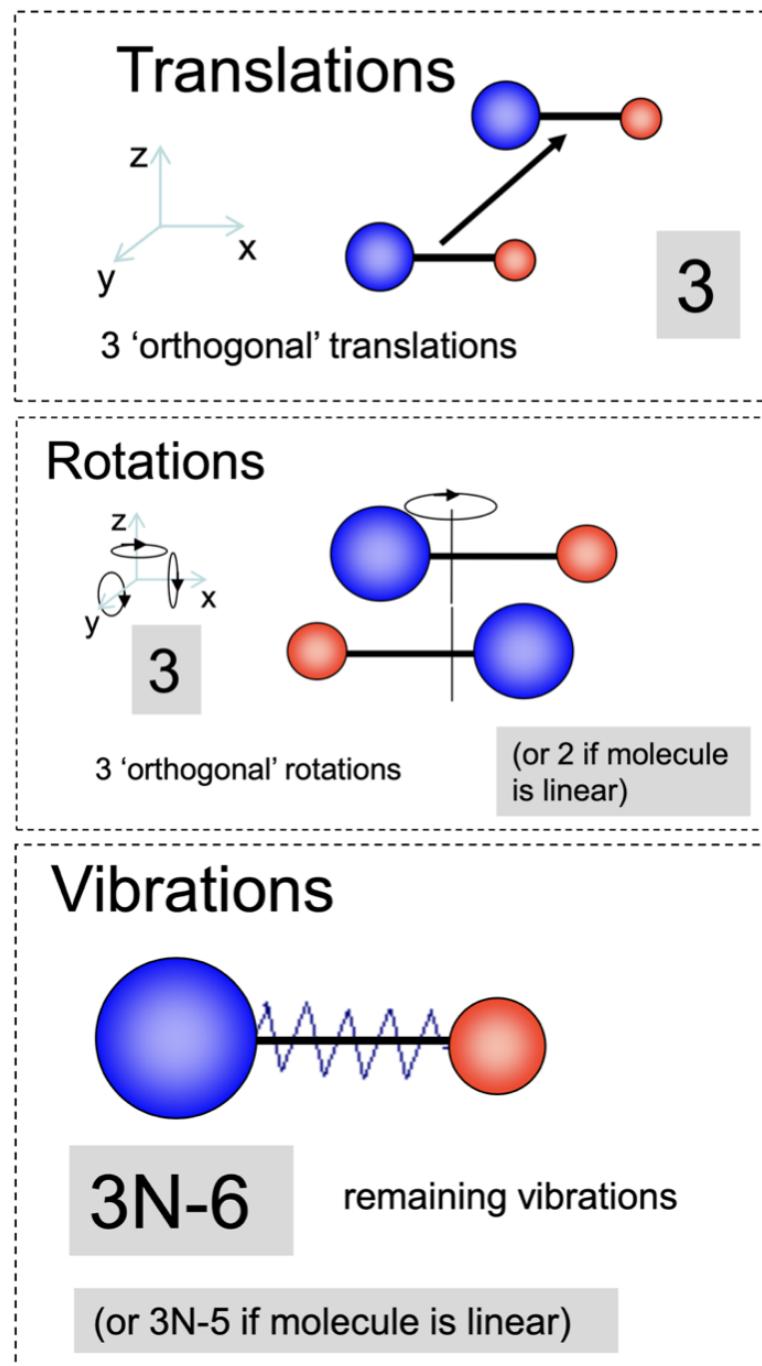


Vibrations



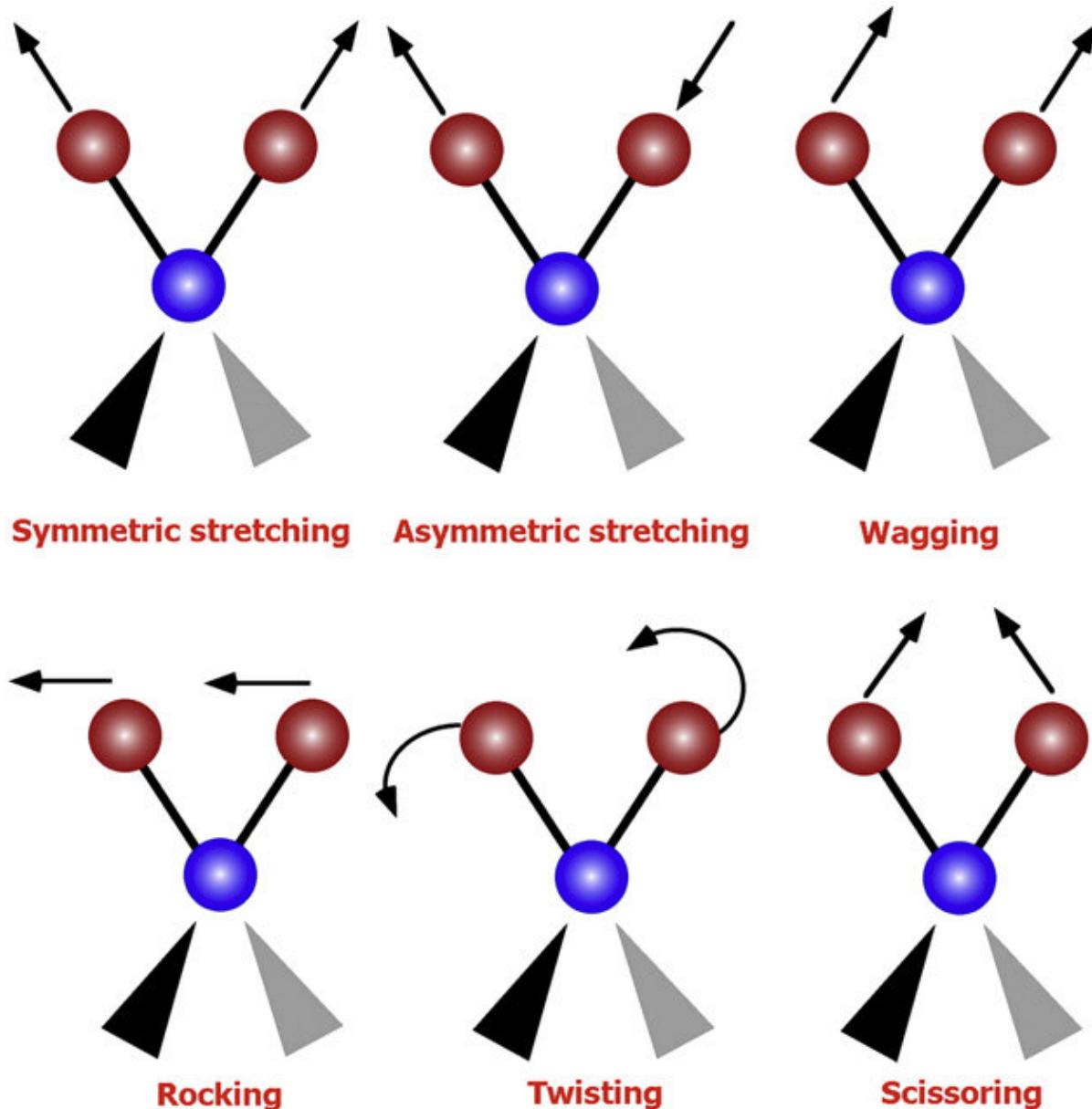
For molecules with $N > 2$ atoms, each of the atoms has 3 ways to move, making the total degrees of freedom (DOF) $3N$. A linear molecule can translate in the x , y and z directions (3 DOF) and can rotate around

2 axis (2 DOF). This means that the number of modes of vibration (the DOF leftover) is $3N - 5$. Non-linear molecules have a third axis of rotation, meaning that the number of vibrational modes becomes $3N - 6$.



Technically, terminology “modes” is referred to as normal modes. Normal mode is an independent, synchronous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode. This concept is introduced as the vibrational motion may be a complicated combination of various forms like stretching and bending, but in the approximation of harmonic distortion (restoring force proportional to deformation) all the motion may be expressed as a superposition of independent harmonic modes, which are the normal modes. Each normal mode has a discrete vibrational frequency, while in some cases, two or more modes may be degenerate.

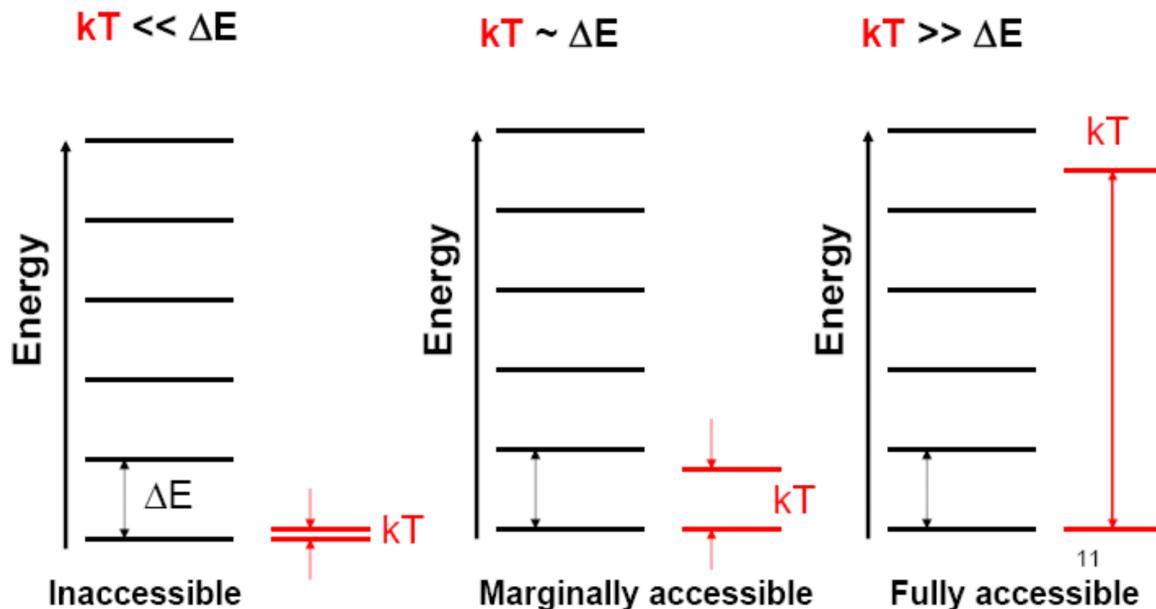
For polyatomic molecules, the [normal modes of vibration](#) are: asymmetric, symmetric, wagging, twisting, rocking and scissoring:



Molecular Spectrum

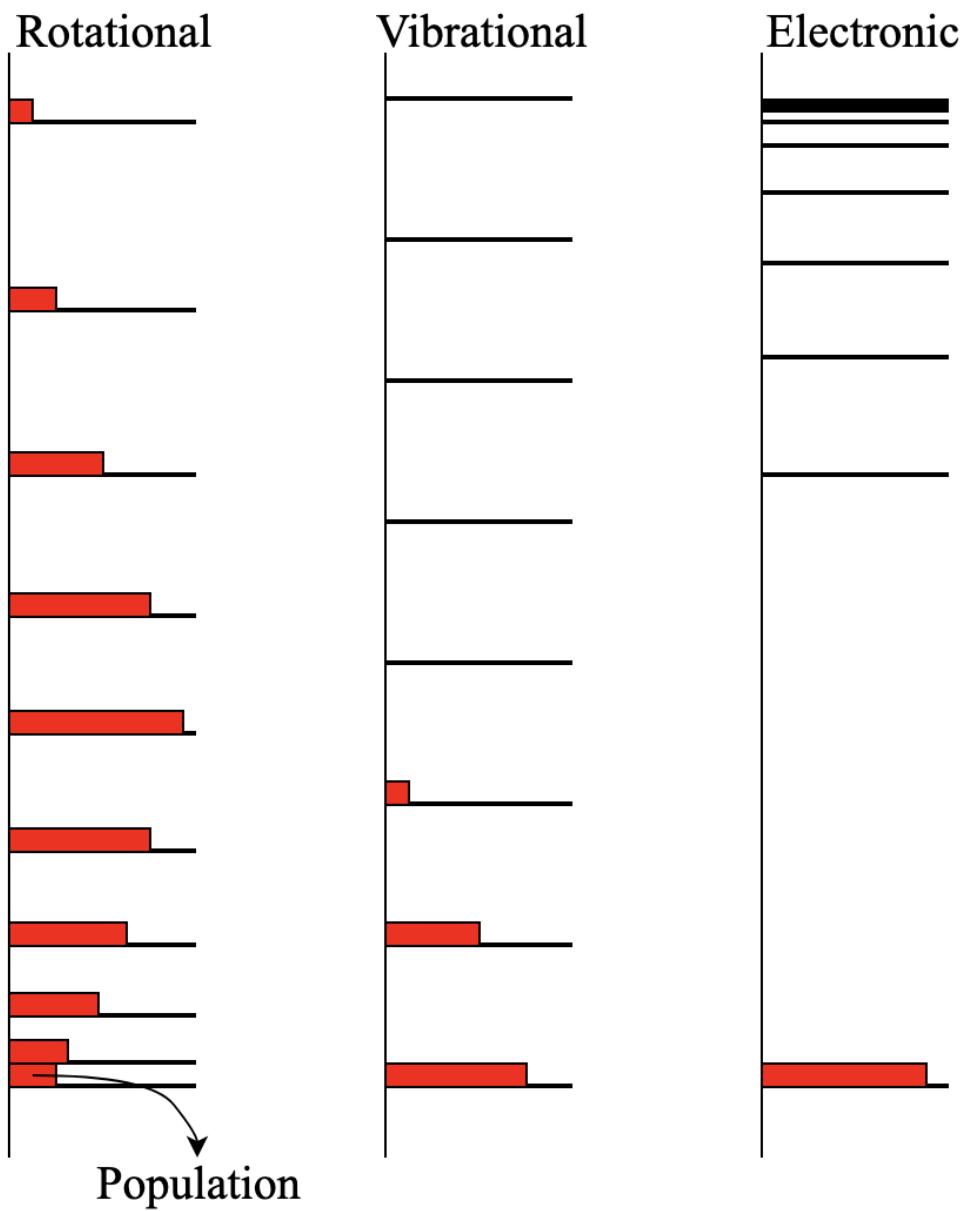
Molecules exhibit not only the aforementioned three modes of motions (vibrational, rotational and vibrational), but also electronic transitions. In any case, the energy levels are quantised, and the energy levels spacing determines whether the transition is accessible at room temperature:

- ▶ If $\Delta E_i \gg kT$, only the lowest energy level will be occupied as very few molecules will have enough energy to reach the next level.
- ▶ If $\Delta E_i \ll kT$, all levels will be evenly populated as they will all have enough energy to jump freely between all energy levels.

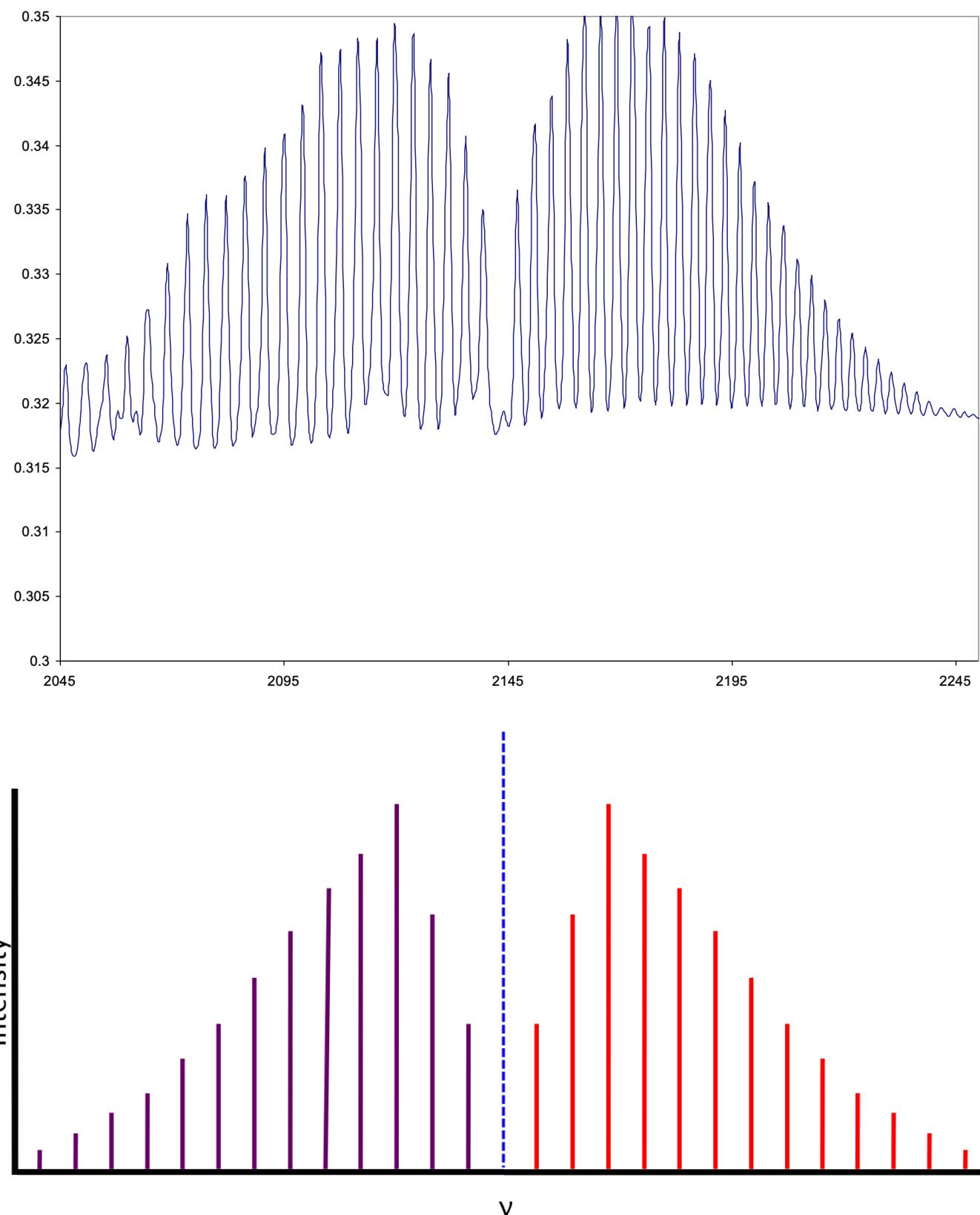


This explains why those various types of energy levels (electronic, vibrational, rotational and translational) are occupied to different extents:

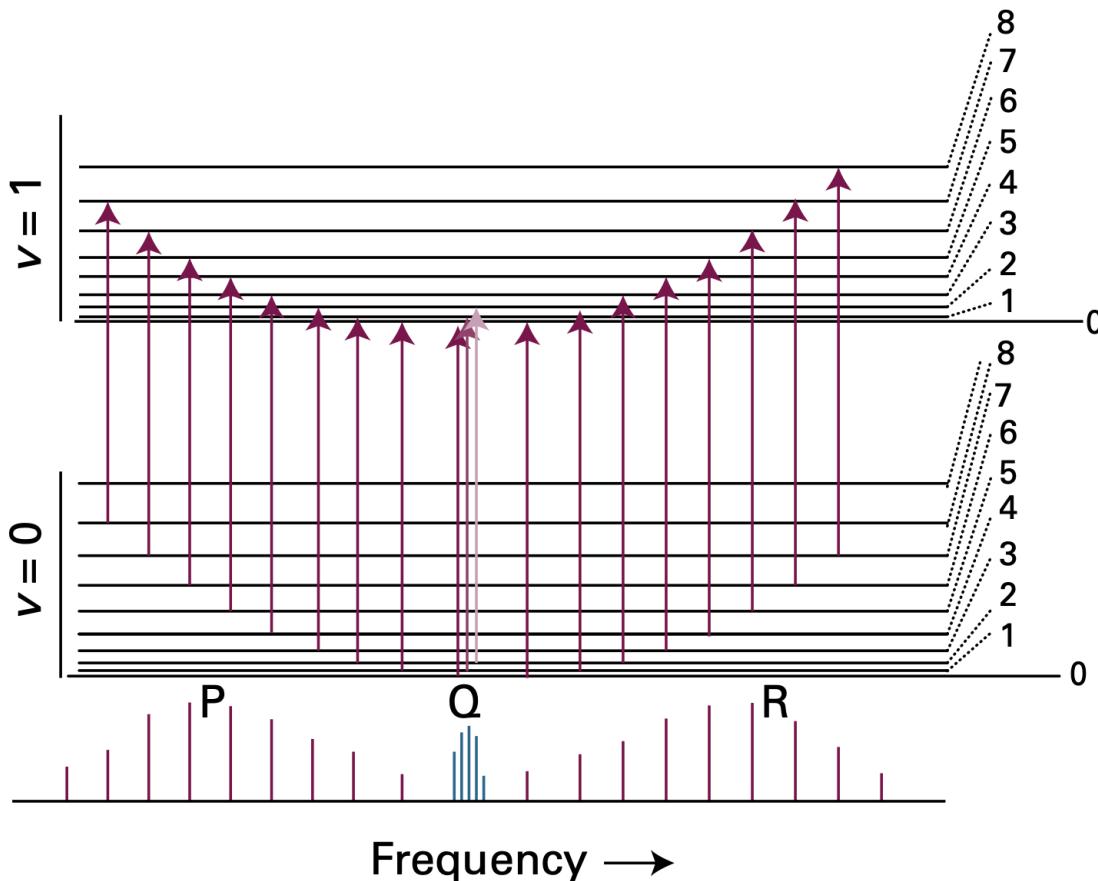
- ▶ The translational energy levels are fully accessible, hence why the levels are usually fully occupied at room temperature.
- ▶ The rotational and vibrational energy levels are marginally accessible. Thus, microwave and infrared radiations are sometimes required to induce such motions.
- ▶ The electronic energy levels are inaccessible as the energy difference is comparatively quite huge, explaining why air does not glow at room temperature. Thus, energy-intense UV or X-ray radiations are required to induce electronic transitions.



In many cases, the rotational and vibrational motions are not completely decoupled. When a molecule undergoes a transition between two energy levels, both rotational and vibrational changes can occur simultaneously, which leads to the appearance of combined rotational-vibrational spectra in spectroscopic measurements.



where the purple and red lines represent the rotational P- and R-branch, the zero-gap blue dotted line represents the rotational Q-branch, which can be used to find the ν .



Infrared Spectroscopy

Selection Rule

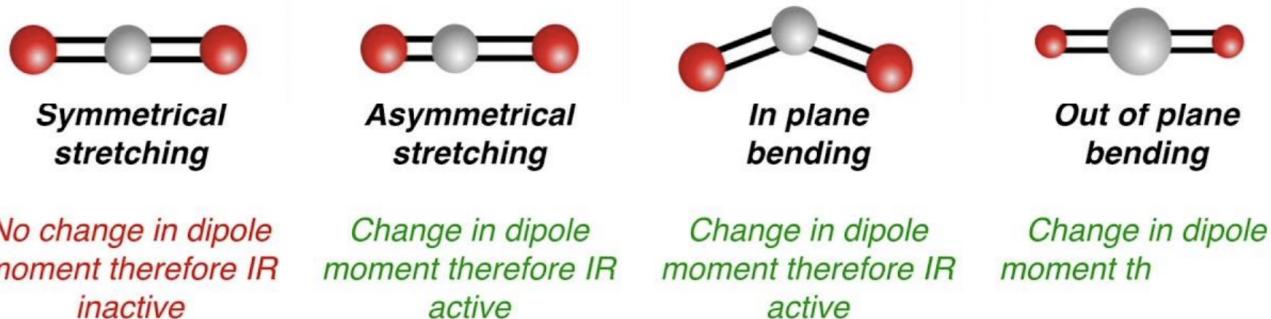
In order for a molecule to be able absorb a photon in spectroscopy, two conditions apply:

- ▶ The photon must have the correct frequency to raise the vibration by one energy level.
- ▶ The molecule must have a changing dipole moment.

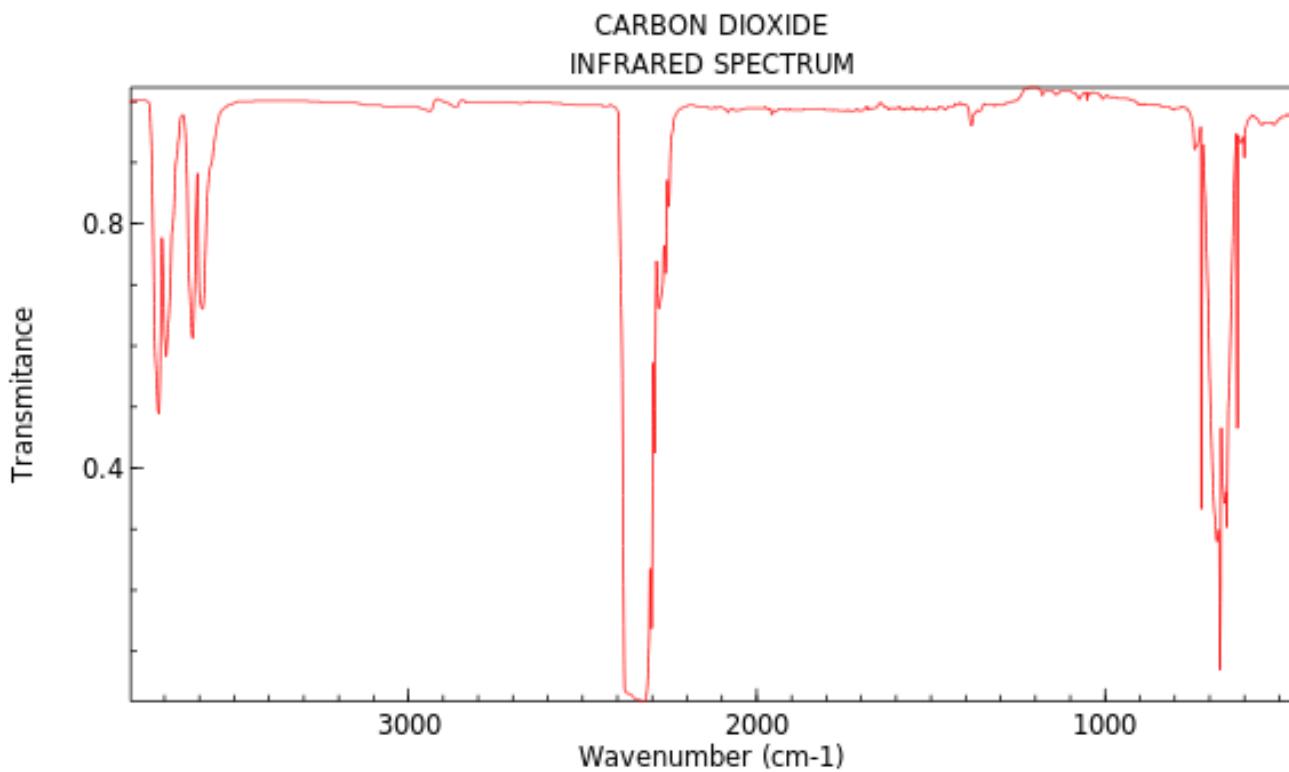
The reason for the latter is because light has an alternating charge (being electro-magnetic). If there is no change in the molecule's dipole (charge), then the light will not be able to interact with it. The molecule must either possess a permanent dipole moment, or undergo a change in dipole moment during vibration, for the vibrational mode to be detectable by IR spectroscopy. Mathematically, for a molecule to be IR-active:

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

where $\mu = qr$ is the dipole moment, q is the charge and r is the distance (bond length). Thus, homonuclear diatomic species like H_2 , N_2 and Br_2 are not IR-active as they do not have a permanent dipole and the only one mode of vibration does not induce dipole moments. In contrast, heteronuclear diatomic HCl and polar polyatomic CH_3Cl , both with a permanent dipole, are IR-active. Nonpolar polyatomic species are slightly trickier. For example, CO_2 has four modes of vibration: symmetric stretching, asymmetric stretching and doubly-degenerate bending:



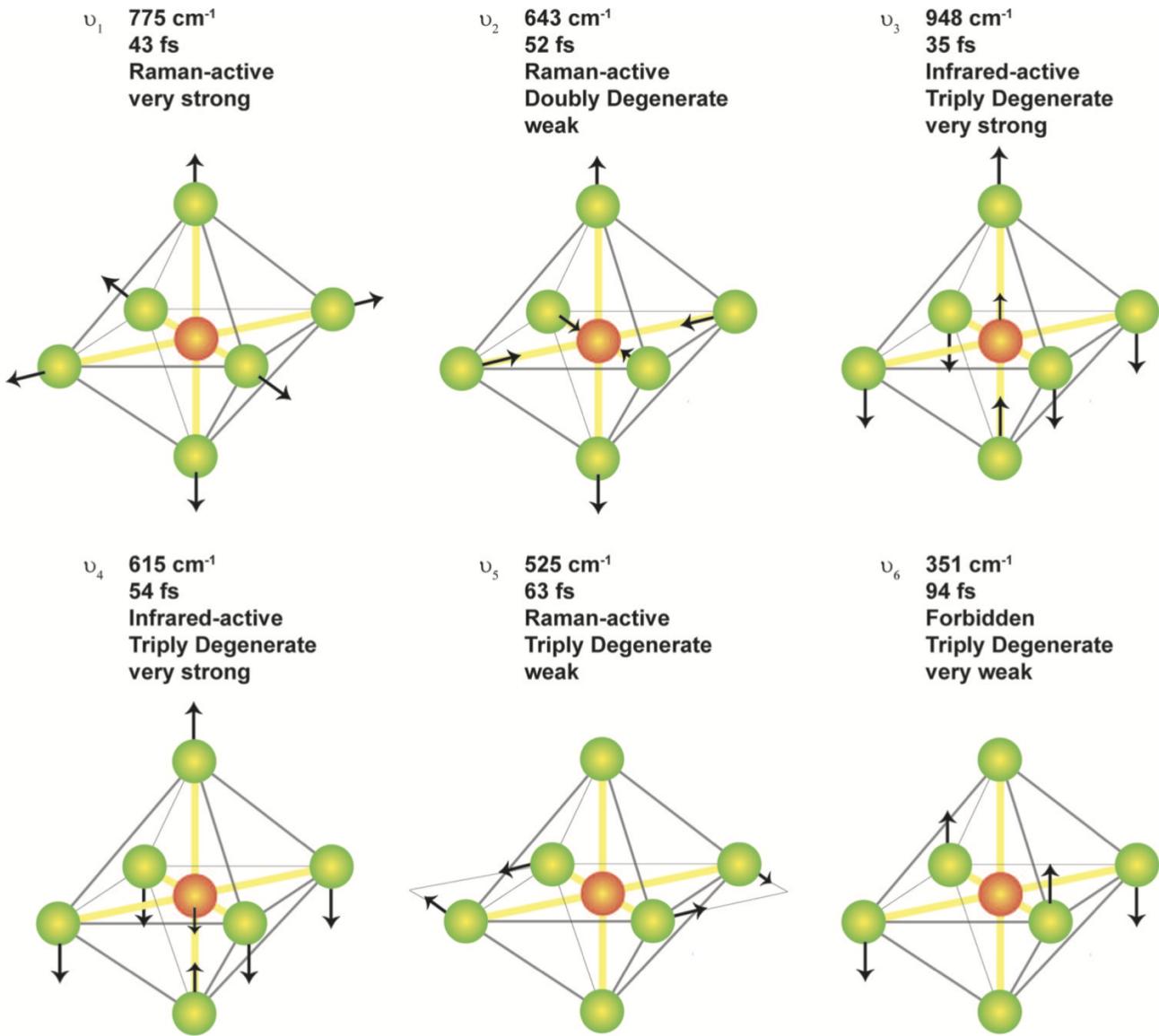
- The symmetric stretching involves both oxygen-carbon bonds expanding and contracting simultaneously. This does not lead to varying dipole moment, and is thus not IR-active.
- The asymmetric stretching involves one bond lengthening while the other shortens. This causes a temporary separation of charges, resulting in a varying dipole moment, and is thus IR-active.
 $\nu_3 = 2349\text{cm}^{-1}$
- The bending modes correspond to the in-plane bending of the molecule. This causes an oscillating dipole moment and is thus IR-active. $\nu_2 = 667\text{cm}^{-1}$



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

The ability of the CO_2 molecule to absorb infrared radiation and traps heat within the atmosphere is primarily why CO_2 is an effective greenhouse gas.

Another example of a nonpolar polyatomic molecule is SF_6 . The [vibrational modes](#) are:



Finally, during molecular vibration, the atoms move back and forth around their equilibrium positions. The amplitude of this motion can vary, resulting in larger or smaller displacements from the equilibrium. However, the vibrational frequency remains constant, as it is determined by the masses of the atoms involved, their bond strengths, and the molecular structure. Therefore, while the extent of vibration may change, the frequency at which the molecule vibrates remains the same.

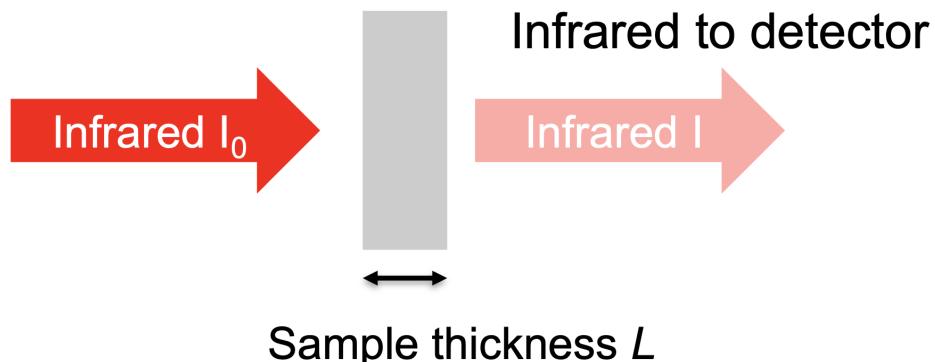
Beer-Lambert Law

The Beer-Lambert Law is a fundamental principle in spectroscopy that relates the concentration of a solute in a solution to the amount of light absorbed by that solution. Assuming a dilute solution and monochromatic light, the Beer-Lambert law states that

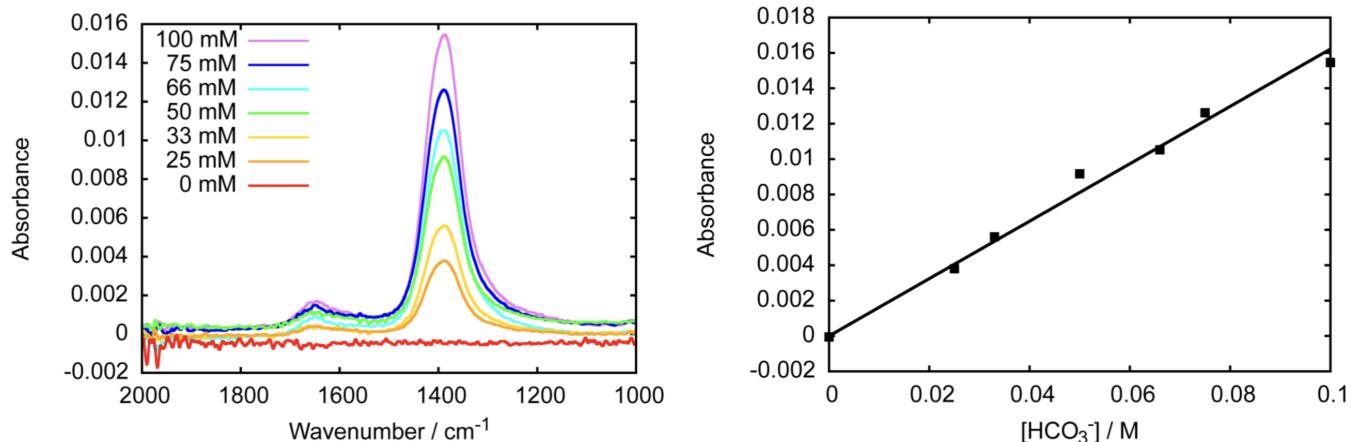
$$A = \varepsilon cl$$

where A is the absorbance of the solution, ε is the molar absorptivity or molar extinction coefficient, c is the concentration of the solute in the solution and l is the path length of the light through the solution (typically measured in cm). The absorbance is:

$$A = -\log_{10} \left(\frac{I}{I_0} \right)$$



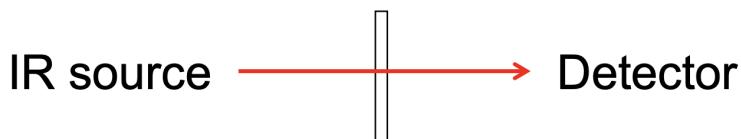
where I is the transmitted light intensity and I_0 is the incident light intensity. By measuring the absorbance of solutions with known concentrations, a linear plot can be obtained to help determine the molar absorptivity:



Sampling Methods

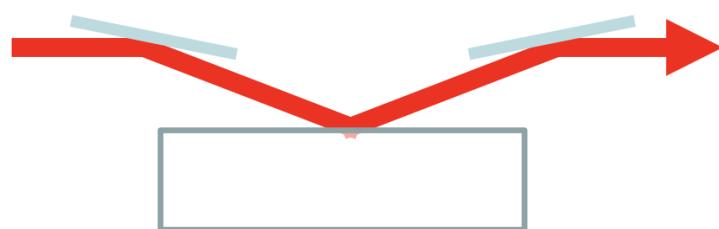
Various sampling methods in infrared spectroscopy are available.

1. Transmission: measure the transmission of infrared light through a sample. This can be achieved using liquid films between transparent salt plates, thin solid films, or by diluting the sample in potassium bromide (KBr) and pressing it into a disc. This method is suitable for bulk measurements.

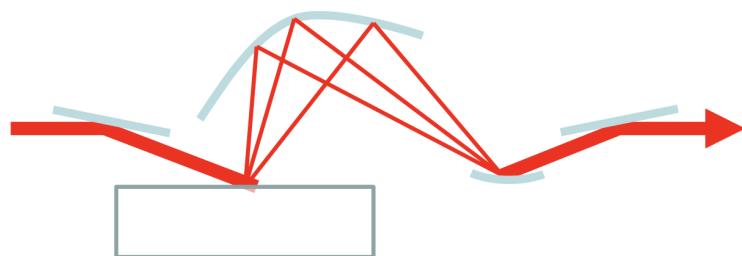


2. External reflection: analyse the reflection of infrared light from the surface of a sample. Two methods are possible specular or diffuse. This method is surface-sensitive and provides information predominantly about the composition and properties of the surface layer.

- ▶ Specular: thin films on reflective substrates or surface coatings are examined by measuring the reflected infrared light.



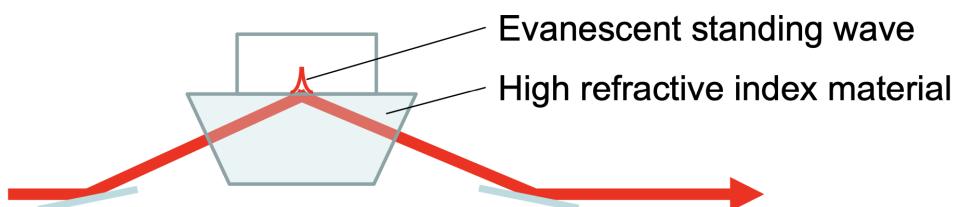
- ▶ Diffuse: this is suitable for the analysis of powdered samples, textured surfaces, fibres, papers, etc., where the reflected light is scattered in multiple directions. Diffuse reflection spectroscopy (DRS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) are commonly used techniques for such measurements.



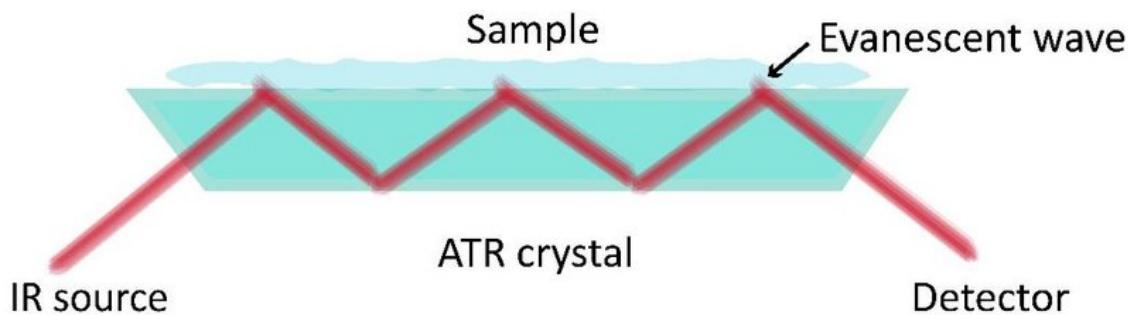
3. Internal reflection: attenuated total reflection (ATR), which is suitable for samples with strongly absorbing properties and provides surface-sensitive information without the need for extensive sample preparation. An infrared beam is directed into a sample at a specific angle, causing it to undergo total internal reflection. As the beam interacts with the sample's surface, its intensity decreases due to absorption, providing information about the sample's surface properties. The penetration depth of ATR represents the depth at which the evanescent wave generated by total internal reflection decays to a negligible intensity, which can be determined by:

$$d_p = \frac{\lambda}{2\pi \cdot (n_1^2 \sin^2 \theta - n_2^2)^{1/2}}$$

where λ is the wavelength, n_1 is the refractive index of the ATR crystal material, n_2 is the refractive index of the sample and θ is the angle of incidence. ATR has a small penetration depth (typically ranging from 0.2 to 3 μm), making it suitable for surface analysis.

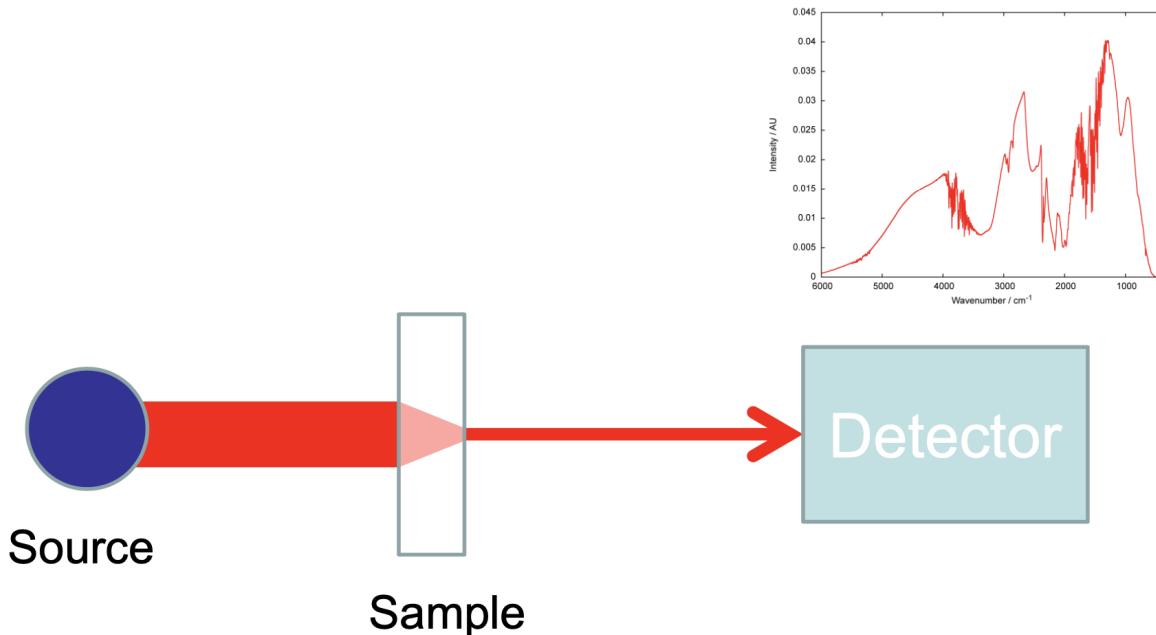


Moreover, multiple-reflection ATR infrared spectroscopy, an extension of the traditional ATR technique, enhances the sensitivity and depth of analysis by incorporating multiple reflections within the ATR crystal. It improves the signal-to-noise ratio and allows for more precise measurements, especially for samples with weak absorption or low concentrations.

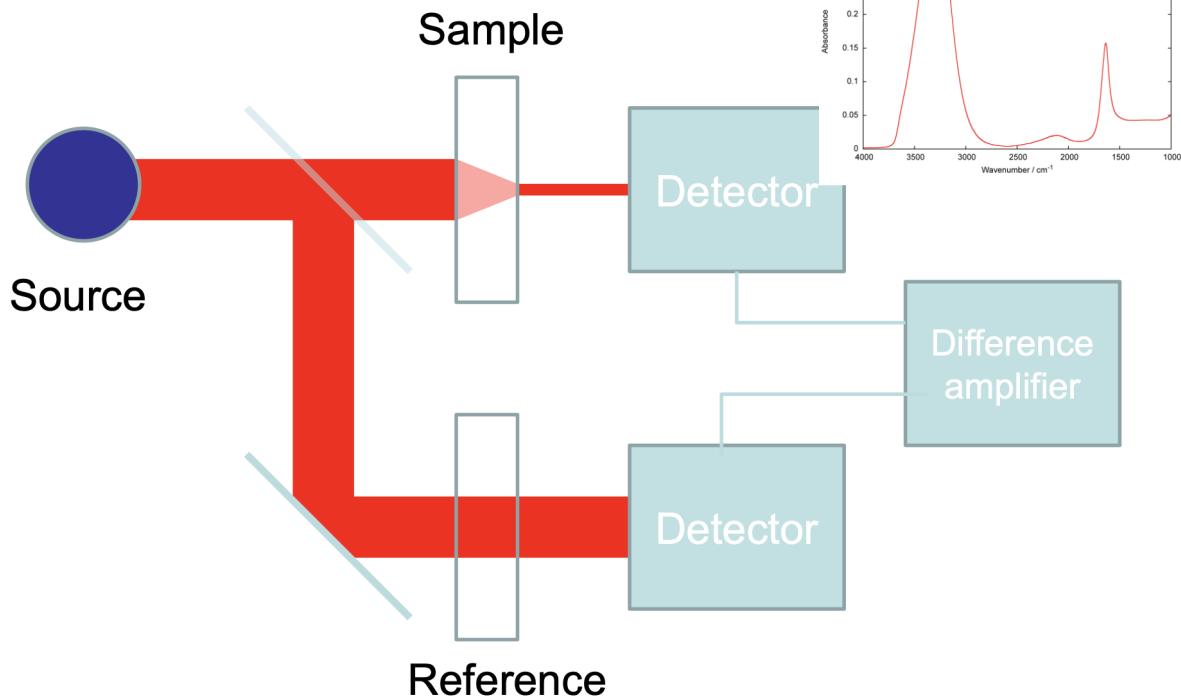


Fourier-Transform Infrared Spectroscopy

A simple IR spectrometer consists of a single beam or IR radiation generated by a source:

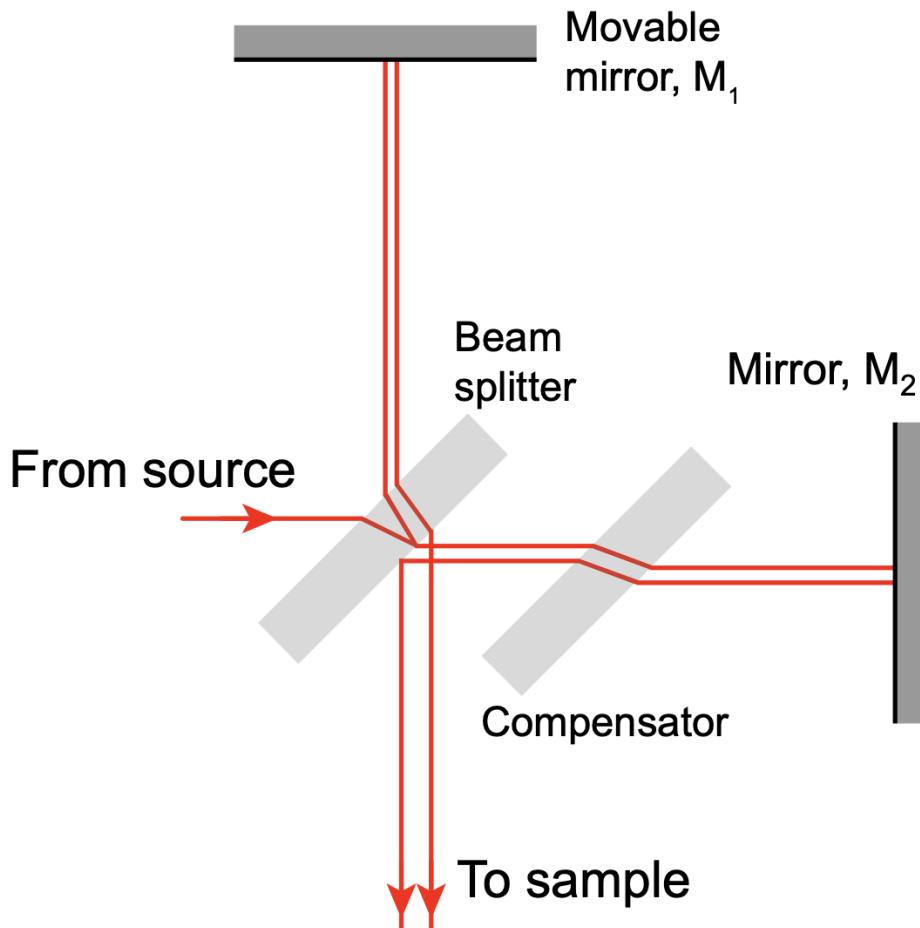


However, this may be more prone to baseline drift and require additional calibration steps to compensate for variations in the source intensity and detector response. An improvement is to incorporate a reference beam, which bypasses the sample, to provide a baseline measurement:



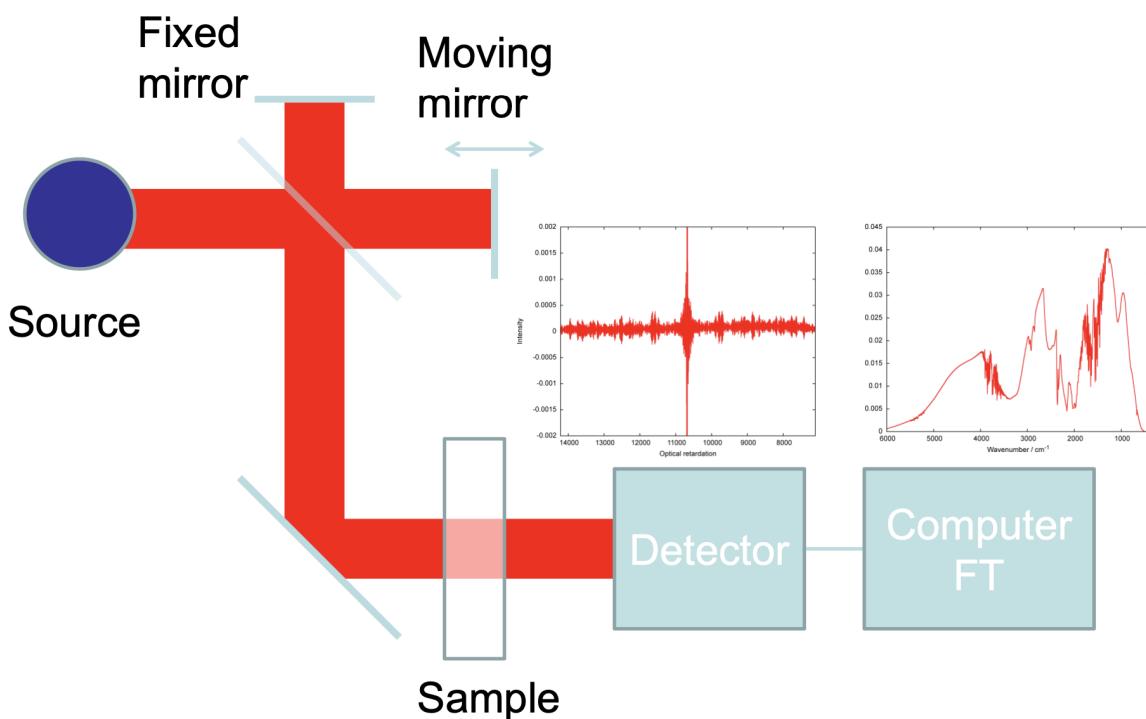
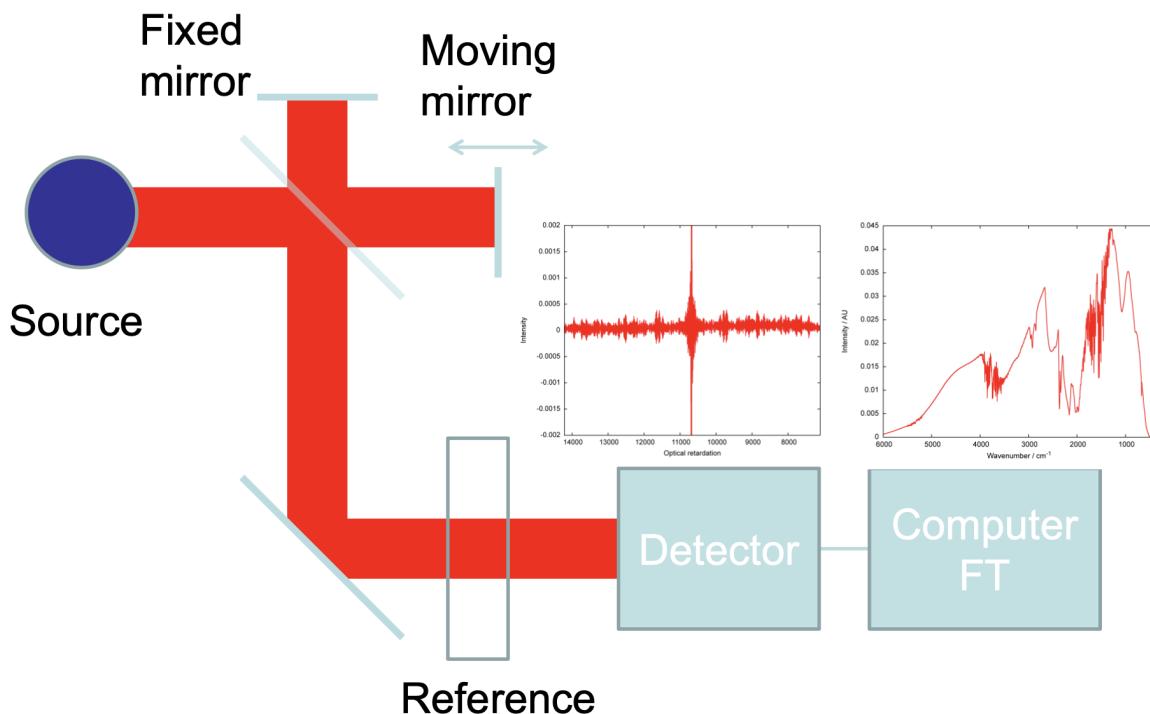
and this technique is the double-beam IR spectrometer. By comparing the intensity of the two beams, absorption or transmission caused by the sample can be determined.

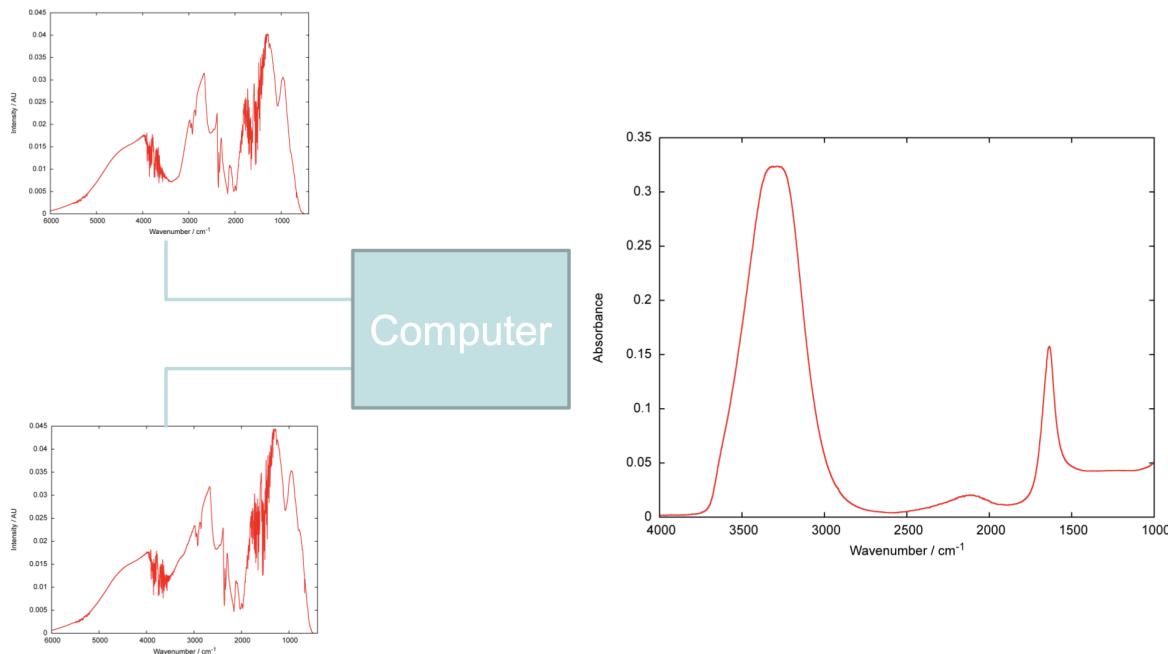
In the traditional IR spectroscopy above, a monochromatic beam of infrared radiation is passed through a sample, and the transmitted or absorbed light is measured as a function of wavelength. This process is repeated for each individual wavelength, resulting in a sequential acquisition of data across the infrared spectrum. Fourier-transform infrared (FTIR) spectroscopy, however, utilises a Michelson interferometer to collect the entire infrared spectrum simultaneously, resulting in faster data acquisition and increased sensitivity. The interferometer splits the infrared beam into two paths; ideally, 50% is refracted towards the fixed mirror and 50% is transmitted towards the moving mirror. Light is reflected from the two mirrors back to the beam splitter.



At the same time, some fraction of the original light passes into the sample compartment. There, the light is focused on the sample. Upon leaving the sample compartment, the light is refocused towards the detector. The difference in optical path length between the two arms to the interferometer is known as the optical path difference (OPD). As the moving mirror moves, the OPD changes accordingly. This variation in the path difference causes distinct interference patterns among light waves, resulting in diverse wavelengths.

An interferogram is obtained by varying the OPD and recording the signal from the detector for various values of the OPD. The form of the interferogram when no sample is present depends on factors such as the variation of source intensity and splitter efficiency with wavelength. This results in a maximum at zero OPD, when there is constructive interference at all wavelengths, followed by series of "wiggles". The position of zero OPD is determined accurately by finding the point of maximum intensity in the interferogram. When a sample is present the background interferogram is modulated by the presence of absorption bands in the sample. By performing a Fourier transform on the interferogram, the spectrum of the sample can be obtained.

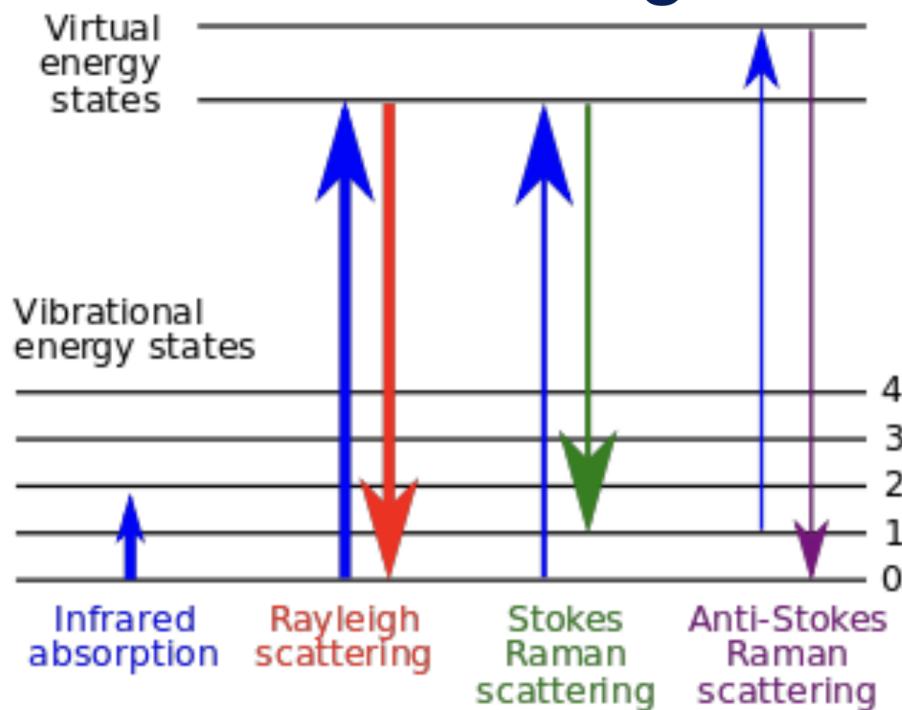




Raman Spectroscopy

While IR spectroscopy involves the absorption of photons, Raman spectroscopy involves the inelastic scattering of photons. Based on the energy shifts observed in the light, the Raman spectrum can be characterised into different regions:

- ▶ Raman scattering (Stokes region): the scattered photons have lower energy (longer wavelength) compared to the incident photons, $h\nu_0 \rightarrow h\nu_0 - h\nu_s$, where ν_s is the vibrational frequency of the molecule. The Stokes region provides information about the vibrational and rotational transitions in the sample molecules.
- ▶ Rayleigh scattering: the majority of the scattered photons that undergo elastic scattering, which do not experience a change in energy or wavelength, $h\nu_0 \rightarrow h\nu_0$. This occurs due to the interaction of incident photons with the electronic structure of the sample, resulting in the re-emission of photons without any energy loss. The Rayleigh light serves as a background in Raman spectroscopy and does not contain information about the sample's vibrational or rotational modes.
- ▶ Raman scattering (Anti-Stokes region): scattered photons have higher energy (shorter wavelength) compared to the incident photons, $h\nu_0 \rightarrow h\nu_0 + h\nu_s$. The anti-Stokes region provides information about higher energy vibrational and rotational transitions.



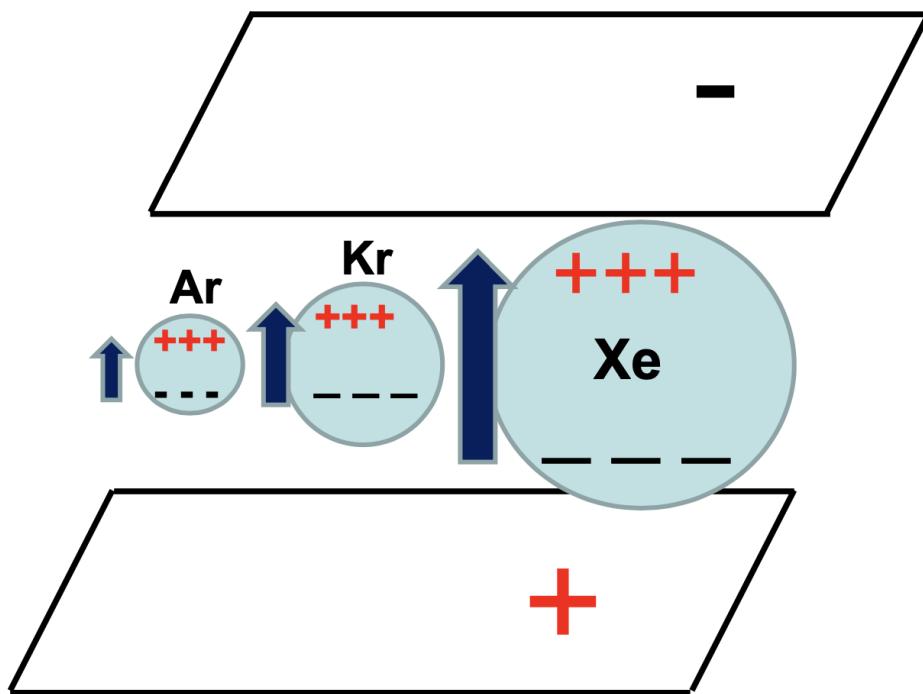
Generally speaking, it is more-likely that Rayleigh and Stokes scattering will occur given that, for anti-Stokes, the bond must already be at a higher energy level (which is unlikely to happen due to the Maxwell-Boltzmann distribution).

Selection Rule

- For a molecule to exhibit a Raman-active vibrational mode, there must be a change in polarizability (α) along the normal mode of vibration.

In simpler terms, this means that there should be a change in the distribution of the electron cloud around the molecule during the vibrational motion. The polarizability α represents the ability of an applied electric field E to induce a dipole moment μ in atom or molecule. When an electric field is applied to a molecule, the positive and negative charges within the molecule experience a separation, resulting in an induced dipole moment. The polarizability of a molecule determines the magnitude of this induced dipole moment.

$$\mu = \alpha E$$



Light or electromagnetic radiation consists of an alternating electric field, E , and a magnetic field, H , perpendicular to the propagating direction and perpendicular to each other. In order for light to interact with a molecule, the molecule must have some movement of charges, such as the presence of polarizable electrons or atoms with partial charges. When a molecule interacts with light, the oscillating electric field of the light can induce a separation of positive and negative charges within the molecule. The ability of electrons and nuclei in a molecule to respond to an external electric field or influence depends on their spatial arrangement and distance from each other. The closer the electrons and nuclei are to each other, the less flexible they are and the weaker the influence of the external field, thus why in a compact molecule with a small distance between its electrons and nuclei, the influence of an external electric field is weak. Vibrations in a molecule, which involve the movement of atoms and the redistribution of charges, can modulate the flexibility of the electrons and nuclei, thus affecting the polarizability and induced dipole moment of the molecule. Therefore, for a molecule to be Raman active:

$$\frac{\delta\alpha}{\delta r} \neq 0$$

Polarizabilities of atoms are isotropic, which means the polarizability is the same regardless of the direction of electric field applied. Polarizabilities of molecules may vary with positions of atoms in the molecule, depending on the molecule's symmetry, size, shape, and electronic structure. Generally, larger and more elongated molecules tend to have higher polarizabilities because their electron clouds are more easily distorted. Additionally, molecules with more delocalised electrons or higher electron density are typically more polarisable.

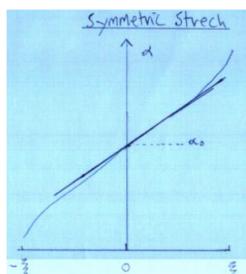
Moreover, since the polarizability of a molecule may not be the same in all spatial directions (anisotropic), a polarizability tensor is used:

$$\begin{bmatrix} \mu'_x \\ \mu'_y \\ \mu'_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

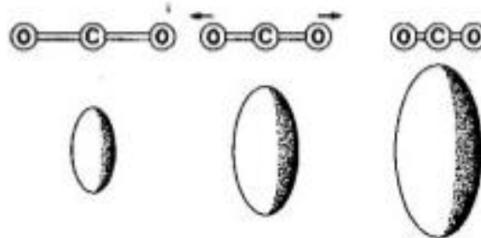
Here, α_{xx} , α_{yy} and α_{zz} represent the diagonal elements of the tensor, which correspond to the polarizability along the x , y , and z directions, respectively. α_{xy} , α_{xz} , α_{yx} , α_{yz} , α_{zx} , α_{zy} represent the off-diagonal elements that represent the coupling between the polarizability along different directions.

The polarizability of a molecule can be represented by an ellipsoid, where the dimensions of the ellipsoid correspond to the polarizability along each direction. The size of the ellipsoid is inversely proportional to $\alpha^{-1/2}$. This means that a larger ellipsoid represents a smaller polarizability, while a smaller ellipsoid represents a larger polarizability. By visualising the ellipsoids representing polarizability in different vibrational states, one can observe how the shape and size of the ellipsoids change, indicating the variation in polarizability during different vibrational modes. If a vibration in molecules changes size, shape, or orientation of ellipsoid, the vibrational mode is likely to be Raman active.

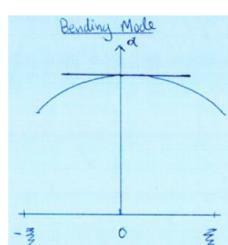
For example, CO₂:



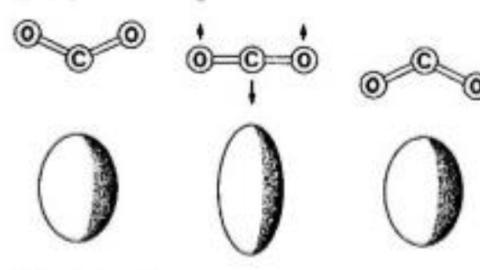
$$\frac{\partial \alpha}{\partial r} \neq 0$$



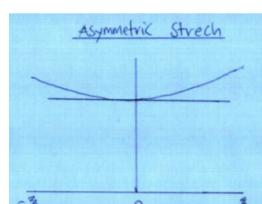
v_1



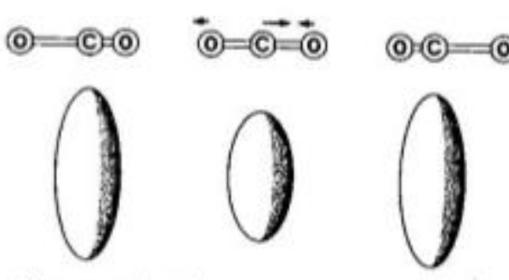
$$\frac{\partial \alpha}{\partial r} \approx 0$$



v_2



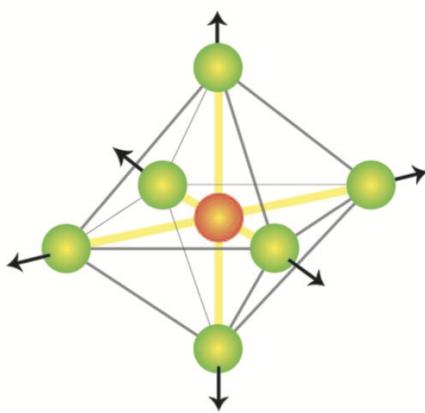
$$\frac{\partial \alpha}{\partial r} \approx 0$$



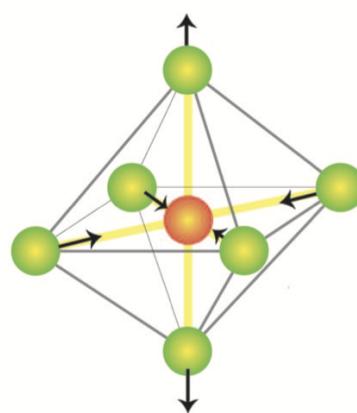
v_3

SF₆:

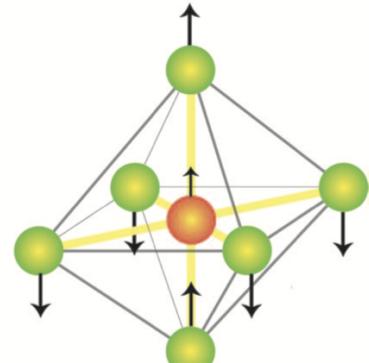
ν_1 **775 cm⁻¹**
43 fs
Raman-active
very strong



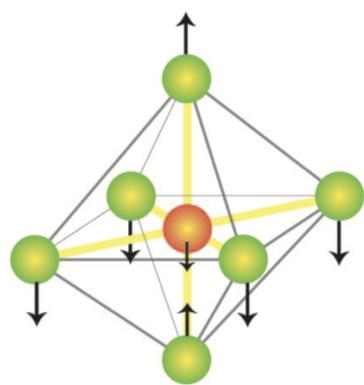
ν_2 **643 cm⁻¹**
52 fs
Raman-active
Doubly Degenerate
weak



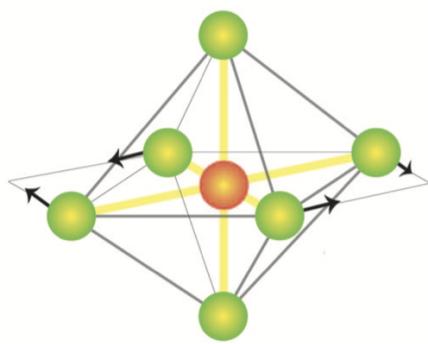
ν_3 **948 cm⁻¹**
35 fs
Infrared-active
Triply Degenerate
very strong



ν_4 **615 cm⁻¹**
54 fs
Infrared-active
Triply Degenerate
very strong



ν_5 **525 cm⁻¹**
63 fs
Raman-active
Triply Degenerate
weak



ν_6 **351 cm⁻¹**
94 fs
Forbidden
Triply Degenerate
very weak

