Chapter 1
Theoretical Aspects

Learning Objectives

- To appreciate the historical background of Raman spectroscopy
- To understand how instrumental improvements opened the way to new Raman spectroscopic applications

The theoretical background of the Raman effect is already extensively described in literature. The Raman effect can be considered as the inelastic scattering of electromagnetic radiation. During this interaction, energy is transferred between the photons and the molecular vibrations. Therefore, the scattered photons have a different energy to the incoming photons.

1.1 Classical Approach

When a molecule is positioned in an electrical field $\mathbf{E}$, an electrical dipole moment $\mathbf{p}$ is induced. The relation between this induced
dipole moment and the electrical field can be expressed as a power series:

\[ p = \alpha \cdot E + (1/2) \cdot \beta \cdot E^2 + (1/6) \cdot \gamma \cdot E^3 \ldots \]  

(1.1)

In this equation, \( \alpha \), \( \beta \) and \( \gamma \) are tensors, which are named polarisability, hyperpolarisability and 2\textsuperscript{nd} hyperpolarisability, respectively. Typically, they are in the range of \( \alpha \sim 10^{-40} \text{C} \cdot \text{V}^{-1} \cdot \text{m}^2 \), \( \beta \sim 10^{-50} \text{C} \cdot \text{V}^{-2} \cdot \text{m}^3 \) and \( \gamma \sim 10^{-60} \text{C} \cdot \text{V}^{-3} \cdot \text{m}^4 \). As these tensors each are a factor 10 billion less intense, the influence of these factors can in many cases be neglected.

**QUESTION 1.1**

Estimate value of the terms in Equation (1.1), when using an electrical field of \( 3 \cdot 10^6 \text{Vm}^{-1} \) (corresponding to a typical laser intensity of ca. \( 10^9 \text{Wm}^{-2} \)).

The induced dipole moment can be thus considered as directly proportional to the electrical field and Equation (1.1) is reduced to:

\[ p = \alpha \cdot E \]  

(1.2)

When studying the Raman effect, the electrical field is caused by electromagnetic radiation. Indeed, light can be considered as an oscillating electrical field. The electrical field vector \( \mathbf{E} \) on the moment \( t \) is described as:

\[ \mathbf{E} = \mathbf{E}_0 \cdot \cos(2\pi \cdot \nu_0 \cdot t) \]  

(1.3)

with \( \nu_0 \) the vibrational frequency of the electromagnetic radiation.

In Equation (1.2) the polarisability \( \alpha \) is a tensor, which is dependent on the shape and dimensions of the chemical bond. As chemical bonds change during vibrations, the polarisability is dependent on the vibrations of the molecule. It can be said that
The polarisability tensor ($\alpha$) is dependent on the normal coordinate $Q$ of the molecule. This relationship can be expressed as a Taylor series:

$$\alpha = \alpha_0 + \sum_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 \cdot Q_k + \frac{1}{2} \sum_{k,l} \left( \frac{\partial^2 \alpha}{\partial Q_k \partial Q_l} \right)_0 \cdot Q_k \cdot Q_l + \ldots$$  

(1.4)

$Q_k$ and $Q_l$ are the normal coordinates that correspond with the $k^{th}$ and $l^{th}$ normal vibration, corresponding with the vibrational frequencies $\nu_k$ and $\nu_l$. In a first approximation, only the first two terms in this equation are maintained. This means that the different (normal) vibrations are considered as totally independent and no cross-terms are included in the equation. Thus, considering the $v^{th}$ normal vibration, Equation (1.4) is reduced to:

$$\alpha_v = \alpha_0 + \alpha'_v \cdot Q_v$$  

(1.5)

with $\alpha'_v$ the derivative of the polarisability tensor to the normal coordinate $Q_v$, under equilibrium conditions.

In a first approximation, the normal coordinate oscillates according to the harmonic oscillator (Intermezzo 1.1). The normal coordinate varies as a function of time according to:

$$Q_v = Q_{v0} \cdot \cos(2\pi \cdot \nu_v \cdot t + \varphi_v)$$  

(1.6)

with $Q_{v0}$ the amplitude of the normal vibration and $\varphi_v$ a phase angle. Substitution of Equation (1.6) for Equation (1.5) gives:

$$\alpha_v = \alpha_0 + \alpha'_v \cdot Q_{v0} \cdot \cos(2\pi \cdot \nu_v \cdot t + \varphi_v)$$  

(1.7)

When considering only the first two terms of the Taylor series (1.4), we assume that the polarisability tensor undergoes a harmonic oscillation, with a frequency $\nu_v$, that equals the vibrational frequency of the normal coordinate of the molecule. By substituting
Equations (1.7) and (1.3) in the (simplified) definition of the dipole moment \( \mathbf{p} \) (Equation (1.2)), we obtain:

\[
\mathbf{p} = \alpha_0 \cdot \mathbf{E}_0 \cdot \cos(2\pi \nu_0 t) + \alpha'_v \cdot \mathbf{E}_0 \cdot Q_v \cdot \cos(2\pi v_v t) \\
\quad \cdot \cos(2\pi v_v t + \varphi_v) \tag{1.8}
\]

By using the trigonometrical formula:

\[
\cos A \cdot \cos B = \frac{1}{2} \left[ \cos(A + B) + \cos(A - B) \right] \tag{1.9}
\]

Equation (1.8) can be modified to:

\[
\mathbf{p} = \alpha_0 \cdot \mathbf{E}_0 \cdot \cos(2\pi \nu_0 t) \\
\quad + \frac{1}{2} \cdot \alpha'_v \cdot \mathbf{E}_0 \cdot Q_v \cdot \cos[2\pi (\nu_0 + v_v) \cdot t + \varphi_v] \\
\quad + \frac{1}{2} \cdot \alpha'_v \cdot \mathbf{E}_0 \cdot Q_v \cdot \cos[2\pi (\nu_0 - v_v) \cdot t - \varphi_v] \tag{1.10}
\]

Therefore, we can consider the induced dipole moment as a function of the vibrational frequencies of the molecule \((\nu_v)\) and of the incident radiation \((\nu_0)\):

\[
\mathbf{p} = \mathbf{p}(\nu_0) + \mathbf{p}(\nu_0 + \nu_v) + \mathbf{p}(\nu_0 - \nu_v) \tag{1.11}
\]

The induced dipole moment can be split into 3 components, each with a different frequency-dependence. The first term in Equation (1.11) corresponds to the elastic scattering of the electromagnetic radiation: the induced dipole moment has the same frequency (hence the same energy) as the incoming radiation. This type of scattering is called ‘Rayleigh scattering’, named after Lord Rayleigh (1842–1919), who used Rayleigh scattering to determine the size of a molecule. The 2nd and 3rd term in Equation (1.11) correspond to the inelastic scattering of light: Raman scattering. The 2nd term corresponds to a higher energy of the scattered radiation, compared to the incident beam (Anti-Stokes scattering), while the last term represents a lowering of the frequency (Stokes scattering).
When using Raman spectroscopy, an intense, monochromatic beam of electromagnetic radiation (usually a laser) is focussed on the sample, and the intensity of the scattered radiation is measured as a function of its wavelength. Usually, in a Raman spectrum the intensity is plotted as a function of the Raman wavenumber \( \omega \), expressed in cm\(^{-1} \), which is related to the difference in frequency between the scattered light and the incident electromagnetic radiation:

\[
\omega = \nu_m - \nu_0 = \frac{\nu_m}{c} - \frac{\nu_0}{c}
\]  

(1.12)

In this expression, the symbols \( \nu_m \) and \( \nu_0 \) stand for the frequency of the scattered (measured) and incident radiation, respectively; \( c \) is the speed of light; wavenumbers are usually expressed in cm\(^{-1} \), so

Figure 1.1 Raman spectrum of the mineral realgar (As\(_4\)S\(_4\)) in the anti-Stokes region, Rayleigh line and Stokes region. The actual intensity of the Rayleigh line is suppressed by a holographic filter in the spectrometer.
be careful when calculating them, as you need to use the appropriate units. Positive wavenumbers correspond with Stokes scattering, while negative wavenumbers correspond with anti-stokes scattering (see Figure 1.1).

**QUESTION 1.2**

The Raman spectrum in Spectrum 1.1 was recorded by using a laser with a wavelength of 785 nm. The most intense Raman band of realgar is positioned at 352 cm$^{-1}$. What are the (absolute) frequencies and wavelengths of the scattered radiation, in the Stokes as well as in the anti-Stokes region?

**INTERMEZZO 1.1 THE HARMONIC OSCILLATOR AND THE POSITION OF THE VIBRATIONAL ENERGY LEVELS**

When discussing molecular vibrations, bonds are often considered as a harmonic oscillator: a diatomic molecule is represented as two balls connected with a spring. For this oscillator Hooke’s law is valid: $F = -k \cdot q$ (with $F$ a force which is in the opposite sense to the displacement $q$, and with $k$ the spring constant). In general, the force of the spring can be described as the (partial) derivative of the energy in function of the displacement: $-F = \partial U/\partial q$. Therefore, the potential energy for a specific displacement $q$ is given by the following Taylor-series:

$$U_q = U_{q=0} + (dU/dq)_{q=0} \cdot q + \frac{1}{2} \cdot (d^2U/dq^2) \cdot q^2 + \ldots$$

For small displacements (i.e. the harmonic oscillator approximation), only the first two terms of this series are considered, and thus: $U = C + \frac{1}{2} \cdot k \cdot q^2$. (In general, the constant term $C$ is set to 0, the energy state in equilibrium position.) In the case of the harmonic oscillator, a parabolic curve is obtained when plotting the potential energy as a function of the displacement.
When substituting this potential energy curve in the Schrödinger equation \( -\frac{\hbar^2}{8\pi^2\mu} \cdot \frac{d^2\Psi}{dq^2} + U \cdot \Psi = E \cdot \Psi \), one can determine the possible energy levels of the harmonic oscillator:

\[
E_v = (v + \frac{1}{2}) \cdot \frac{\hbar}{2\pi} \sqrt{\frac{k}{\mu}},
\]

with the vibrational quantum number \( v = 0, 1, 2, \ldots, \infty \). \( \mu \) is the reduced mass of the molecule \( \left( \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \right) \). It can be noted that for the harmonic oscillator approximation, the vibrational energy levels are equidistant (see Figure Intermezzo 1.1).

![Figure Intermezzo 1.1 Harmonic oscillator.](image)

### 1.2 Selection Rule

From Equation (1.10) it can be seen that the Raman effect only happens if \( \alpha'_v \neq 0 \). Therefore, during the considered normal vibration a change in polarisability should happen:

\[
\alpha'_v = \left( \frac{\partial \alpha}{\partial Q_v} \right)_0 \neq 0 \quad (1.13)
\]
Opposite to this, in infrared spectroscopy there is a change in (permanent) dipole moment during the vibration. In principle, on ground of this selection rule, it can be determined whether a vibration is Raman or infrared active. However, only for very simple molecules this can be done by hand: vibrations of more complex molecules can be evaluated by using quantum mechanics and group theory.

**QUESTION 1.3**

Describe the different vibrations in a CO$_2$ molecule. Which of these vibrations is infrared active and which is Raman active?

Consider a homonuclear diatomic molecule (e.g. H$_2$). In this case, the polarisability is a function of the internuclear distance. This can be understood by thinking that, when the internuclear distance is larger, the electrons are relatively further away from the nuclei and thus can be moved more easily. During this vibration, a change in polarisability of the molecule occurs and thus the vibration is Raman active. The dipole moment does not change and the vibration is infrared inactive.

Analogously, in a heteronuclear diatomic molecule (e.g. HCl) polarisability is also dependent on the bond distance. Moreover, since the size of the dipole moment is dependent on the charge separation, during a vibration there is a change of the dipole moment. The vibration is thus Raman and infrared active.

For triatomic molecules, different cases can be distinguished, depending on the number of different types of atoms (1;2 or 3) and depending on the linearity of the molecule. For a linear molecule of the type ABA (e.g. CO$_2$), 4 normal vibrations can be distinguished: symmetrical stretch vibration, asymmetrical stretch and 2 bending vibrations (degenerated). Of these, only the symmetrical stretch is Raman active, whereas the other vibrations are infrared active.
For nonlinear molecules of the type ABA (e.g. H$_2$O), 3 normal vibrations can be distinguished (symmetrical and asymmetrical stretch, symmetrical bending vibration) that are infrared and Raman active. In general it can be stated that, in a centrosymmetric molecule Raman active vibrations are infrared inactive and vice versa. Moreover, from practice we know that vibrations that give rise to very intense infrared bands are generally rather weak Raman scatterers.

To determine the Raman and/or infrared activity of vibrations in complex molecules, quantum mechanics and group theory are used. The total vibrational wave function $\psi_v$ can be written as the product of different wave functions $\psi_i (n_i)$, with $\psi_i$ the $i^{th}$ normal vibration that is currently in the $n_i^{th}$ state:

$$\psi_v = \psi_1(n_1) \cdot \psi_2(n_2) \cdot \ldots \cdot \psi_k(n_k) = \prod_{j=1}^{k} \psi_i(n_i) \quad (1.14)$$

A fundamental transition is the transition form a state with all normal vibrations in the ground state $\psi_i(0)$ to a state with all vibrations but one in the ground state. That particular vibration is in the first excited state $\psi_i(1)$:

$$\prod_{i} \psi_i(0) \rightarrow \psi_j(1) \cdot \prod_{i \neq j} \psi_i(0) \quad (1.15a)$$

This vibrational transition can be concisely written as:

$$\psi_v^0 \rightarrow \psi_v^{j=1} \quad (1.15b)$$

The induced dipole moment is given by Equation (1.2). The amplitude of the transition moment which is induced during transition 1.15, is expressed as:

$$[p_{0}]_{j=1}^{0} = \int \psi_v^{j=1} \cdot \tilde{\alpha} \psi_v^0 d\tau \cdot E_0 \quad (1.16)$$
The operator $\hat{\alpha}$ is the polarisability (cf. Equation (1.1)) and $\tau$ is the spatial coordinate. Here, we only consider the time-independent part (i.e. the amplitude) of the transition moment, which allows us to use the time-independent part of the perturbation theory. In analogy with Equation (1.2), we can consider the integral in Equation (1.16) as the quantum mechanical equivalent of the polarisability tensor. This integral can in a simply way be noted in the Dirac notation:

$$[\alpha]_{j=1}^{0} = \int \psi_{j=1}^{*} \hat{\alpha} \psi_{0} d\tau = \langle \psi_{j=1}^{*} | \alpha | \psi_{0} \rangle$$  \hspace{1cm} (1.17)$$

Polarisability is a function of the normal coordinate. We assume harmonicity, and thus we only substitute the first two terms of Equation (1.4), leading to:

$$[\alpha]_{j=0} = \alpha_{0} \cdot \langle \psi_{j=1}^{*} | \psi_{0} \rangle + \sum_{k} \left( \frac{\partial \alpha}{\partial Q_{k}} \right)_{0} \cdot \langle \psi_{j=1}^{*} | Q_{k} | \psi_{0} \rangle$$  \hspace{1cm} (1.18)$$

From this equation, the quantum mechanical description of the border conditions of the Raman effect can be derived. Because of the orthogonality of the wave functions, the value of the integral in the first term is:

$$\langle \psi_{j=1}^{*} | \psi_{0} \rangle = 0 \text{ if } j \neq 0$$ \hspace{1cm} (1.19a)

$$\langle \psi_{j=1}^{*} | \psi_{0} \rangle = 1 \text{ if } j = 0$$ \hspace{1cm} (1.19b)

This term corresponds to Rayleigh scattering. The second part of Equation (1.18) describes the Raman scattering. The condition for the Raman effect to happen is that both factors in this term differ from 0. The first factor indicates that the polarisability should change during the vibration, whereas the second factor only differs from 0 if the wave function $\psi_{j=1}^{i}$ and the normal coordinate $Q_{k}$ are determined by the same quantumnumber ($j = k$). When considering
Stokes Raman scattering, the transition from the ground state to the first excited vibrational state \( j = 1 \) is involved.

\[
\langle \psi_j^1 | Q_k | \psi^0 \rangle \neq 0 \quad \text{if} \quad j = k = 1
\]  

(1.20)

As a consequence, for Stokes scattering, Equation (1.18) should be written as:

\[
[a]_{j=1 \leftarrow 0} = \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 \cdot \langle \psi_j^1 | Q_k | \psi^0 \rangle
\]  

(1.21)

The selection rule states that the polarisability for the considered transition (Stokes Raman) should differ from 0. To evaluate this, it is not necessary to calculate the integral as such; based on its symmetry properties it can be determined whether it is different from 0 or not. This is only the case if \( \psi_j^1 \) and \( Q_k \) belong to a different symmetry class, which means that all possible symmetry operations are transformed in the same way. Based on the symmetry properties of a molecule, it can be determined how a certain vibration transforms, how its symmetry class can be determined, and whether a vibration is Raman active or not. These studies are the subject of group theoretical examinations. When considering (crystalline) solids, not only the symmetry of the ‘molecule’ or the ion (e.g. \( \text{CO}_3^{2-} \)) should be taken into account, but also the geometry in the crystalline structure. Symmetry of the cavity that contains the group plays an important role.

**INTERMEZZO 1.2 THE ANHARMONIC OSCILLATOR AND THE POSITION OF VIBRATIONAL ENERGY LEVELS**

In this discussion, molecular vibrations are considered as harmonic oscillations. In reality, however, this is not the case and harmonic oscillations are a simplified model. If molecular vibrations were harmonic oscillations, atoms could approach each
other until they overlap entirely – which obviously is impossible. Moreover, atoms would always oscillate around their equilibrium distance, also if they had been taken a long distance apart. This is not the case as molecular bonds break when the interatomic distance is too large.

Therefore, there are deviations of the model of the harmonic oscillator. The curve describing the potential energy of the anharmonic oscillator (see Figure Intermezzo 1.2) as a function of the distance between the atoms’ nuclei, is named the Morse curve, with the equation $U = D_e \cdot (1 - e^{-\beta q})^2$. The Morse curve is presented in the illustration below. It can be seen that atoms can approach each other less easily, compared to the harmonic oscillator. Moreover, if atoms are sufficiently far apart (i.e. when they are no longer bound to each other), there is no change in the potential energy curve.

![Morse curve illustration](image)

Figure Intermezzo 1.2 Anharmonic oscillator.

A consequence of the introduction of the anharmonic oscillator is that the distance between consecutive energy levels is not equal. In spectroscopy, this is seen by the occurrence of sum peaks and overtones.
1.3 Energy Levels and Group Frequencies

The result of the Schrödinger equation for a particle in a box tells us that only a limited number of energy levels are allowed:

\[ E_\nu = (\nu + \frac{1}{2}) \cdot h \nu_v \quad (\nu = 0, 1, 2, \ldots) \quad (1.22) \]

With \( \nu \) the vibrational quantum number, \( h \) Planck’s constant \((h = 6.6260755 \cdot 10^{-34} \text{ J} \cdot \text{s})\) and \( \nu_v \) the molecular vibrational frequency. During the transition of one vibrational level to the next, the difference in quantum numbers between begin and end state should equal 0 or ±1. This is a consequence of the use of the harmonic oscillation approximation.\(^1\)

If the difference equals 0, Rayleigh scattering is considered, otherwise Stokes or anti-Stokes (Raman) scattering is discussed. It is thus clear that the overall energy difference for a Raman transition equals ± \( h \cdot \nu_v \). This energy difference is plotted on the horizontal axis of a Raman spectrum, expressed as Raman wavenumbers (Equation (1.12)).

The position of a Raman band in the spectrum is determined by the energy difference between the ground state and the first vibrationally excited state (Figure 1.2).

As a consequence of the harmonic oscillation approximation, the vibrational frequency can be expressed as:

\[ \nu_v = \frac{1}{2} \cdot \pi \cdot \sqrt{\frac{\kappa}{\mu}} \quad (1.23) \]

with \( \kappa \) the force constant of the bond and \( \mu \) the reduced mass. For a diatomic molecule, the reduced mass is defined as:

\[ \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad (1.24) \]

\(^1\)This approach is usually allowed for traditional Raman spectroscopic experiments. Overtones and sumpeaks (that do not obey this approximation) are usually weak.
with $m_1$ and $m_2$ the masses of the atoms constituting the bond. For more complex systems, where multiple atoms are involved, this equation can easily be expanded.

Equation (1.23) forms the basis for the interpretation of Raman spectra. From this equation, it appears that two factors determine the Raman band position: the force constant of the bond and the type of vibration ($\kappa$) and the reduced mass ($\mu$). Once these two properties are known, the Raman band position can be calculated. Opposite, one can calculate the force constant of a bond from the Raman band position (provided the (reduced) mass is known). Since $\kappa$ and $\mu$ are relatively stable for a specific type of bond or a particular functional group, for a series of functional groups so-called group frequencies can be determined. These characteristic wavenumbers give an indication about the region where a particular Raman band can be expected, but don’t say whether this band is present or not, as this is dependent on the selection rules (§ 1.2) and the final
The appearance of the spectrum is strongly dependent on the symmetry of the molecule. A typical example of this is the Raman spectrum of substituted benzene molecules, where the appearance of the spectrum not only is determined by the substituents, but mainly by the number of substituents and their relative positions on the benzene ring (symmetry see §5.3.3).

The idea of group frequencies is based on the simplification that vibrations in a specific functional group are independent of the other vibrations in the molecule. These group frequencies have mainly practical value for the interpretation of Raman spectra of organic molecules. Often Raman spectra of inorganic molecules are more influenced by the symmetry properties of the molecule. Moreover, strong band shifts occur frequently as well as possible overlap between functional groups. For instance, there is overlap between the regions of total symmetrical stretch vibration of the carbonate ($CO_3^{2−}$) and sulphate ($SO_4^{2−}$) ions. In Table 1.1 some group frequencies of organic molecules are mentioned.

Note that stretching vibrations are usually abbreviated with the Greek letter $\nu$ ($\nu$), while bending vibrations have the symbol $\delta$ ($\delta$) and vibrations involving rotations are assigned the Greek letter $\rho$ ($\rho$).

**Discussion Topic 1.1**

In Table 1.1 some general trends can be observed:

- vibrations where H-atoms are involved, usually occur at higher wavenumbers;
- $\nu$(C–C) have lower group frequencies than $\nu$(C=C) and than $\nu$(C≡C);
- stretching vibrations have higher group frequencies than the corresponding bending vibrations.

Explain why.
Answer:

From Equation (1.24) it can be seen that molecules involving light atoms (like hydrogen) have a smaller reduced mass than molecules with large atoms. As a consequence their vibrational frequency is higher (Equation 1.23). Opposite to this, inorganic materials, that often contain heavy atoms or ions, usually have Raman bands at lower wavenumbers. This property can be used to distinguish between spectra of inorganic or organic materials.

From Equation (1.23) it can be seen that the force constant $\kappa$ is the second factor that influences the Raman band position. Bonds with high force constants (more or less synonym of ‘strong bonds’) can give rise to bands at high wavenumber positions. This can be seen in the group frequencies of the series $\nu(C\equiv C)$, $\nu(C=\equiv C)$, and $\nu(C-C)$.

When evaluating Table 1.1 we also see that stretch vibrations occur at high wavenumbers, compared to bending vibrations. During stretch vibrations the bond length changes, while during bending vibrations only the bond angle is changed. Since another type of vibration is involved, another force constant should be used. Changing a bond length requires more energy than bending it, hence the difference in Raman band positions.

The force constant is strongly dependent on inter- and intramolecular interactions. For instance, hydrogen bonding can cause a band shift in some molecules. Substituents on a functional group can as well cause a change in the force constant $\kappa$. Electron donors or electron acceptors influence the electron density of the bond, and thus also its force constant, which is observed as a shifting Raman band.
### Table 1.1  Some group frequencies for functional groups in organic compounds.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>Raman-intensity¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H stretch</td>
<td>ν(O–H)</td>
<td>3650–3000</td>
</tr>
<tr>
<td>N–H stretch</td>
<td>ν(N–H)</td>
<td>3500–3300</td>
</tr>
<tr>
<td>C–H stretch of alkenes</td>
<td>ν(≡C−H)</td>
<td>3350–3300</td>
</tr>
<tr>
<td>C–H stretch of alkenes</td>
<td>ν(= C–H)</td>
<td>3100–3000</td>
</tr>
<tr>
<td>C–H stretch of alkanes</td>
<td>ν(−C−H)</td>
<td>3000–2750</td>
</tr>
<tr>
<td>C≡C stretch of alkenes</td>
<td>ν(C≡C)</td>
<td>2250–2100</td>
</tr>
<tr>
<td>C–C stretch of alkenes</td>
<td>ν(C=C)</td>
<td>1750–1450</td>
</tr>
<tr>
<td>C–C stretch of aliphatic chains and cycloalkanes</td>
<td>ν(C−C)</td>
<td>1150–950</td>
</tr>
<tr>
<td>CC stretch of aromates [(substituted) benzene molecules]</td>
<td>ν(CC)</td>
<td>1600, 1580, 1500, 1450, 1000</td>
</tr>
<tr>
<td>C═O stretch</td>
<td>ν(C=O)</td>
<td>1870–1650</td>
</tr>
<tr>
<td>Antisymmetric C–O–C stretch</td>
<td>ν_sym(COC)</td>
<td>1150–1060</td>
</tr>
<tr>
<td>Symmetrical C–O–C stretch</td>
<td>ν_sym(COC)</td>
<td>970–800</td>
</tr>
<tr>
<td>CH₂ bending vibrations, antisymmetric CH₃ bend</td>
<td>δ(CH₂), δ_sym(CH₃)</td>
<td>1470–1400</td>
</tr>
</tbody>
</table>

[(continued overleaf)]
Table 1.1 (continued).

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Wavenumbers (cm(^{-1}))</th>
<th>Raman-intensity(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric CH(_3) bend</td>
<td>(\delta_{\text{sym}}(\text{CH}_3))</td>
<td>1380</td>
</tr>
<tr>
<td>CH(_2) in phase twist</td>
<td>(\delta(\text{CH}_2))</td>
<td>1305–1295</td>
</tr>
<tr>
<td>Symmetric bending of aliphatic chains (C(_n) with n=3 . . . 12) (=chain expansion)</td>
<td>(\delta_{\text{sym}}(\text{CC}))</td>
<td>425–150</td>
</tr>
<tr>
<td>Amide I band (CONH stretch)(^2)</td>
<td>Amide I</td>
<td>1670–1630</td>
</tr>
<tr>
<td>Amide III band (C–N stretch, coupled with opening of the CNH angle)(^2)</td>
<td>Amide III</td>
<td>1350–1250</td>
</tr>
</tbody>
</table>

\(^1\)s strong, m medium, w weak, v very (see Intermezzo 1.3).

\(^2\)Vibrations of the bonds in an amide function can not be considered independently. The amide I and III bands are the most important Raman active vibrations of this functional group. Group frequencies of this functional group can be defined more precisely when primary, secondary or tertiary amides are considered separately.

The force constant of the bond is also influenced by the hybridisation state of the considered atoms. In Table 1.1 this can be seen when comparing the band positions of the \(\nu(\text{C–H})\) stretching vibration for alkanes, alkenes and alkynes. In the first case, the carbon atom is sp\(^3\) hybridised, whereas in the other cases its hybridisation is sp\(^2\) and sp, respectively. We can see that, in this series, the relative percentage s-character of the hybridised carbon atom rises. The higher the percentage s-character of the carbon atom, the higher the force constant \(\kappa\).
1.4 Raman Intensity

The overall intensity of a Raman band is the result of a whole series of influences. Basically, they can be divided into two groups:

\[ I = \alpha \cdot \beta \]  

(1.25)$^2$

where \( \alpha \) refers to parameters related to the sample and \( \beta \) are parameters that are instrument-related. Jawhari et al. (T. Jawahari, P.J. Hendra, H.A. Wills and M. Judkins, Spect. Chim. Acta A 46, 161–70 (1990)) express this last group of parameters as:

\[ \beta = B \cdot V \cdot F_{\text{instr}} \]  

(1.26)

where \( B \) is related to the intensity of the source of radiation, \( V \) is the analysed volume and \( F_{\text{instr}} \) is a group of instrument-dependent factors, like detector efficiency or measurement geometry (see also Chapter 2). In this paragraph, Raman intensity is considered from a fundamental point of view, and instrumental factors are not taken into account here.

In general, the intensity of scattered light equals the change in electromagnetic flux \( d\Phi \), considered over a specific solid angle \( \Omega \):

\[ I = d\Phi / d\Omega \]  

(1.27)

Intensity has as units \( \text{W} \cdot \text{steradian}^{-1} \). The solid angle \( \Omega \) describes a circle with area \( A \), on a distance \( r \) of the source of the scattered radiation, resulting in:

\[ dA = r^2 \cdot d\Omega \]  

(1.28)

For a specific considered area \( A \) (e.g. the size of the collection optics), the measured intensity is inversely proportional to the square of the distance to the source.

$^2$Here, the symbol \( \alpha \) represents a group of parameters, not polarisability.
The intensity of the light that is scattered in a certain direction by a dipole with a specific orientation in space is given by:

\[
I = \frac{d\Phi}{d\Omega} = \frac{\pi^2 \cdot c \cdot \bar{\nu}^4 \cdot p_0^2 \cdot \sin^2 \theta}{2 \cdot \varepsilon_0}
\] (1.29)

Here, \(\bar{\nu} = \frac{1}{\lambda}\) is the \textit{absolute} wavenumber\(^3\) of the electromagnetic radiation, \(p_0\) is the amplitude of the induced oscillating dipole moment, \(c\) is the speed of light and \(\varepsilon_0\) (\(\approx 8.854187817 \cdot 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}\)) is the permittivity of vacuum. \(\theta\) is the angle between the direction of the dipole moment and the direction in which the measurement is done. In reality, intensity is not measured in exactly one direction, but should be integrated over a solid angle \(\Omega\) (centred around \(\theta\)) and this expression should be integrated over this solid angle.

\[
\Delta \Phi = \frac{\pi^2 \cdot c \cdot \bar{\nu}^4 \cdot p_0^2}{2 \cdot \varepsilon_0} \int_{\theta-\Delta\theta}^{\theta+\Delta\theta} \int_{\phi-\Delta\phi}^{\phi+\Delta\phi} \sin^3 \theta \, d\theta \, d\phi
\] (1.30)

If \(\bar{\nu}\) is expressed in \(\text{cm}^{-1}\) in Equations (1.29) and (1.30), \(p_0\) in \(\text{C} \cdot \text{m}\), \(\Phi\) in \(\text{W}\) and \(I\) in \(\text{W} \cdot \text{sr}^{-1}\), then we obtain the following expression, if all constants are grouped:

\[
I = 1.6709 \cdot 10^{28} \cdot \bar{\nu}^4 \cdot \sin^2 \theta \cdot p_0^2
\] (1.29‘)

\[
\Delta \Phi = 1.6709 \cdot 10^{28} \cdot \bar{\nu}^4 \cdot p_0^2 \int_{\theta-\Delta\theta}^{\theta+\Delta\theta} \int_{\phi-\Delta\phi}^{\phi+\Delta\phi} \sin^3 \theta \, d\theta \, d\phi
\] (1.30‘)

In Equations (1.30) and (1.30‘), \(p_0\) is independent of the orientation. It can be seen that the measured intensity is proportional to \(\bar{\nu}^4\), and as a consequence, the Raman signal is seriously stronger, the shorter the laser wavelength that is used – certainly a reason

\(^3\)In Equation (1.29) the absolute wave number is used \(\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}\), opposite to the Raman wave number \(\nu_{\text{R}} = \frac{\nu}{c}\). The relation between both is: \(\nu = \nu_{\text{R}} \pm \nu_{\text{R}} = \nu_{\text{0}} \pm \nu_{\text{v}}\), with \(\nu_{\text{0}}\) laser frequency.
why UV-Raman spectroscopy is an interesting technique. From Equations (1.29) to (1.30) it can be seen that the measured intensity is proportional to the square of the amplitude of the polarisability and we see as well a strong dependence on the orientation \((\sin^2 \theta)\) of the measured Raman effect. Apart from this, the polarisability \(\alpha\) is also dependent on the direction, as this is basically a tensor (i.e. an operator that changes one vector in another). The direction of the induced dipole is not always the same as those of the electrical field vector. In a Cartesian coordinate system, Equation (1.2) can be written as:

\[
\begin{pmatrix}
p_x \\
p_y \\
p_z \\
\end{pmatrix} =
\begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz} \\
\end{pmatrix} \cdot \begin{pmatrix}
E_x \\
E_y \\
E_z \\
\end{pmatrix}
\]

\(1.31\)

with the vectors \(\mathbf{p}\) and \(\mathbf{E}\) expressed as their respective components \(p_x, p_y, p_z\) and \(E_x, E_y, E_z\). The polarisability tensor \(\alpha\) is expressed in a matrix. Usually, the polarisability tensor is symmetrical \((\alpha_{ij} = \alpha_{ji})\), which requires us to consider 6 components. However, two properties are independent of the axes chosen: the average polarisability \(\bar{\alpha}\) and the anisotropy factor \(\gamma^4\). These variables are defined as:

\[
\bar{\alpha} = \frac{1}{3} \cdot (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
\]

\(1.32\)

\[
\gamma^2 = \frac{1}{2} \cdot \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 \cdot (\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \right]
\]

\(1.33\)

The polarisability tensor can be split into two components: an isotropic tensor \(\alpha_{iso}\) and an anisotropic tensor \(\alpha_{aniso}\). \(\alpha_{iso}\) can be expressed as a diagonal matrix, with the diagonal elements equalling \(\bar{\alpha}\). In \(\alpha_{aniso}\) the diagonal elements equals \(\alpha_{ii} - \bar{\alpha}\),

---

4 Don’t confuse with the hyper polarisability, for which the same symbol is used (Equation (1.1)).
while the other elements are equal to the respective components $\alpha_{ij}$. As a consequence, the polarisability can be expressed as a sum:

$$\alpha = \alpha_{\text{iso}} + \alpha_{\text{aniso}}$$  \hspace{1cm} (1.34)

Totally isotropic systems have an anisotropy $\gamma$ of 0 and the anisotropic polarisability tensor $\alpha_{\text{aniso}} = 0$, since the mixed terms $\alpha_{ij}$ are equal to 0.

Let’s consider a molecule with a fixed position and orientation in space. We choose our axis system so that the molecule is in the origin of the axis system and the incident beam is along the x-axis (Figure 1.3). In Raman spectroscopy, two types of measurement geometry are often encountered:

- the traditional 90° geometry, where the scattered light is measured perpendicular to the incident beam;
- the back-scattering geometry, where the light is measured that is back-scattered in the direction of the laser.

The electrical field vector $\mathbf{E}$ of the incident light can be decomposed in two vectors, perpendicular to each other: $\mathbf{E}_y$ and $\mathbf{E}_z$; since the field vector is perpendicular to the direction of propagation, the third component $\mathbf{E}_x = 0$. For unpolarised light, in a certain period of time, the average amplitudes for both components have equal sizes.

For Rayleigh scattering, in the 90° geometry, we can state that:

$$p_y = \alpha_{yx} \cdot E_x + \alpha_{yz} \cdot E_z$$  \hspace{1cm} (1.35)

$$p_z = \alpha_{zx} \cdot E_x + \alpha_{zz} \cdot E_z$$  \hspace{1cm} (1.36)

When considering Raman scattering, the derivative of the polarisability to the normal coordinate has to be considered (i.e. the second term in Equation (1.18)). Similar equations as (1.35) and
Theoretical Aspects

Figure 1.3 Schematical representation of two traditional measurement geometries: (a) 90° geometry and (b) back-scattering geometry.

(1.36) can be obtained, with the replacement of the polarisability with its first derivative. In back-scattering geometry, for Rayleigh scattering, we find:

\[
\begin{align*}
\mathbf{p}_x &= \alpha_{xx} \cdot \mathbf{E}_x + \alpha_{xz} \cdot \mathbf{E}_z \\
\mathbf{p}_z &= \alpha_{zx} \cdot \mathbf{E}_x + \alpha_{zz} \cdot \mathbf{E}_z
\end{align*}
\]  (1.37)
When considering a molecule with a specific orientation in space (e.g. when describing a monocrystal), the intensity of the scattered radiation as a function of the orientation can be described as: (note that, for unpolarised light: $E_x = E_z = E$):

- in 90° geometry:

$$I_y^{(Rayleigh)} = \text{Const} \cdot (\alpha_{zy}^2 \cdot E_z^2 + \alpha_{xy}^2 \cdot E_x^2)$$
$$= \text{Const} \cdot (\alpha_{zy}^2 + \alpha_{xy}^2) \cdot E^2 \quad (1.38)^5$$

$$I_z^{(Rayleigh)} = \text{Const} \cdot (\alpha_{zz}^2 \cdot E_z^2 + \alpha_{xz}^2 \cdot E_x^2)$$
$$= \text{Const} \cdot (\alpha_{zz}^2 + \alpha_{xz}^2) \cdot E^2 \quad (1.39)$$

$$I_y^{(Raman)} = \text{Const} \cdot (\alpha'_{zy}^2 \cdot E_z^2 + \alpha'_{xy}^2 \cdot E_x^2)$$
$$= \text{Const} \cdot (\alpha'_{zy}^2 + \alpha'_{xy}^2) \cdot E^2 \quad (1.40)$$

$$I_z^{(Raman)} = \text{Const} \cdot (\alpha'_{zz}^2 \cdot E_z^2 + \alpha'_{xz}^2 \cdot E_x^2)$$
$$= \text{Const} \cdot (\alpha'_{zz}^2 + \alpha'_{xz}^2) \cdot E^2 \quad (1.41)$$

- in back-scattering geometry:

$$I_z^{(Rayleigh)} = \text{Const} \cdot (\alpha_{zz}^2 \cdot E_z^2 + \alpha_{xz}^2 \cdot E_x^2)$$
$$= \text{Const} \cdot (\alpha_{zz}^2 + \alpha_{xz}^2) \cdot E^2 \quad (1.39)$$

$$I_x^{(Rayleigh)} = \text{Const} \cdot (\alpha_{zx}^2 \cdot E_z^2 + \alpha_{xx}^2 \cdot E_x^2)$$
$$= \text{Const} \cdot (\alpha_{zx}^2 + \alpha_{xx}^2) \cdot E^2 \quad (1.42)$$

$$I_z^{(Raman)} = \text{Const} \cdot (\alpha'_{zz}^2 \cdot E_z^2 + \alpha'_{xz}^2 \cdot E_x^2)$$
$$= \text{Const} \cdot (\alpha'_{zz}^2 + \alpha'_{xz}^2) \cdot E^2 \quad (1.41)$$

---

^5In these equations, a series of parameters are grouped as ‘Const’. This term is different for Rayleigh or Raman scattering. It is, amongst others, function of the used laser wavelength. See also Equation (1.29).
\[ I_x^{\text{(Raman)}} = \text{Const} \cdot (\alpha'_{zx}^2 \cdot E_z^2 + \alpha'_{xx}^2 \cdot E_x^2) \]
\[ = \text{Const} \cdot (\alpha'_{zx}^2 + \alpha'_{xx}^2) \cdot E^2 \] (1.43)

The total intensity can be considered as the sum of the corresponding expressions. For 90° geometry \( I_{\text{tot},x} \) and for back-scattering geometry \( I_{\text{tot},y} \) the following expressions can be obtained, respectively:

\[ I_{\text{tot},x}^{\text{(Rayleigh)}} = \text{Const} \cdot (\alpha_{zy}^2 + \alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{zz}^2) \cdot E^2 \] (1.44)

\[ I_{\text{tot},x}^{\text{(Raman)}} = \text{Const} \cdot (\alpha'_{zy}^2 + \alpha'_{xy}^2 + \alpha'_{xz}^2 + \alpha'_{zz}^2) \cdot E^2 \] (1.45)

\[ I_{\text{tot},y}^{\text{(Rayleigh)}} = \text{Const} \cdot (\alpha_{xx}^2 + 2 \cdot \alpha_{xz}^2 + \alpha_{zz}^2) \cdot E^2 \] (1.46)

\[ I_{\text{tot},y}^{\text{(Raman)}} = \text{Const} \cdot (\alpha'_{xx}^2 + 2 \cdot \alpha'_{xz}^2 + \alpha'_{zz}^2) \cdot E^2 \] (1.47)

When considering a molecule with an isotropic polarisability tensor, the terms \( \alpha_{jk} \) disappear and the retrieved expression is further simplified.

**Discussion Topic 1.2**

What happens if we work with linearly polarised light?

**Answer:**

*Depending on the orientation of the plane of polarisation, in relation to the orientation of the molecule, different results can be obtained, considering Equations (1.38)–(1.43). In these cases, \( E_x \) no longer equals \( E_z \). By changing the plane of polarisation, it is possible to make either \( E_x \) or \( E_z \) disappear.*

In practice, it is impossible to record a Raman spectrum of a single molecule. The total signal intensity equals the sum of the
contributions of all molecules in the analysed volume $V$. When considering a group of randomly oriented molecules, the intensity has to be averaged over all possible orientations of the system, in relation to the considered electrical field. Typical examples of such systems with randomly oriented molecules are gasses, ideal fluids, finely dispersed powders (without preferential orientation) and amorphous materials. For these products, we need to consider the average squares of the polarisability. For a symmetrical polarisability tensor – thinking on Equations (1.32) and (1.33) – we can consider:

$$
\overline{\alpha_{xx}^2} = \overline{\alpha_{yy}^2} = \overline{\alpha_{zz}^2} = \frac{45 \cdot \alpha^2 + 4 \cdot \gamma^2}{45} \quad (1.48)^6
$$

$$
\overline{\alpha_{yx}^2} = \overline{\alpha_{yz}^2} = \overline{\alpha_{zx}^2} = \frac{\gamma^2}{15} \quad (1.49)
$$

$$
\overline{\alpha_{xx}\alpha_{yy}} = \overline{\alpha_{yy}\alpha_{zz}} = \overline{\alpha_{zz}\alpha_{xx}} = \frac{45 \cdot \alpha^2 - 2 \cdot \gamma^2}{45} \quad (1.50)
$$

Other product terms equal 0. Now it is possible, by using an analogous approach as for a specifically oriented molecule, to define the Rayleigh- and Raman-intensities for randomly oriented molecules. Indeed, by using Equations (1.44) to (1.47) we obtain:

- for the $90^\circ$ geometry:

$$
I_y(\text{Rayleigh}) = \text{Const} \cdot \left( \overline{\alpha_{zy}^2} \cdot \mathbf{E}_z^2 + \overline{\alpha_{xy}^2} \cdot \mathbf{E}_x^2 \right)
$$

$$
= \text{Const} \cdot \frac{2 \cdot \gamma^2}{15} \cdot \mathbf{E}^2 \quad (1.51)
$$

$$
I_z(\text{Rayleigh}) = \text{Const} \cdot \left( \overline{\alpha_{zz}^2} \cdot \mathbf{E}_z^2 + \overline{\alpha_{xz}^2} \cdot \mathbf{E}_x^2 \right)
$$

$$
= \text{Const} \cdot \frac{45 \cdot \alpha^2 + 7 \cdot \gamma^2}{45} \cdot \mathbf{E}^2 \quad (1.52)
$$

\(^6\text{Note: the square of the average polarisability } \overline{\alpha^2} = \frac{1}{9} \cdot (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2 \text{ is different from the average of the square of one of the components of the polarisability tensor } \overline{\alpha_{ij}^2}.\)
\[ I_y(\text{Raman}) = \text{Const} \cdot (\alpha'_{zy} \cdot E_z^2 + \alpha'_{xy} \cdot E_x^2) \]
\[ = \text{Const} \cdot \frac{2 \cdot \gamma^2}{15} \cdot E^2 \quad (1.53) \]
\[ I_z(\text{Raman}) = \text{Const} \cdot (\alpha'_{zz} \cdot E_z^2 + \alpha'_{xz} \cdot E_x^2) \]
\[ = \text{Const} \cdot \frac{45 \cdot \overline{\alpha}^2 + 7 \cdot \gamma^2}{45} \cdot E^2 \quad (1.54) \]

- for the back-scattering geometry:

\[ I_z(\text{Rayleigh}) = \text{Const} \cdot (\alpha^2_{zz} \cdot E_z^2 + \alpha^2_{xz} \cdot E_x^2) \]
\[ = \text{Const} \cdot \frac{45 \cdot \overline{\alpha}^2 + 7 \cdot \gamma^2}{45} \cdot E^2 \quad (1.52) \]
\[ I_x(\text{Rayleigh}) = \text{Const} \cdot (\alpha^2_{zx} \cdot E_z^2 + \alpha^2_{xx} \cdot E_x^2) \]
\[ = \text{Const} \cdot \frac{45 \cdot \overline{\alpha}^2 + 7 \cdot \gamma^2}{45} \cdot E^2 \quad (1.55) \]
\[ I_z(\text{Raman}) = \text{Const} \cdot (\alpha'_{zz} \cdot E_z^2 + \alpha'_{xz} \cdot E_x^2) \]
\[ = \text{Const} \cdot \frac{45 \cdot \overline{\alpha}^2 + 7 \cdot \gamma^2}{45} \cdot E^2 \quad (1.54) \]
\[ I_x(\text{Raman}) = \text{Const} \cdot (\alpha'_{zx} \cdot E_z^2 + \alpha'_{xx} \cdot E_x^2) \]
\[ = \text{Const} \cdot \frac{45 \cdot \overline{\alpha}^2 + 7 \cdot \gamma^2}{45} \cdot E^2 \quad (1.56) \]

The degree of depolarisation \( \rho_n \) is defined as the ratio \( I_y/I_z \) and in 90° geometry, it can be measured by using a polariser. From

\( \rho_n \): The index \( n \) shows that we consider the depolarisation ratio for unpolarised light. It is also possible to consider the degrees of depolarisation \( \rho || \) and \( \rho \perp \) when using planary polarised light, polarised in the \( xy \) or \( yz \) plane, respectively (for the geometry: see Figure 1.3).
Equations (1.53) to (1.54) it results that the numerical value of the degree of depolarisation equals:

$$\rho_n = \frac{I_y}{I_z} = \frac{6 \cdot \gamma^2}{45 \cdot \bar{\alpha}^2 + 7 \cdot \gamma^2} = \frac{6 \cdot \gamma'^2}{45 \cdot \bar{\alpha}'^2 + 7 \cdot \gamma'^2} \quad (1.57)$$

For totally isotropic systems $\rho_n = 0$, while for totally anisotropic systems $\rho_n = 6/7$. The total intensity of the scattered light is given by the sum of its components. For 90° geometry and for back-scattering geometry, this is, respectively:

$$I_{\text{tot},x \ (\text{Rayleigh})} = \text{Const} \cdot \frac{45 \cdot \bar{\alpha}^2 + 13 \cdot \gamma^2}{45} \cdot E^2 \quad (1.58)$$

$$I_{\text{tot},x \ (\text{Raman})} = \text{Const} \cdot \frac{45 \cdot \bar{\alpha}'^2 + 13 \cdot \gamma'^2}{45} \cdot E^2 \quad (1.59)$$

$$I_{\text{tot},y \ (\text{Rayleigh})} = \text{Const} \cdot \frac{90 \cdot \bar{\alpha}^2 + 14 \cdot \gamma^2}{45} \cdot E^2 \quad (1.60)$$

$$I_{\text{tot},y \ (\text{Raman})} = \text{Const} \cdot \frac{90 \cdot \bar{\alpha}'^2 + 14 \cdot \gamma'^2}{45} \cdot E^2 \quad (1.61)$$

In a Raman spectrum, clearly a difference in intensity can be found depending on the different areas in the spectrum. Usually the Rayleigh line is much more intense than the (Stokes or anti-Stokes) Raman bands are. In practice, the Rayleigh line is strongly suppressed with a filter. From Figure 1.1 it can be seen that the intensities in the Stokes region are more intense than the Raman bands in the anti-Stokes region. This can be explained by the Boltzmann distribution, describing the distribution of the molecules over the different energy levels. To understand this, in expression (1.29) we should not simply consider the amplitude of the induced dipole moment $p_0$ but rather its quantum mechanical equivalent: the dipole transition moment. For the Rayleigh transition, with the
same beginning and final state, the quantum mechanical approach results in similar formulas as the classical approach. Stokes and anti-Stokes transitions have a different starting and final situation. Due to the orientation dependence of the dipole transitions, for Rayleigh, Stokes and anti-Stokes transitions, each time a set of three equations can be described, for the following forms, respectively:

Rayleigh:

\[
[p_{x0}^{(1)}]_{b\leftarrow b} = \alpha_{xx} \cdot E_{x0} + \alpha_{xy} \cdot E_{y0} + \alpha_{xz} \cdot E_{z0}
\] (1.62)

Stokes:

\[
[p_{x0}^{(1)}]_{v_b+1\leftarrow v_b} = \sqrt{(v_b + 1) \cdot h \over 8 \cdot \pi^2 \cdot c \cdot v_v} \cdot (\alpha'_{xx} \cdot E_{x0} + \alpha'_{xy} \cdot E_{y0} + \alpha'_{xz} \cdot E_{z0})
\] (1.63)

Anti-Stokes:

\[
[p_{x0}^{(1)}]_{v_b-1\leftarrow v_b} = \sqrt{v_b \cdot h \over 8 \cdot \pi^2 \cdot c \cdot v_v} \cdot (\alpha'_{xx} \cdot E_{x0} + \alpha'_{xy} \cdot E_{y0} + \alpha'_{xz} \cdot E_{z0})
\] (1.64)

In these equations, the index 0 refers to the amplitude (=time-independent part) of the dipole transition moment. The index b refers to the first situation. The superscript (1) indicates that the approximation of electrical harmonicity is used in these equations. In other words, this means that Equation (1.2) is used instead of Equation (1.1). A consequence of this approximation is that we only consider transitions with a change in vibrational quantumnumber of \(\Delta v = \pm 1\) (for Raman transitions).

\(^8\)The first term in this equation is the quantum mechanical analogue of \(Q_{v0}\), the amplitude of the normal vibration.
INTERMEZZO 1.3 RAMAN INTENSITY ANNOTATIONS

In literature, for some molecules, a list of Raman band positions is given. Often, the authors also provide an indication of the relative Raman band intensities in the spectrum. Therefore, a list of abbreviations is used, indicating band intensities ranging from very strong (vs) to very weak (vw). Sometimes authors also include indications like br (broad band) or sh (shoulder). For band intensities, there are two systems commonly used – one system with 5 classes, another one with two more intermediate classes. Although no strict rules exist about when this or another band intensity annotation should be given, we provide here an indicative table, to provide the relative band intensity annotations.

<table>
<thead>
<tr>
<th>Annotation</th>
<th>Relative intensity (relative to most intense band intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very strong (vs)</td>
<td>100–90%</td>
</tr>
<tr>
<td>Strong (s)</td>
<td>90–75%</td>
</tr>
<tr>
<td>Medium to strong (m-s)</td>
<td>75–65%</td>
</tr>
<tr>
<td>Medium (m)</td>
<td>65–35%</td>
</tr>
<tr>
<td>Medium to weak (m-w)</td>
<td>35–25%</td>
</tr>
<tr>
<td>Weak (w)</td>
<td>25–10%</td>
</tr>
<tr>
<td>Very weak (vw)</td>
<td>10–0%</td>
</tr>
</tbody>
</table>

Further Reading

P. Vandenabeele, L. Moens, J. Raman, Spectrosc. 43 (2012), 1545–50.
An importance difference between classical and quantum mechanical approximation is in the presence of the factors \((v_b + 1)^{1/2}\) and \(v_b^{1/2}\) in the equations of the Stokes and anti-Stokes dipole transition moment, respectively. Note that, as in the expression for the intensity of the scattered light (Equation (1.29)) contains the square of the dipole (transition) moment, there is a multiplication with a whole quantumnumber.

At normal measurement temperatures, most molecules are in the vibrational ground state \((v_b = 0)\), although some molecules might be in an excited vibrational state \((v_b = 1, 2, \ldots)\). The intensity of a certain Stokes transition \((v_b + 1 \leftarrow v_b)\) is proportional to \(N_{v_b} \cdot (v_b + 1)\), where \(N_{v_b}\) equals the number of molecules in the vibrational state \(v_b\). The occupation of a specific energy level is given by the Boltzmann distribution:

\[
N_{v_b} = N \cdot \frac{e^{-E_{v_b}/kT}}{\sum_i e^{-E_i/kT}} = N \cdot \frac{e^{-\left(v_b + \frac{1}{2}\right)hc\nu_v/kT}}{\sum_i e^{-\left(v_i + \frac{1}{2}\right)hc\nu_v/kT}} \tag{1.65}
\]

In this equation, \(N\) is the total molecule population, \(k\) is the Boltzmann constant \((k = 1.380658 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1})\) and \(T\) is the temperature (in K). Since the harmonic oscillation approximation is considered, the wavenumbers for the different transitions with \(\Delta v = 1\) coincide \((i.e. \ 1 \leftarrow 0, 2 \leftarrow 1, 3 \leftarrow 2, \ldots)\) and the measured intensity of a certain vibration is proportional to \(\sum_{v_b} [N_{v_b} \cdot (v_b + 1)]\). If, in this equation \(N_{v_b}\) is replaced by Equation (1.65), we obtain:

\[
\sum_{v_b} [N_{v_b} \cdot (v_b + 1)] = \frac{N}{1 - e^{hc\nu_v/kT}} \tag{1.66}
\]

For anti-Stokes transitions, by an analogy, we obtain:

\[
\sum_{v_b} (N_{v_b} \cdot v_b) = \frac{N}{e^{hc\nu_v/kT} - 1} \tag{1.67}
\]
These equations can now be implemented in the general intensity equation. Following Equations (1.59) and (1.61), for a group of \( N \) molecules, randomly oriented in space the intensity of the Stokes Raman band in \( 90^\circ \) and back-scattering geometry, respectively, can be given by:

\[
I_{tot,x}(\text{Stokes}) = \frac{h \cdot N \cdot (\nu_0 - \nu_v)^4}{8 \cdot \varepsilon_0^2 \cdot c \cdot \nu_v} \cdot \frac{45 \cdot \alpha'^2 + 13 \cdot \gamma'^2}{45} \cdot \frac{E^2}{1 - e^{-h \cdot c \cdot \nu_v / kT}}
\]  \hspace{1cm} (1.68)

\[
I_{tot,y}(\text{Stokes}) = \frac{h \cdot N \cdot (\nu_0 - \nu_v)^4}{8 \cdot \varepsilon_0^2 \cdot c \cdot \nu_v} \cdot \frac{90 \cdot \alpha'^2 + 14 \cdot \gamma'^2}{45} \cdot \frac{E^2}{1 - e^{-h \cdot c \cdot \nu_v / kT}}
\]  \hspace{1cm} (1.69)

For anti-Stokes transitions, these expressions can be obtained for \( 90^\circ \) and back-scattering geometry, respectively:

\[
I_{tot,x}(\text{anti-Stokes}) = \frac{h \cdot N \cdot (\nu_0 + \nu_v)^4}{8 \cdot \varepsilon_0^2 \cdot c \cdot \nu_v} \cdot \frac{45 \cdot \alpha'^2 + 13 \cdot \gamma'^2}{45} \cdot \frac{E^2}{e^{h \cdot c \cdot \nu_v / kT} - 1}
\]  \hspace{1cm} (1.70)

\[
I_{tot,y}(\text{anti-Stokes}) = \frac{h \cdot N \cdot (\nu_0 + \nu_v)^4}{8 \cdot \varepsilon_0^2 \cdot c \cdot \nu_v} \cdot \frac{90 \cdot \alpha'^2 + 14 \cdot \gamma'^2}{45} \cdot \frac{E^2}{e^{h \cdot c \cdot \nu_v / kT} - 1}
\]  \hspace{1cm} (1.71)

From these equations, and in agreement with Figure 1.1, it can be seen that the intensity of anti-Stokes radiation is lower than that of Stokes-Radiation. As a consequence, for analytical purposes, Stokes radiation is usually used.
We see in the first instance a linear relationship between the measured intensity and the number of molecules in the sampled volume, which can form the basis for quantitative measurements. In this approach, we didn’t take degeneration into account: the fact that two different vibrations may correspond to the same energy level.

We see that in both cases (90° geometry as well as back-scattering geometry) the ratio between the intensity of Stokes and anti-Stokes scattering equals:

$$\frac{I_{\text{Stokes}}}{I_{\text{anti-Stokes}}} = \frac{(\nu_0 - \nu_k)^4}{(\nu_0 + \nu_k)^4} \cdot e^{\frac{\hbar \cdot c \cdot \nu_k}{k \cdot T}}$$  \hspace{1cm} (1.72)

In theory, we see that we can use this expression to use our Raman spectrometer as an expensive thermometer.

**Discussion Topic 1.3**

How can we measure the temperature of analysis from a Raman spectrum?

**Answer:**

*By using Equation (1.72), it is possible to calculate the temperature T. For a given Raman band, at band the ratio is made of the Stokes intensity at position $\nu_k$ and the anti-Stokes intensity at position $-\nu_k$. The laser wavelength, expressed in wavenumbers, is also used in this expression. The only nonconstant parameter is the temperature T, which can thus be calculated. In practice, this approach is hampered by the occurrence of wavelength-dependent sensitivity of the detector, which has to be taken into account when making the intensity ratio. Also, someone has to correct for the occurrence of fluorescence and eventually also for wavelength-dependent self-absorption of the sample. Moreover, when irradiated with*
laser light, the sample may warm up, resulting in a changing occupation of the energy levels. Especially if Stokes and anti-Stokes radiation are not measured simultaneous, this may seriously influence the estimation of the temperature.

Recording a Raman spectrum can sometimes be hampered by the occurrence of absorption, by the analyte molecule or by the matrix. A typical example of this interference is the influence of water on the spectrum. The three normal vibrations of water are Raman active, but the bands can clearly be distinguished, and unless infrared spectroscopy, little interference is expected. However, water strongly absorbs radiation in the infrared region of the spectrum and when recording a spectrum in an aqueous solution, one should take these absorption effects into account. One the one hand, laser light with wavenumber $\nu_0$ can be absorbed, while on the other hand the scattered light with wavenumber $\nu = \nu_0 \pm \nu_v$ may be absorbed as well.

In some other cases, the Raman scattered light is much more intense than initially expected. Enhancement of the Raman signal can be caused by different reasons, often related to time-dependent effects. The previous equations are not able to deal with this, since only the amplitude of the electrical field (i.e. the time-independent part) was involved. One of the most important time-dependent effects is the Resonance Enhanced Raman effect. Intuitively, we can understand this from Figure 1.2: the schematical diagram of the different transitions. The (in-)elastic scattering of the light is presented as an absorption-emission mechanism. In this case, the molecule reaches during a short time an excited state $\Delta E = h \cdot \nu_0$ higher than the initial state. This virtual energy level is usually situated in a ‘forbidden’ zone. However, in the case of resonance enhancement, this energy level coincides with a stable electronic state. As the absorption process in this case can be considered as an ‘allowed’ transition, the absorption-emission process has a higher
probability of occurrence, which means that we can expect a higher Raman intensity than initially thought.

1.5 Raman Bandwidth

The Raman bandwidth is determined by a number of factors. Firstly, there is natural band broadening, which is a direct consequence of the Heisenberg uncertainty principle \( (ca. 10^{-8} \text{ cm}^{-1}) \). Raman spectra of gases may also undergo Doppler broadening \( (ca. 10^{-3} \text{ cm}^{-1} \text{ at } 300 \text{ K}) \), which is dependent on temperature and pressure. Most spectrometers have insufficient resolution to detect these effects.

However, for most materials – being amorphous or nonideal single crystals – the local molecular neighborhood is the most important source of band broadening. From Equation (1.23) we know that the Raman band position in a spectrum is determined by two factors: the reduced mass of the atoms and the force constant of the bond. Chemical environment does not influence the reduced mass; however, it does influence the force constant of the chemical bond. A different chemical environment may cause a shift in the Raman band position. If each of these bonds present in the measured volume of the sample does not have the same chemical environment, there may be a range of slightly different force constants, which consequently may cause band broadening. This clearly explains why Raman bands of amorphous materials are broader than those of crystalline materials.

The second parameter in Equation (1.23) that determines the band position is the mass of the contributing atoms. Differences in atomic mass (i.e., different isotopes) give rise to different Raman band positions. If these different Raman bands are closer than the spectral resolution of the spectrometer, the Raman bands are observed as a single (broader) band.
For Raman spectra of gasses and fluids, another type of Raman band broadening is to be considered: in these materials, also rotation-vibration transitions are possible. During a stretching vibration, the bond length varies as a cosinus equation with time (Equation (1.6)). The angular momentum (and thus the rotational energy) of the molecule is dependent on the bond distance. Thus, rotational and vibrational energy of the molecule are coupled; for each vibrational transition, there are different roto-vibrational transitions, allowing the energy to be raised or lowered with a number of rotational quantum steps. Rotational quantum steps are much lower than vibrational transitions, so that each fundamental vibrational transition can be associated with a number of roto-vibrational bands, being slightly lower or higher than the fundamental transition. Again, if the spectral resolution of the spectrometer is insufficient to resolve them, this causes band broadening. Therefore, freezing liquids sometimes allows to obtain sharper Raman bands. However, a different aggregation state may cause sharper bands, but sometimes at different positions in the Raman spectrum, for instance due to the occurrence of hydrogen bonding. The change in molecular environment again changes the force constant of the bond and consequently of the Raman band position.

Apart from these theoretical aspects, instrumental parameters have an influence on the Raman bandwidth. An important characteristic is the spectral resolution of the spectrometer. In dispersive systems, this is mainly determined by the line density of the spectrometer grating, the size of the entrance slit, the pixel size of the CCD detector and the distance between grating and detector (focal length of the spectrometer). For Fourier-transform spectrometers, the spectral resolution is mainly determined by the travel distance of the moving mirror in the interferometer, as this determines the number of fringes per wavenumber in the interferrogram (see Chapter 4, Section 4.4.2). Apart from this, the wavelength stability of the laser
is of importance. This can be influenced by the working temperature of the system, and often lasers are equipped with an internal temperature calibration system. Laser side-bands are removed by using a filter system.

1.6 The General Appearance of a Raman Spectrum

**QUESTION 1.4**

Complete the following paragraph.

Every Raman spectrum (Figure 1.1) has a very intense band at 0 cm\(^{-1}\): the line, caused by __________ scattering of electromagnetic radiation. Normally the intensity of this line is suppressed by using appropriate filters.

At positive wavenumbers, __________ Raman bands are observed, while at negative wavenumbers, one can find __________ Raman bands. We know that __________ Raman scattering is more intense than __________ scattering, as a consequence of the __________ distribution.

Stokes and anti-Stokes bands are positioned symmetrically to the Rayleigh line. The observed Raman bands correspond with transitions for which there is a change in __________ of the molecule. By using group theory, it is possible to study whether certain transitions will give rise to a Raman band or not.

The Raman band position is dependent on the __________ of the bond, as well as of the __________ of the constituting atoms. As a consequence, __________ can be defined. Bonds with relatively heavy elements (typically inorganic materials, such as metal oxides) give rise to Raman bands at relatively __________ wavenumbers. Moreover, crystalline materials can undergo lattice vibrations: these can hardly be considered as intramolecular vibrations, but are merely vibrations of larger units relative to
each other. The corresponding Raman bands are observed at __________ wavenumbers and are strongly dependent on the local symmetry. Amorphous materials give in general rise to __________ Raman bands, compared to crystalline materials.

1.7 Summary

The theoretical aspects of Raman spectroscopy have been introduced in this chapter. We have discussed the selection rule for Raman spectroscopy, namely that during a Raman active vibration, a change in polarisability occurs. To be able to interpret Raman spectra, it is important to know the different factors that determine the position of a Raman band and we have discussed the concept of group frequencies. In this chapter, also the influence of the laser wavelength on the Raman spectra has been described and we have determined the different factors that influence the Raman bandwidth.

Further Reading