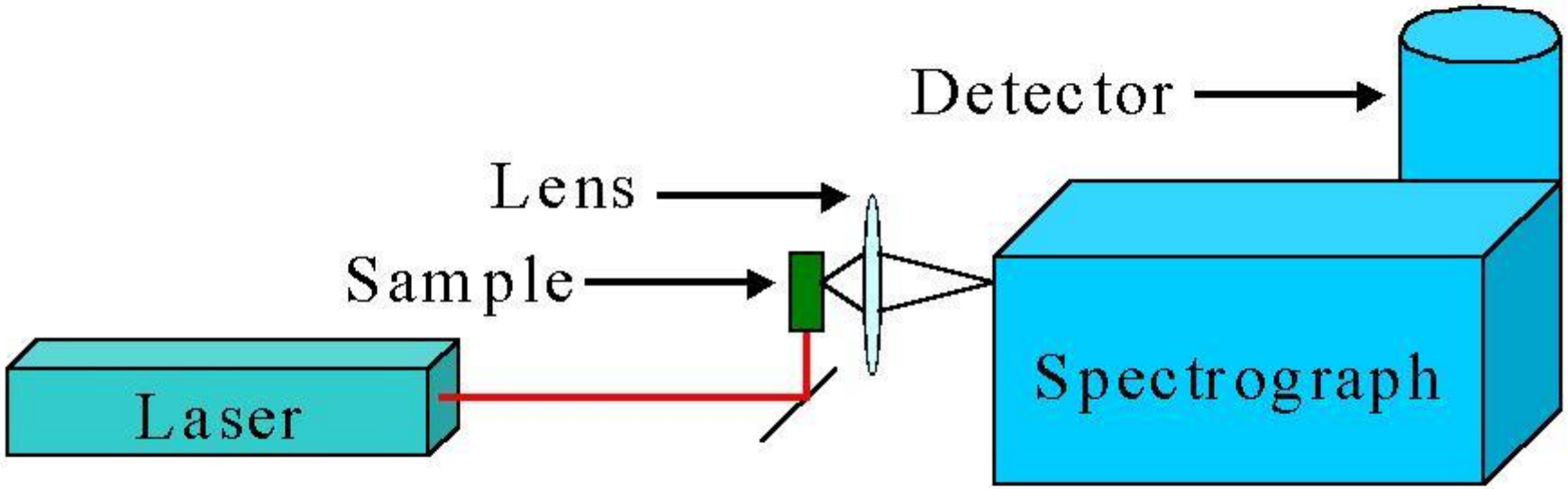
Raman Spectroscopy

- Experimental Configuration
- Classical Polarizability
- The Depolarization Ratio

NC State University

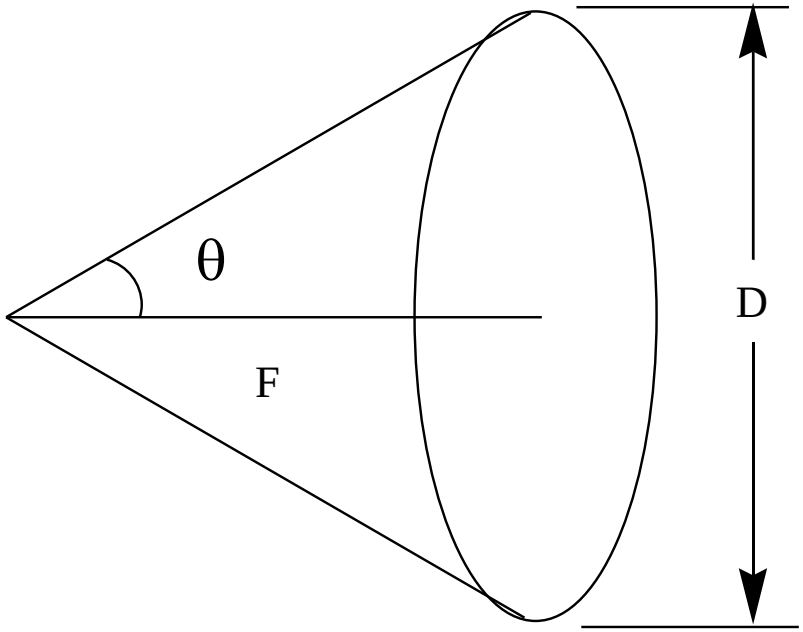
Experimental Raman Apparatus



Inelastic light scattering produces a frequency shift. There is exchange of energy between the vibrations of the molecule and the incident photon.

Collection of scattered light

Although we discuss the light scattered along Y it must be understood that light is in fact scattered into all directions. The solid angle of a sphere is 4π stearadians and the solid angle collected is $d\Omega$ where $d\Omega < 4\pi$. For example, if the f-number of a collection lens is 1 then the geometry for collection is



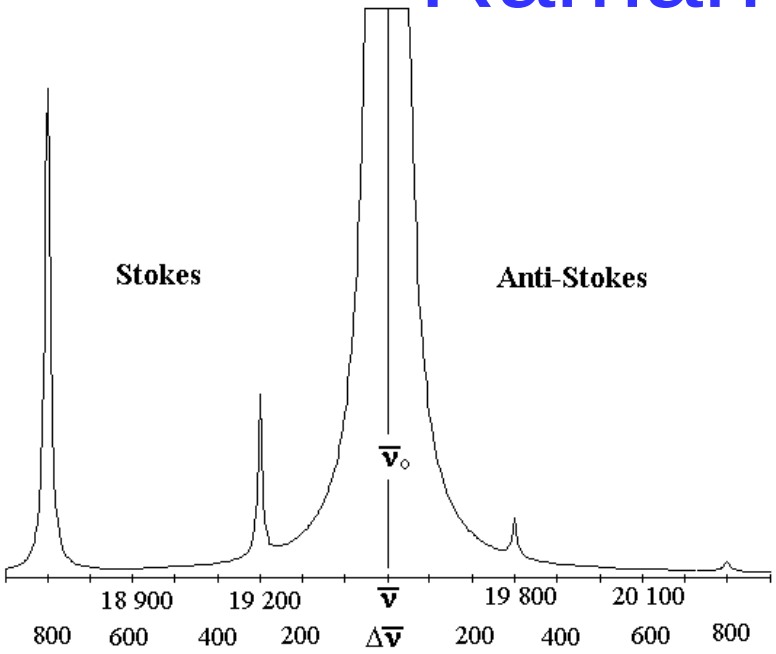
Collection of scattered light

In this case since D = F we have θ = arctan(1/2) = 26.56^o = 0.147π radians. The solid angle here can be calculated by integrating the differential volume element $d\Omega = d\phi \sin\theta d\theta$ over the limits 0 to 2π and 0 to 0.147π.

$$\int_0^{2\pi} d\phi \int_0^{0.147\pi} \sin\theta d\theta = \left(2\pi\right)\left(-\cos\theta\right)\Big|_0^{0.147\pi}$$

When we evaluate the integral over the limits shown we find that the second term is approximately 0.1. So the solid angle defined by f/1 collection optics is 0.4π stearadians. This arrangement leads to collection of about 10% of the total light scattered from the sample.

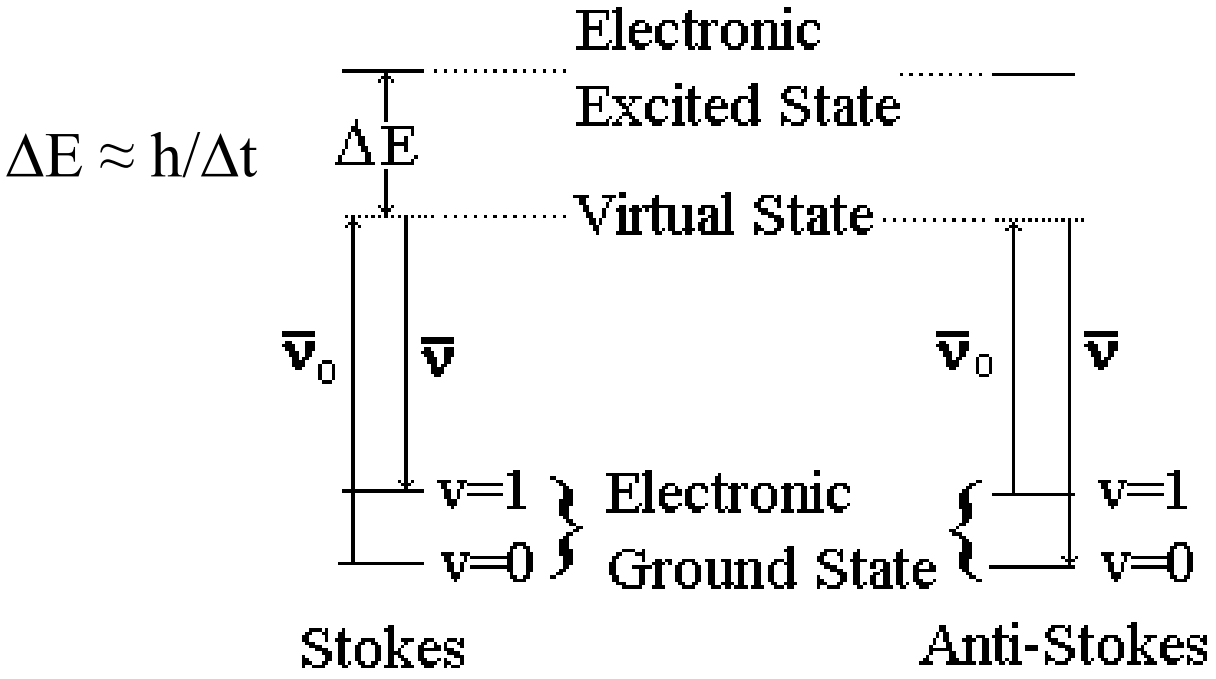
Raman scattering



The Raman spectrum of a compound with vibrational modes at 300 and 800 cm^{-1} observed with a 19,500 cm^{-1} exciting line at 300K. The very strong line at n_o is due to Rayleigh scattering. The anti-Stokes component of the Raman scattering is weaker than the Stokes component by $\exp(-E_{vib}/kT)$.

In **normal Raman**, the scattering is not from a stationary state but from a virtual state. Virtual states can be considered as stationary states that have been spread out by the uncertainty principle, $\Delta E\ \Delta t \approx h$ where ΔE is the amount by which the photon's energy fails to be in resonance with the closest lying excited state and Δt is the time the system can spend in this state.

Stokes and anti-Stokes



The two types of normal Raman scattering.

Since $\Delta t \approx (c)^{-1}$, if the exciting line, n_0 is 20,000 cm^{-1} and the lowest excited state is 30,000 cm^{-1}, then $\Delta E = 1x10^4$ cm^{-1} and $\Delta t \approx (1x10^4 \times 3x10^{10})^{-1} \approx 3$ fs or about a vibrational period - normal Raman scattering is a very fast process.

Molecular polarizability

What fraction of the molecules will undergo scattering will depend upon how the electrons are affected by the electric field, *i.e.*, on the molecule's **polarizability** (α).

One can view the process as the photon initiating an oscillating dipole (μ) in the molecule as the electrons oscillate with the electric field; it is then the oscillating dipole that radiates the scattered photon (much like a radio transmitter).

The strength of this induced dipole is proportional to the electric field of the photon. The proportionality constant is the molecular polarizability, α. Since the dipole and the electric field are actually vectors, the polarizability is a tensor.

$$\boldsymbol{\mu}_{ind} = \boldsymbol{\alpha\varepsilon}$$

The polarizability tensor

$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \end{pmatrix}$$

where α_{xz} ($\neq 0$) is a measure of how strongly the z-component of the electric field (z-polarization) induces a dipole in the x-direction: **this implies that the vibration interacts with the electric field in such a way so as to rotate the polarization of the electric field**.

Indeed, one of the important pieces of information available from Raman scattering is the polarization change that the incoming photon undergoes.

Classical description of Raman scattering

The molecular vibration at ω_v alters the polarizability according to:

$$\alpha_{molecule} = \alpha_M + \frac{\partial \alpha_M}{\partial Q} \Delta Q cos(\omega_v t)$$

A transition dipole moment from state i to f is created by

Interaction of radiation at frequency ω_0.

$$\mu_{fi} = \frac{\partial \alpha_M}{\partial Q} \Delta Q cos(\omega_v t) E_0 \cos(\omega_0 t)$$

$$= \frac{\partial \alpha_M}{\partial Q} \frac{\Delta Q}{2} E_0 \left(\cos([\omega_0 - \omega_V]t) + \cos([\omega_0 + \omega_V]t) \right)$$

The depolarization ratio

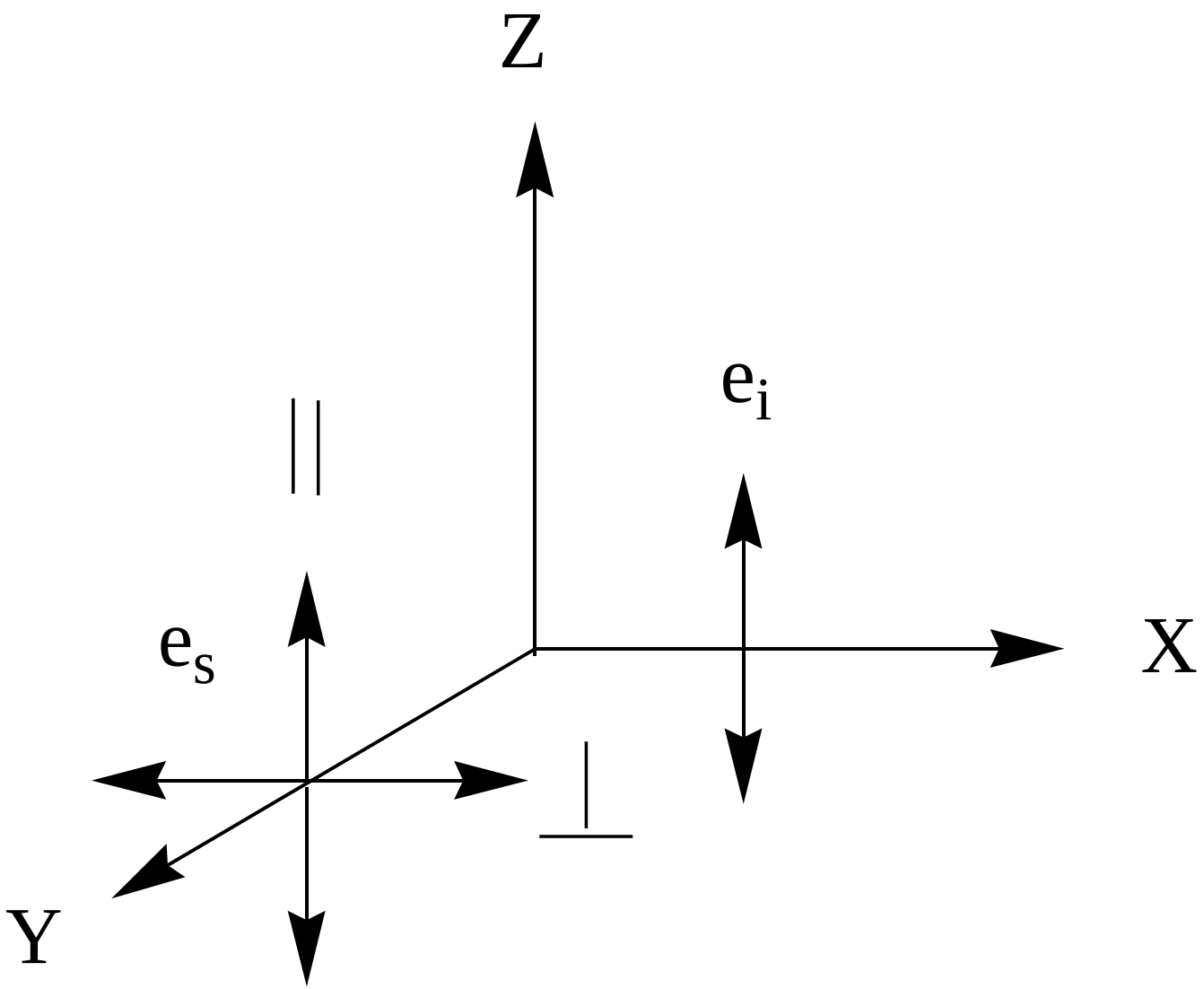
The intensity of scattered radiation which is polarized perpendicular to that of the incoming radiation is defined as $I_{\perp}$ and that of the radiation parallel to the incoming radiation as $I_{\parallel}$ then the **depolarization ratio**, ρ is defined as,

$$\rho = I_{\perp}/I_{\parallel}$$

When the polarizability tensor is diagonal, the vibration does not rotate the electric vector: all of the intensity will remain parallel to the incoming radiation and $\rho = 0$. This is **isotropic scattering**.

However, if any of the off-diagonal elements of the polarizability tensor are non-zero, then there is intensity in $I_{\perp}$ and $\rho > 0$.

Geometry for polarization measurement



Definition of an invariant

For a rank 2 tensor (e.g. transition polarizability) we can write down three rotational invariants, Σ_J, that are linear combinations of the α_{JM} that are independent of reference frame. These are

$$\Sigma^J = \sum_{M=-J}^{J} \left(\alpha^J{}_M\right)^2$$

where J = 0, 1, 2… and M = 0 , $\pm$ 1 ,…, $\pm$ J. Each Σ_J is called an invariant because it is independent of orientation. The length of a vector is independent of its orientation. That is the same thing as saying that for the vector **m**, the combination $m_x^2 + m_y^2 + m_z^2$ is a rotational invariant.

Three invariants of a second-rank tensor

A second rank tensor has three invariants,

$$\Sigma^0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)^2$$

$$\Sigma^1 = \frac{1}{2}\left\{\left(\alpha_{xy} - \alpha_{yx}\right)^2 + \left(\alpha_{xz} - \alpha_{zx}\right)^2 + \left(\alpha_{zy} - \alpha_{yz}\right)^2\right\}$$

$$\Sigma^2 = \frac{1}{2}\left\{\left(\alpha_{xy} + \alpha_{yx}\right)^2 + \left(\alpha_{xz} + \alpha_{zx}\right)^2 + \left(\alpha_{zy} + \alpha_{yz}\right)^2\right\}$$

$$+\frac{1}{3}\left\{\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2\right\}$$

The invariants are

Σ^0 isotropic part

Σ^1 anti-symmetric anisotropy

Σ^2 symmetric anisotropy

Invariants in the lab frame

The isotropic part of the polarizability is proportional to the square of the trace of the polarizability tensor $\Sigma_0 = (\mathrm{Tr}\alpha)^2/3$. The trace of tensor a (written as $\mathrm{Tr}\alpha$) is the sum of diagonal elements of the tensor.

Therefore, Σ_2 represents the deviation of the polarizability from spherical symmetry.

The lab frame components $|\alpha_{ZZ}|^2$ and $|\alpha_{XZ}|^2$ can be written as linear combinations of the invariants.

$$\left(\alpha_{ZZ}\right)^2 = \frac{1}{3}\Sigma^0 + \frac{2}{15}\Sigma^2$$

$$\left(\alpha_{XZ}\right)^2 = \frac{1}{6}\Sigma^1 + \frac{1}{10}\Sigma^2$$

Regimes of Raman polarization

The depolarization ratio is:

$$\rho = \frac{\left(\alpha_{zx}\right)^2}{\left(\alpha_{zz}\right)^2}$$

Using the invariants the depolarization ratio is

$$\rho = \frac{5\Sigma^1 + 3\Sigma^2}{10\Sigma^0 + 4\Sigma^2}$$

Thus, we see that isotropic Raman ($\Sigma^1 = 0$) is polarized and $\rho = 0$ (for a molecule of spherical symmetry)
and anisotropic Raman ($\Sigma^0 = 0$) is depolarized and hence $\rho = 3/4$

Non-resonant Raman scattering

The form of α in the molecular frame depends on the symmetry of the vibration. For non-resonant Raman the polarizability tensor is symmetric and therefore the anti-symmetric anisotropy Σ^1 is zero. Inspection of the anti-symmetric anisotropy shows that it is zero when $\alpha_{rs} = \alpha_{sr}$.

Σ^2 depends on non-zero off diagonal terms and on differences in the diagonal terms. It is not necessarily zero in non-resonant Raman scattering.

Non-resonant Raman Scattering: Totally symmetric modes

The polarizability tensor for a totally symmetric vibrational mode preserves this symmetry. These are the modes that we think of a Franck-Condon active modes in absorption spectroscopy. The Cartesian Raman tensor for any totally symmetric mode is of the form:

$$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

For molecules with spherical symmetry a = b = c.
Symmetric top molecules have two equal components, so a = b $\neq$ c.
Asymmetric top molecules have a $\neq$ b $\neq$ c.

Non-resonant Raman Scattering: Totally symmetric modes

For example, the Raman polarizability tensor for any totally symmetric mode of a totally symmetric molecule (CCl_4 or SF_6) has three equivalent diagonal components and so

$$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$$

Thus, $\Sigma^1 = \Sigma^2 = 0$ and $\rho = 0$.

However, there are two other cases

Symmetric top

$$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

Asymmetric top

$$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

It is often convenient to write out the totally and non-totally symmetric part of the polarizability,

$$\alpha = \alpha \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \beta$$

where we define the average polarizability:

$$\alpha = \frac{Tr\alpha}{3} = \frac{\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)}{3}$$

and the tensor β is the anisotropy of the polarizability

$$\beta = \begin{pmatrix} \left(\alpha_{xx} - \alpha\right) & \alpha_{yx} & \alpha_{zx} \\ \alpha_{xy} & \left(\alpha_{yy} - \alpha\right) & \alpha_{zy} \\ \alpha_{xz} & \alpha_{yz} & \left(\alpha_{zz} - \alpha\right) \end{pmatrix}$$

Polarized modes

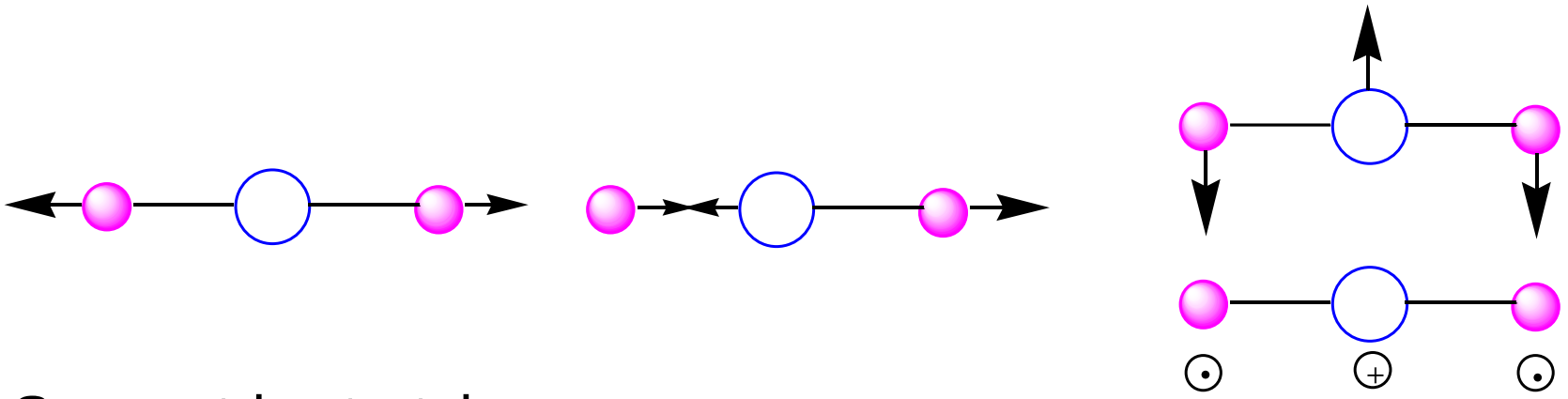
We can treat three cases for molecules of high symmetry. Here we ignore off-diagonal terms (e.g. a_{xy} etc.)

1. Spherical symmetry (e.g. T_d, O_h)
   $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$; $\Sigma_0 = 3\alpha^2$ $\alpha_1 = 0$; $\alpha_2 = 0$
   $\rho = 0$

2. Axial symmetry (e.g. D_{4h}) (symmetric top)
   $\alpha_{xx} = \alpha_{yy}$ but $\alpha_{zz} = 0$; $\Sigma_0 = 4/3\alpha^2$; $\Sigma_1 = 0$; $\Sigma_2 = 2/3\alpha^2$
   $\rho = 1/8$

3. Different symmetry axes (e.g. D_{2h}) (asymmetric top)
   $\alpha_{xx} >> \alpha_{yy}$ and α_{zz} which are approximately 0.
   $\Sigma_0 = 1/3\alpha^2$; $\Sigma_1 = 0$; $\Sigma_2 = 2/3\alpha^2$
   $\rho = 1/3$

Normal modes - CO_2



Symmetric stretch
ν_1 2289 cm^{-1}
(Raman active)

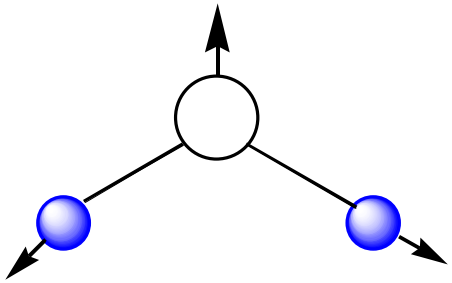
Asymmetric stretch
ν_3 2349 cm^{-1}
(IR active)

Bends
ν_2 667 cm^{-1}

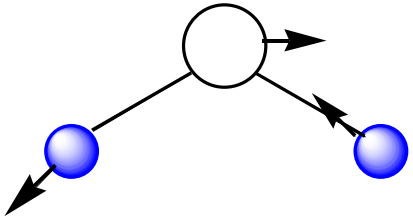
(IR active)

There are 4 normal modes (3N - 5). Three of them are infrared active since they show a dipole moment change in their motion.

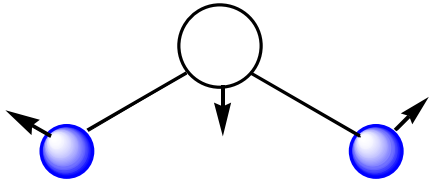
Normal modes - water



Symmetric Stretch
ν_1 3825 cm^{-1}



Asymmetric Stretch
ν_3 3935 cm^{-1}



Bend
ν_2 1654 cm^{-1}

There are 3 normal modes (3N - 6). All of them are infrared active since all show a dipole moment change in their motion. The harmonic approximation can be applied to each normal mode.