Normal Modes

In general, the nuclei of a vibrating polyatomic molecule undergo complex movement about their equilibrium positions; but it is always possible to decompose this motion into a sum of vibrations – normal modes – for which the deviations are in phase.

Potential energy:
$$V = \tfrac{1}{2}\sum_{i\,j} k_{ij}\xi_i\xi_j \qquad \xi = \text{deviation}$$
from equilibrium

Generalized Force Constant:
$$k_{ij} = \left[\frac{\partial^2 V}{\partial\xi_i\partial\xi_j}\right]_0 \qquad$$
Evaluated at the equilibrium position

i and j both range from 1 to 3N.

Normal Coordinates are defined as the linear combinations
$$Q_i = \sum_k c_{ik}q_k = \sum_k c_{ik}m_k^{\frac{1}{2}}\xi_k \qquad q = \text{mass-weighted}$$
coordinate

such that
$$V = \tfrac{1}{2}\sum_i K_i Q_i^2 = \sum_i V_i$$

and
$$T = \tfrac{1}{2}\sum_i m_i\dot{\xi}_i^2 = \tfrac{1}{2}\sum_i \dot{Q}_i^2$$

i.e. the potential energy is diagonal just like the kinetic energy.

This general treatment applies to all $3N$ degrees of freedom, but 3 of these are translational, 3 are rotational (2 for linear molecules).

Thus $3N$-6 displacements correspond to vibrations ($3N$-5 for linear molecules).

Vibrational Spectra of Polyatomics

Once the complex vibrational motion of a molecule has been decomposed into normal modes the vibrational frequencies, zero-point energies, etc. associated with each mode can be treated to a good approximation as independent of each other.

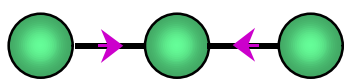$$\hat{H} = \sum_i \hat{H}_i = \tfrac{1}{2}\sum_i \left\{ -\hbar^2 \frac{\partial^2}{\partial Q_i^2} + K_i Q_i^2 \right\} \qquad \text{Separation of variables}$$

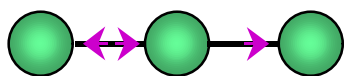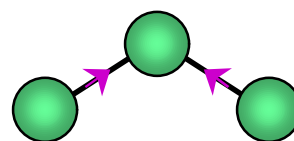$$\Psi = \prod_{i=1}^{3N-6} \psi_i(Q_i) \qquad \hat{H}_i \psi_i = E_i \psi_i$$

Each mode can be treated as a simple harmonic oscillator.

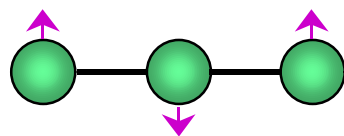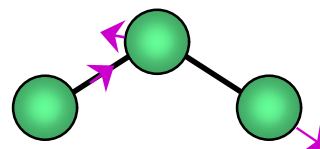$$E = \sum_i \hbar\omega_i (v_i + \tfrac{1}{2}) \qquad \Delta E = \hbar\omega_i$$

Electric dipole transitions are only allowed for modes in which the dipole moment changes. Such modes are called IR active.
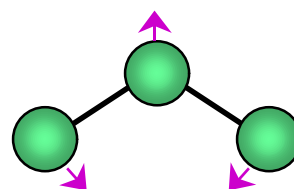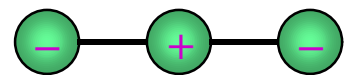
symmetric stretch

asymmetric stretch

symmetric bend

Raman Spectroscopy

Raman effect $\equiv$ inelastic scattering of light by molecules.

• Light may deposit energy during the scattering interaction
   by exciting internal modes of the molecule.

• Light may gain energy if the molecule is already excited.

A monochromatic beam is used for irradiation.
Detection is in a perpendicular direction.
Since the molecular energy is quantized the scattered light
includes components shifted in frequency from the excitation
source by discrete amounts.

The Rayleigh line is due to light scattered at ν_{exc}

Stokes lines are at lower frequencies: $\nu \ll \nu_{exc}$

anti-Stokes lines are at higher frequencies: $\nu \gg \nu_{exc}$

The intensity of the Stokes lines is usually greater than the
anti-Stokes, which depend on population of excited states.
Both are weaker than Rayleigh scattering.

The Raman effect depends on the polarizability of molecules.

The polarizability is a measure of how easily a dipole moment
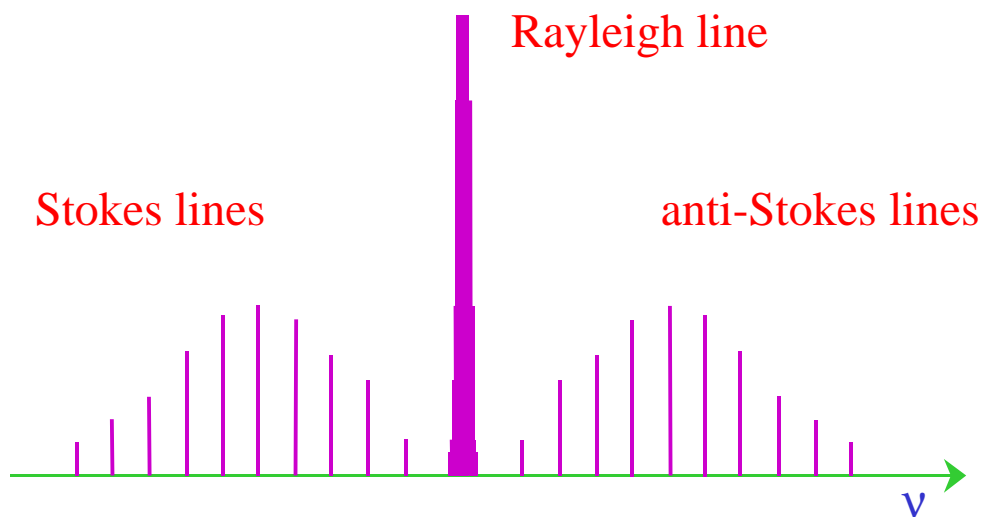is induced when the molecule is placed in an electric field.

Rotational Raman Spectroscopy

For linear molecules, $\qquad E_J = BJ(J+1)$

Selection rule: $\quad \Delta J = \pm 2$ (and 0)

$$\Delta E = B(4J+6)$$

$$\nu = \nu_{exc} \pm (B/h)(4J+6)$$

Rayleigh line

Stokes lines

anti-Stokes lines

ν

Note: A linear molecule with a centre of symmetry has no dipole moment, and is therefore invisible to regular microwave spectroscopy. It *does* have a Raman spectrum, however, but the intensities depend on nuclear spin.

Vibrational Raman Spectroscopy

Pure vibration

$$\Delta v = 0, \pm 1, \pm 2, \, ...$$

$$\nu = \nu_{exc} - \omega_0 / 2\pi, \qquad \nu_{exc} + \omega_0 / 2\pi$$

anti-Stokes often too weak to observe

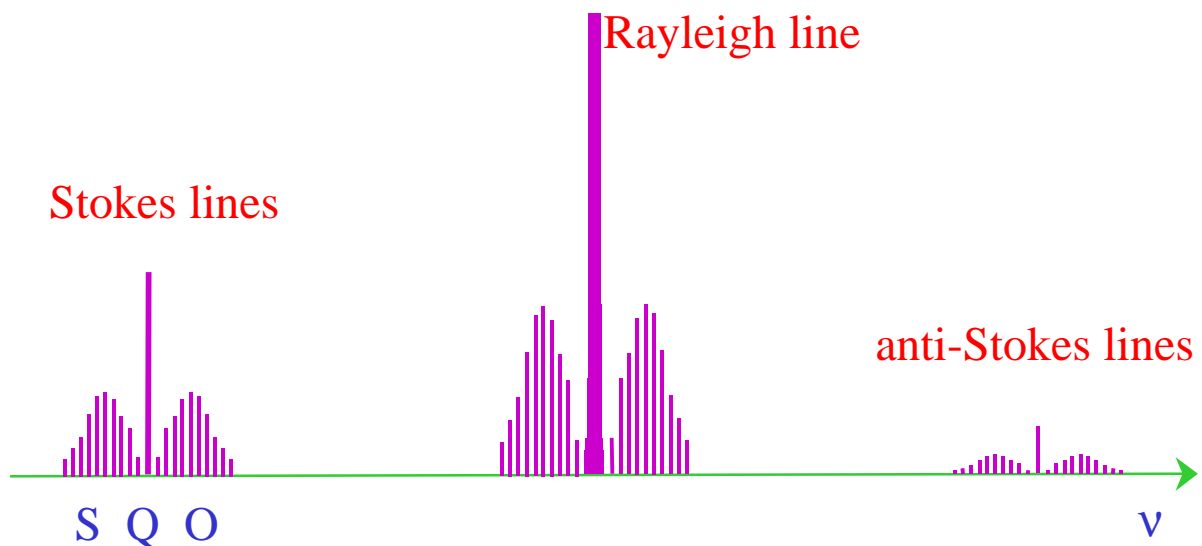**Rotational fine structure of diatomics**

$$\Delta v = +1 \quad \Delta J = 0, \pm 2$$

$\Delta J = 0 :$ $\quad \Delta \nu_Q = \nu_{vib}$

$\Delta J = +2 :$ $\quad \Delta \nu_S = \nu_{vib} + B(4J + 6) \qquad J = 0, 1, 2, \, ...$

$\Delta J = -2 :$ $\quad \Delta \nu_O = \nu_{vib} - B(4J + 6) \qquad J = 2, 3, 4, \, ...$

Rayleigh line

Stokes lines

anti-Stokes lines

S Q O

ν

Symmetry and Selection Rules

The intensity of a stimulated electric dipole transition is proportional to the square of the transition dipole moment:

$$I \propto |\mu_{mn}|^2 = |\mu_{mn}^x|^2 + |\mu_{mn}^y|^2 + |\mu_{mn}^z|^2$$

where $\mu_{mn}^x = \langle m|\mu^x|n \rangle$ etc.,

Rotational transitions have no intensity if there is no dipole moment.

Vibrational transitions are allowed, even if the dipole moment is zero, provided that a dipole is created in the vibrational mode:

$$\mu_{mn}^x = \mu_0^x \langle m|n \rangle + \langle m|\Delta\mu^x|n \rangle$$

$$= \quad 0 \quad + \frac{d\mu}{dx}\langle m|x|n \rangle$$

Specific Selection Rules are derived by considering the conditions for which integrals such as $\langle m|x|n \rangle$ are non-zero.

If only one of x, y or z gives a non-zero integral, the mode is active only for the corresponding plane polarized light.

In simple cases integrals can be shown to be zero by inspecting the even–odd symmetry of the wavefunctions.

More generally, Group Theory is used to analyze symmetry.

Integrals of Even/Odd Functions

Suppose $I = \int_{-\infty}^{+\infty} F(x)\,dx$

Then $\quad I = \int_{-\infty}^{0} F(x)\,dx + \int_{0}^{+\infty} F(x)\,dx$

$$= \int_{0}^{+\infty} F(-x)\,dx + \int_{0}^{+\infty} F(x)\,dx$$

For $F(x)$ odd $\quad F(-x) = -F(x) \quad \Rightarrow \quad I = 0$

For $F(x)$ even $\quad F(-x) = F(x) \quad \Rightarrow \quad I \neq 0$

Since x is an odd function,

$\mu_{mn}^{x} = \langle m|\mu^{x}|n\rangle = 0$ unless $\psi_{m}^{*}\psi_{n}$ is *also* odd.

Group Theory and Selection Rules

$\langle m|\hat{O}|n \rangle = 0$ unless the direct product of the irreducible representations spanned by $\langle m|$, $\hat{O}$ and $|n\rangle$ contains the totally symmetric representation A_1.

Translation: a spectroscopic transition is allowed between two states if the product of their wavefunctions has the same symmetry as the relevant operator.

↳ same row of the molecule's character table

Infrared Spectroscopy
The electric dipole transition operator belongs to the same symmetry species as the functions x, y and z.

Raman Spectroscopy
The relevant functions are those of the polarizability tensor: x^2, y^2, z^2, xy, yz, zx (and combinations)

Exclusion Rule
Fundamental transitions in centrosymmetric molecules are either electric dipole (infrared) or Raman active, never both.