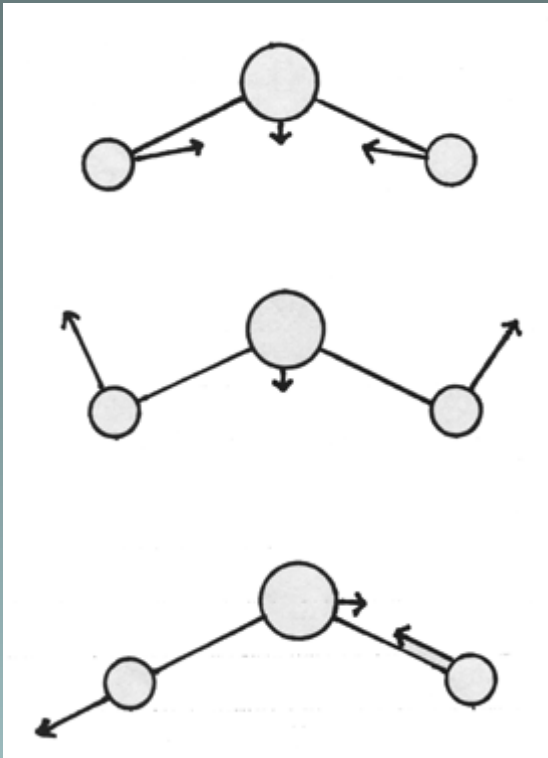


## Part A.2

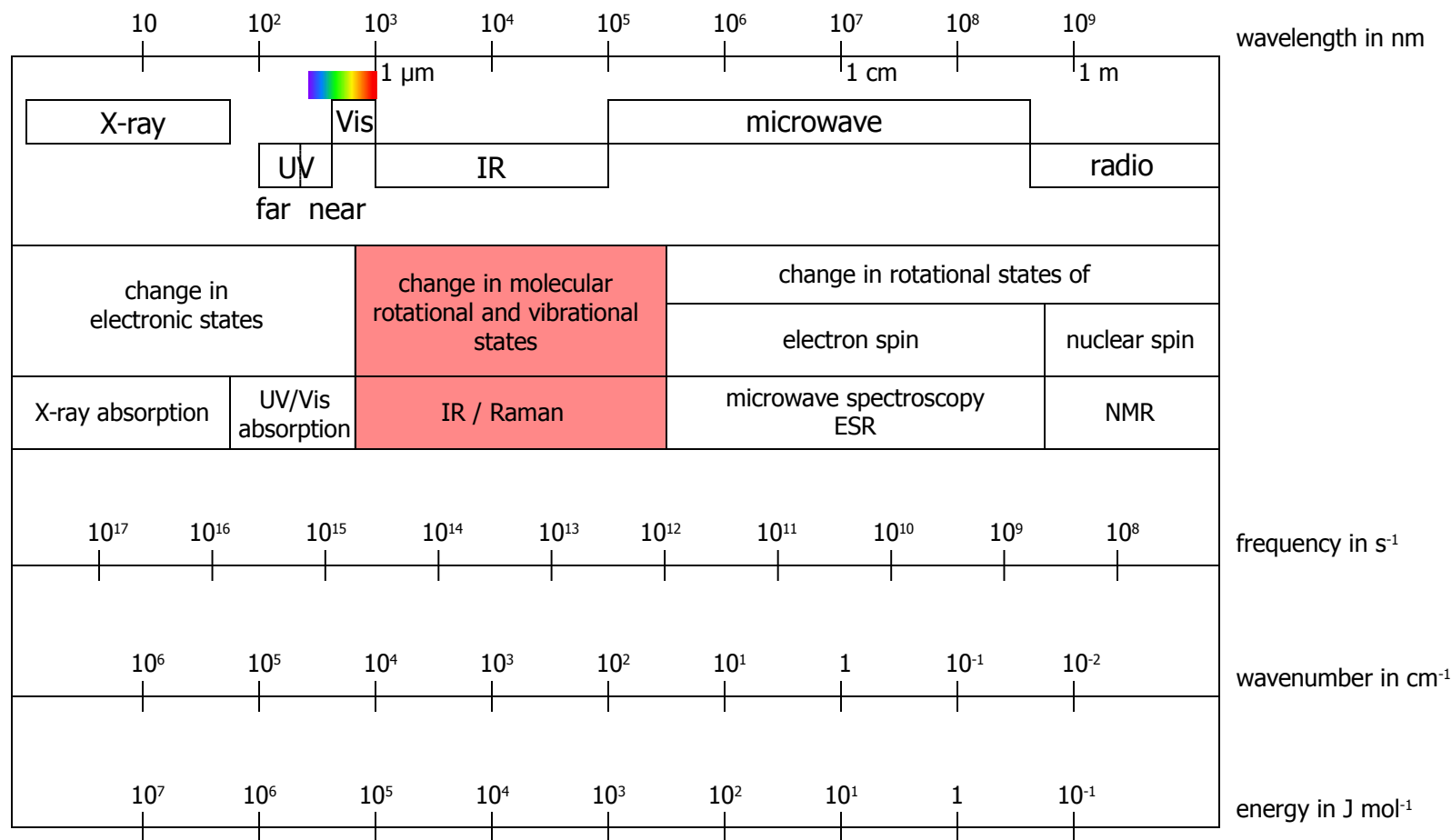
## Rota-vibrational spectroscopy I

# Rota-vibrational spectroscopy I

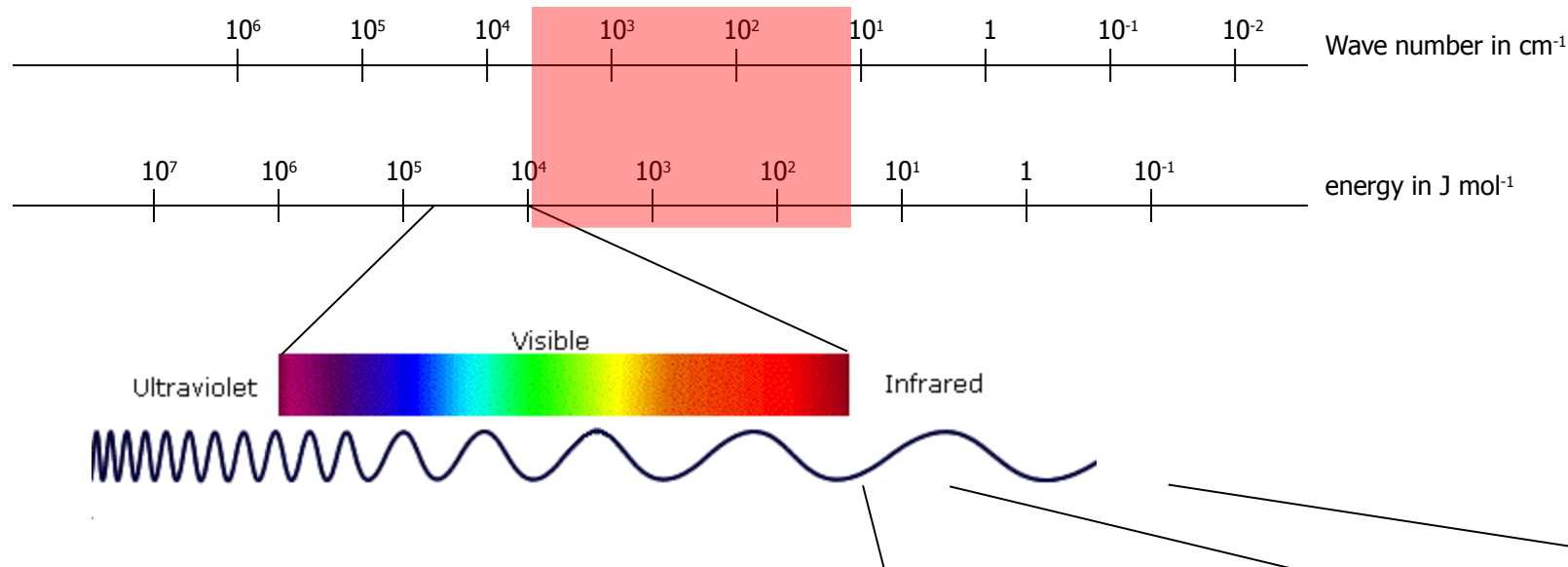


Energy region for vibrational spectroscopy  
Vibration in polyatomic molecules  
Mechanical description of vibration  
Effects of atomic mass on vibration  
Quantum mechanical description of vibration  
Rota-vibrational transitions (IR)  
Raman effect  
Infrared and Raman spectroscopy  
Rota-vibrational transitions (Raman)

# Energy region for rota-vibrational spectroscopy



# Energy region for rota-vibrational spectroscopy



Spectr.	Wavenumber	Energy
Raman	$4000 - 50 \text{ cm}^{-1}$	$50 - 0.5 \text{ kJ mol}^{-1}$
IR	$4000 - 400 \text{ cm}^{-1}$	$50 - 5 \text{ kJ mol}^{-1}$

## Near IR

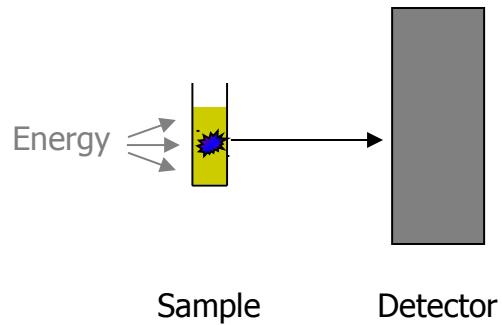
The region "near to visible light" and uses visible light optics. This is a high energy region: it probes the anharmonic vibrations (overtones and combinations), nearly all are CH, NH, and OH related. The reflectivity can be a problem.

## Mid IR

From  $400 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$ . The region of bending, stretching and breathing; functional groups, "fingerprint region".

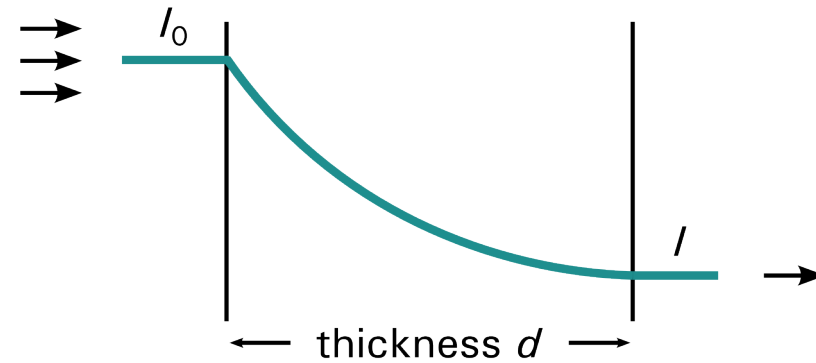
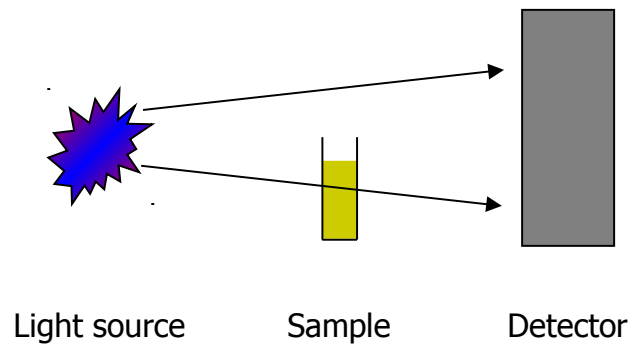
# Light emission and absorption

## Emission

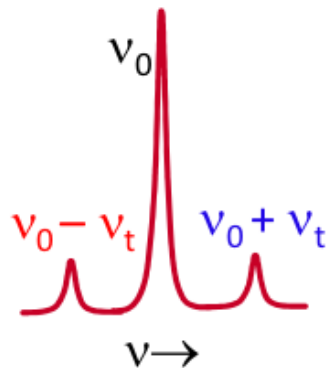
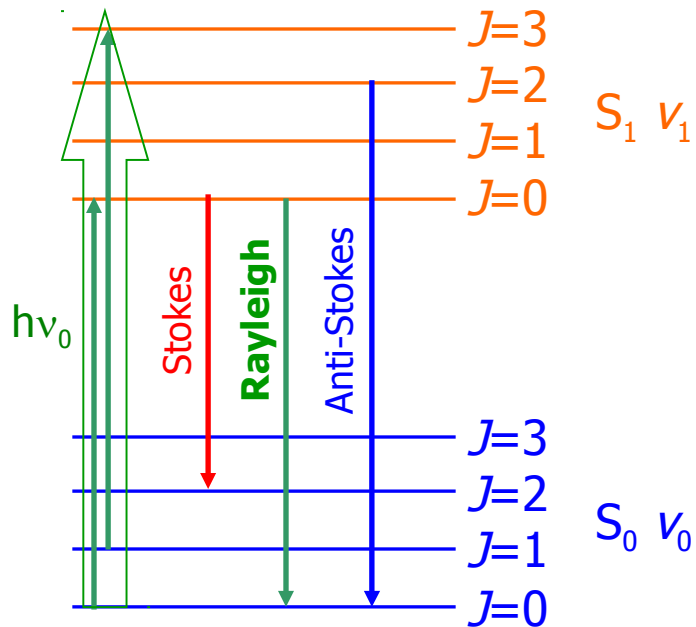


Infrared spectroscopy is absorption spectroscopy, Raman spectroscopy is emission spectroscopy.

## Absorption



# Raman effect



The strongest scattering is **Rayleigh scatter**. This is elastic scattering, i.e. the energy of the scattered photon is the same as the energy of the absorbed photon.

Raman scattering is inelastic: the scattered photon has a different energy than the incident photon.

**Stokes lines** are those in which the photon has lost energy to the molecule:

$$\nu_0 - \nu_t \quad \nu_t \text{ is the Raman shift}$$

**Anti-Stokes** lines are those in which the photon has gained energy from the molecule:

$$\nu_0 + \nu_t \quad \nu_t \text{ is the Raman shift}$$

Since molecular energy levels are quantised, this produces discrete lines from which we can gain information on the molecule itself.

Anti-Stokes lines are less intense than Stokes lines.

Fluorescence sometimes interferes with the Stokes lines.

## Vibration in polyatomic molecules

---

The position and orientation of a molecule does not change on the time scale of a vibrational transition.

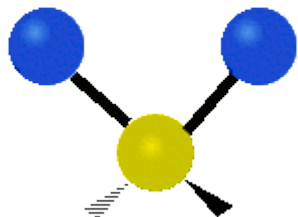
All atoms move through their equilibrium configurations at the same time – they are in phase.

Amplitudes and speeds depend on atomic masses and bond strength / stiffness.

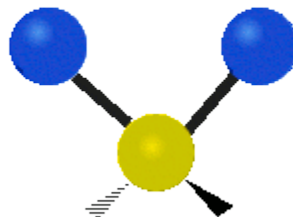
# Modes of vibration

---

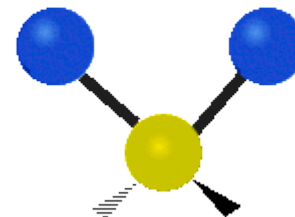
symmetrical stretching



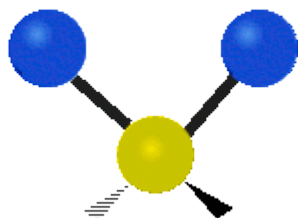
asymmetrical stretching



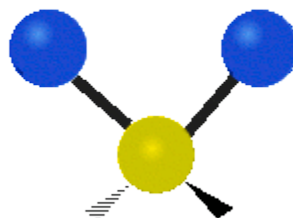
scissoring



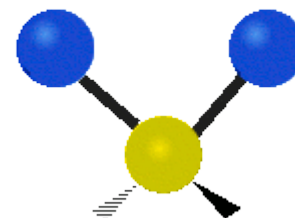
rocking



wagging



twisting





## Modes of vibration

---

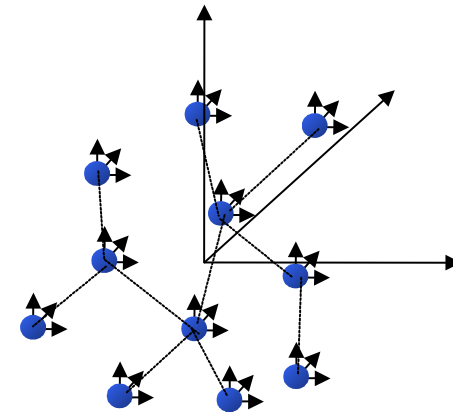
For a molecule with  $N$  atoms there are  **$3 \cdot N$  degrees of freedom**

3 modes are translation (in  $x$ -,  $y$ -,  $z$ -direction)

3 modes are rotation (around  $x$ -,  $y$ -,  $z$ -axis)

$\Rightarrow 3 \cdot N - 6$  modes are vibration

A linear molecule has only  $3 \cdot N - 5$  vibration modes, since rotation around its molecular axis cannot be observed.



# Modes of vibration

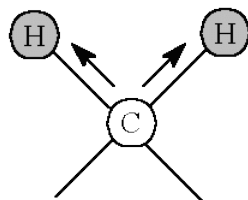
$$N = 5:$$

$$3 \cdot N - 6 = 9$$

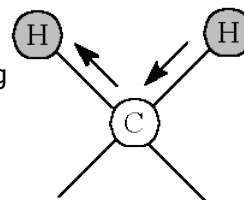
vibration modes, e.g.  $\text{CH}_2\text{Cl}_2$

$C_{2v}$

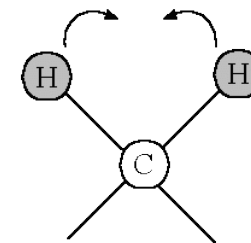
Mode 9  
C-H symmetric stretching  
 $3077 \text{ cm}^{-1}$   
IR active  
Raman active



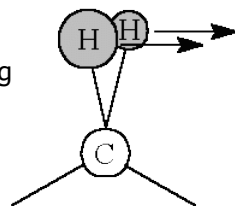
Mode 8  
C-H asymmetric stretching  
 $3037 \text{ cm}^{-1}$   
IR active  
Raman active



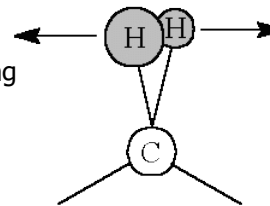
Mode 7  
H-C-H in-plane scissoring  
 $1327 \text{ cm}^{-1}$   
IR active  
Raman active



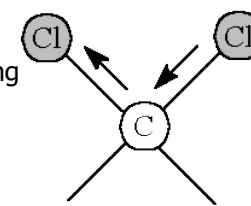
Mode 6  
H-C-H out-of-plane wagging  
 $1218 \text{ cm}^{-1}$   
IR active  
Raman active



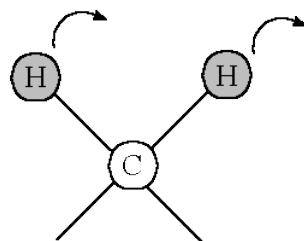
Mode 5  
H-C-H out-of-plane twisting  
 $1057 \text{ cm}^{-1}$   
IR inactive  
Raman active



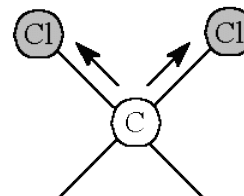
Mode 4  
C-Cl asymmetric stretching  
 $874 \text{ cm}^{-1}$   
IR active  
Raman active



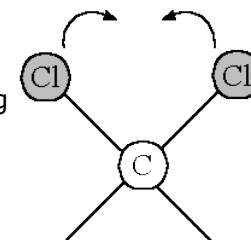
Mode 3  
H-C-H in-plane rocking  
 $863 \text{ cm}^{-1}$   
IR active  
Raman active



Mode 2  
C-Cl symmetric stretching  
 $771 \text{ cm}^{-1}$   
IR active  
Raman active



Mode 1  
Cl-C-Cl in-plane scissoring  
 $313 \text{ cm}^{-1}$   
IR active  
Raman active

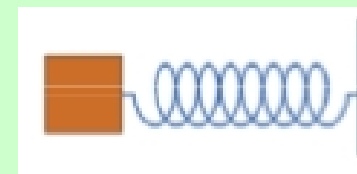


## Mechanical description of vibration

---

The force required to extend a spring is given by Hooke's law

$$F = -k \cdot x, \text{ with } k \text{ being the **force constant**}$$



Newtonian mechanics delivers the description of the harmonic oscillator

$$x(t) = A \cdot \cos(2\pi \cdot \nu \cdot t), \text{ with } \nu = 1/(2\pi) \cdot (k/\mu)^{1/2}$$

The reduced mass  $\mu$  is given by

$$\mu = m_A \cdot m_B / (m_A + m_B) \text{ or } 1/\mu = 1/m_A + 1/m_B$$

The potential energy  $V$  is a quadratic function of the coordinate  $x$

$$V \sim k \cdot (x-x_0)^2 \Rightarrow k = d^2V/dx^2, \text{ i.e. **the force constant is the second derivative of the potential (= bond) energy**}$$

## Effects of atomic mass on vibration

---

Newtonian mechanics deliver the description of the harmonic oscillator

$$x(t) = A \cdot \cos(2\pi \cdot \nu \cdot t), \text{ with } \nu = 1/(2\pi) (k/\mu)^{1/2} = 1/(2\pi) [k / (1/m_A + 1/m_B)]^{1/2}$$

The reduced mass  $\mu$  is given by

$$\mu = m_A \cdot m_B / (m_A + m_B) \text{ or } 1/\mu = 1/m_A + 1/m_B$$

Isotopes affect the energy required for transition: C=<sup>14</sup>N and C=<sup>15</sup>N

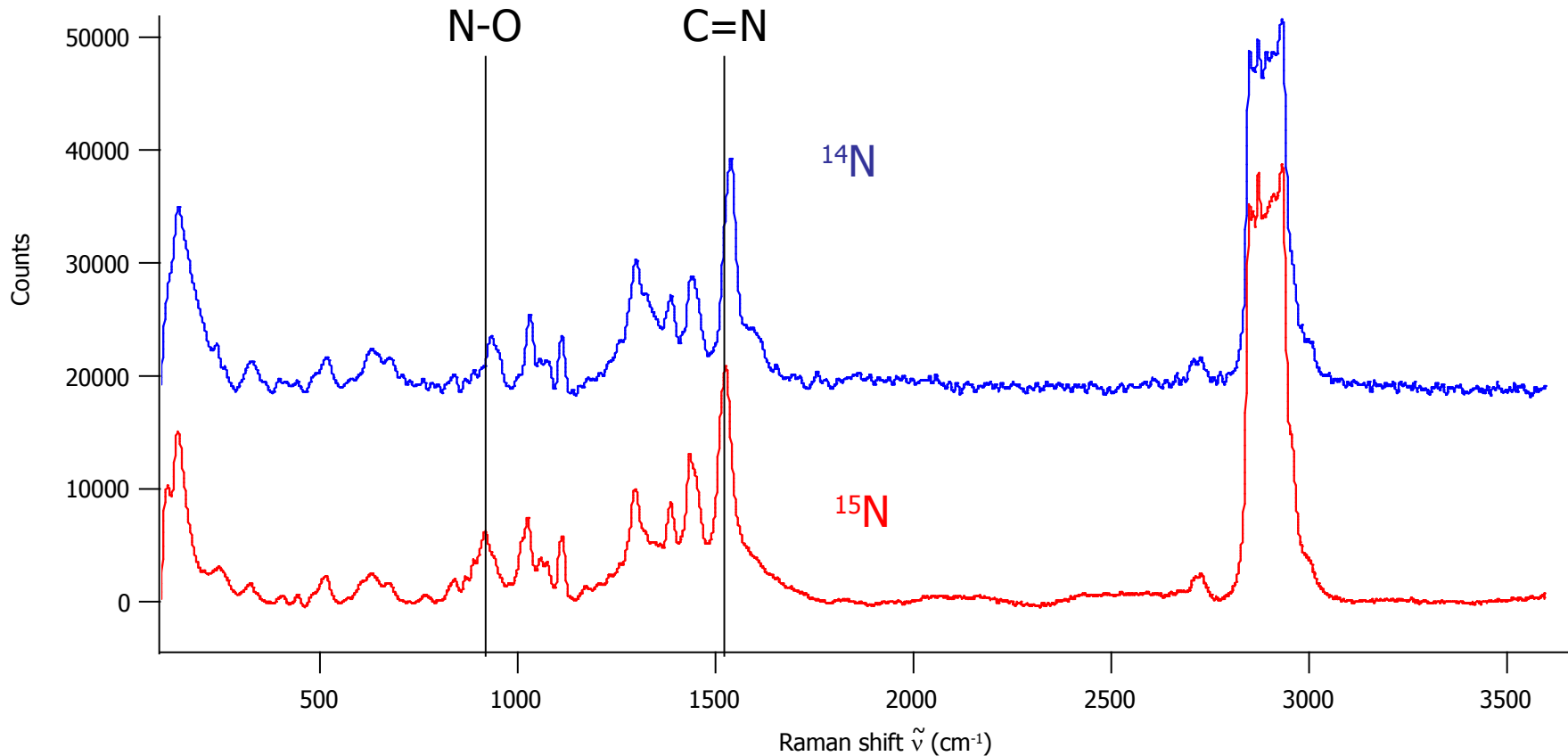
$$\nu = 1/(2\pi) \cdot (k/\mu)^{1/2} = 1/(2\pi) \cdot [k / (1/m_{\text{C-12}} + 1/m_{\text{N-14}})]^{1/2}$$

$$\nu = 1/(2\pi) \cdot (k/\mu)^{1/2} = 1/(2\pi) \cdot [k / (1/m_{\text{C-12}} + 1/m_{\text{N-15}})]^{1/2}$$

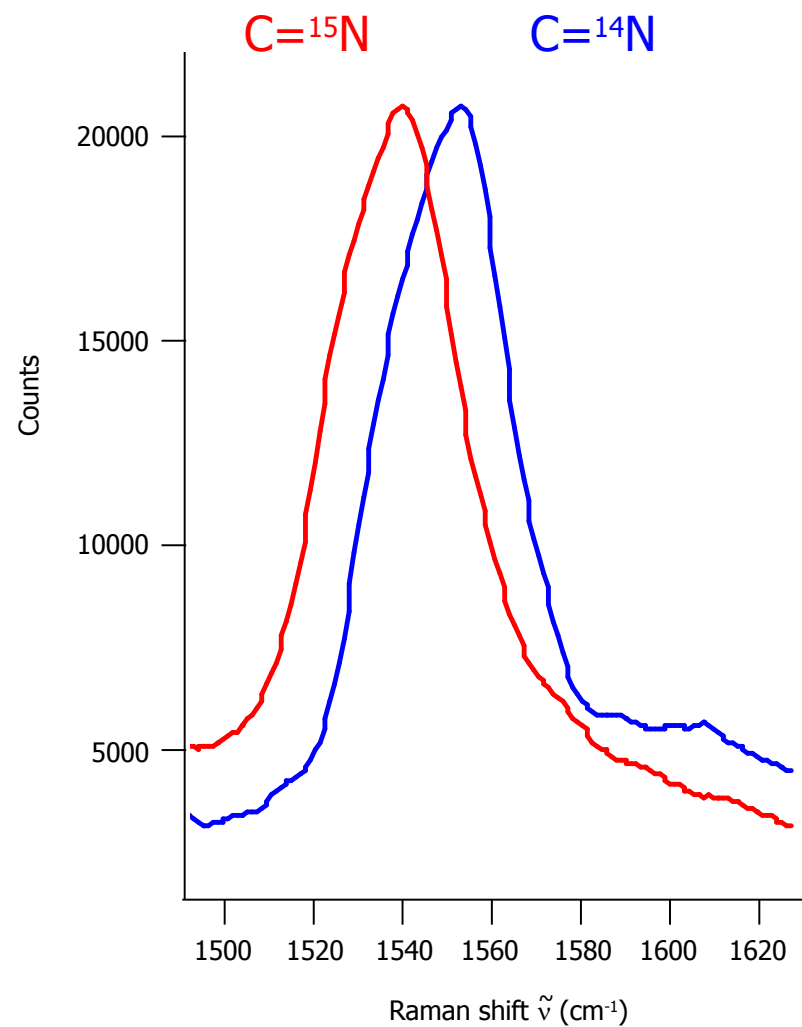
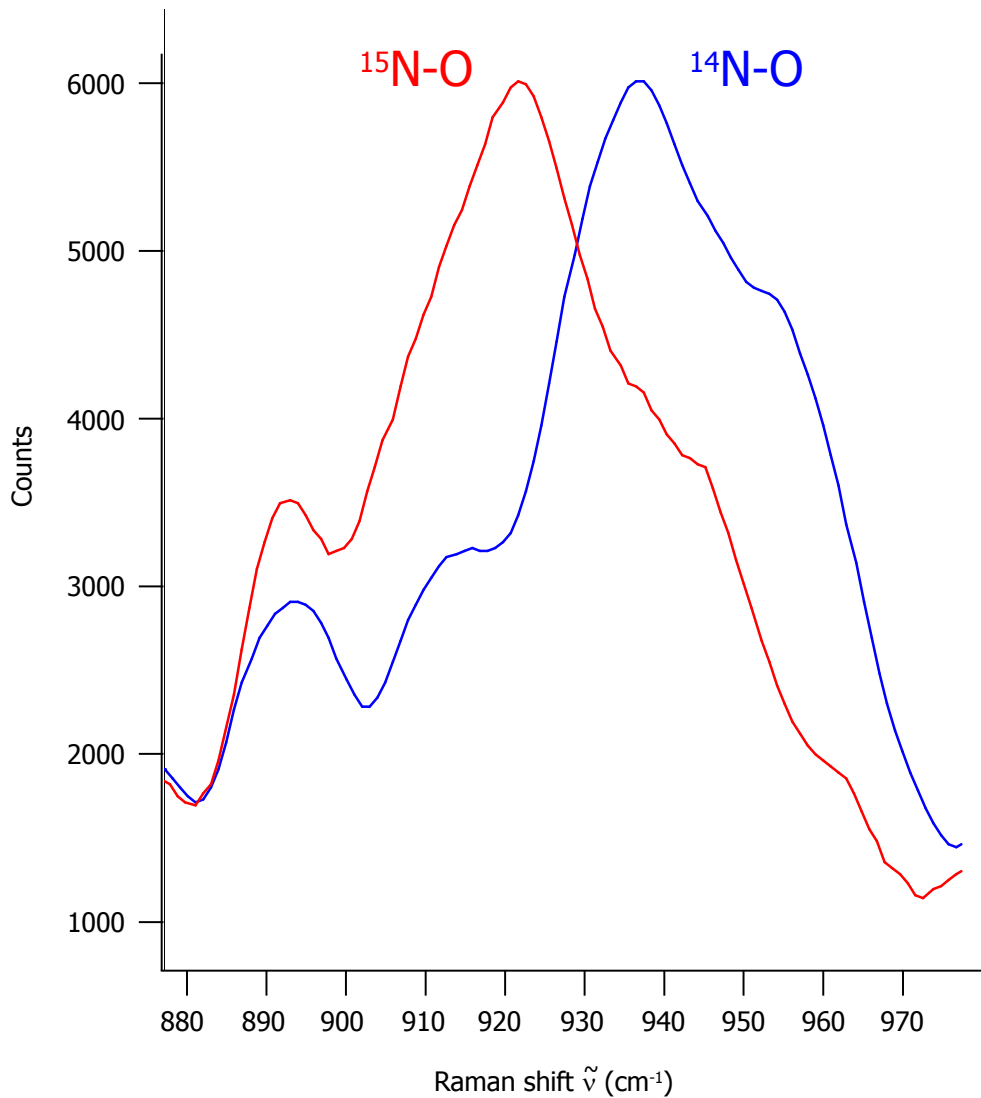
# Effects of atomic mass on vibration

Newtonian mechanics deliver the description of the harmonic oscillator

$$x(t) = A \cdot \cos(2\pi \cdot \nu \cdot t), \text{ with } \nu = 1/(2\pi) \cdot (k/\mu)^{1/2} = 1/(2\pi) \cdot [k / (1/m_A + 1/m_B)]^{1/2}$$



# Effects of atomic mass on vibration



Calculate a force constant for the C=N bond if the mass of C is 12 and N is 14.

The band is observed at 1560 cm<sup>-1</sup>.

$$\nu = 1/(2 \cdot \pi) \cdot (k/\mu)^{1/2}$$

# Quantum mechanical description of vibration

---

## Newtonian mechanical description of vibration

The potential energy  $V$  is quadratic function of the coordinate  $x$

$$V = k \cdot (x - x_0)^2$$

A classical harmonic oscillator can take any potential energy  $V$ .

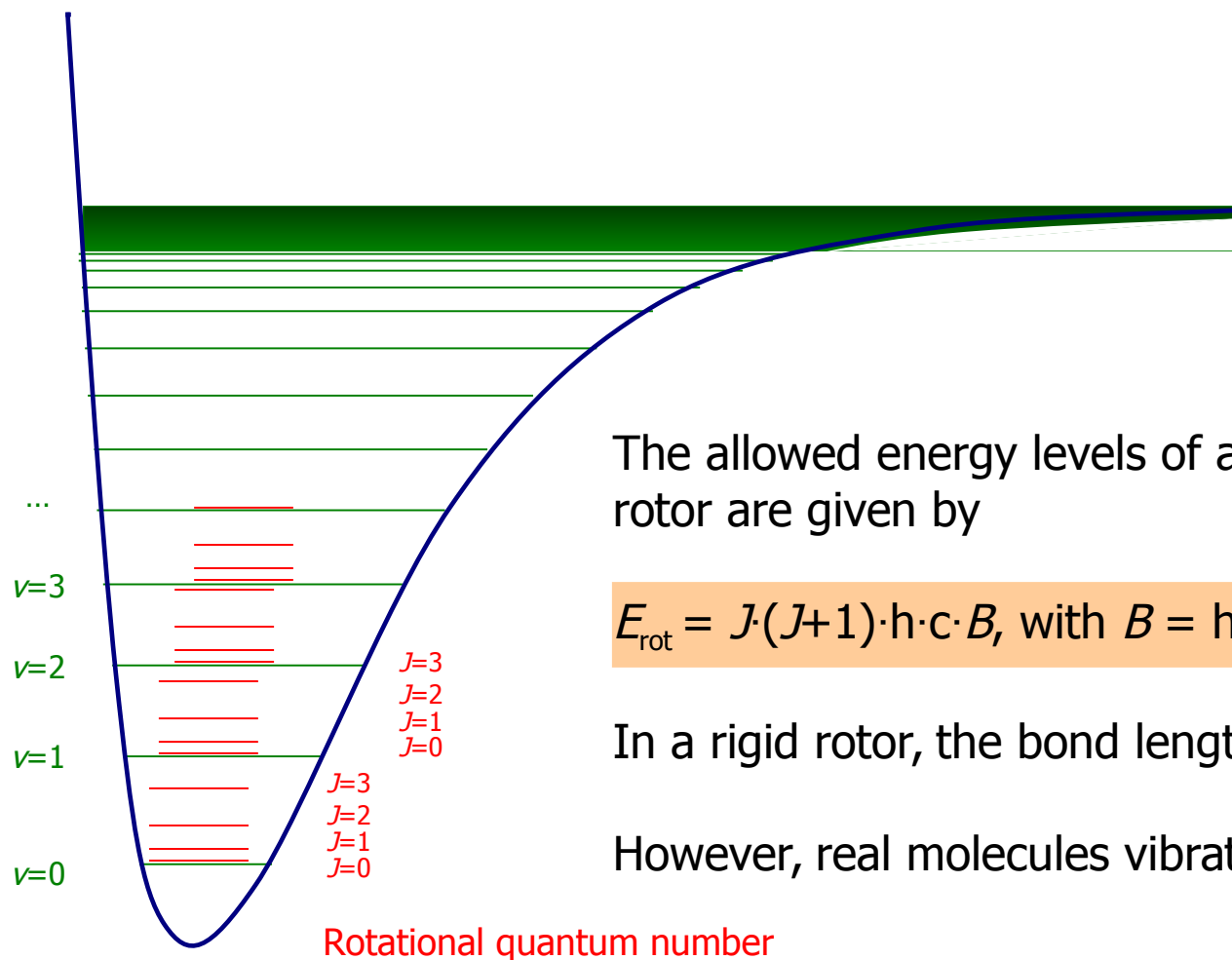
## Quantum mechanical description of vibration

The allowed energy levels of a quantum mechanical harmonic oscillator are discretely spaced and can be calculated for each vibrational quantum number  $\nu$

$$E_{\text{vib}} = (\nu + 1/2) \cdot h \cdot \nu$$



# Rotational levels are overlaid onto the vibrational states of a molecule



The allowed energy levels of a quantum mechanical rigid rotor are given by

$$E_{\text{rot}} = J(J+1) \cdot h \cdot c \cdot B, \text{ with } B = h / (8\pi^2 \cdot c \cdot \mu \cdot r^2), [B] = 1 \text{ cm}^{-1}$$

In a rigid rotor, the bond length  $r$  does not change.

However, real molecules vibrate and rotate, hence  $r$  varies.

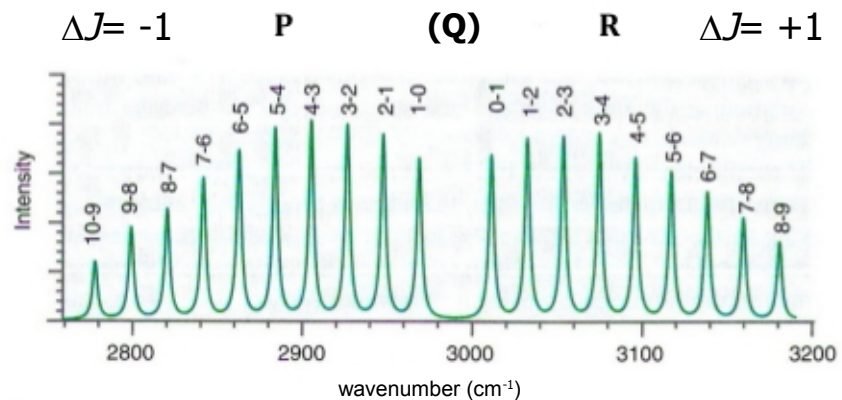
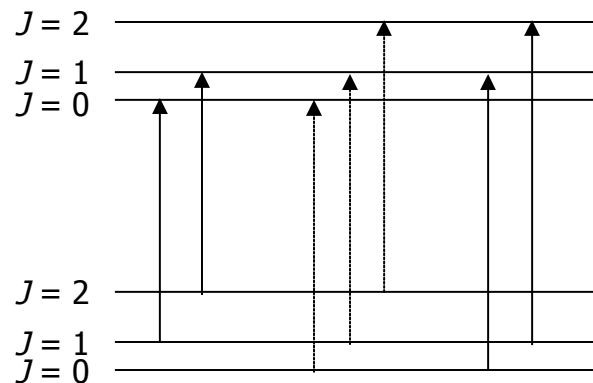
Vibrational quantum number

Rotational quantum number

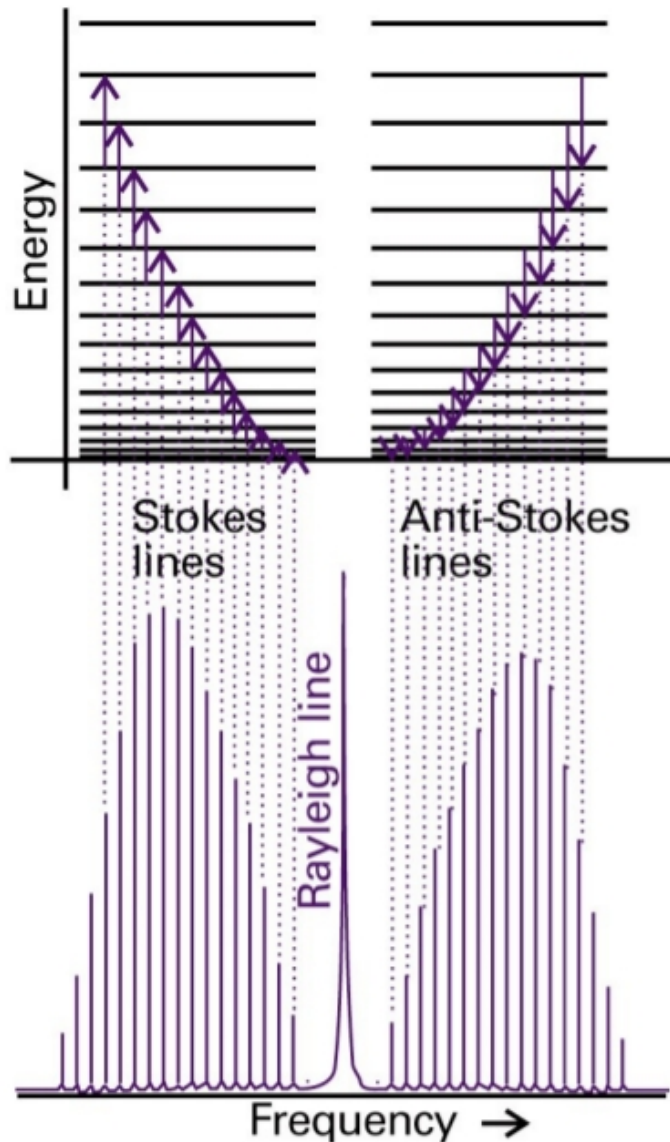
# Rota-vibrational transitions by infrared absorption

Selection rules for infrared absorption of a linear molecule:

$$\Delta v = \pm 1 \text{ and } \Delta J = \pm 1$$



# Rotational transitions by Raman scattering (linear molecule)



$$\Delta J = 0, \pm 2$$

Assuming a rigid rotor:  $F(J) = BJ(J+1)$

$\therefore$  Stokes lines are observed at:

$$\bar{\nu} = \nu_0 - \{F(J+2) - F(J)\} = \nu_0 - B(4J + 6)$$

and Anti- Stokes lines at:

$$\bar{\nu} = \nu_0 + \{F(J) - F(J-2)\} = \nu_0 + B(4J - 2)$$

*n.b.* 1<sup>st</sup> Anti-Stokes line is  $J = 2$

i.e.,

- a gap of  $6B$  between  $\nu_0$  and 1<sup>st</sup> lines of each branch
- lines in each branch of equal spacing =  $4B$

# Bond length determination by rota-vibrational analysis

$$E_{\text{rot}} = J \cdot (J+1) \cdot h \cdot c \cdot B, \text{ with } B = h / (8\pi^2 \cdot c \cdot \mu \cdot r^2), [B] = 1 \text{ cm}^{-1}$$

In a rigid rotor, the bond length  $r$  does not change.  
However, real molecules vibrate and rotate, hence  $r$  varies.

The bond distance  $r_e$  can then be calculated from

$$r_e = [h / (8\pi^2 \cdot c \cdot \mu \cdot B_e)]^{1/2}$$

Problem:

The rotational constant  $B$  depends on the vibrational state.

At higher vibrational states,  $B$  will be smaller:

The molecule rotates slower, because the bond length is larger.

$$B_1 (v=1) < B_0 (v=0)$$

These can be determined from different transitions:

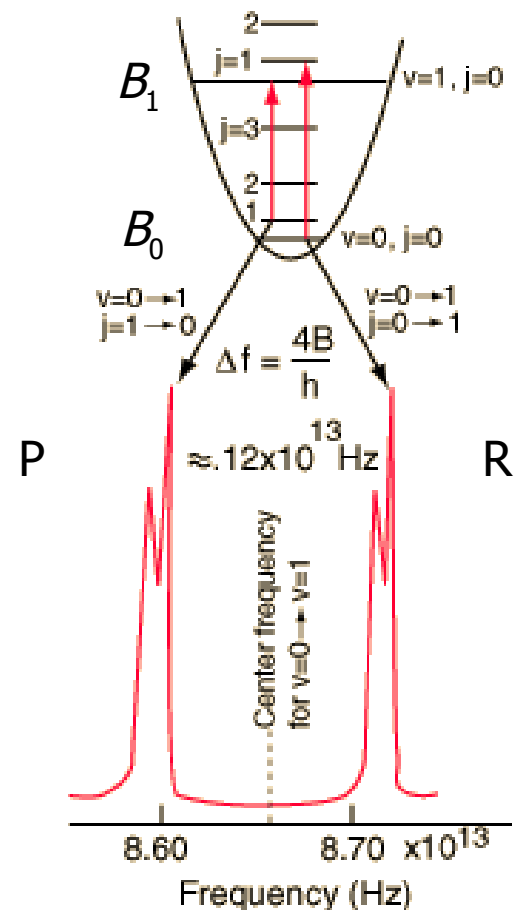
$$E(R_j) - E(P_j) \sim 4 \cdot B_1 \cdot (J + 1/2)$$

$$E(R_{j-1}) - E(P_{j+1}) \sim 4 \cdot B_0 \cdot (J + 1/2)$$

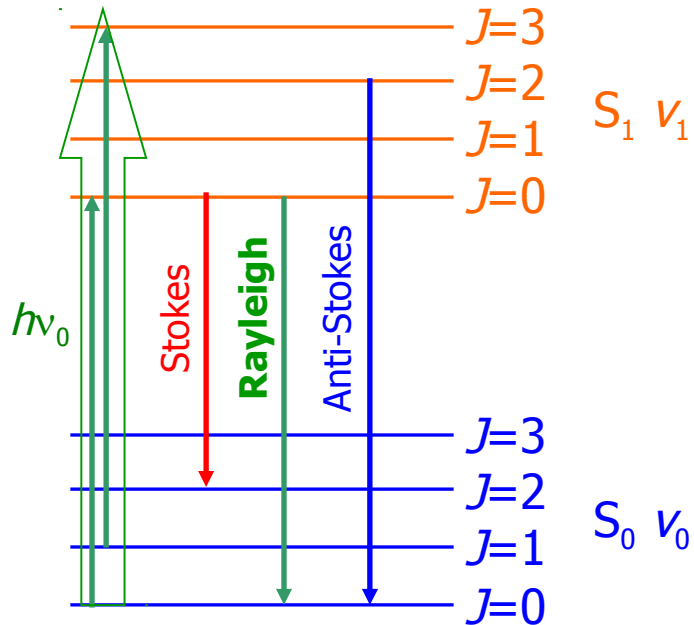
The following equation can be established for  $B_0, B_1, \dots$

$$B_v = B_e - \alpha_e (v + 1/2)$$

From the multiple equations,  $B_e$  and  $\alpha_e$  can be determined.



# Raman effect



The strongest scattering is **Rayleigh scatter**. This is elastic scattering, i.e. the energy of the scattered photon is the same as the energy of the absorbed photon.

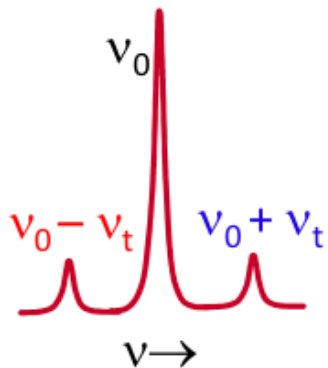
Raman scattering is inelastic: the scattered photon has a different energy than the incident photon.

**Stokes lines** are those in which the photon has lost energy to the molecule:

$$\nu_0 - \nu_t \quad \nu_t \text{ is the Raman shift}$$

**Anti-Stokes** lines are those in which the photon has gained energy from the molecule:

$$\nu_0 + \nu_t \quad \nu_t \text{ is the Raman shift}$$

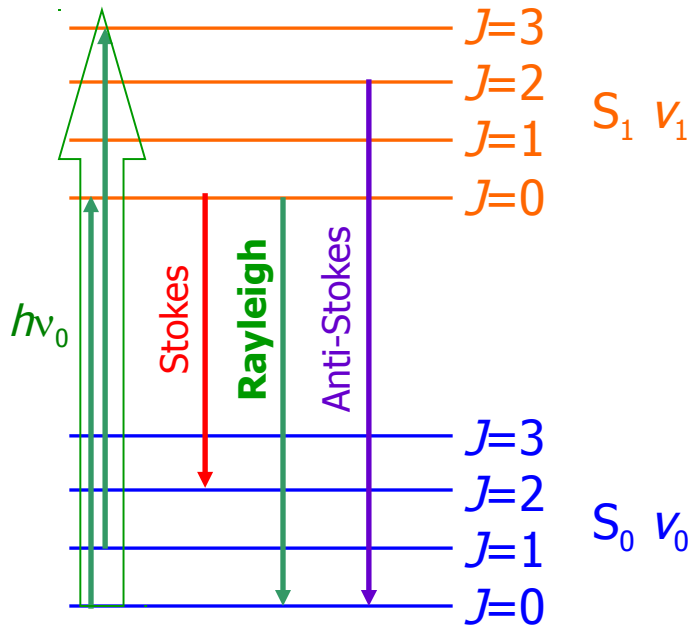


Since molecular energy levels are quantised, this produces discrete lines from which we can gain information on the molecule itself.

Anti-Stokes lines are less intense than Stokes lines.

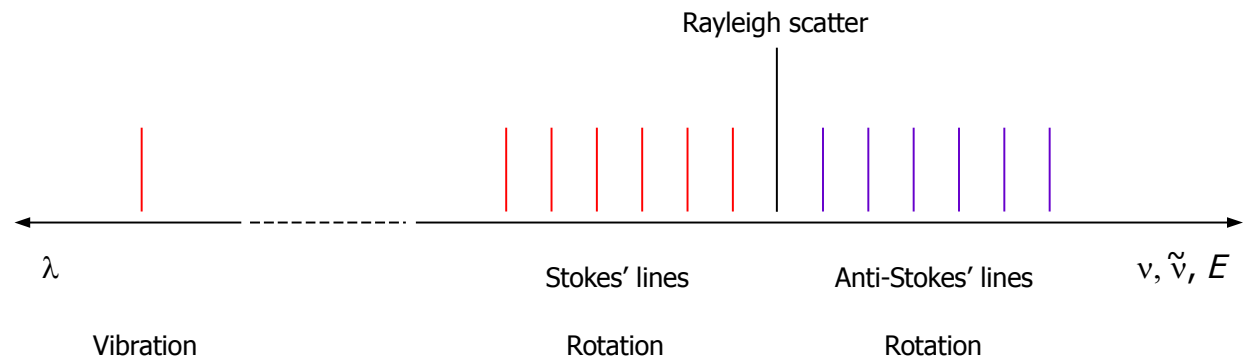
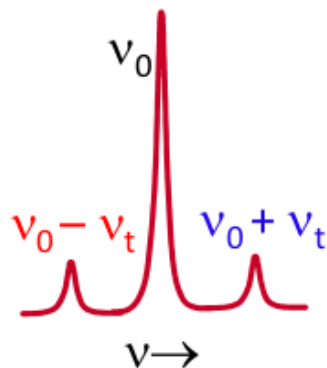
Fluorescence sometimes interferes with the Stokes lines.

# Raman effect



An incident photon  $h \cdot \nu_0$  might be scattered inelastically:

- \* The photon might transfer energy onto the molecule and activate rotation (or vibration): **Stokes' lines**
- \* The photon might get energy from a molecule that jumps from a higher to a lower rotation state: **Anti-Stokes' lines**

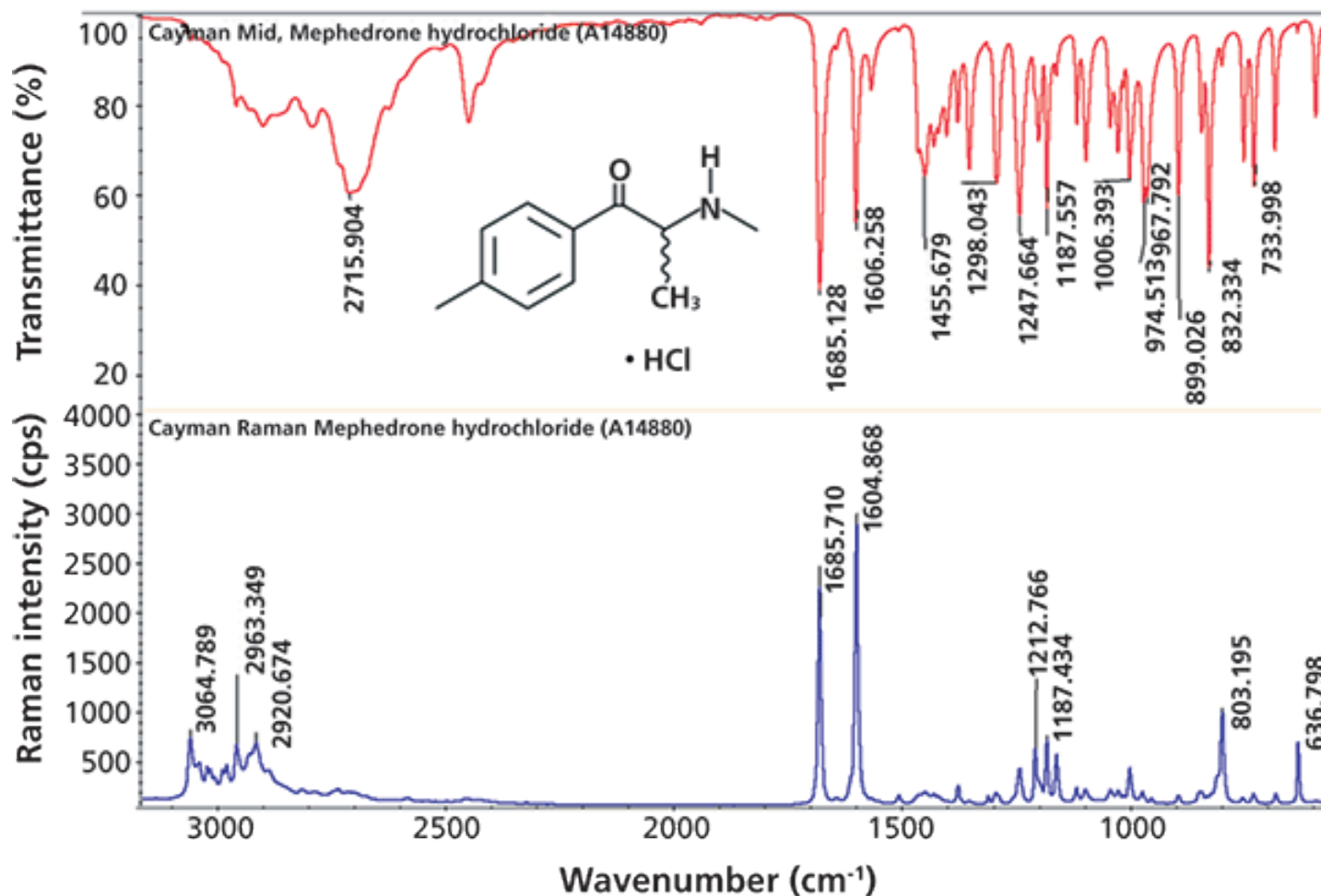


## Scattering intensity

$$I_{\text{scatter}} = \frac{8 \cdot \pi^4 \cdot \alpha^2}{\lambda^4 \cdot r^2} \cdot (1 + \cos^2 \theta) \cdot I_0$$

$\alpha$	Polarisability of particle
$\lambda$	Wavelength of incident radiation
$I_0$	Incident intensity
$\theta$	Angle between incident and scattered ray
$r$	Distance of sample to detector

## Different bands are observed in infrared and Raman spectra



Comparison of FT-IR and Raman spectra from mephedrone, a psychoactive compound commonly known as "meow meow".



# Infrared and Raman spectroscopy: gross selection rules

## IR selection rule

A transition is IR-active if there is:

- a change in **dipole momentum**
- a change in the quantum numbers  $\Delta v = \pm 1, \Delta J = \pm 1$

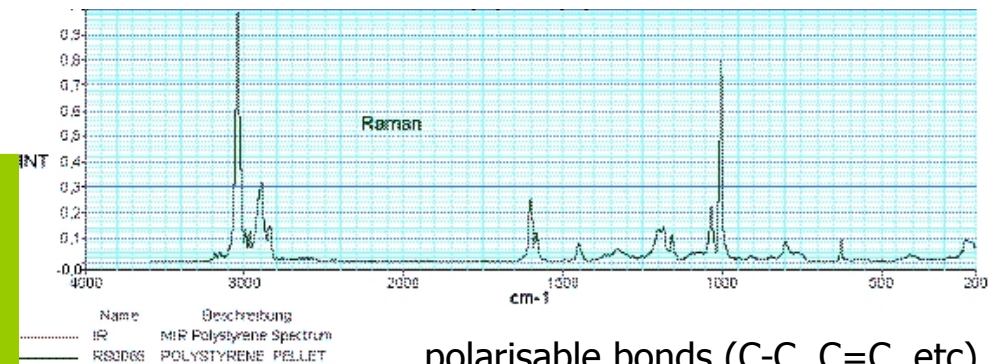


polar bonds (C=O, O-H, etc)

## Raman selection rule

A transition is Raman-active if there is:

- a change in **polarisation**
- a change in the quantum numbers  $\Delta v = \pm 1, \Delta J = 0, \pm 2$



polarisable bonds (C-C, C=C, etc)

# Infrared and Raman spectroscopy: gross selection rules

## IR selection rule

A transition is IR-active if there is:

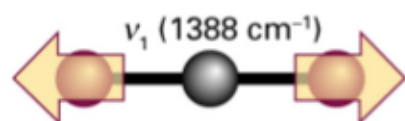
- a change in **dipole moment**
- a change in the quantum numbers  $\Delta v = \pm 1, \Delta J = \pm 1$

## Raman selection rule

A transition is Raman-active if there is:

- a change in **polarisation**
- a change in the quantum numbers  $\Delta v = \pm 1, \Delta J = 0, \pm 2$

## Example: O=C=O



symmetrical stretching

Dipole moment

+

+

Polarisability

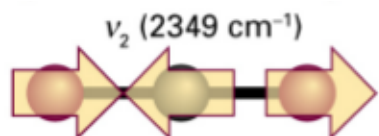


IR

-

Raman

+



asymmetrical stretching

+

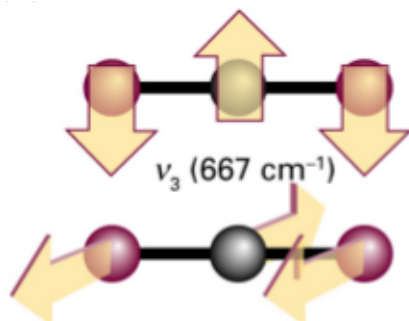
+

→



+

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wagging

+

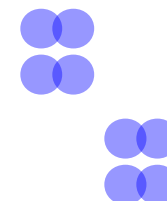
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# Infrared and Raman spectroscopy: gross selection rules

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## IR selection rule

A transition is IR-active if there is:

- a change in **dipole moment**
- a change in the quantum numbers  $\Delta v = \pm 1, \Delta J = \pm 1$

## Raman selection rule

A transition is Raman-active if there is:

- a change in **polarisation**
- a change in the quantum numbers  $\Delta v = \pm 1, \Delta J = 0, \pm 2$

Symmetry dictates which modes are active in Raman or IR  
Rule of thumb:

asymmetric mode

symmetric mode

## Rule of mutual exclusion

In a centrosymmetric molecule (i.e. one with a centre of inversion symmetry) a vibrational mode may be either IR active or Raman active but not both.

## Further reading

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Hofmann, A., Simon, A., Grkovic, T. & Jones, M. (2014) *Methods of Molecular Analysis in the Life Sciences*. Cambridge University Press. Section 2.7.

### **Textbooks and reviews on infrared spectroscopy**

Beekes M., Lasch P. & Naumann D. (2007) Analytical applications of Fourier transform-infrared (FT-IR) spectroscopy in microbiology and prion research. *Veterinary Microbiology* 123, 305-319.

Ganim Z., Chung H.S., Smith A.W., Deflores L.P., Jones K.C. & Tokmakoff A. (2008) Amide I two-dimensional infrared spectroscopy of proteins. *Accounts of Chemical Research* 41, 432-441.

Hind A.R., Bhargava S.K. & McKinnon A. (2001) At the solid/liquid interface: FTIR/ATR - the tool of choice. *Advances in Colloid and Interface Science* 93, 91-114.

Kazarian S.G. & Chan K.L.A. (2006) Applications of ATR-FTIR spectroscopic imaging to biomedical samples. *Biochimica et Biophysica Acta* 1758, 858-867.

Pretsch E., Bühlmann P. & Badertscher, M. (2009) *Structure determination of organic compounds*. 4th edition, Springer Verlag, Berlin, Heidelberg. (A compendium with tables of spectral data.)

Tonouchi M. (2007) Cutting-edge terahertz technology. *Nature Photonics* 1, 97-105.

### **Web sites on infrared spectroscopy**

Infrared spectroscopy: a tutorial

<http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/infrared.htm>

Organic Chemistry at CU Boulder: IR spectroscopy tutorial

<http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html>

### **Textbooks and reviews on Raman spectroscopy**

Benevides J.M., Overman S.A. & Thomas G.J. Jr. (2004) Raman spectroscopy of proteins. *Current Protocols in Protein Science*, Chapter 17, Unit 17.8.

Wen Z.Q. (2007) Raman spectroscopy of protein pharmaceuticals. *Journal of Pharmaceutical Sciences* 96, 2861-2878.

### **Web sites on Raman spectroscopy**

Raman spectroscopy at the University of Bath

<http://people.bath.ac.uk/pysdw/newpage11.htm>