

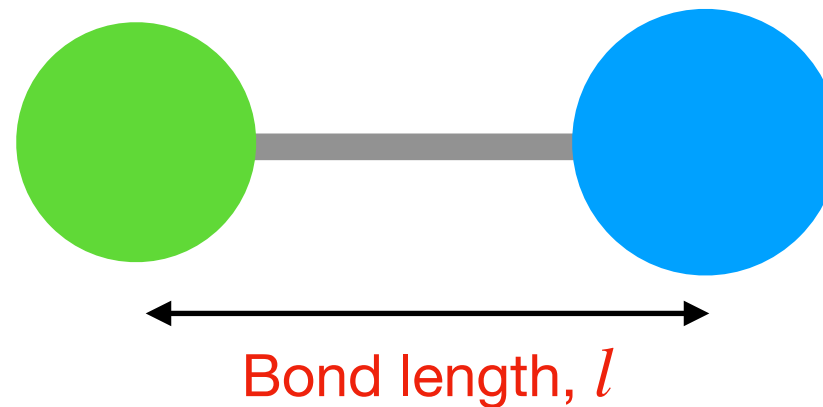
Today's class:

Infra-red Spectroscopy

This lecture follows the materials from the following books

- *Physical Chemistry for Life Sciences, by PW Atkins and JD Paula, Oxford, 2006*
- *Prescott's Principles of Microbiology, McGraw-Hill 2009*

Molecular vibrations



The simplest model that describes molecular vibrations is the harmonic oscillator

Hooke's law

Restoring force is proportional to displacement, x

$$F = -kx$$

k = force constant or strength of bond

x = any change in the length of the bond

E.g. $x = l(t) - l_0$, l_0 being the equilibrium bond length

Potential energy of a harmonic oscillator

$$\text{Force, } F = -\frac{dV}{dx}$$

V = potential energy

$$dV = -Fdx$$

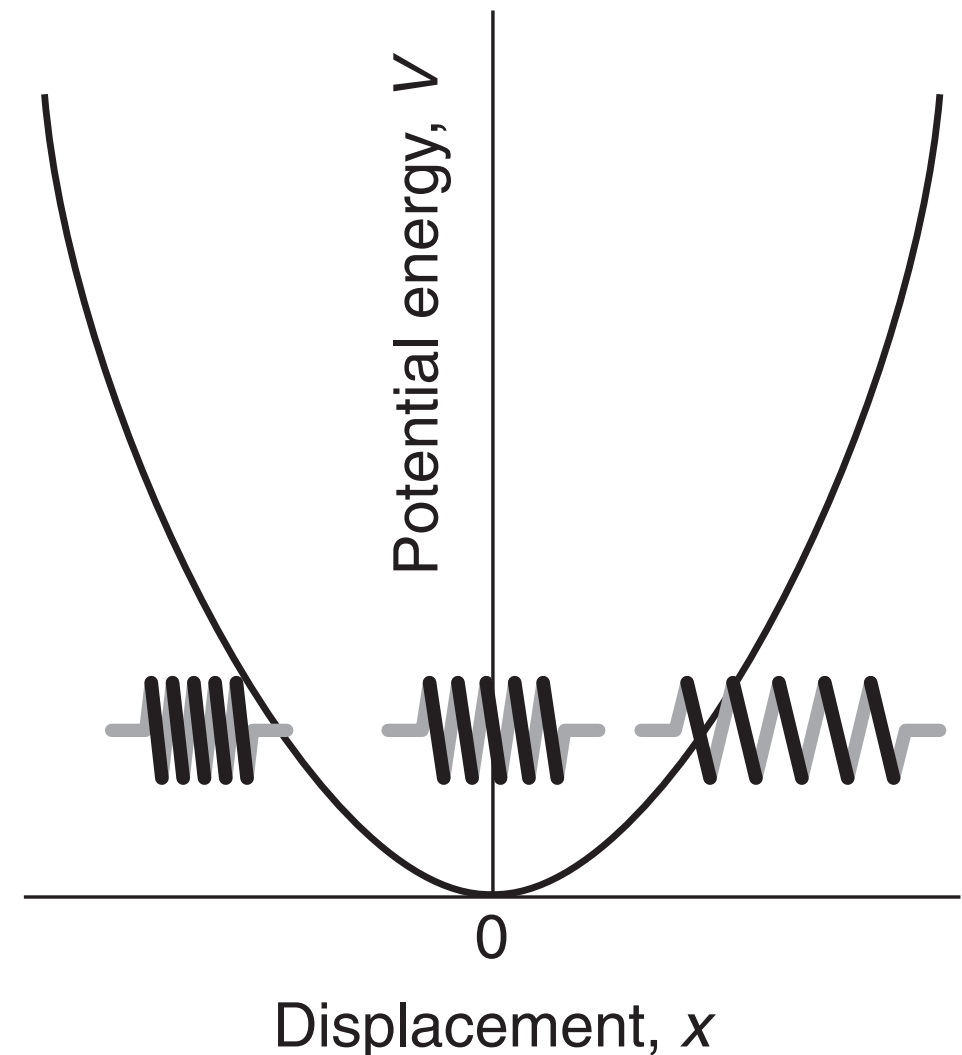
$$\Rightarrow \int_{V(0)}^{V(x)} dV = -\int_0^x Fdx$$

$$\Rightarrow V(x) - V(0) = \int_0^x kxdx$$

$$\Rightarrow V(x) - V(0) = \frac{kx^2}{2}$$

choosing $V(0) = 0$,

$$V(x) = \frac{1}{2}kx^2$$



Parabolic potential energy

Vibrational energy levels for a diatomic molecule

Solving the Schrödinger equation, we get the following energy levels

$$E_v = \left(v + \frac{1}{2} \right) h\nu \quad \text{where, } v = 0, 1, 2, \dots$$

Frequency of vibration

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

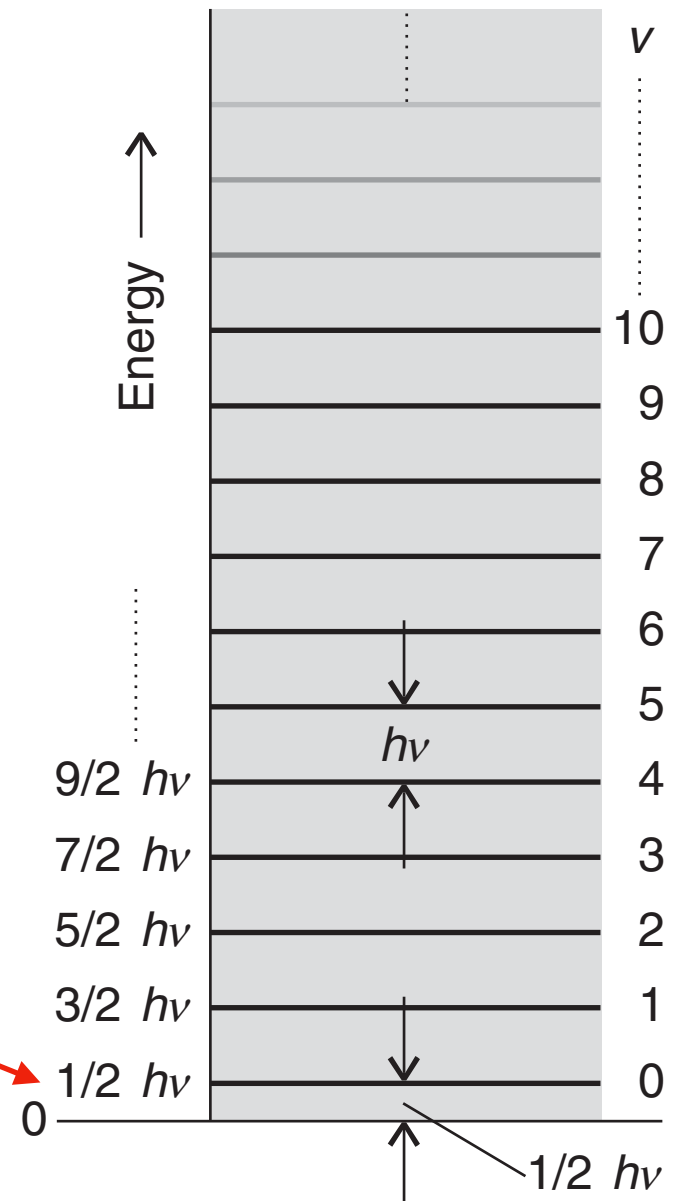
$$\text{where, } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Reduced mass

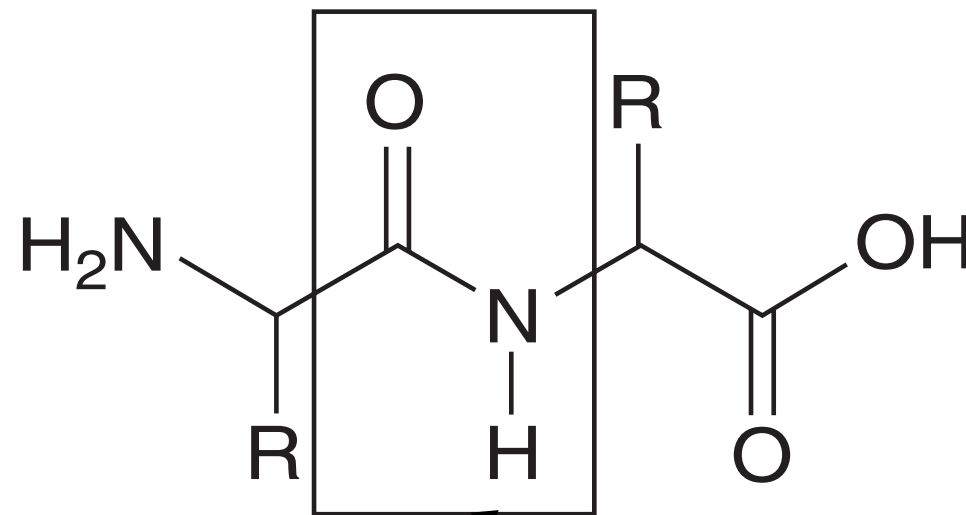
The energy for the lowest vibrational state is not zero

$$\text{for } v = 0, \quad E_v = \frac{1}{2} h\nu$$

Zero point energy



Vibration of the N-H bond of the peptide link



The peptide link

$^{15}\text{N} - ^1\text{H}$

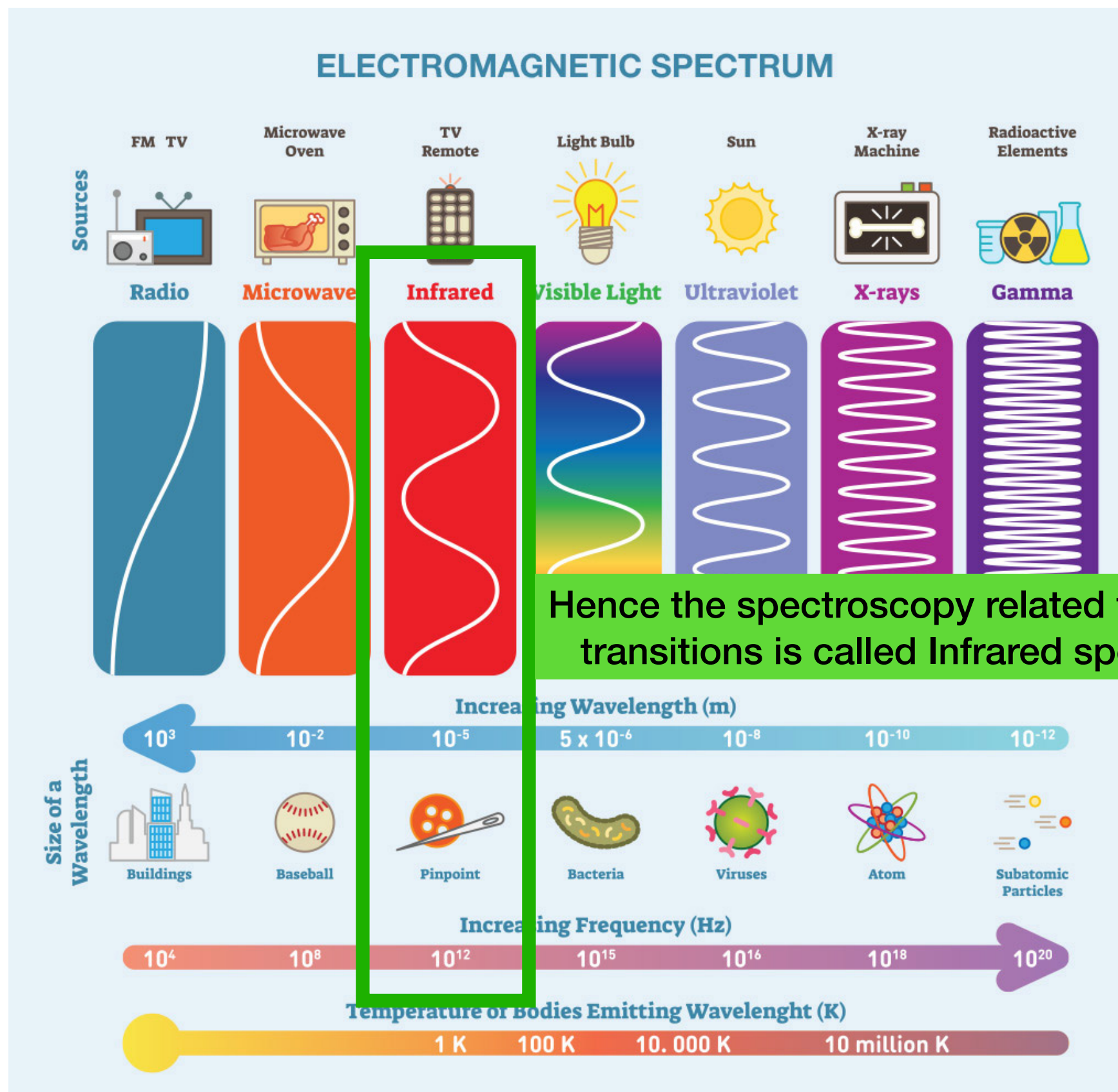
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_{NH}}{\mu}} \quad \text{where, } \mu = \frac{m_N m_H}{m_N + m_H} \quad 1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$k_{NH} \approx 300 \text{ Nm}^{-1} \quad \Rightarrow \quad \nu = ??$$

$$\nu \approx 67 \text{ THz} \quad \Rightarrow \quad h\nu \approx 4.5 \times 10^{-20} \text{ J}$$

Which is region of the electromagnetic spectrum is this?

Types of radiations by wavelength and frequency

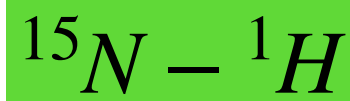


Significance of the reduced mass for molecular vibration



$$\text{reduced mass, } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\text{for } m_1 \gg m_2 \implies \mu \approx \frac{m_1 m_2}{m_1} = m_2$$



$$\mu = \frac{15 \times 1}{15 + 1} = 0.94 \text{ amu} \approx m_H$$



$$\mu = \frac{12 \times 16}{12 + 16} = 6.86 \text{ amu}$$

Not close to either
 m_C or m_O

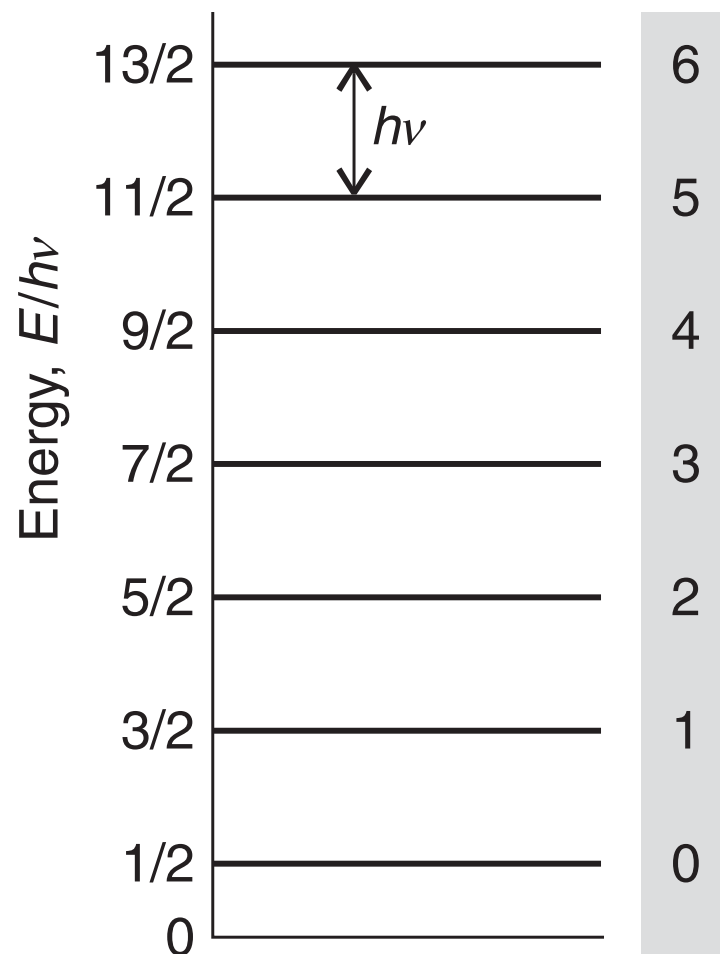
For homonuclear
diatomic molecules

$$\mu = \frac{m \times m}{m + m} = \frac{m}{2}$$

Vibrational transitions

The energy of typical vibrational excitation $\approx 10^{-20} - 10^{-19} J$ and the frequency of exciting radiation should be $\approx 10^{12} - 10^{14} Hz$

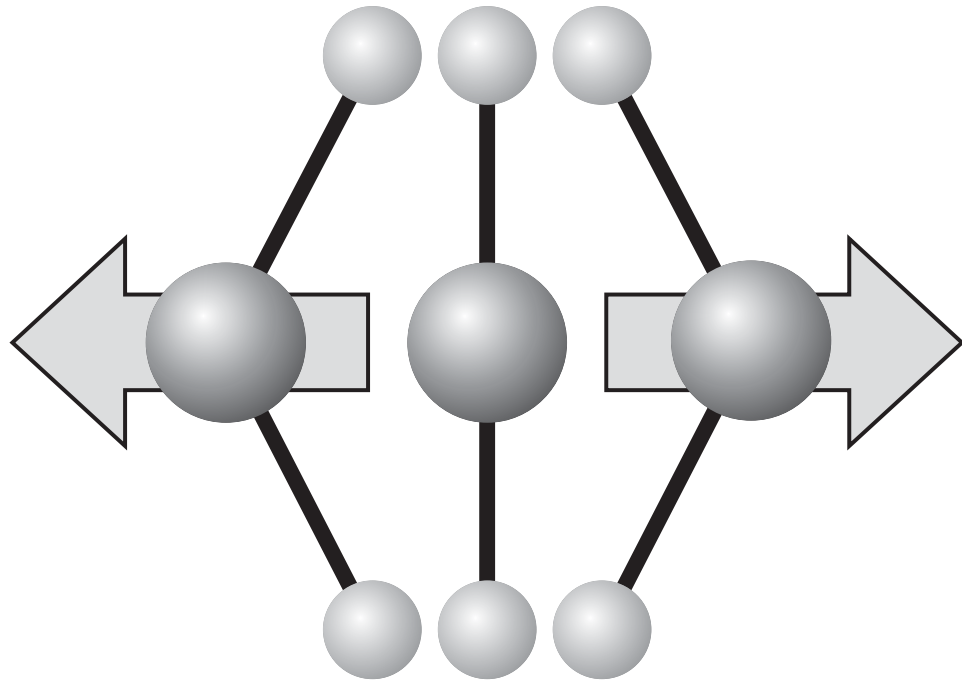
This frequency range corresponds to infrared radiation, so vibrational transitions are observed by infrared or IR spectroscopy.



In IR spectroscopy, transitions are normally expressed in terms of their wavenumbers $\bar{\nu} = 1/\lambda$

$$\bar{\nu}_{IR} \approx 300-3000 \text{ cm}^{-1}$$

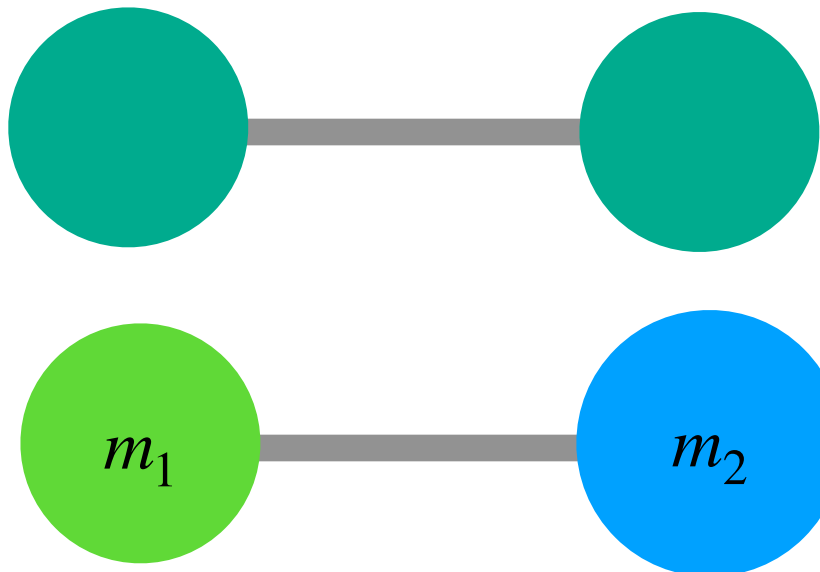
Selection rules for IR spectroscopy



The gross selection rule for IR absorption spectra = the electric dipole moment of the molecule must change during the vibration.

No permanent dipole is needed, but if a dipole is developed during vibration the molecule is IR active

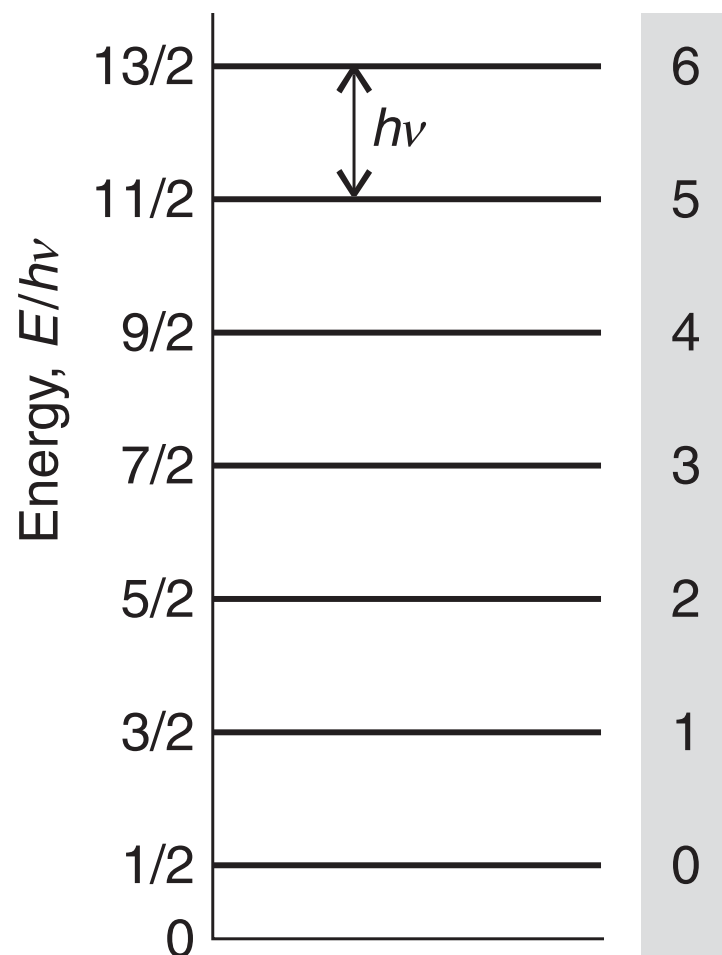
If some vibrational mode of a molecule has no changing dipole moment that mode is IR inactive



A homonuclear diatomic molecule is IR inactive

A heteronuclear diatomic molecule is IR active

Selection rules for IR spectroscopy ...contd



The specific selection rule for infrared absorption spectra is

$$\Delta v = \pm 1$$

Change in energy from v to $v + 1$ is given by

$$\begin{aligned} \Delta E &= E_{v+1} - E_v \\ &= \left(v + 1 + \frac{1}{2} \right) h\nu - \left(v + \frac{1}{2} \right) h\nu = h\nu \end{aligned}$$

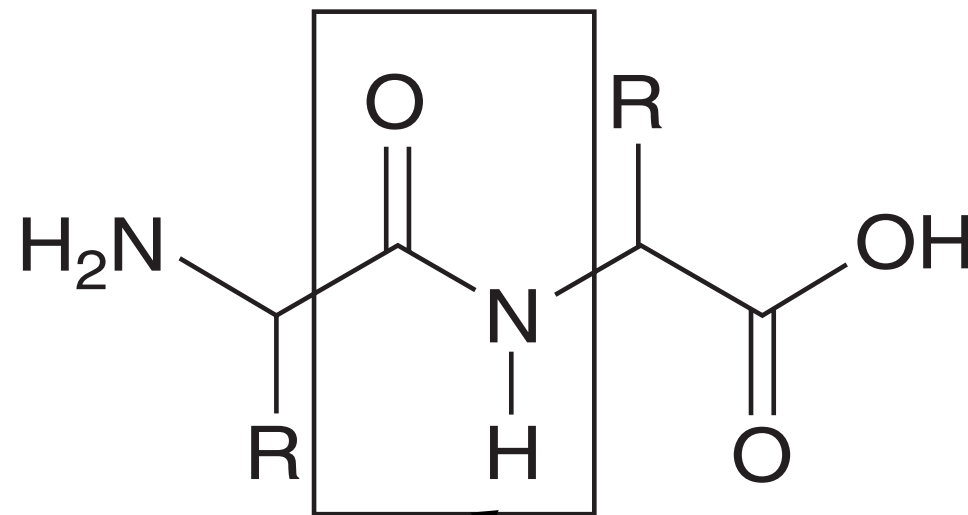
At room temperature, most molecules are at $v = 0$ state

Most important vibrational transition is the transition from $v = 0$ to $v = 1$ state

$\bar{\nu}_{0 \rightarrow 1}$ = fundamental wavenumber

$\nu_{0 \rightarrow 1}$ = fundamental frequency

Computing the fundamental wavenumber



The peptide link



$$k_{\text{CO}} \approx 1.2 \text{ kNm}^{-1}$$

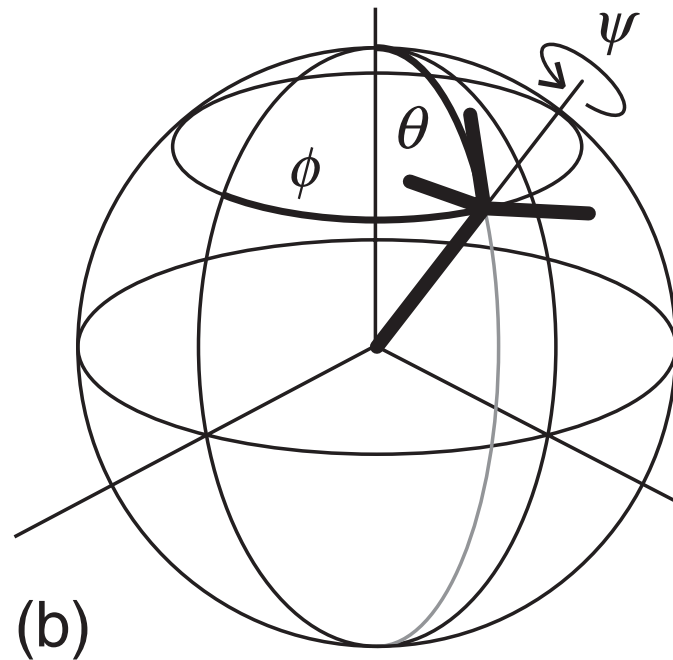
$$\mu = \frac{12 \times 16}{12 + 16} = 6.86 \text{ amu}$$

$$\bar{\nu}_{0 \rightarrow 1} = ??$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k_{\text{CO}}}{\mu}}$$

$$\Rightarrow \bar{\nu} \approx 1700 \text{ cm}^{-1}$$

The vibrations of polyatomic molecules



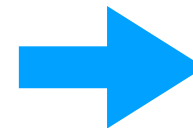
For a non-linear molecule of N atoms,

Total degrees of freedom = $3N$

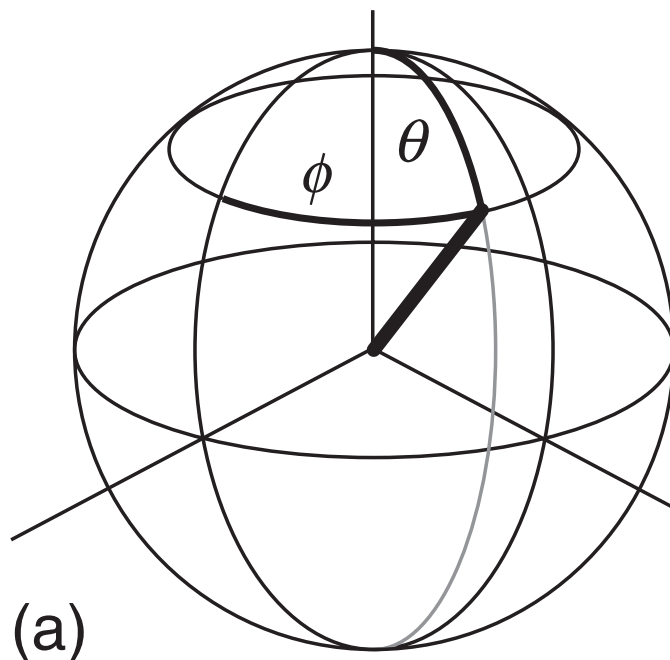
How many are not vibrational modes?

Translational modes of the whole molecule = 3

Rotational modes of the whole molecule = 3



Vibrational modes = $3N - 6$

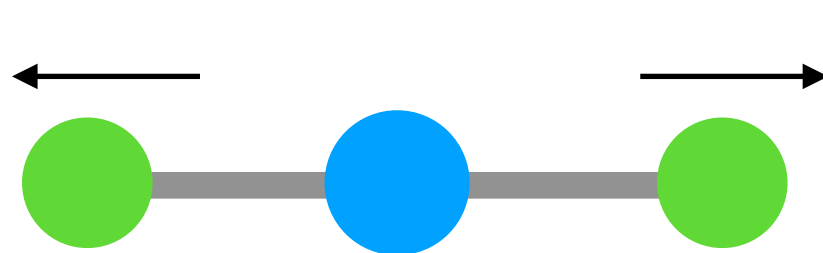


For linear molecules there is one less rotational mode

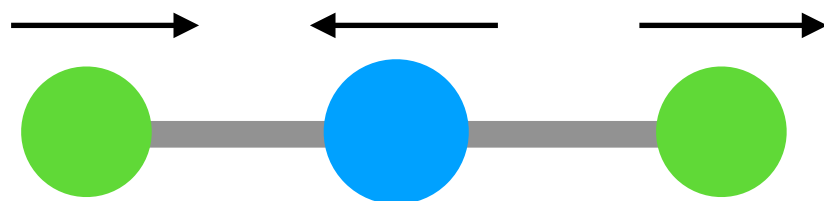
So, vibrational modes for linear molecules = $3N - 5$

The vibrational modes of carbon dioxide

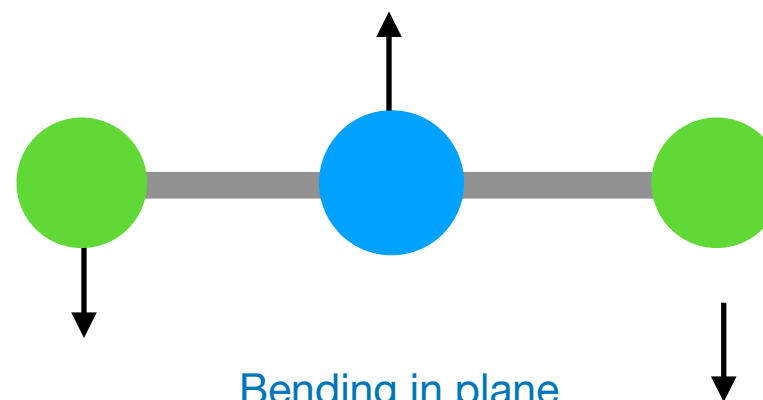
$$\text{No of vibrational modes} = 3N - 5 = 3 \times 3 - 5 = 4$$



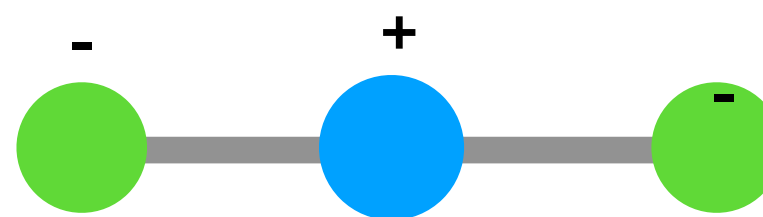
Symmetric stretching



Antisymmetric stretching



Bending in plane



Bending out of plane

Symmetric stretching modes has no change in dipole moment \Rightarrow IR inactive

Degenerate bending modes, same energy

The gross selection rule for IR active modes = the electric dipole moment of the molecule must change during a given vibrational mode. Thus a molecule can have active and inactive modes

Typically, bending modes have lower force constant (and hence a lower frequency) than stretching modes