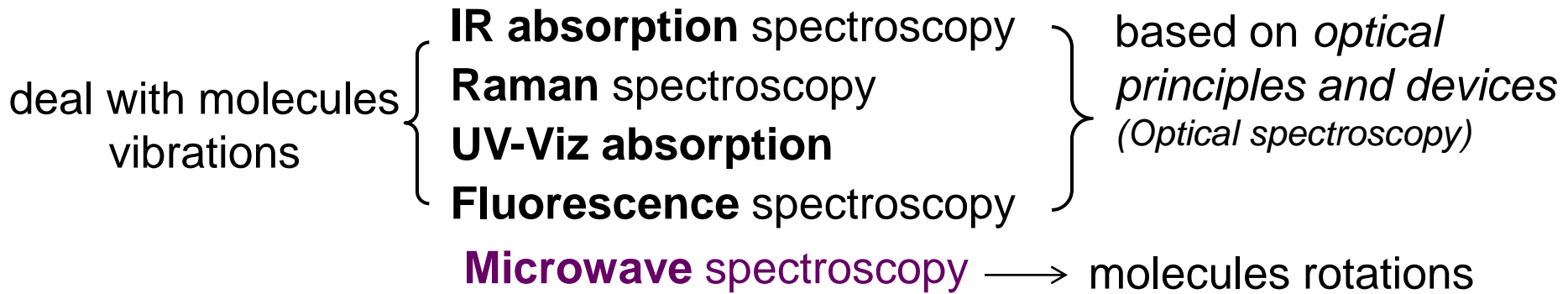


Vibrational spectroscopy

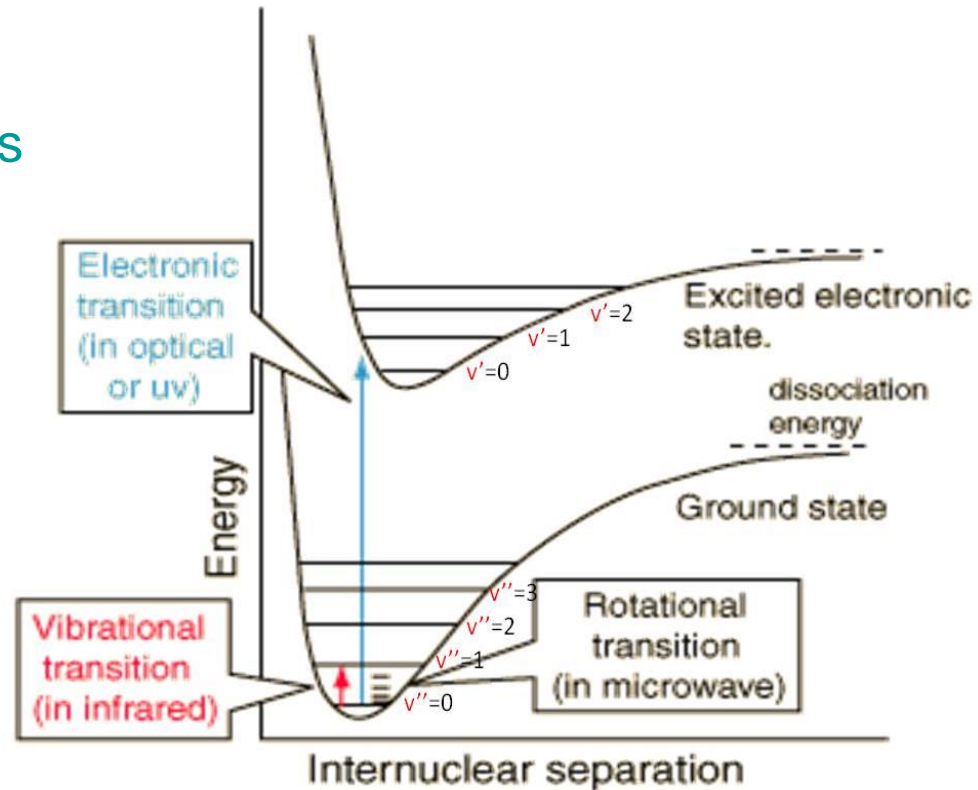


Electromagnetic radiation can determine a molecule to change his energy! (rotational, vibrational, electronic)

A lot of energy levels !!!

- rotational
- vibrational
- electronic

(ground state / excited state)



What is spectroscopy?

Spectroscopy study the **properties of matter** through its interaction with electromagnetic radiation (different frequency components).

Latin: “spectron” — ghost (or spirit)

Greek: “σκοπειν” — (scopie = to see)

In spectroscopy, we aren't looking directly at the molecules (the matter), we study its “ghost”, obtained from the interaction of electromagnetic waves with molecules.

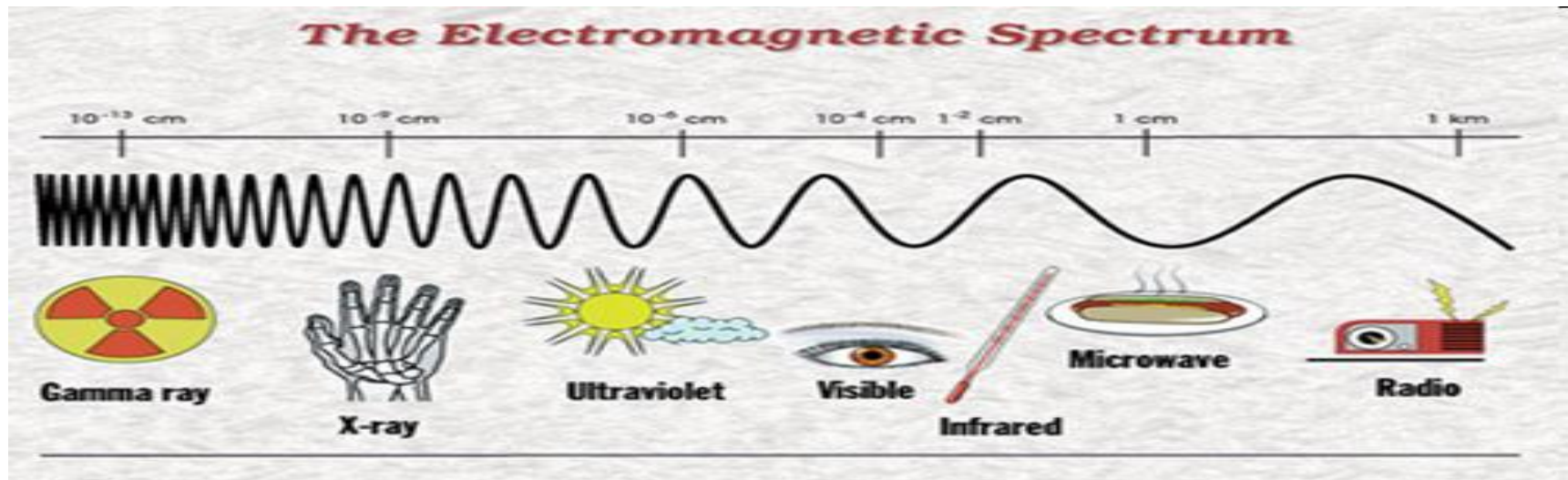
Different type of spectroscopy (incident electromagnetic waves with different frequency/wavelength/wavenumber/energy) involve different picture (**different spectrum**).

	RMN	RES	Micro waves	Raman IR	Visible	UV Fluorescence	X -Ray	Γ - Ray
λ [m]	10^2	1	10^{-2}	10^{-4}	10^{-6}	10^{-8}	10^{-10}	10^{-12}
$\bar{\nu}$ [cm ⁻¹]	10^{-4}	10^{-2}	1	10^2	10^4	10^6	10^8	10^{10}
ν [Hz]	3×10^6	3×10^8	3×10^{10}	3×10^{12}	3×10^{14}	3×10^{16}	3×10^{18}	3×10^{20}

From **spectroscopy** measurements we can extract different information (energies of electronic, vibrational, rotational states; structure and symmetry of molecules; dynamic information, etc).

Goal: to understand:

- how **electromagnetic radiations** interacts with matter and
- how we can use the obtained information in order to understand the sample.



Spectroscopy applications

	Gas	Liquid	Solid
Finger print	IR, Raman Microwave	IR, Raman UV-Vis, MS NMR	IR, Raman UV-Vis, MS X-Ray diff.
Functional groups	IR, Raman MS NMR	IR, Raman MS NMR	IR, Raman MS, NMR Mossbauer
Molecular symmetry	IR, Raman Microwave e-diffraction	IR, Raman MS NMR	IR, Raman MS, NMR Mossbauer
Bond distances Bond angles	IR, Raman Microwave e-diffraction	EXAFS LC-NMR/MS	X-Ray diff. neutron diff.
Electronic structure	UV-Vis UPS ESR	UV-Vis UPS ESR	UV-Vis, UPS, ESR Mossbauer, NQR X-Ray diff. neutron diff.

EXAFS: Extended X-Ray Absorption Fine Structure,

MS: Mass Spectrometry,

NQR: Nuclear Quadrupolar Resonance,

LC-MNR/MS: Liquid Chromatograph Nuclear Magnetic Resonance Mass Spectrometer,

UPS: Ultraviolet photoemission spectroscopy

Questions:

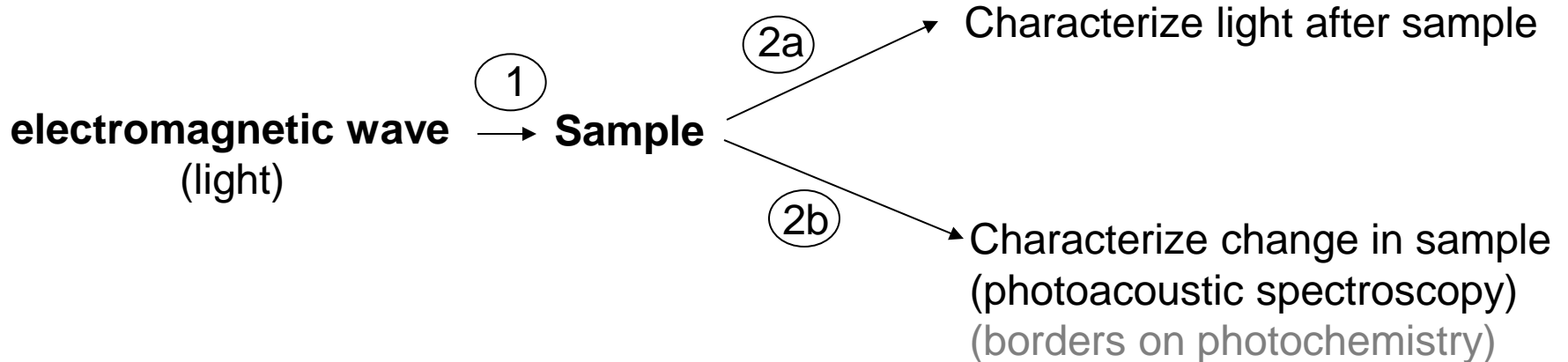
What does light do to sample?

How do we produce a spectrum?

What does a spectrum measure?

*Interaction of light with a sample can influence - the sample
- the light*

The basic idea:



(1) excitation; (2) detection

In vibrational spectroscopy we measure *how a sample modifies the incident light*, in order to understand what light do to the sample!

1) **Absorption:** The sample can absorb a part of incident light

A change in the intensity appear: **emergent light differs from incident light**

Sample attenuates the incident light (at particular frequencies).

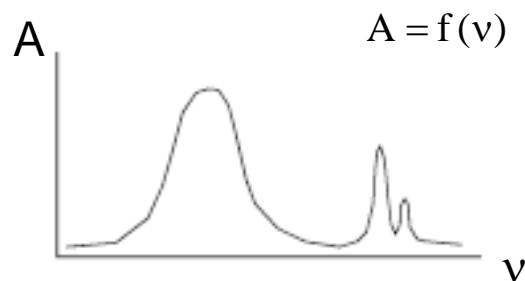
Two type of measurements:

→ absorbance $A = \log(I_0/I)$

→ transmission $T = I/I_0$



If we measure the absorbance of light on entire range of incident radiation, we will obtained **the absorption spectrum**.



$$A = f(\nu) \quad A = f(\lambda) \quad A = f(\bar{\nu})$$

ν - frequency (Hz, 1/s)

$$\nu = c \cdot \bar{\nu}$$

λ - wavelength (nm, μm)

$$\lambda = \frac{c}{\nu}$$

$\bar{\nu}$ - **wavenumber** (cm^{-1})

$$\bar{\nu} = \frac{1}{\lambda}$$

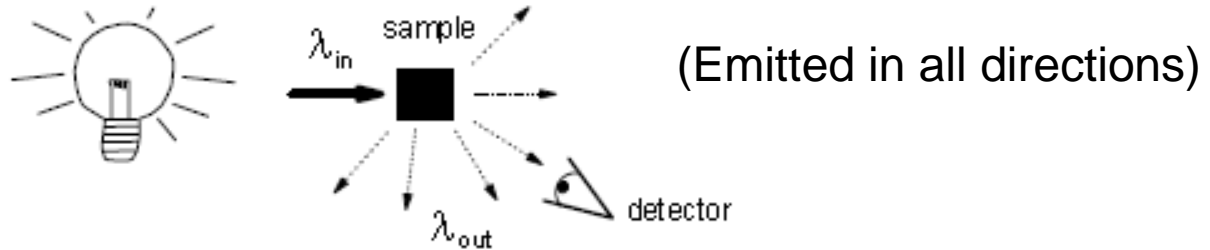
Microwaves absorption (involve rotational transitions)

Infrared absorption (involve vibrational transitions)

UV-Vis absorption (involve electronical transitions)

2) Emission:

Excitation can **induces** emission of light from the sample (usually of different frequency from incident light!).



same frequency:

Rayleigh scattering

different frequency

Raman scattering (vibrational transitions are involved)

Fluorescence (emission from excited electronic singlet states)

Phosphorescence (emission from excited electronic triplet states)

3) Optical Rotation:

Phase change of light incident on sample (rotation of polarization plane)

(- no spectroscopy)

An *electromagnetic wave* is composed from an electric field (E_x) and a magnetic field (H_y) that are perpendicular each other, and perpendicular to the direction of travel (Oz).

The wave equation for electromagnetic waves arises from Maxwell's equations:

$$E_x = E_0 \sin(2\pi\nu \cdot t - (2\pi/\lambda) \cdot z)$$

$$H_y = H_0 \sin(\omega t - kz)$$

ω angular frequency ($\omega = 2\pi\nu$) [radians/sec]

k wave vector ($k = 2\pi/\lambda = \omega/c$)

ν frequency ($\nu = \omega/2\pi$) [sec^{-1} , Hertz]

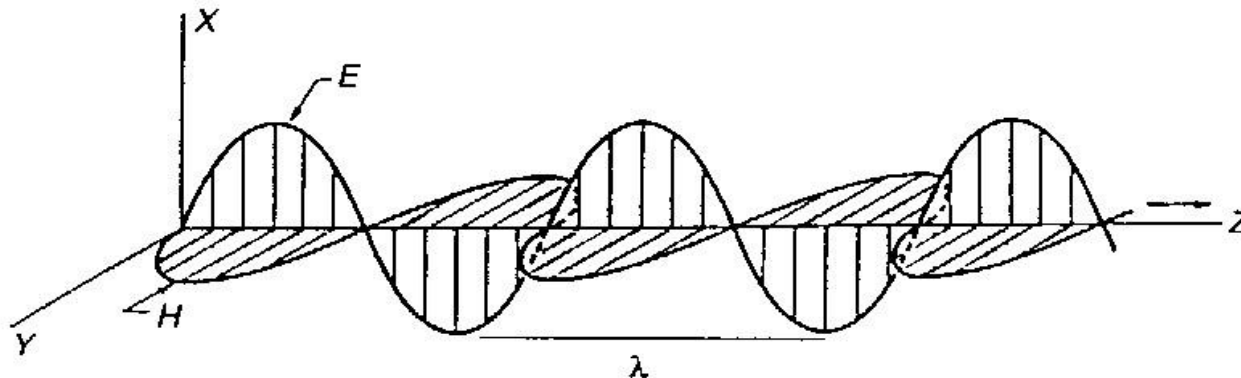
λ wavelength (nm, Å)

$\bar{\nu}$ wavenumber (cm^{-1})

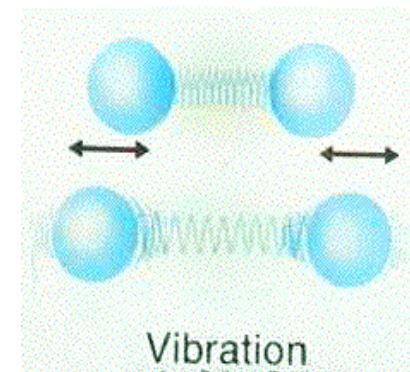
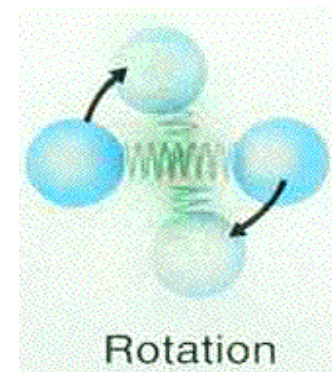
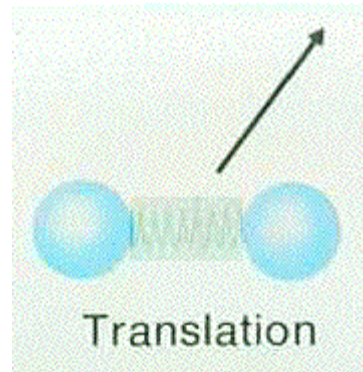
c light speed ($3 \cdot 10^8$ m/s)

E energy ($E = h \cdot \nu$) [J], energy can be expressed as cm^{-1} using E/hc !

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

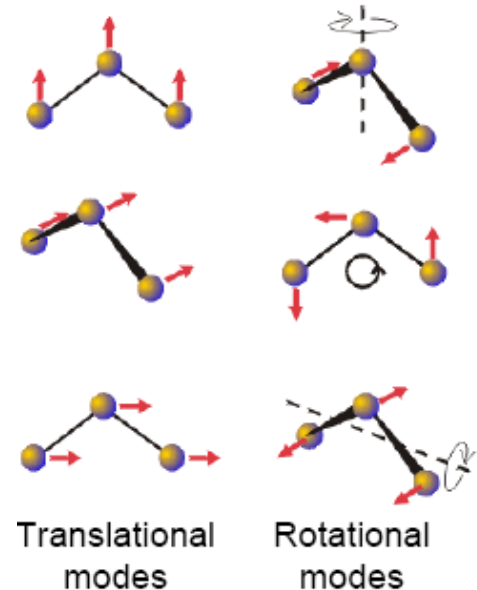


Types of molecule motion



Motion of whole molecule

- **Translational motion:** whole molecule changes its location in three dimensional space
- **Rotational motion:** whole molecule spins around an axis in three dimensional space



Motion within molecule

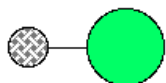
- **Vibrational motion:** motion that changes the shape of the molecule (**periodic motion of atoms**)
 - stretching (bonds length deformation)
 - bending (bonds angle deformation)

Molecular vibrations

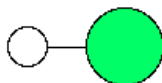
A **molecular vibration** occurs when atoms in a molecule are in periodic motion. The frequency of the periodic motion is known as the **vibration frequency**.

A molecular vibration is a periodic distortion of a molecule from its equilibrium geometry.

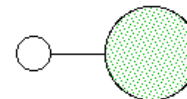
The energy required for a molecule to vibrate is not continuous (is quantized) and is (generally) in the infrared region of the electromagnetic spectrum.



D-F

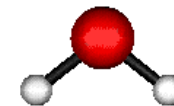
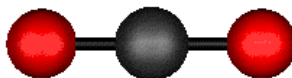


H-F

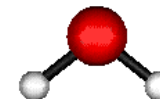


H-Cl

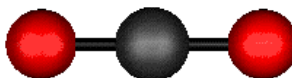
symmetrical stretching



asymmetrical stretching



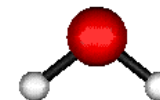
bending



CO₂



N₂O



H₂O

Vibrational motion of 3 atoms group:

Symmetrical stretching	Asymmetrical stretching	Scissoring
Rocking	Wagging	Twisting

In plane vibrations

- stretching
- scissoring
- rocking

Out of plane vibrations

- wagging
- twisting

Stretching:

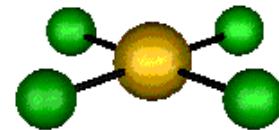
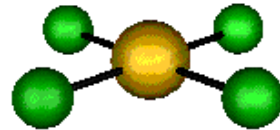
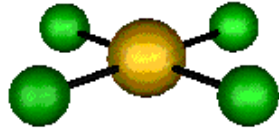
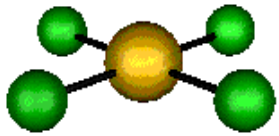


Molecular vibrations can be classified in

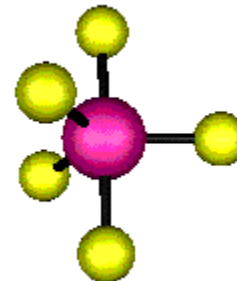
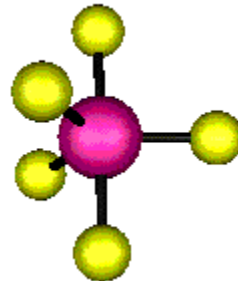
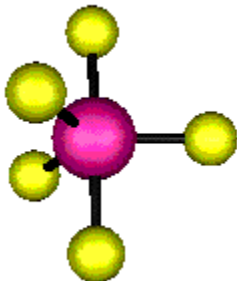
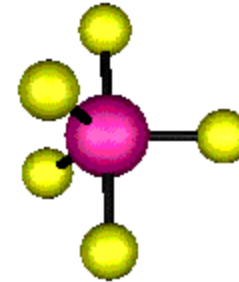
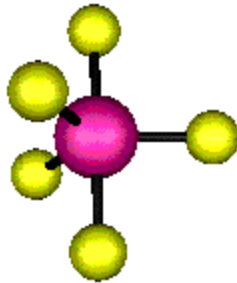
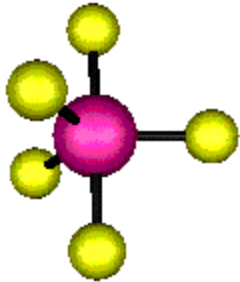
- stretching
- bending
- torsion (more than 3 atoms involved)

Bending or Deformation:



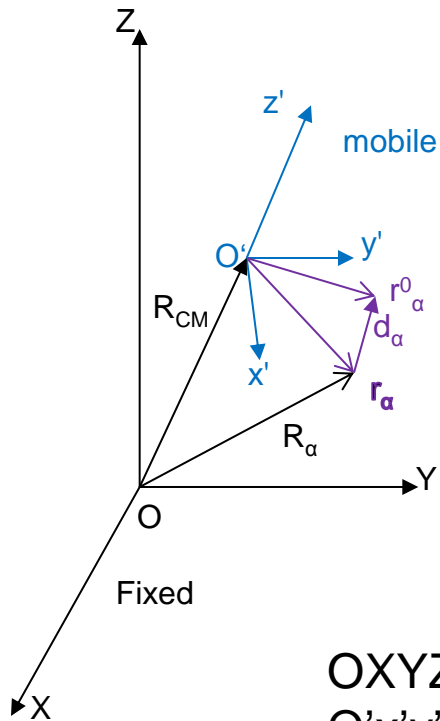


http://www2.ess.ucla.edu/~schauble/molecular_vibrations.htm



Molecular vibrations of molecules

Isolated molecule → total energy (E), linear momentum (p) and angular momentum (M) are constants.



$$E = E_c + V = \text{const}$$

$$\vec{p} = \sum_{\alpha} m_{\alpha} \cdot \frac{d\vec{R}_{\alpha}}{dt} = \text{const}$$

$$\vec{M} = \sum_{\alpha} \vec{R}_{\alpha} \times \vec{p}_{\alpha} = \text{const}$$

$$E_c = \frac{1}{2} \sum_{\alpha} m_i \cdot \left(\frac{d\vec{R}_{\alpha}}{dt} \right)^2$$

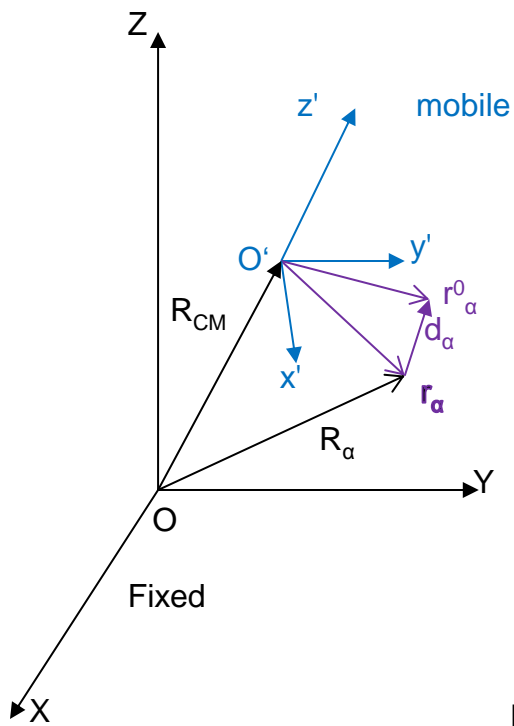
E_c - kinetic energy

V - potential energy (=?)

OXYZ: fixed reference frame

O'x'y'z': center of mass reference frame

$$\vec{R}_{CM} = \frac{\sum m_{\alpha} \cdot \vec{R}_{\alpha}}{\sum m_{\alpha}}$$



In the **center of mass reference frame (CM)**, linear momentum (p) and angular momentum (M) are zero!

$$\left\{ \begin{array}{l} \vec{p} = \sum m_\alpha \cdot \vec{r}_\alpha = 0 \\ \vec{M} = \sum_\alpha m_\alpha \cdot \vec{r}_\alpha^0 \times \vec{r}_\alpha = 0 \end{array} \right.$$

r_α^0 - equilibrium position

Eckart conditions:

$$\left\{ \begin{array}{l} \sum_\alpha m_\alpha \cdot \vec{d}_\alpha = 0 \\ \sum_\alpha m_\alpha \cdot \vec{r}_\alpha^0 \times \vec{d}_\alpha = 0 \end{array} \right. \quad \vec{d}_\alpha = \vec{r}_\alpha - \vec{r}_\alpha^0$$

Only movement which meet the Eckart conditions are vibrations!

The kinetic energy of an isolated molecule in the center of mass reference frame (CM):

$$\frac{d\vec{R}_\alpha}{dt} = \frac{d\vec{R}}{dt} + \vec{\omega} \times \vec{r}_\alpha + \frac{d\vec{r}_\alpha}{dt}$$

α atom speed
(fixed frame)

translational
speed

rotational
speed

relative
speed
(CM frame)

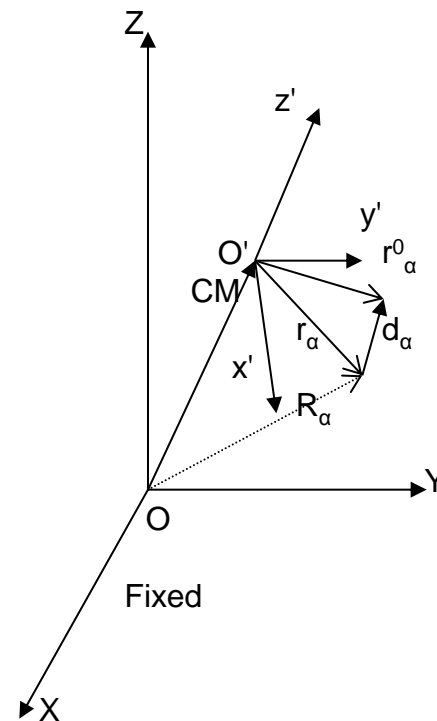
$$E_c = \frac{1}{2} \sum m_\alpha \cdot \left(\frac{d\vec{R}_\alpha}{dt} \right)^2 = T_{tr} + T_{rot} + T_{vib} + T_{cor} \quad - \text{total kinetic energy}$$

$$T_{tr} = \frac{1}{2} \sum m_\alpha \cdot \vec{R}^2 \quad - \text{pure translational kinetic energy}$$

$$T_{rot} = \frac{1}{2} \sum_\alpha m_\alpha \cdot (\vec{\omega} \times \vec{r}_\alpha)^2 \quad - \text{pure rotational kinetic energy}$$

$$T_{vib} = \frac{1}{2} \sum m_\alpha \cdot \vec{r}_\alpha^2 \quad - \text{pure vibrational kinetic energy}$$

$$T_{cor} = \vec{\omega} \sum m_\alpha (\vec{d}_\alpha \times \vec{r}_\alpha) \quad - \text{roto-vibrational kinetic energy}$$



We almost can separate the kinetic energy of the three type of molecule motion!!!

Diatomic molecule vibration

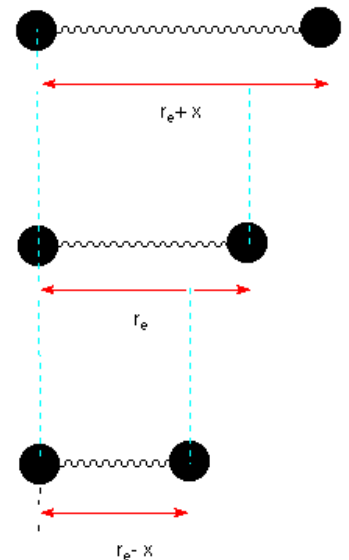
The simplest model to describe the **vibration of a diatomic molecule** (two atoms linked by a chemical bond) is the classical analog of a **spring connecting two bodies**.

The **strength of the bond** corresponds to the **force constant k** of the spring

The spring behavior gives us a description of **how the molecule energy changes if we distort the bond**.

When the spring equation ($F = -kx$) is applied to the vibrating particles **the frequency of the vibration** is related to the **masses of the particles** and to the **force constant k** .

In a similar way, the frequency of the molecule vibration (ν) is related to the **masses of the atoms (μ)** and to the **strength of the chemical bond (k)**.

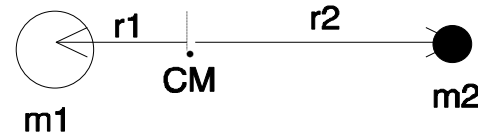


The molecule is considered isolated, so total energy (E), linear momentum (p) and angular momentum (M) are constants.

$$E = E_c + V(x) = \text{const.}$$

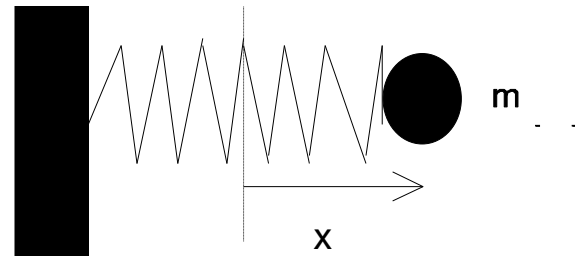
$$\vec{p} = m_1 \cdot \dot{\vec{R}}_1 + m_2 \cdot \dot{\vec{R}}_2 = \text{const}$$

$$\vec{M} = \vec{R}_1 \times \vec{p}_1 + \vec{R}_2 \times \vec{p}_2 = \text{const}$$



$$E_c = \frac{1}{2} (m_1 v_1^2 + m_2 v_2^2) = \frac{1}{2} \mu v^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduce mass}$$



In order to describe the molecule vibration we must **define the potential energy (V)** of the molecule.

The potential energy of a **harmonic oscillator (ideal molecule)** is $V(x) = 1/2k \cdot x^2$ where $V(x)$ = potential energy,

k = chemical bond (force constant)

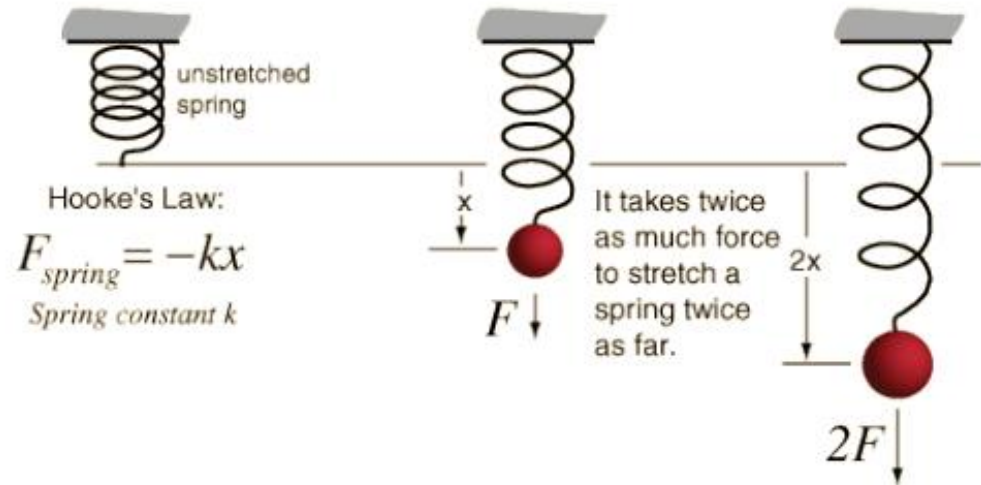
x = elongation/compression of the bond from its equilibrium position

At the equilibrium position, the potential energy is zero!

The Harmonic Oscillator Approximation → Classical description

The vibration motion of a diatomic molecule is model with a "*Simple Harmonic Oscillator*" (SHO) using Hooke's law as a linear restoring force.

Classically:
$$F = ma = m \frac{d^2x}{dt^2} = -kx$$



The exact classical solution (depends upon the initial conditions) generally take the form:

$$x(t) = A \sin(2\pi\nu t) = A \sin(\omega t)$$

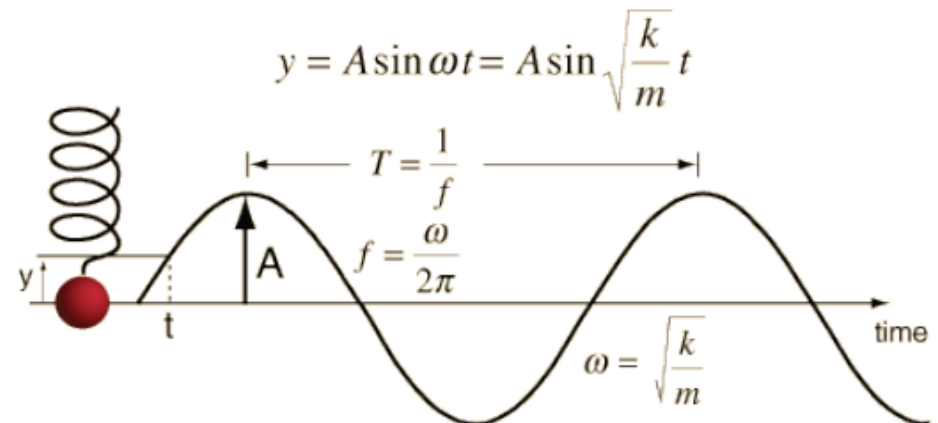
$$\omega = 2\pi\nu = \sqrt{\frac{k}{m}}$$

- k is the force constant of the spring in N/m

The frequency of oscillation is given by:

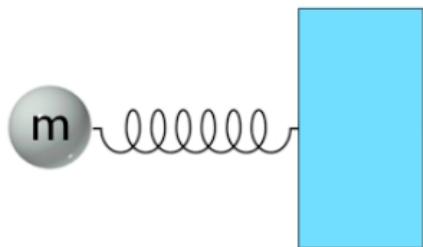
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

The frequency ν does not depend on the amplitude (A).



The vibration of a diatomic molecule (ideal molecule):

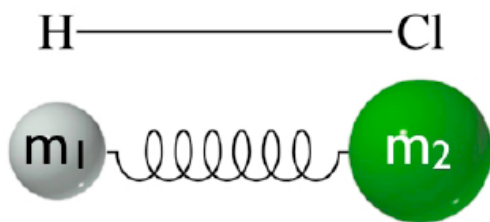
Simple harmonic oscillator → the mass m is fixed to a wall:



The frequency of oscillation is given by:

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

Diatomic molecules → there are two masses, m_1 and m_2 .



The **frequency of vibration** is given by:

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

k bond force constant

μ reduce mass

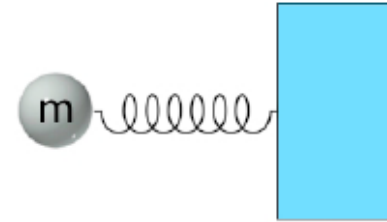
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Simple harmonic oscillator (SHO) → Quantum Mechanical

To get the QM solution, we need the potential energy stored in the SHO:

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

Hamiltonian:
$$H = E_c + V = \frac{p^2}{2\mu} + \frac{1}{2}kx^2$$



Schrödinger equation:
$$\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$$

When we solve the Schrödinger equation, we always obtain two things:

1. a set of wave functions (eigenstates):

2. a set energies (eigenvalues):

$$|\Psi_n\rangle \quad n = 1, 2, 3, \dots$$

$$E_n = h\nu\left(n + \frac{1}{2}\right) \quad n - \text{quantum number}$$

The energy of a vibrating molecule is quantized!

The vibrations energy levels are:

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

or

$$E_v = hc\bar{\nu}\left(v + \frac{1}{2}\right)$$

v - vibrational quantum number ($v = 0, 1, 2, 3, \dots$)

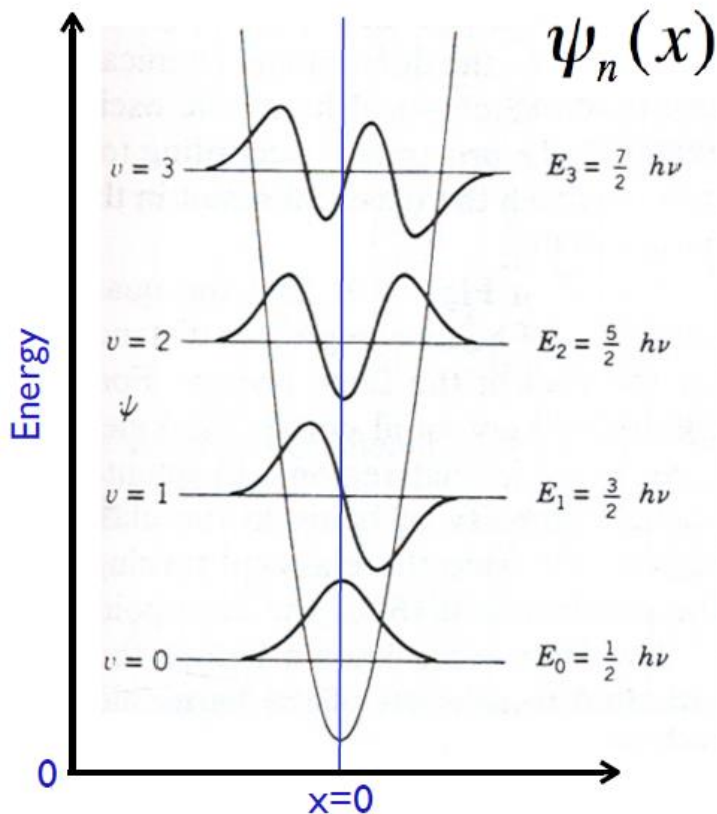
Diatomic molecule - one vibration! (stretching)

Energy levels:	$E_v = hc\bar{\nu}\left(v + \frac{1}{2}\right)$	$E_v = h\nu\left(v + \frac{1}{2}\right)$	$\bar{\nu}$ wavenumber ν frequency
Wavenumber:	$\bar{\nu} = \frac{1}{2\pi \cdot c} \sqrt{\frac{k}{\mu}}$	$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$	μ reduce mass k force constant

Wavefunctions	$\Psi_v(x) = N_v \exp\left[-\frac{1}{2}x^2\right] H_v(x)$ $N_v^2 = \left(\frac{4\pi m\nu}{h}\right)^{\frac{1}{2}} \frac{1}{2^v v!}$	}	$H_v(x) =$ Hermite polynomials $H_0(x) = 1$ $H_1(x) = 2x$ $H_2(x) = 4x^2 - 2$ $H_3(x) = 8x^3 - 12x$ $H_{v+1} = 2xH_v - 2vH_{v-1}$
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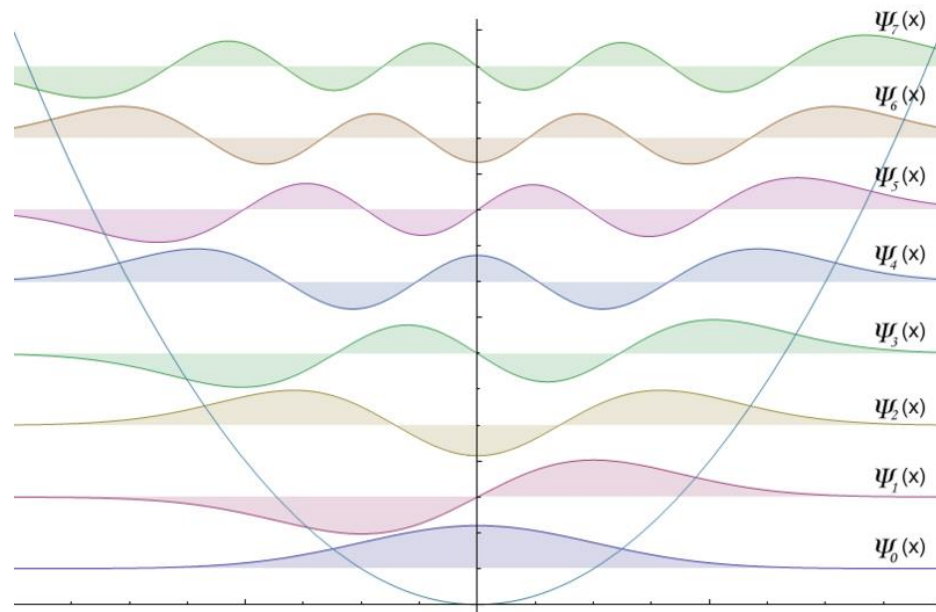
The simple harmonic oscillator wave functions (solutions to the one dimensional Schrödinger equation) are known as the "Hermite Polynomials".

The vibrational wave functions of a simple harmonic oscillator have **alternate parity** (even/odd \leftrightarrow symmetry/asymmetry).



SHO Wave functions

Wave function representations for the first eight quantum states. →



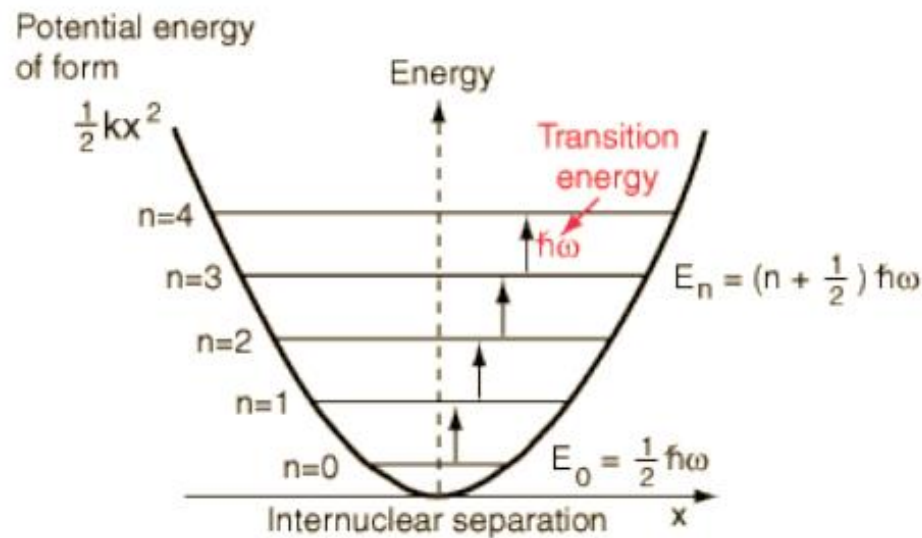
$$E_{v+1} - E_v = h \cdot c \cdot \bar{\nu}$$

The **distance** between two adjacent levels ($E_{v+1} - E_v$) is **$h \cdot c \cdot \bar{\nu}$** !

For an ideal molecule, the vibrational energy levels are equidistant!

For the simple harmonic oscillator: quantum mechanical **predicts** the **existence of discrete, evenly spaced, vibrational energy levels**.

$$E_v = hc\bar{\nu} \left(v + \frac{1}{2} \right) \quad v = 0, 1, 2, 3, \dots$$



► v - vibrational quantum number

► For the ground state ($v = 0$), $E_0 = 1/2 \cdot h \cdot c \cdot \bar{\nu}$

$$E_0 = 1/2 \cdot h \cdot c \cdot \bar{\nu}$$

$E_0 \neq 0!!!$

This is called the **zero point energy**.

Even in ground state there is some kind of vibration!

Anharmonic oscillator → real molecule!

If a **more realistic potential (V)** is used in the Schrödinger Equation, **the energy levels get scrunched together!**

Using Taylor series near equilibrium position:

$$V(r) = V(r_0) + \left(\frac{dV}{dr}\right)_{r=r_0} (r-r_0) + \frac{1}{2!} \left(\frac{d^2V}{dr^2}\right)_{r=r_0} (r-r_0)^2 + \frac{1}{3!} \left(\frac{d^3V}{dr^3}\right)_{r=r_0} (r-r_0)^3 + \dots$$

- in equilibrium position we have a *minimum*, so $\left(\frac{dV}{dr}\right)_{r=r_0} = 0$

- we supposed zero potential in equilibrium position: $V(r_0) = 0$

harmonic:

- we consider only term 2

$$V(r) = \frac{1}{2} \left(\frac{d^2V}{dr^2}\right) (r-r_0)^2$$

- we neglected superior terms 3, 4, 5, ...

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

anharmonic:

- we consider terms 3 and 4

$$V(x) = \frac{1}{2} kx^2 - gx^3 + ex^4$$

- we neglect terms 5,6, ...

$$V(r) = \frac{1}{2!} \left(\frac{d^2V}{dr^2}\right)_{r=r_0} (r-r_0)^2 + \frac{1}{3!} \left(\frac{d^3V}{dr^3}\right)_{r=r_0} (r-r_0)^3 + \frac{1}{4!} \left(\frac{d^4V}{dr^4}\right)_{r=r_0} (r-r_0)^4$$

Morse potential – close to real molecule potential:

$$V = D_e (1 - e^{-a(r-r_0)})^2$$

$$V(r) = \frac{1}{2} \left(\frac{d^2V}{dr^2} \right) (r-r_0)^2 + \frac{1}{3!} \left(\frac{d^3V}{dr^3} \right) (r-r_0)^3 + \frac{1}{4!} \left(\frac{d^4V}{dr^4} \right) (r-r_0)^4$$

$$V(x) = \frac{1}{2} kx^2 - gx^3 + ex^4 \quad k = 2D_e a^2; \quad g = D_e a^3 \quad e = \frac{7}{12} D_e a^4$$

From Schrödinger equation:

$$E_v = (v+1/2)h\nu_0 - x_e(v+1/2)^2h\nu_0$$

$$x_e = \frac{h\nu_0}{4D_e}$$

ν_0 - harmonic oscillator frequency

v - quantum number

x_e - anharmonicity constant

D_e - dissociation energy

► For the ground state ($v = 0$): $E_0 = 1/2 \cdot h\nu_0 (1 - 1/4 \cdot x_e)$

► The **distance** between two adjacent levels ($E_{v+1} - E_v$) depend on vibrational quantum number (v):

$$E_{v+1} - E_v = h\nu_0 (1 - 2x_e(v+1))$$

The anharmonicity constant is small: $x_e \sim 0.005 - 0.02$

The anharmonicity constant (x_e) and dissociation energy (D_e) are linked, they are specific to molecule!

Dissociation energy = the distance between the minimum of the potential curve and the continuum!

$[D_e] = \text{J}$

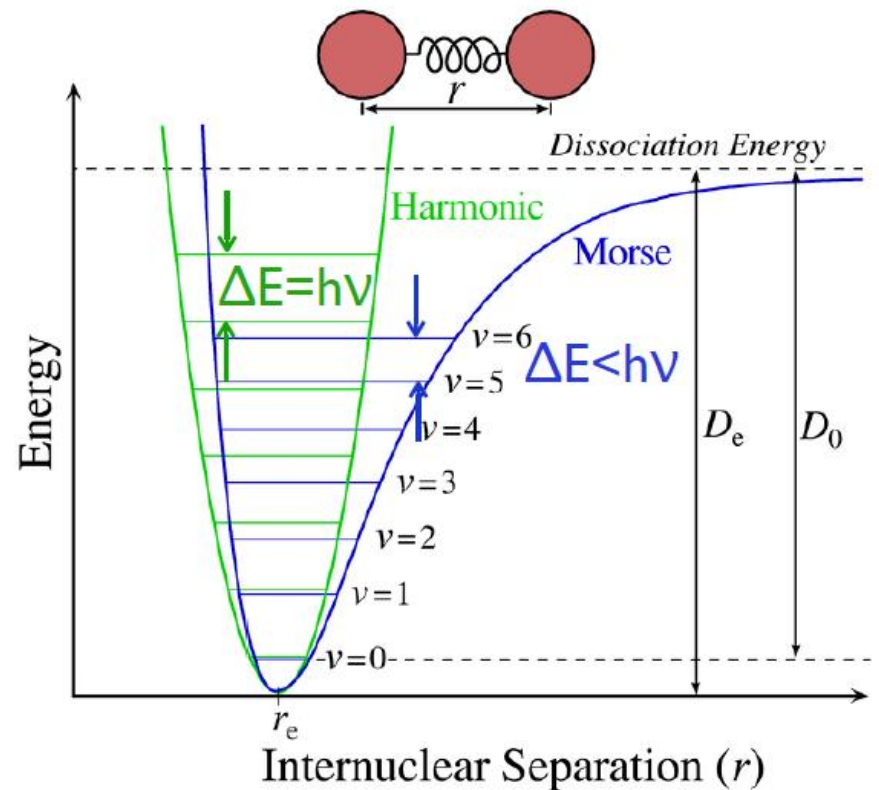
$$D_e = D_0 + \frac{1}{2} h\nu_0 - \frac{1}{4} x_e h\nu_0$$

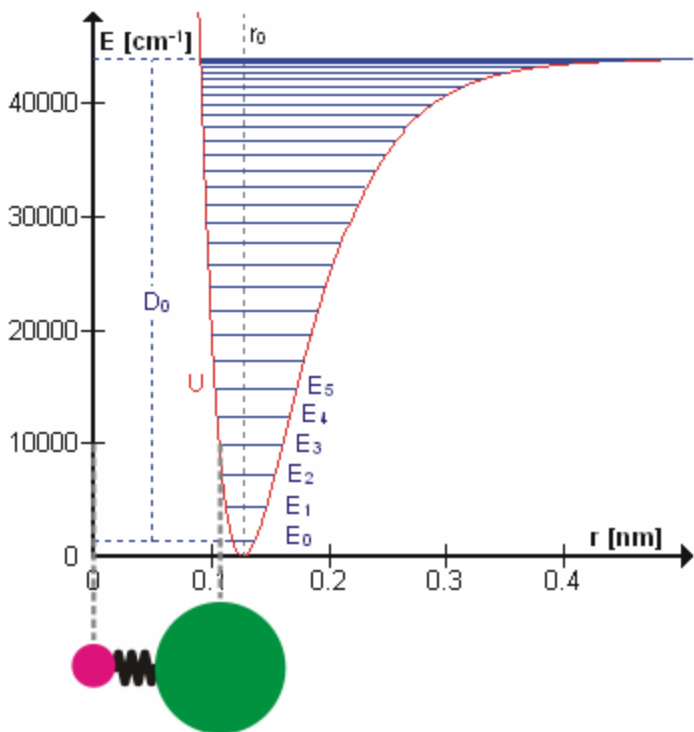
$$x_e = \frac{h\nu_0}{4D_e}$$

$[D_e] = \text{cm}^{-1}$

$$D_e = D_0 + \frac{1}{2} \bar{\nu}_0 - \frac{1}{4} x_e \bar{\nu}_0$$

$$x_e = \frac{\bar{\nu}_0}{4D_e}$$

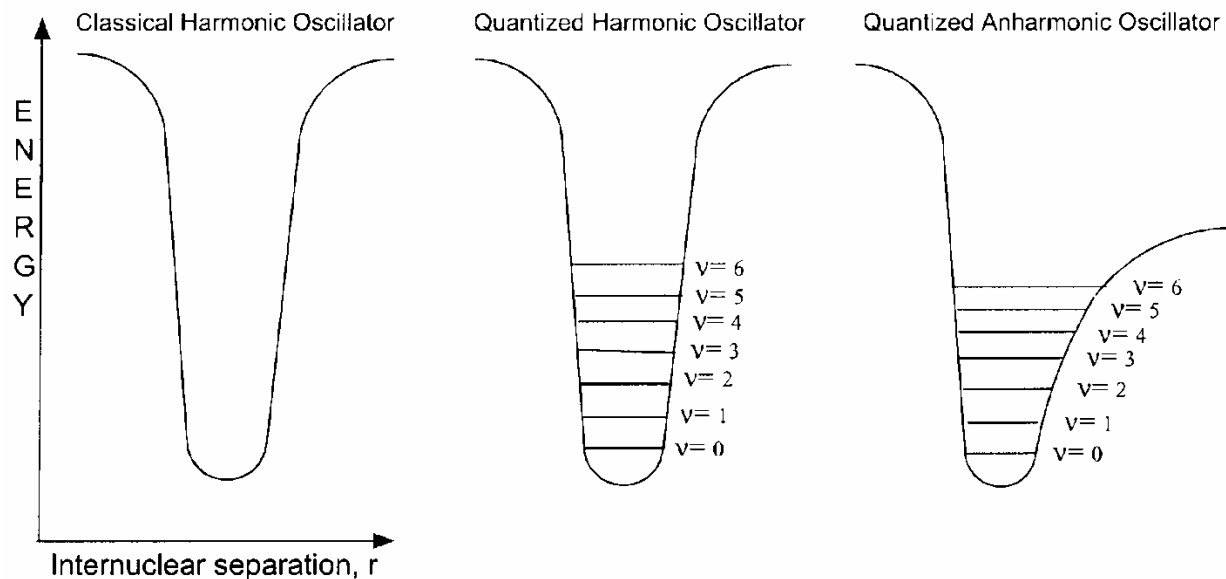




In harmonic approximation the number of vibrational levels is infinite!

In anharmonic approximation the number of vibrational levels is finite!

When energy increase the molecule can dissociate.



Vibration of polyatomic molecules. Normal modes

For a molecule with N atoms, each atom has three *motional degrees of freedom*. Thus, the molecule possesses a total of **$3N$ degrees of freedom**.

Chemical bonds serve to *constrain* the motion of the atoms to well defined vibrational modes (normal modes).

Linear molecules have **three unique translations**, but only **two unique rotations**.

The rotation about the bond axis does not count, since it changes neither positions of the atoms, nor does it change the angular momentum.

Thus, from the total of $3N$ degrees of freedom, we subtract three translations and two rotations, leaving **$3N-5$ vibrational degrees of freedom**.

Non-linear molecules have **three unique translations**, and **three unique rotations**.

Thus, from the total of $3N$ degrees of freedom, we subtract three translations and three rotations, leaving **$3N-6$ vibrational degrees of freedom**.

The number of “normal modes” is equal to the vibrational degree of freedom.

Normal modes

The vibrations of a molecule are given by its normal modes.

A normal mode is a molecular vibration where some or all atoms vibrate together with the same frequency in a defined manner.

Normal modes are basic vibrations in terms of which any other vibration is derived by superposing suitable modes in the required proportion.

No normal mode is expressible in terms of any other normal mode. Each one is pure and has no component of any other normal mode (i.e. they are orthogonal to each other).

Linear molecules have **$3N - 5$ normal modes**, where N is the number of atoms.

Non-linear molecules have **$3N - 6$ normal modes**.

Non-circular molecules have **$N-1$ stretching modes**.

Linear molecules have **$2N-4$ bending modes**.

Non-linear molecules have **$2N-5$ bending modes**.

The normal modes are described in normal coordinate (Q).

cartesian coordinate (x_i)

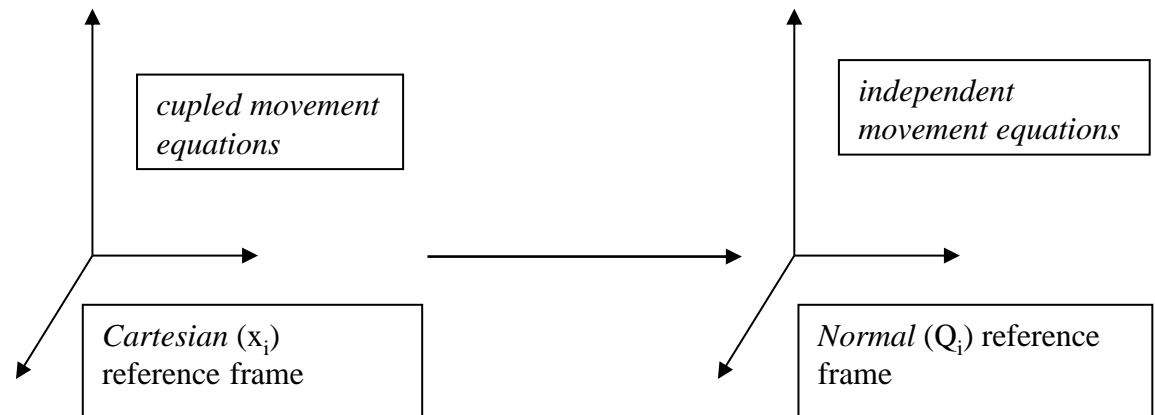


ponderat coordinate (q_i)

$$q_i = \sqrt{m_i} \cdot x_i$$



normal coordinate (Q_i): the normal amplitudes depend from ponderat amplitudes!



$$A_{ij} = \frac{A^{q_{ij}}}{\left(A^{q_{ij}^2} + A^{q_{ij}^2} + A^{q_{ij}^2} \right)^{1/2}}$$

The amplitude of normal mode are **normal** and **orthogonal** to each other.

$$\sum_i A_{is}^2 = 1 \quad \sum_i A_{ias}^2 = 1 \quad \sum_i A_{itr}^2 = 1$$

$$\begin{aligned} A_{1s}A_{1as} + A_{2a}A_{2as} + A_{3s}A_{3as} &= 0 \\ A_{1s}A_{1tr} + A_{2a}A_{2tr} + A_{3s}A_{3tr} &= 0 \\ A_{1tr}A_{1as} + A_{2tr}A_{2as} + A_{3tr}A_{3as} &= 0 \end{aligned}$$

Characteristics of Normal Modes

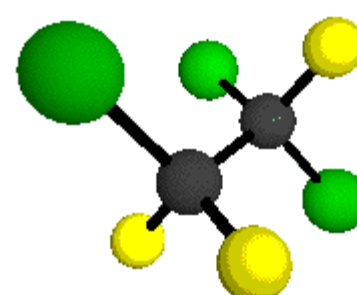
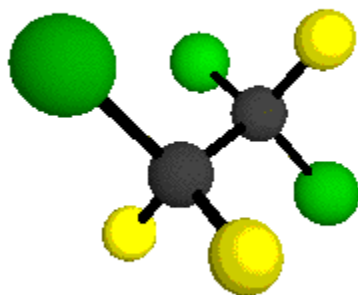
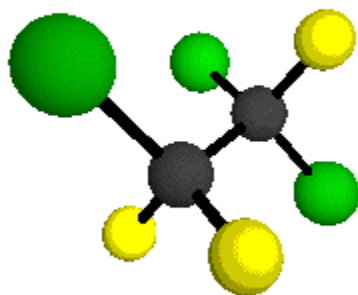
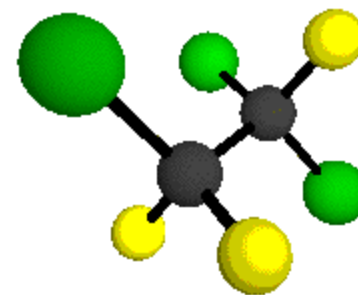
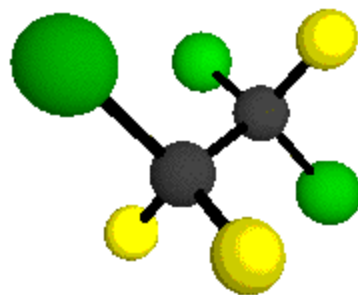
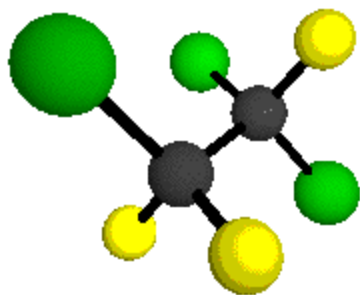
1. Each normal mode acts like a simple harmonic oscillator.
2. All atoms oscillate with same frequency.
A normal mode is a concerted motion of many atoms.
3. The center of mass doesn't move.
4. All atoms pass through their equilibrium positions at the same time.
5. Normal modes are independent; they don't interact.

Normal modes are useful in order to describe the vibration of polyatomic molecules!

All atoms oscillate with same frequency.

The center of mass doesn't move.

All atoms pass through their equilibrium positions at the same time.



Polyatomic molecules

In normal coordinates (Q):

$$E_c = \frac{1}{2} \sum_k \dot{Q}_k^2 \quad V = \frac{1}{2} \sum_k \lambda_k Q_k^2$$

$$-\frac{\hbar^2}{8\pi^2} \sum_k \frac{\partial^2 \Psi}{\partial Q_k^2} + \frac{1}{2} \sum_k \lambda_k Q_k^2 \Psi = E \Psi$$

Schrödinger equation can be split in 3N independent differential equations.

$$-\frac{\hbar^2}{8\pi^2} \frac{d^2 \Psi_k}{dQ_k^2} + \frac{1}{2} \lambda_k Q_k^2 \Psi_k = E_k \Psi_k$$

Total wavefunction: $\Psi(Q_1, Q_2, \dots, Q_k, \dots) = \Psi(Q_1) \Psi(Q_2) \dots \Psi(Q_k) \dots$

Total energy: $E_{total} = \sum_k \left(\nu_k + \frac{1}{2} \right) \hbar \nu_k$

An excited vibrational state (of a **polyatomic molecule**) involve more than one level of energy (**more than one vibrational quantum number must be used!**).

$k = 0, 1, \dots, 3N-5$ for linear molecules;

$k = 0, 1, \dots, 3N-6$ for nonlinear molecules;

Ex:

Normal modes of vibration for CO₂ molecule:

- 4 normal modes ($3 \cdot 3 - 5 = 4$), but 2 are *degenerated* (bending modes).

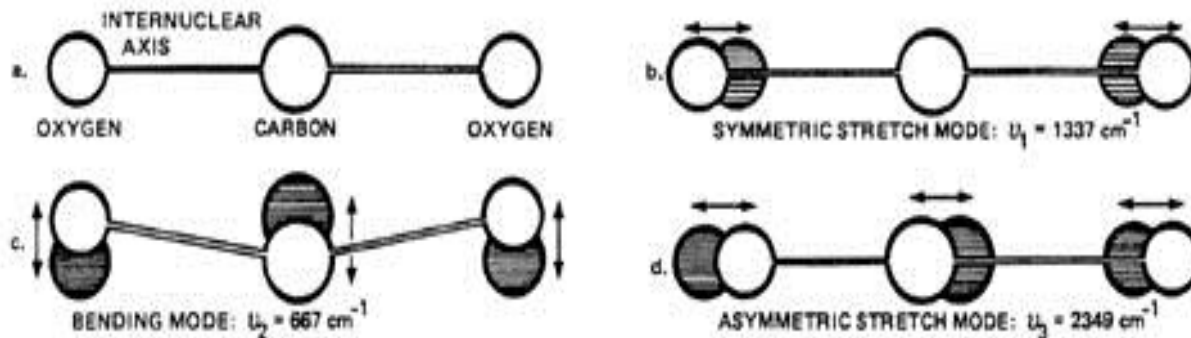
CO₂ have 3 different vibrations (normal modes)!

The vibrational energy state of CO₂ molecule can be described by *three quantum numbers*: ($\nu_1 \nu_2 \nu_3$)

ν_1 = Symmetric stretching quantum number.

ν_2 = Bending quantum number.

ν_3 = Asymmetric stretching quantum number.



$E(000)$ - the vibrational ground state of molecule; (is not 0!)

$$E_{(000)} = \frac{1}{2} h(\nu_1 + \nu_2 + \nu_3)$$

$E(100)$ - the first excited symmetric stretching state;

$E(001)$ - the first excited asymmetric stretching state;

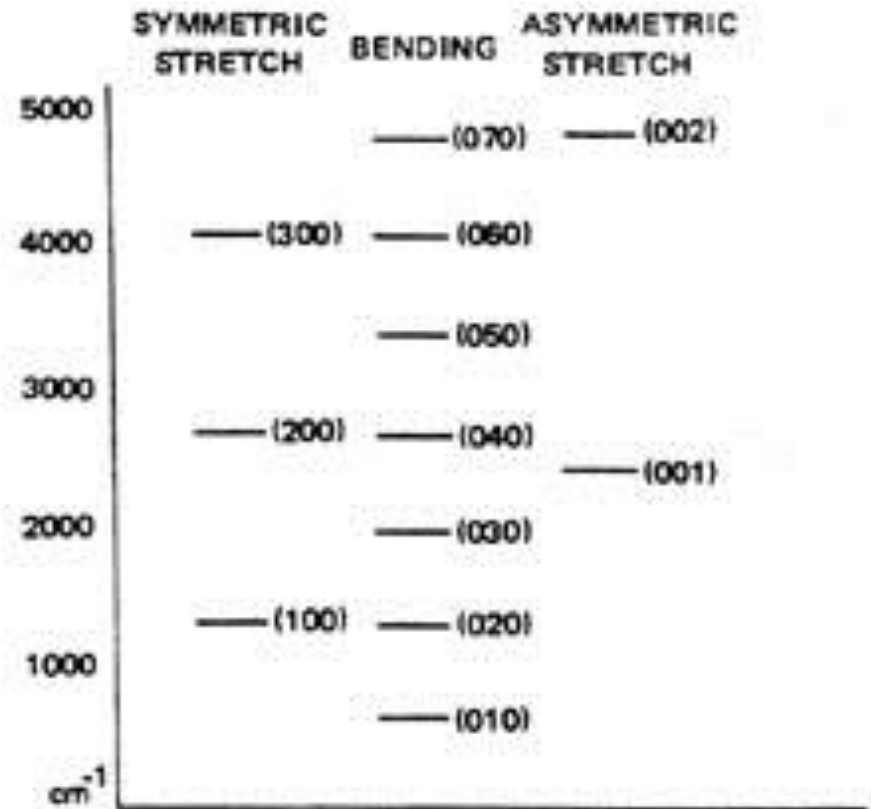
$E(010)$ - the first excited bending state;

$E(020)$ - two quanta of the excited bending state;

and so on.

$$E_{(\nu_1, \nu_2, \nu_3)} = \left(\nu_1 + \frac{1}{2}\right) h \nu_1 + \left(\nu_2 + \frac{1}{2}\right) h \nu_2 + \left(\nu_3 + \frac{1}{2}\right) h \nu_3$$

Vibrational energy levels in the electronic ground state of CO_2 :



Summary

Harmonic oscillator

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

$$E_v = h\nu(v + \frac{1}{2}) \quad E_v = hc\bar{\nu}(v + \frac{1}{2})$$

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

$$D_e = D_0 + \frac{1}{2}h\nu_0$$

$$\nu = \frac{c}{\lambda} = c\bar{\nu}$$

$$\omega = 2\pi\nu$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$m = M \cdot u$$

$$u = 1,66 \cdot 10^{-27} \text{ kg}$$

M - molar mass

u - atomic mass unit (amu)

Anharmonic oscillator

$$\bar{\nu}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$E_v = (v + \frac{1}{2})h\nu_0 - x_e(v + \frac{1}{2})^2 h\nu_0$$

$$E_v = (v + \frac{1}{2})hc\bar{\nu}_0 - x_e(v + \frac{1}{2})^2 hc\bar{\nu}_0$$

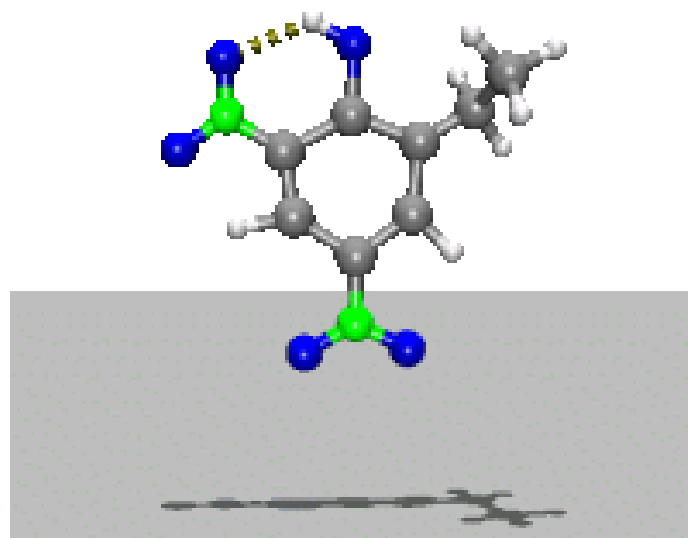
$$V(x) = \frac{1}{2}kx^2 - gx^3 + ex^4$$

$$k = 2D_e a^2 \quad g = D_e a^3$$

$$e = \frac{7}{12} D_e a^4$$

$$\chi_e = \frac{h\nu_0}{4D_e}$$

$$D_e = D_0 + \frac{1}{2}h\nu_0 - \frac{1}{4}\chi_e h\nu_0$$



http://molecularmodelingbasics.blogspot.ro/2010_07_01_archive.html

Questions:

1. For the following molecules: NH_3 , C_6H_6 (cyclic), C_{10}H_8 , CH_4 , C_2H_2 (linear).
 - a) find the number of vibrational modes
 - b) find the number of stretching modes
 - c) find the number of bending modes
2. Calculate the vibrational frequency of CO given the following data:
 $M_{\text{C}} = 12.01 \text{ u}$, $M_{\text{O}} = 16 \text{ u}$, $k = 1.86 \cdot 10^3 \text{ kg/s}^2$
3. Calculate the vibrational energy in (Joules) of a normal mode in question 2, in its ground state of $v = 0$.
4. Assuming the force constant to be the same for H_2O and D_2O . A normal mode for H_2O is at 3650 cm^{-1} . Do you expect the corresponding D_2O wave number to be higher or lower? Why?
5. The wavenumber of the fundamental vibrational transition of $^{79}\text{Br}^{81}\text{Br}$ is 320 cm^{-1} . Calculate the force constant of the bond (in N/m).

$$1 \text{ u} = 1.67 \cdot 10^{-27} \text{ kg}, c = 3 \cdot 10^8 \text{ m/s}, h = 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$$