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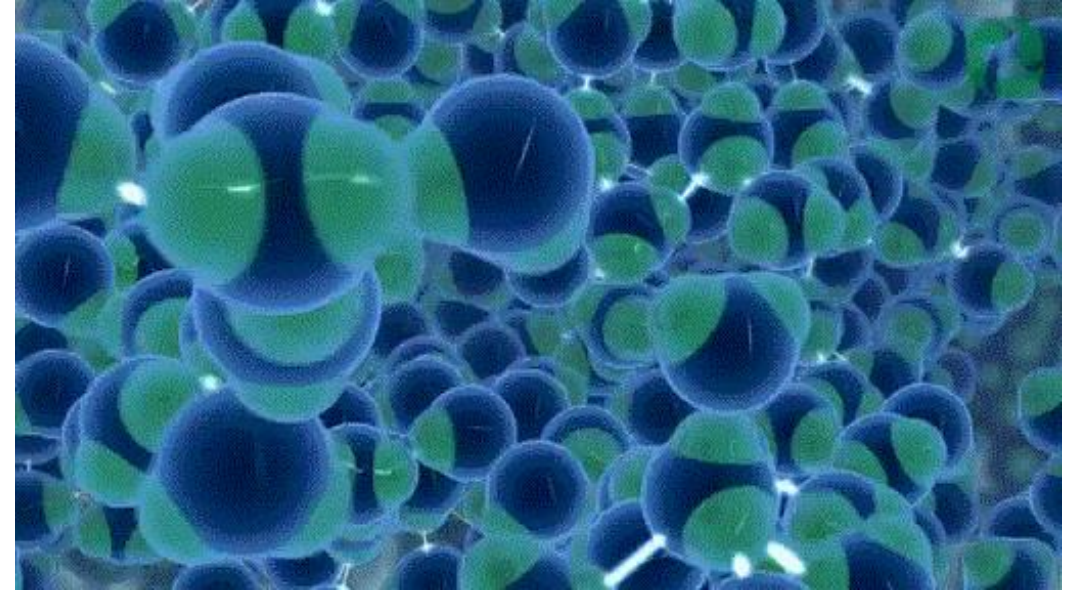
PEN205 MODERN PHYSICS

Molecules and Solids – I

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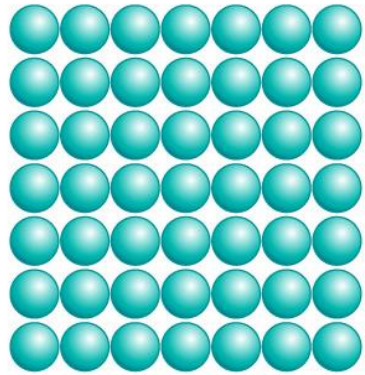
OUTLINE

- Molecular Bonds
- Energy States and Spectra of Molecules
- Bonding in Solids
- Free-Electron Theory of Metals
- Band Theory of Solids
- Electrical Conduction in Metals, Insulators, and Semiconductors



States of Matter

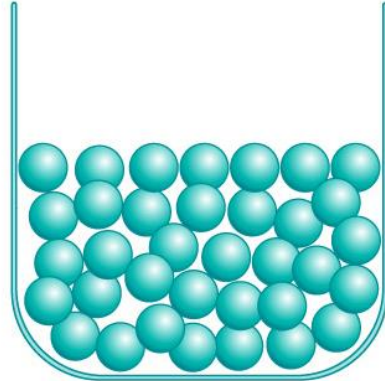
increasing energy



Solid

The molecules that make up a solid are arranged in regular, repeating patterns. They are held firmly in place but can vibrate within a limited area.

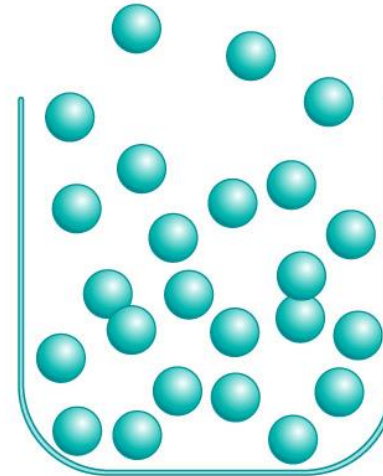
they form a regular array



Liquid

The molecules that make up a liquid flow easily around one another. They are kept from flying apart by attractive forces between them. Liquids assume the shape of their containers.

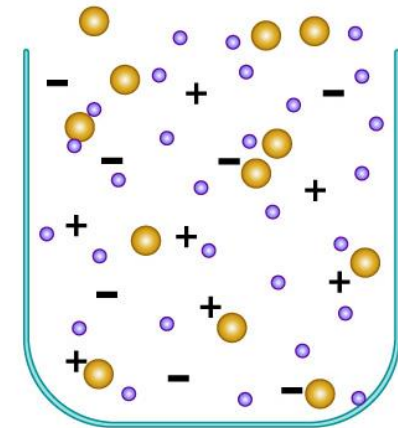
they do NOT form a regular array



Gas

The molecules that make up a gas fly in all directions at great speeds. They are so far apart that the attractive forces between them are insignificant.

random atomic arrangement



Plasma

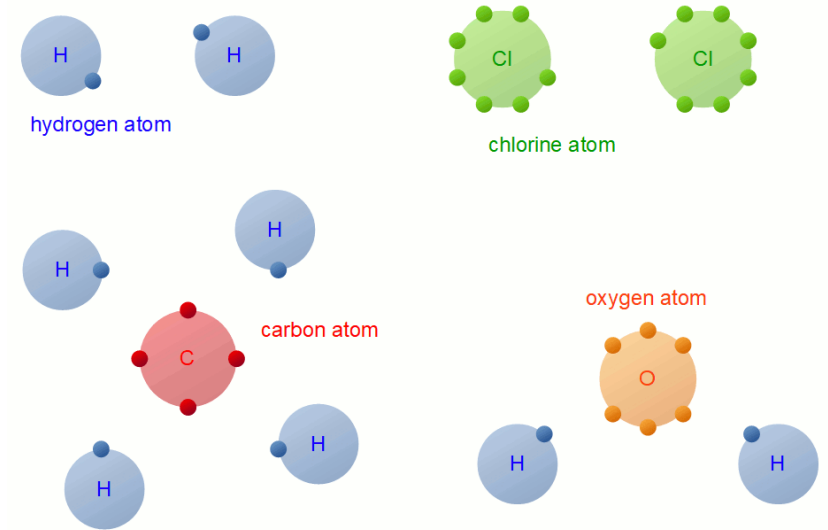
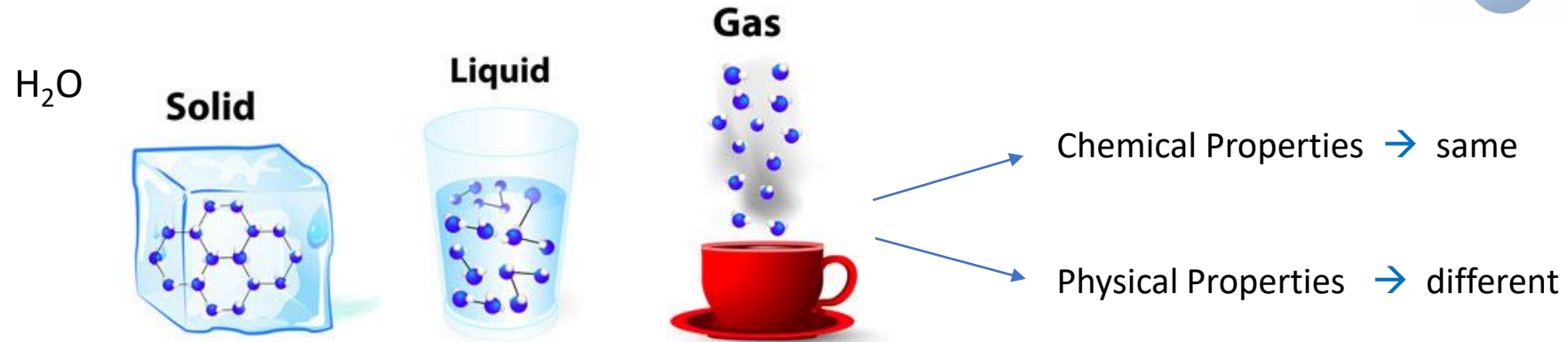
At the very high temperatures of stars, atoms lose their electrons. The mixture of electrons and nuclei that results is the plasma state of matter.

Molecular Bonds

Aggregates of atoms → Molecules

Gases, liquids and solids are all made up of atoms, **molecules**, and/or ions.

Molecules in different phases of the same material are not different.
But their arrangement and degree of movement are different.



The bonding mechanisms in a molecule are fundamentally due to electric forces between atoms (or ions).

Electric force is conservative → the forces between atoms in the system of a molecule are related to a potential energy function.

A stable molecule is expected at a configuration for which the potential energy function for the molecule has its minimum value.

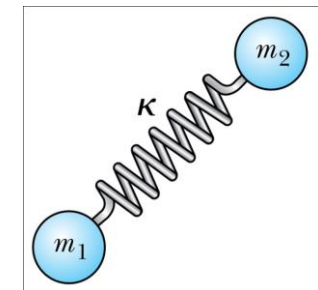
A potential energy function that can be used to model a molecule must take into account two known properties of the molecular bond:

1- At very small separation between atoms: the force between atoms is repulsive. Here;

- Some of their electron shells overlap, resulting in repulsion between the shells.
- This repulsion is partly electrostatic in origin and partly the result of the exclusion principle
- Because all electrons must obey the exclusion principle, some electrons in the overlapping shells are forced into higher energy states and the system energy increases as if a repulsive force existed between the atoms.

2- At larger separation between atoms: the force between atoms is attractive.

- If that were not true, the atoms in a molecule would not be bound together.



The potential energy of an atom pair can be positive or negative, depending on the separation between the atoms.

When two atoms are separated by an infinite distance, the force between them is zero, as is their electrostatic energy.

The potential energy for a system of two atoms can be represented by an expression of the form ;

$$U(r) = -\frac{A}{r^n} + \frac{B}{r^m}$$



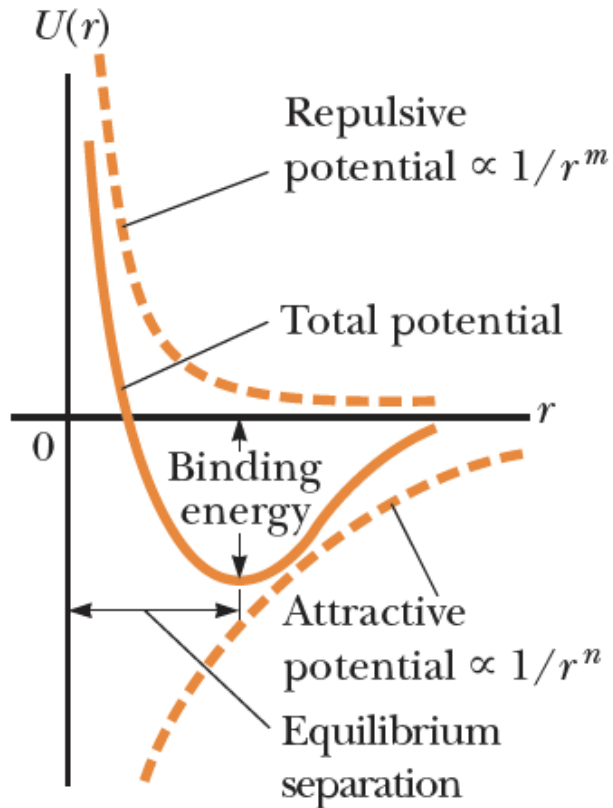
$$U(r) = -\frac{A}{r^n} + \frac{B}{r^m}$$

r : internuclear separation distance between the two atoms

n, m : integers (parameters related with the type of molecular bonding)

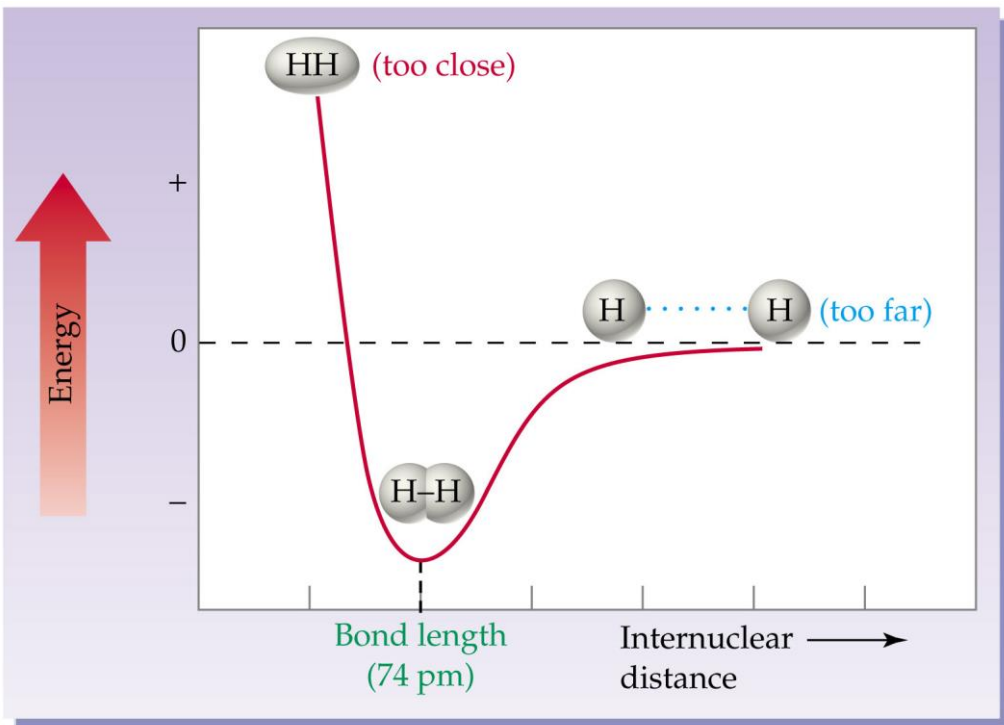
A, B : constants related with repulsive and attractive forces

The combination of attractive and repulsive forces creates a stable molecular structure.



→ At large separation distances between the two atoms, the slope of the curve is positive, corresponding to a net attractive force.

→ At the equilibrium separation distance, the attractive and repulsive forces just balance. At this point, the potential energy has its minimum value and the slope of the curve is zero.

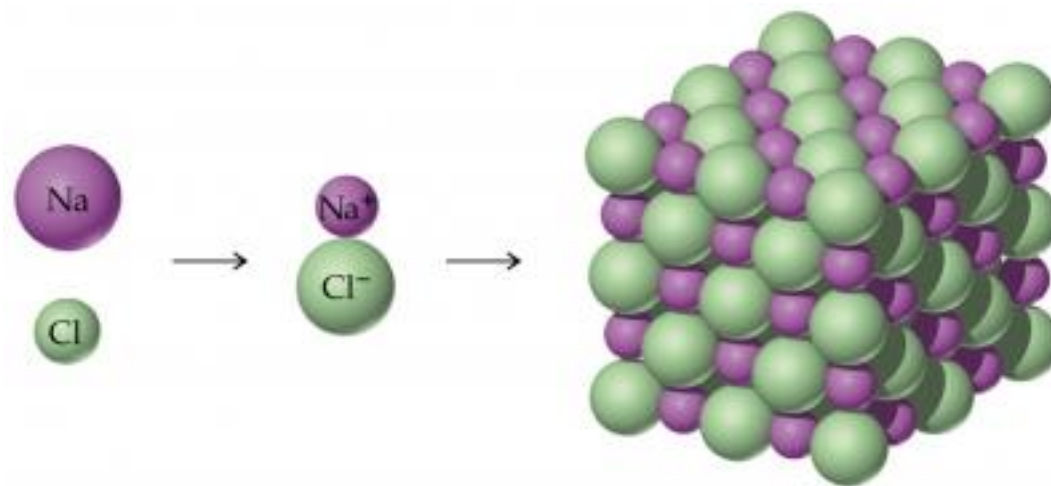


binding energy is roughly equal to the depth of the potential well.

Binding energy is the mechanical energy required to disassemble a whole into its separate parts.

A bound system typically has a lower potential energy than the sum of its constituent parts — this is what keeps the system together.

eg. ; NaCl crystal is more stable than free Na and Cl atoms

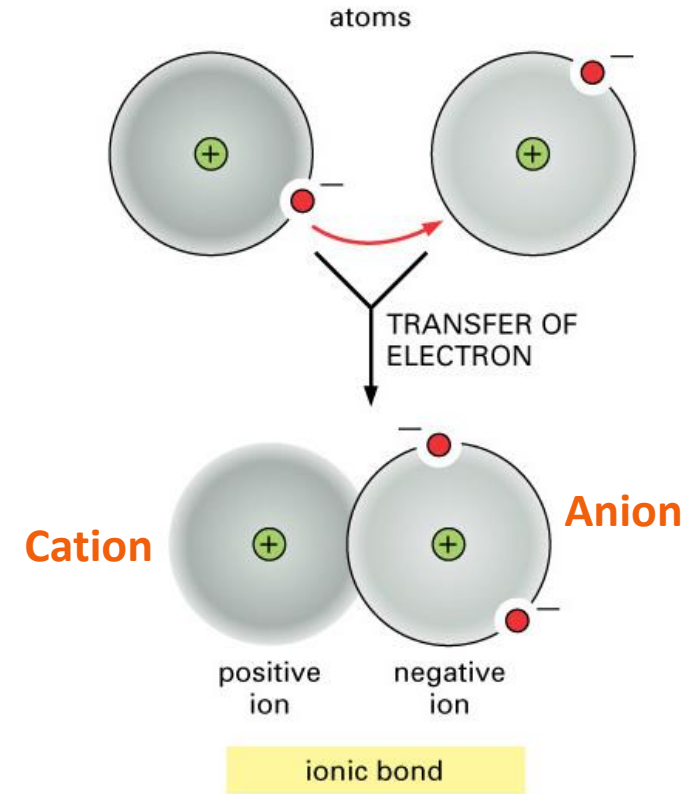


Bonding Types

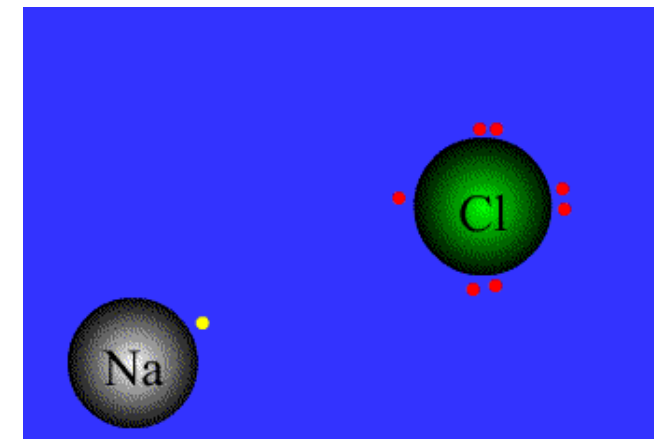
Ionic Bonding

When two atoms combine in such a way that one or more outer electrons are transferred from one atom to the other.

Ionic bonds are fundamentally caused by the Coulomb attraction between oppositely charged ions.



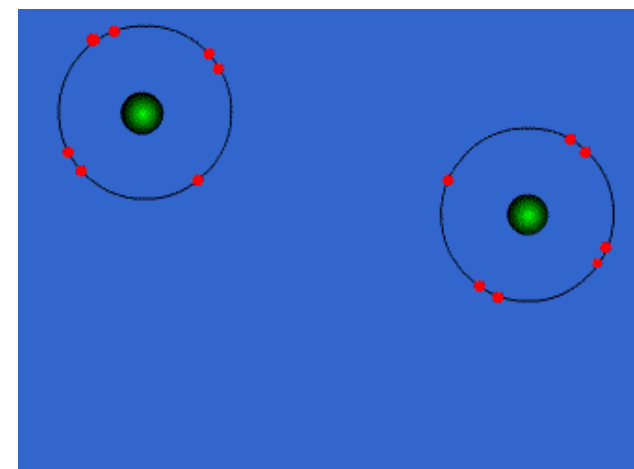
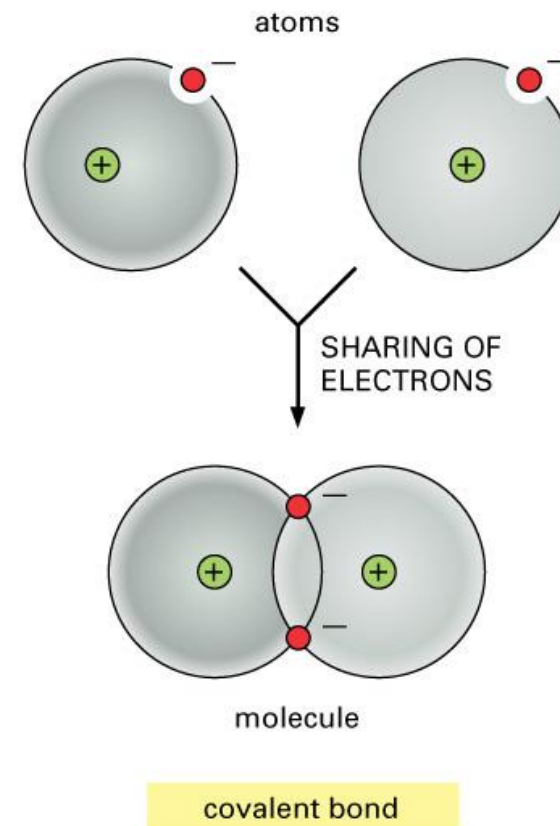
Property	Explanation
High melting and boiling points	Separating ions bonded with strong electrostatic forces require high thermal energy.
Weak electrical conductivity	There are no free charges to move and conduct electricity.
Hard, not scratched easily	Ions are bonded to crystal lattice tightly and they can not move easily.
Fragile	Trying to change the crystal structure causes them to break because ions with the same charges repel each other strongly.



Covalent Bonding

In this bonding type, electrons supplied by either one or both atoms are shared by the two atoms.

Property	Explanation
Very high melting and boiling points	Each atom are bonded with strong covalent bonds. In order to melt a solid with covalent bonds, one needs to break it and give very high thermal energy.
Very weak electrical conductivity	Electrons are bonded tightly and can not move easily within the crystal lattice.
Hard, not scratched easily	Ions are bonded to lattice tightly and can not move easily.
Fragile	Trying to change the crystal structure causes them to break because ions with the same charges repel each other strongly.



➤ Ionic bonds

➤ Covalent bonds



Occur between atoms to form molecules or ionic solids
So, they can be described as bonds **within molecules**.

There are two additional types of bonds ;

➤ Van der Waals bonds

➤ Hydrogen bonds



occur **between molecules**

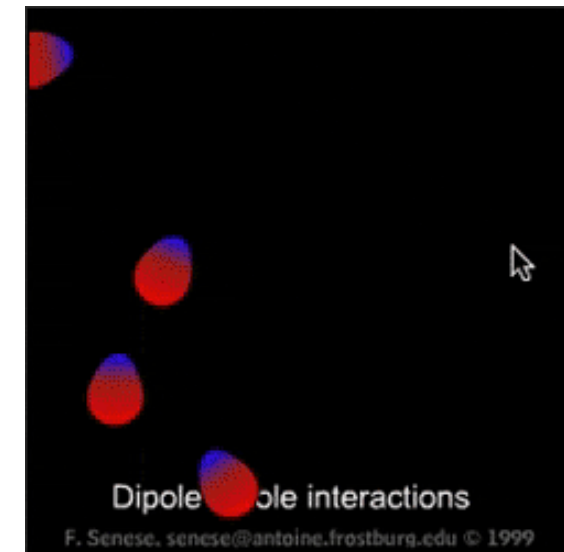
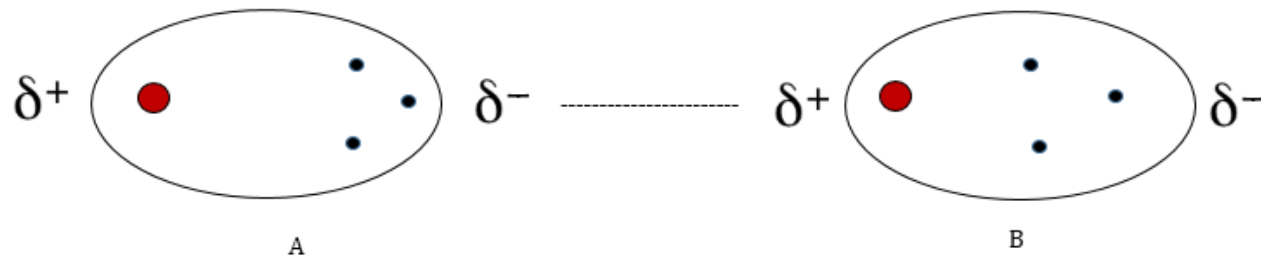
Van der Waals Bonding

How do two neutral molecules whose net charge is zero interact with each other by means of the electric force?



- While being electrically neutral, a molecule has a charge distribution with positive and negative centers at different positions in the molecule.
- As a result, the molecule may act as an electric dipole.
- Because of the dipole electric fields, two molecules can interact such that there is an attractive force between them.

These weak electrostatic forces are called **van der Waals forces**.



Hydrogen Bonding

Hydrogen has only one electron → it is expected to form a covalent bond with only one other atom within a molecule.

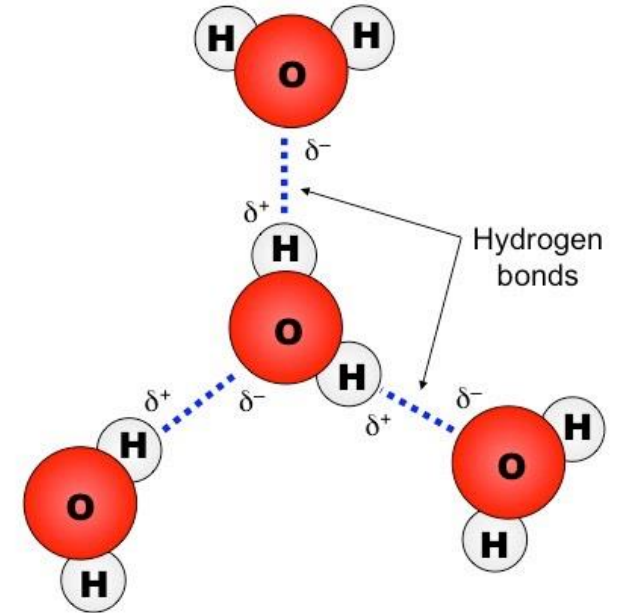
But a hydrogen atom can also form a second type of bond between molecules called a **hydrogen bond**.

eg. water molecule : H₂O

In the two covalent bonds in this molecule, the electrons from the hydrogen atoms are more likely to be found near the oxygen atom than near the hydrogen atoms.

This leaves bare (unshielded) protons at the positions of the hydrogen atoms.

This unshielded positive charge can be attracted to the negative end of another polar molecule.

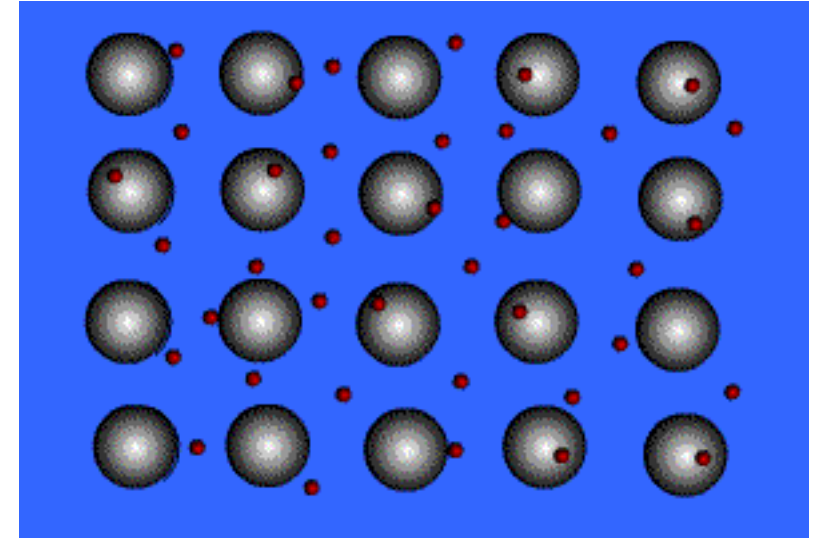


The bonds within a water molecule are **covalent**,
but the bonds between water molecules in ice are **hydrogen bonds**.

Metallic Bonds

The outer electrons in the metal atoms are relatively free to move throughout the material and the number of such mobile electrons in a metal is large.

Free valence electrons are shared by a number of atoms.



Metallic bonding constitutes the electrostatic attractive forces between the delocalized electrons and the positively charged metal ions.

Bonding in metals is a result of many metal atoms being so close to one another that their outermost energy levels overlap. Because of this overlapping, metallic bonds extend throughout the metal in all directions.

This bond is *direction independent*, therefore shape deformation does not effect the metallic bond.

Bond types

Ionic bonds

- High melting point
 - Hard and fragile
 - Nonconductor
- NaCl, CsCl, ZnS

Covalent bonds

- Very high melting point
 - Very hard
 - Usually nonconductor
- Diamond, graphite

Hydrogen bonds

- Low melting point
 - Soft and fragile
 - Usually nonconductor
- Ice, organic solids

Van der Waals bonds

- Low melting point
 - Soft and fragile
 - Nonconductor
- Ne, Ar, Kr, Xe

Metallic bonds

- Various melting points
 - Various hardness
 - Conductor
- Fe, Cu, Ag

Primary Bonds → (Chemical bonds, strong)

- Ionic
- Covalent
- Metallic

Secondary Bonds → (Physical bonds, weaker)

- Van der Waals
- Hydrogen

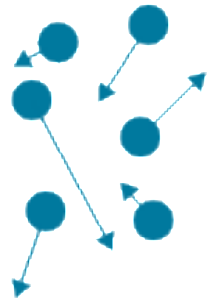
Energy States and Spectra of Molecules

Let's consider an individual molecule in the gaseous phase.

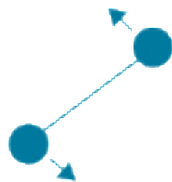
The energy (E) of the molecule can be divided into four categories:

1. **Electronic energy:** Due to the interaction between electrons and nucleus of the molecule
2. **Translational energy:** Due to the motion of the molecule's center of mass through space
3. **Rotational energy:** Due to the rotation of the molecule around its center of mass
4. **Vibrational energy:** Due to the vibration of the atoms in molecule

$$E = E_{\text{el}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$$



Translational K. E.



Rotational K. E.



Vibrational K. E.

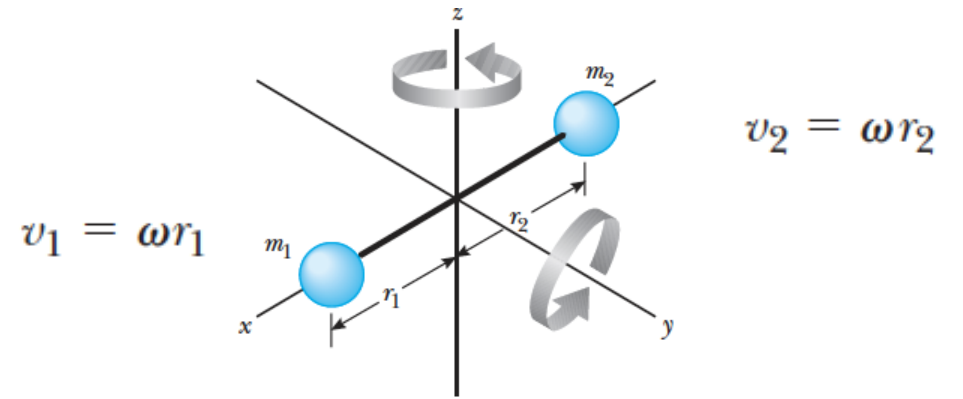
E_{rot} and E_{vib} → give spectral lines in the microwave and infrared regions of the electromagnetic spectrum

Significant information about molecule

Rotational Motion of Molecules

Let's consider the rotation of a molecule around its center of mass.

A diatomic molecule has only two rotational degrees of freedom;



Classical mechanics:

$$E_{rot} = \frac{1}{2} I \omega^2$$

$$I = \left(\frac{m_1 \cdot m_2}{m_1 + m_2} \right) r^2 = \mu r^2$$

$I\omega$: Angular momentum
is continuous

I : moment of inertia

μ : reduced mass of molecule

Quantum mechanics:

Angular momentum is quantized;

$$I\omega = \sqrt{J(J+1)}\hbar, \quad J = 0, 1, 2, \dots$$

J : rotational quantum number

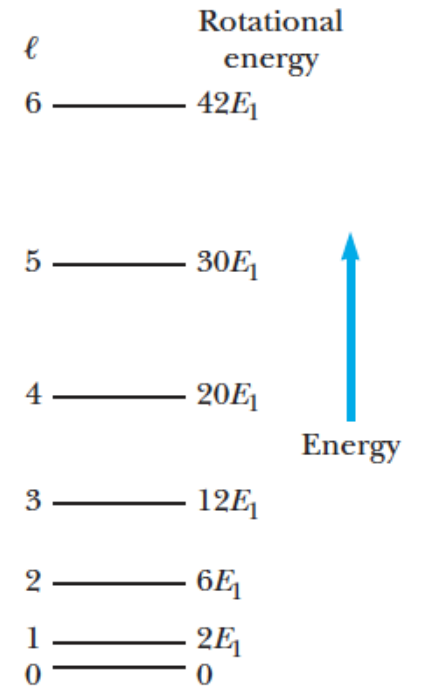
$$E_{rot} = \frac{1}{2} I \omega^2 = \frac{1}{2I} (I\omega)^2$$

$$E_{rot} = \frac{(\sqrt{J(J+1)}\hbar)^2}{2I}$$

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1)$$

Rotational energy is quantized and depends on the rotational inertia of the molecule.

For most molecules, transitions between adjacent rotational energy levels result in radiation that lies in the **microwave** range of frequencies ($f \sim 10^{11}$ Hz)



The allowed rotational energies of a diatomic molecule

Vibrational Motion of Molecules

Let's consider a flexible molecule in which the atoms are bonded together by "effective springs"

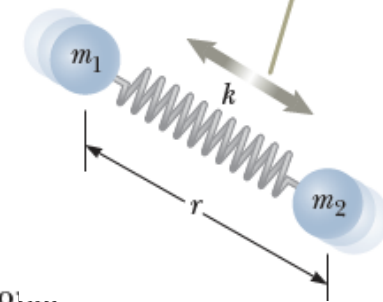
Here, we can apply the *particle in simple harmonic motion analysis model* to the molecule as long as the atoms in the molecule are not too far from their equilibrium positions.

According to classical mechanics, the frequency of vibration for the system

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

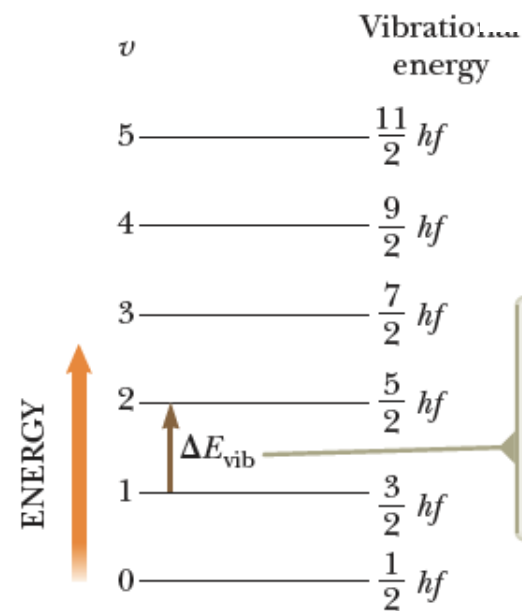
k : spring constant
 μ : reduced mass

$$\mu = m_1 m_2 / (m_1 + m_2)$$



According to QM → a molecule vibrates in quantized states

Allowed vibrational energies → $E_{\text{vib}} = (v + \frac{1}{2})hf$ $v = 0, 1, 2, \dots$



v is an integer called the **vibrational quantum number**

$$E_{\text{vib}} = (v + \frac{1}{2}) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad v = 0, 1, 2, \dots$$

Transitions between vibrational states corresponds to **IR** region.

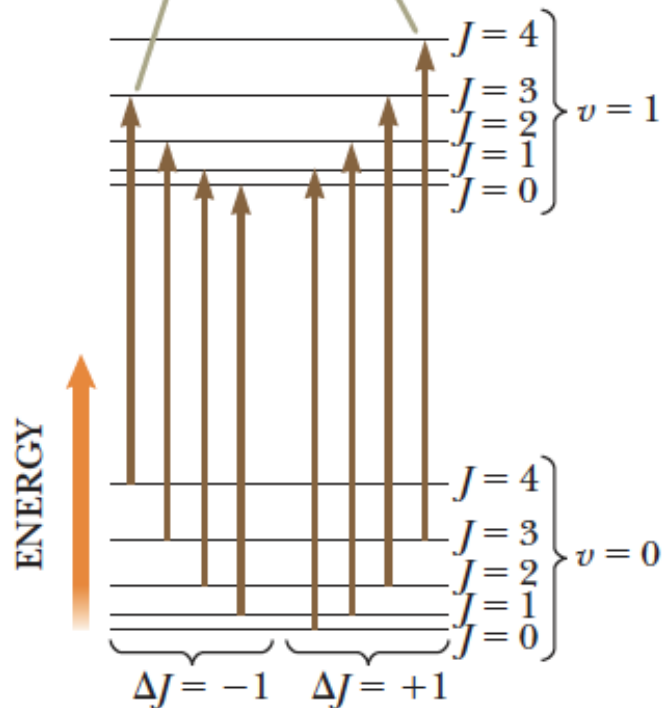
At ordinary temperatures, most molecules have vibrational energies corresponding to the $v = 0$ state because $\Delta E_{\text{vib}} \gg k_B T$

In general, a molecule vibrates and rotates simultaneously.

These motions are independent of each other, so the total energy of the molecule for these motions is;

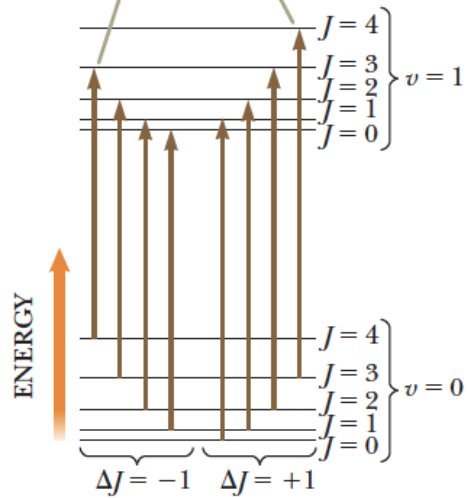
$$E = \left(v + \frac{1}{2}\right)hf + \frac{\hbar^2}{2I}J(J + 1)$$

The transitions obey the selection rule $\Delta J = \pm 1$ and fall into two sequences, those for $\Delta J = +1$ and those for $\Delta J = -1$.



- For each allowed value of the vibrational quantum number v , there is a complete set of rotational levels corresponding to $J=0, 1, 2, \dots$
- The energy separation between successive rotational levels is much smaller than the separation between successive vibrational levels.
- As said earlier, most molecules at ordinary temperatures are in the $v=0$ vibrational state; these molecules can be in various rotational states

The transitions obey the selection rule $\Delta J = \pm 1$ and fall into two sequences, those for $\Delta J = +1$ and those for $\Delta J = -1$.



When a molecule absorbs a photon with the appropriate energy;

- the vibrational quantum number ν increases by one unit
- while the rotational quantum number J either increases or decreases by one unit

Therefore, the molecular absorption spectrum consists of two groups of lines;

$$\Delta J = +1 \quad \Delta \nu = +1$$

$$\Delta J = -1 \quad \Delta \nu = +1$$

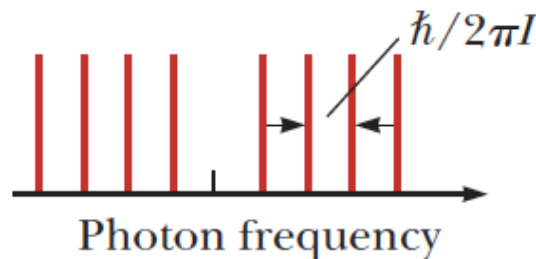
The energies of the absorbed photons can be calculated as ;

$$E_{\text{photon}} = \Delta E = hf + \frac{\hbar^2}{I} (J + 1) \quad J = 0, 1, 2, \dots \quad (\Delta J = +1)$$

Generates the series of equally spaced lines higher than the frequency f

$$E_{\text{photon}} = \Delta E = hf - \frac{\hbar^2}{I} J \quad J = 1, 2, 3, \dots \quad (\Delta J = -1)$$

Generates the series of equally spaced lines lower than the frequency f

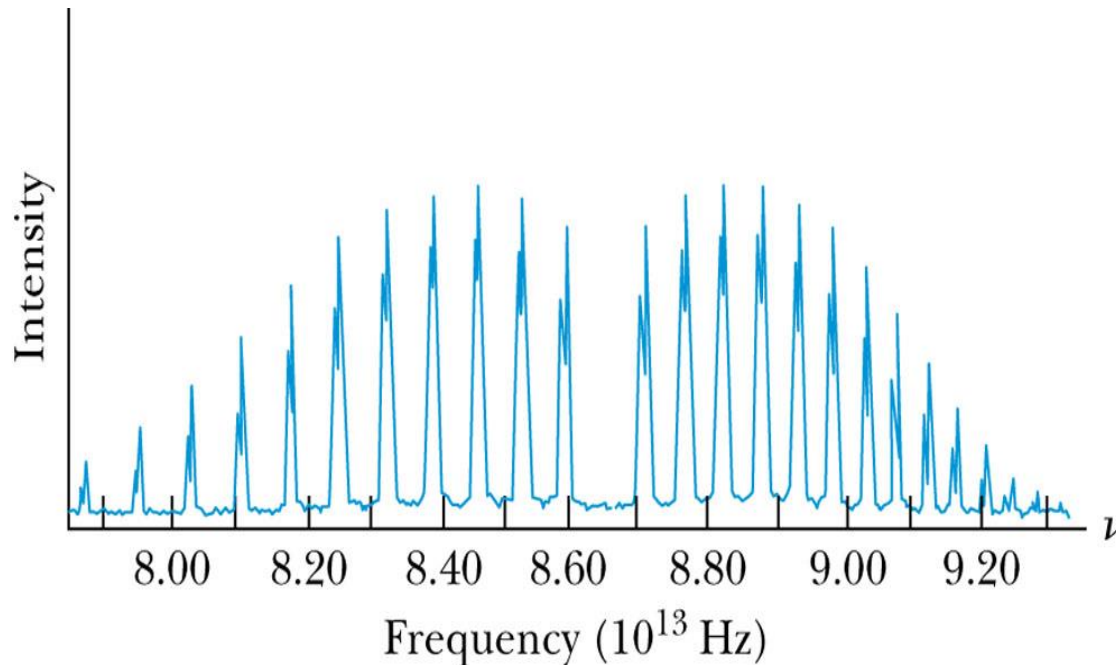


the expected frequencies in the absorption spectrum of the molecule; these same frequencies appear in the emission spectrum.

The experimental absorption spectrum of the HCl molecule reinforces before-mentioned model...

But one peculiarity seems to be: **each line is split into a doublet**

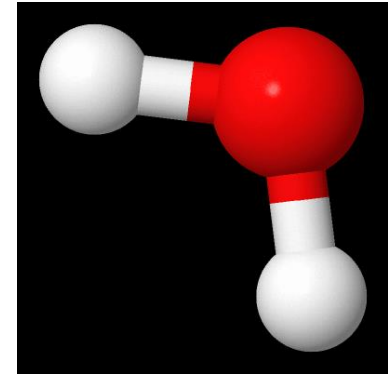
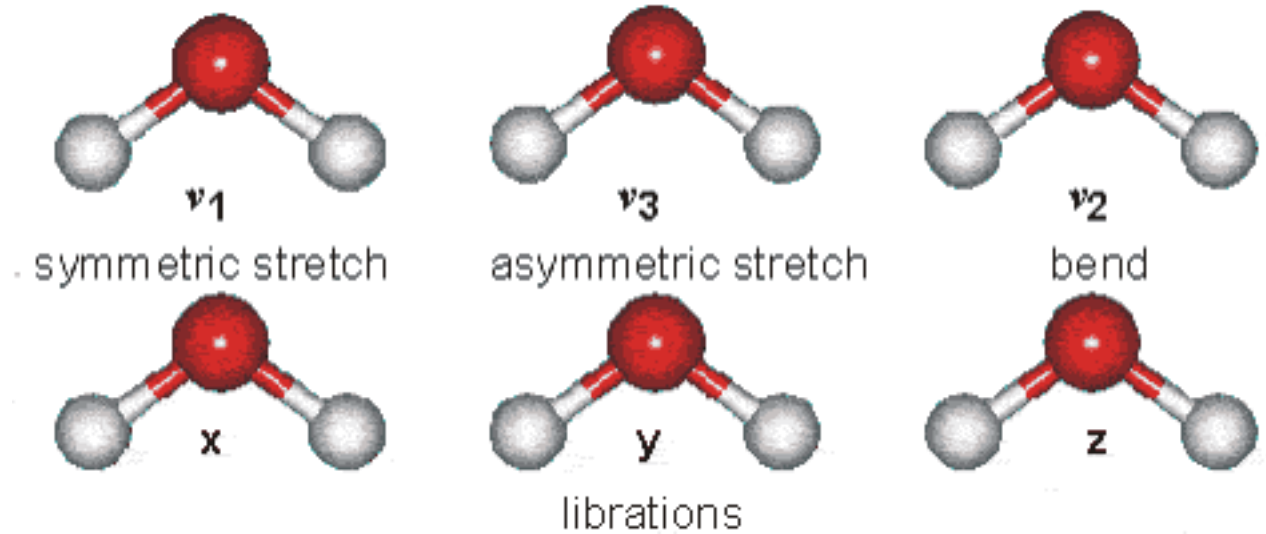
This doubling occurs because two chlorine isotopes (Cl-35 and Cl-37) were present in the sample used to obtain this spectrum. Because the isotopes have different masses, the two HCl molecules have different values of I .



The central frequency

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

Not all spectral lines appear with the same intensity, because even the allowed transitions occur at different rates.

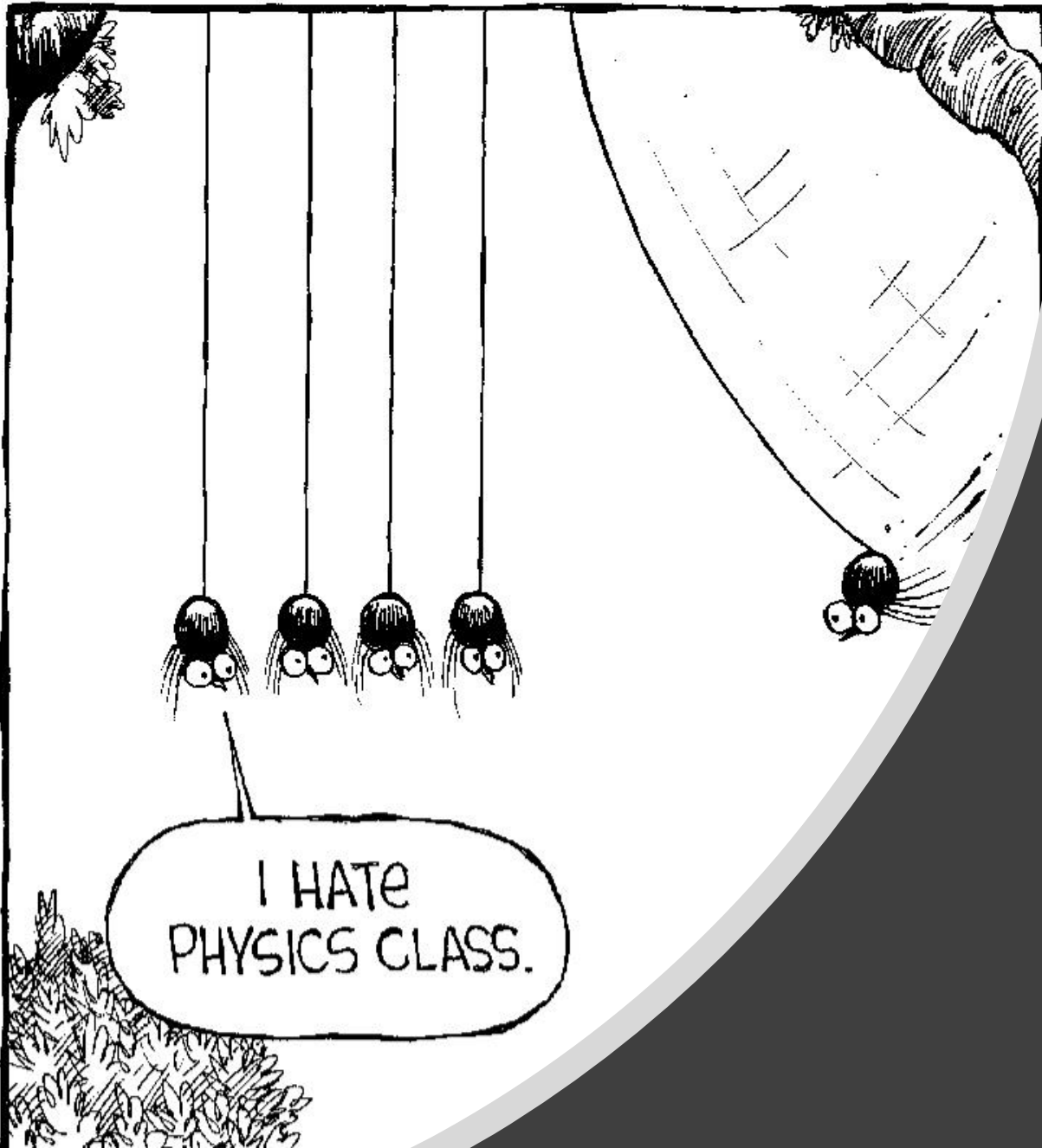


Fourier transform infrared spectroscopy (FTIR)

- vibrational spectroscopy that relies on the absorbance, transmittance or reflectance of infrared light.
- depends on a change in the dipole moment
- measures absolute frequencies at which a sample absorbs radiation

Raman Spectroscopy

- probes molecular vibrations to provide a molecular fingerprint of materials
- Depends on a change in polarizability of a molecule
- Measures relative frequencies at which a sample scatters radiation



Homework:

Study the "Rotation and vibration of CO molecule" examples in your textbook