

# Fundamentals in Biophotonics

*Quantum nature of atoms, molecules –  
matter*

Aleksandra Radenovic

aleksandra.radenovic@epfl.ch

EPFL – Ecole Polytechnique Federale de Lausanne

Bioengineering Institute IBI



ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE

26. 03. 2018.

# Quantum numbers

•The four quantum numbers-are discrete sets of integers or half-integers.

–*n*: Principal quantum **number-The first describes the electron shell, or energy level, of an atom**

–*l* : Orbital angular momentum quantum number-as **the angular quantum number or orbital quantum number) describes the subshell, and gives the magnitude of the orbital angular momentum through the relation**

$$L^2 = \hbar(l + 1)$$

–*m<sub>l</sub>*:Magnetic (azimuthal) quantum number

(refers, to the direction of the angular momentum vector. The magnetic quantum number m does not affect the electron's energy, but it does affect the probability cloud)- magnetic quantum number determines the energy shift of an [atomic orbital](#) due to an external magnetic field-Zeeman effect

–**s spin- intrinsic angular momentum** Spin "up" and "down" allows two electrons for each set of spatial quantum numbers.

The restrictions for the quantum numbers:

- $n = 1, 2, 3, 4, \dots$
- $\ell = 0, 1, 2, 3, \dots, n - 1$
- $m_\ell = -\ell, -\ell + 1, \dots, 0, 1, \dots, \ell - 1, \ell$
- 

–Equivalently:

$$n > 0$$

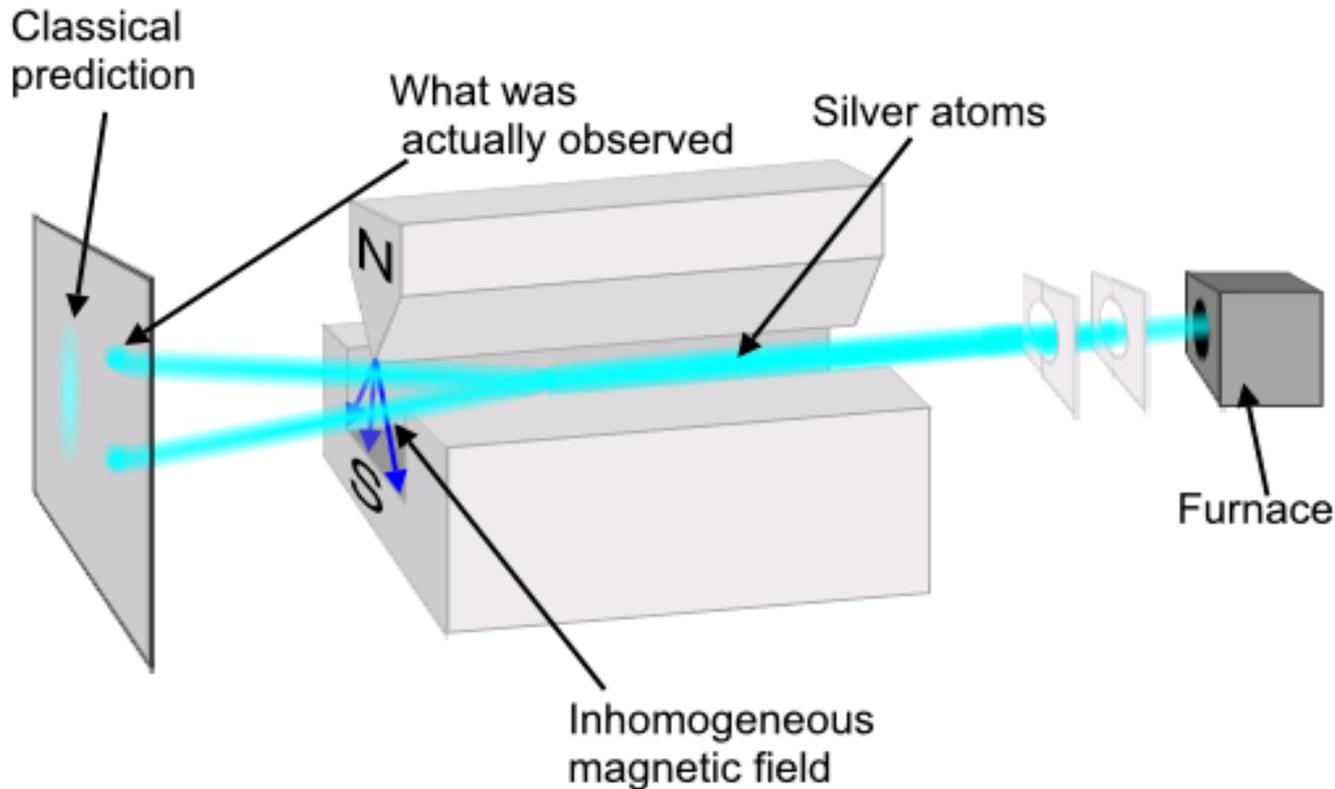
$$\ell < n$$

$$|m_\ell| \leq \ell$$

The energy levels are:

$$E_n = -\frac{E_0}{n^2}$$

# Stern-Gerlach experiment



If the particles were classical spinning objects, one would expect the distribution of their spin angular momentum vectors to be [random and continuous](#). Each particle would be deflected by a different amount, producing some density distribution on the detector screen. Instead, the particles passing through the Stern–Gerlach apparatus are deflected either up or down by a specific amount. This was a measurement of the quantum [observable](#) now known as [spin](#), which demonstrated possible outcomes of a measurement where the observable has [point spectrum](#).

# Hydrogen Atom Radial Wave Functions

• First few radial wave functions  $R_{n\ell}$

Sub-scripts on  $R$  specify the values of  $n$  and  $\ell$ .

**Table 7.1** Hydrogen Atom Radial Wave Functions

$n$	$\ell$	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

# Solution of the Angular and Azimuthal Equations

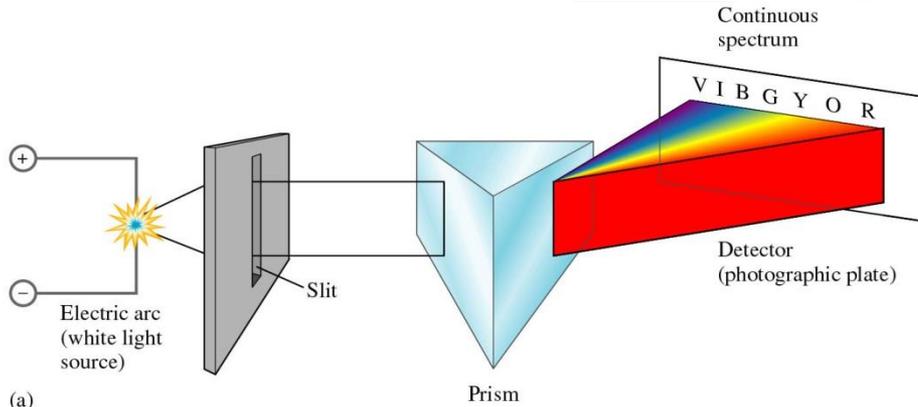
- The radial wave function  $R$  and the spherical harmonics  $Y$  determine the probability density for the various quantum states. The total wave function  $\psi(r, \theta, \phi)$
- depends on  $n$ ,  $\ell$ , and  $m_\ell$ .
- The wave function becomes

$$\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r) Y_{n\ell m_\ell}(\theta, \phi)$$

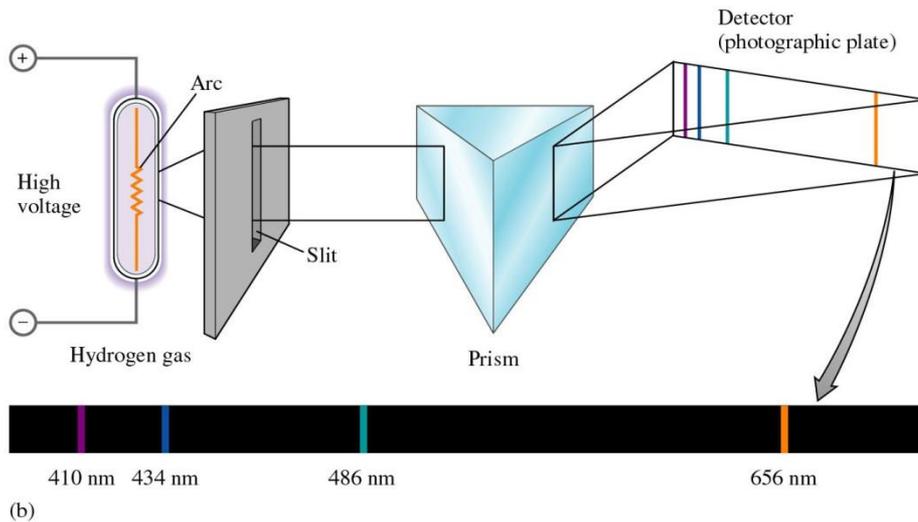
The four quantum numbers  $n$ ,  $\ell$ ,  $m$ , and  $s$  specify the complete and unique [quantum state](#) of a single electron in an atom called its [wavefunction](#) or [orbital](#).

# Bohr atom model

- In 1913, the Danish scientist Niels Bohr proposed an improvement. In his model, he placed each electron in a **specific** energy level.



Light Bulb

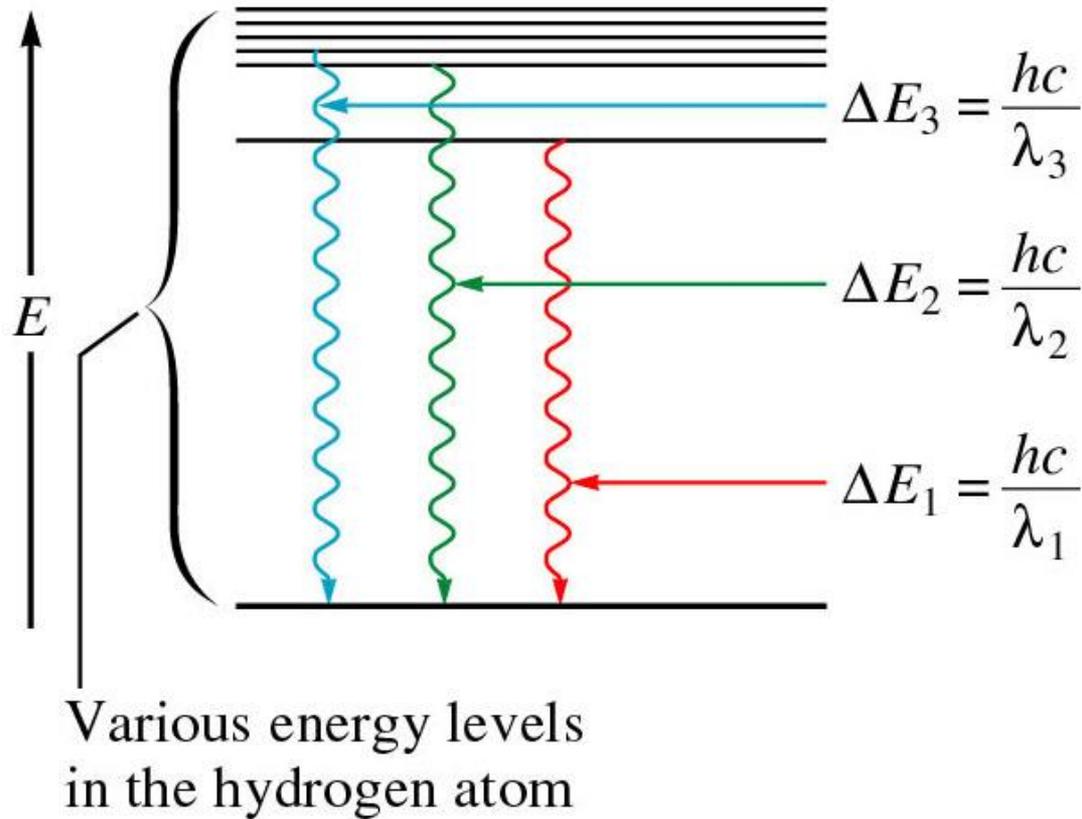


Hydrogen Lamp

Quantized, not continuous

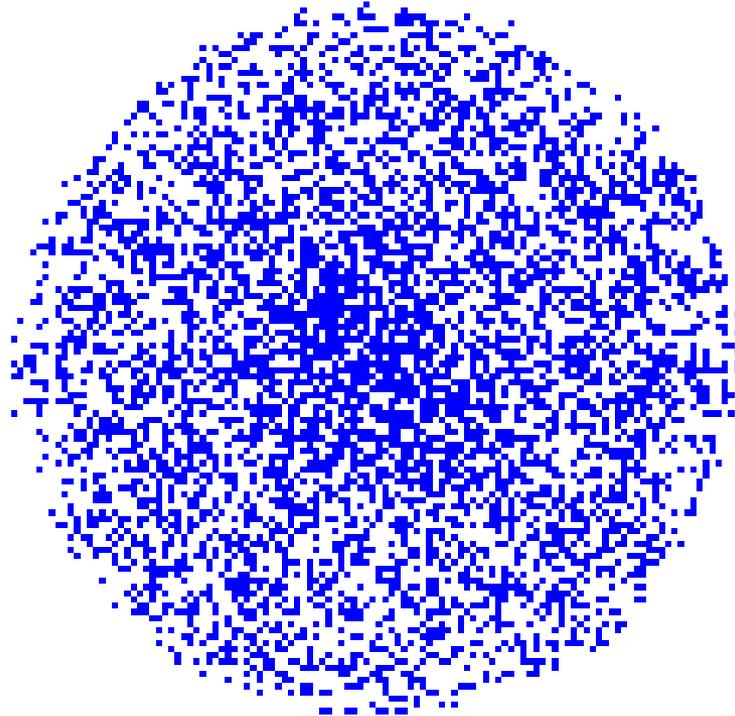
# Emission spectrum of Hydrogen atom

- We can use the emission spectrum to determine the energy levels for the hydrogen atom.



# Bohr atom model

- According to Bohr's atomic model, electrons move in definite orbits around the nucleus, much like planets circle the sun. These orbits, or energy levels, are located at certain distances from the nucleus
- In fact, it is impossible to determine the exact location of an electron. The probable location of an electron is based on how much energy the electron has.
- According to the modern atomic model, an atom has a small positively charged nucleus surrounded by a large region in which there are enough electrons to make an atom neutral.



# Probability Distribution Functions

- We use the wave functions to calculate the probability distributions of the electrons.
- The “position” of the electron is spread over space and is not well defined.
- We may use the radial wave function  $R(r)$  to calculate radial probability distributions of the electron.
- The probability of finding the electron in a differential volume element  $d\tau$  is:

$$dP = \psi^*(r, \theta, \phi) \psi(r, \theta, \phi) dx dy dz$$

where the differential volume element in spherical polar coordinates is

$$dx dy dz = r^2 \sin \theta dr d\theta d\phi$$

At the moment, we'll consider only the radial dependence. So we should integrate over all values of  $\theta$  and  $\phi$ :

$$P(r) dr = r^2 R^*(r) R(r) dr \int_0^\pi |f(\theta)|^2 \sin \theta d\theta \int_0^{2\pi} |g(\phi)|^2 d\phi$$

The  $\theta$  and  $\phi$  integrals are just constants.

# Probability Distribution Functions

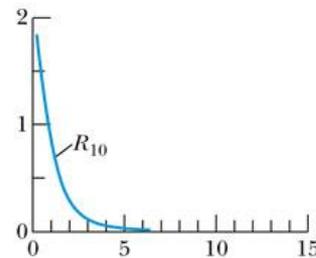
- So the radial probability density is  $P(r) = r^2 |R(r)|^2$  and it depends only on  $n$  and  $\ell$ .

$$P(r) dr = r^2 |R(r)|^2 dr$$

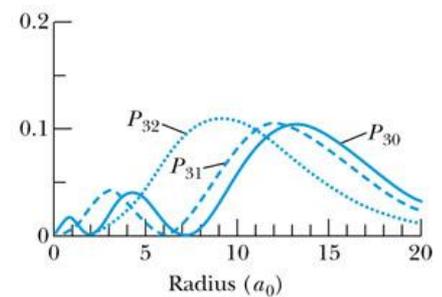
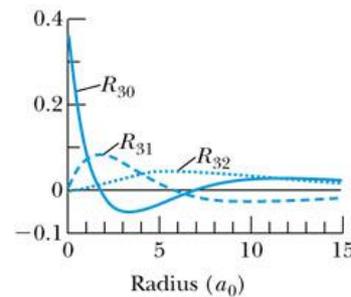
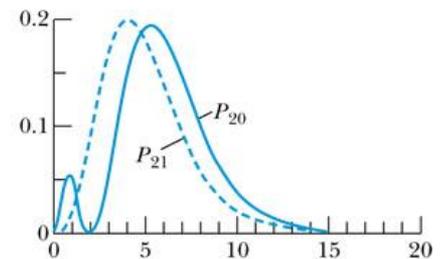
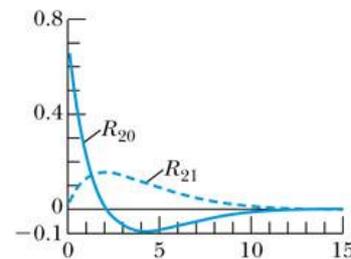
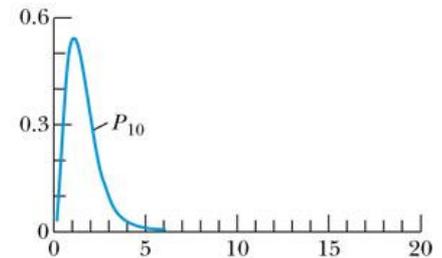
$R(r)$  and  $P(r)$  for the lowest-lying states of the hydrogen atom.

Note that  $R_{n0}$  is maximal at  $r = 0$ ! But the  $r^2$  factor reduces the probability there to 0. Nevertheless, there's a nonzero probability that the electron is inside the nucleus.

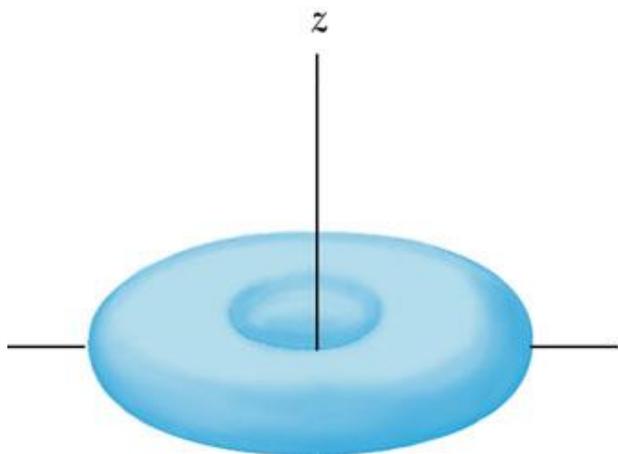
Radial wave functions ( $R_{n\ell}$ )



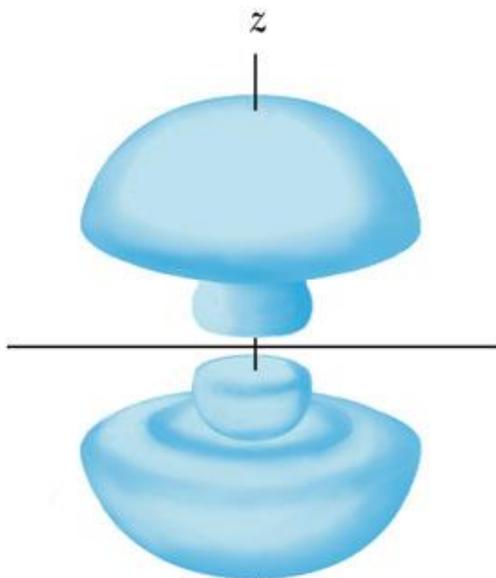
Radial probability distribution ( $P_{n\ell}$ )



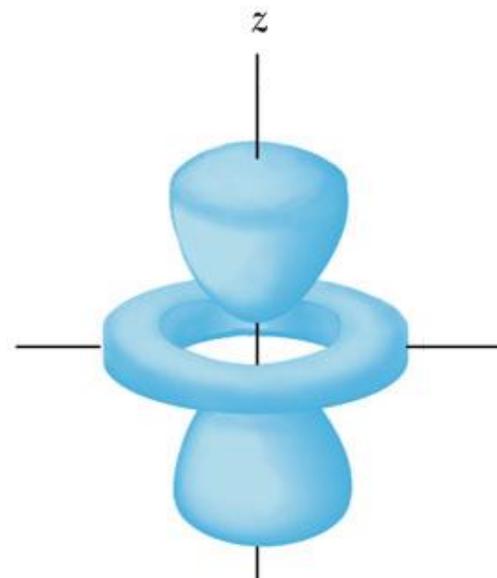
# Probability Distribution Functions



$$\begin{aligned}n &= 2 \\ \ell &= 1 \\ m_\ell &= \pm 1\end{aligned}$$



$$\begin{aligned}n &= 3 \\ \ell &= 1 \\ m_\ell &= 0\end{aligned}$$



$$\begin{aligned}n &= 3 \\ \ell &= 2 \\ m_\ell &= 0\end{aligned}$$

In chemistry and spectroscopy, " $\ell = 0$ " is called an s orbital, " $\ell = 1$ " a p orbital, " $\ell = 2$ " a d orbital, and " $\ell = 3$ " an f orbital. The value of  $\ell$  ranges from 0 to  $n - 1$ , because the first p orbital ( $\ell = 1$ ) appears in the second electron shell ( $n = 2$ ), the first d orbital ( $\ell = 2$ ) appears in the third shell ( $n = 3$ ), and so on:[\[4\]](#)

# Molecules are combinations of multi-electron atoms.

- When more than one atom is involved, the potential and the wave function are functions *of way more than one position (a position vector for each nucleus and electron)*:

$$V = V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad \Psi = \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t)$$

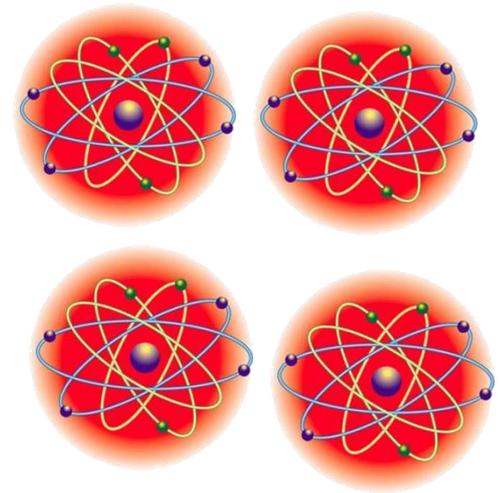
Solving the Schrodinger Equation in this case is even harder than for multi-electron atoms.

$$\left[ \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) \right] \Psi(\mathbf{r}; \mathbf{R}) = E_{el} \Psi(\mathbf{r}; \mathbf{R}).$$

Serious approximation methods are required.

The only force that binds atoms together in molecules is the **Coulomb force**.

But aren't most atoms electrically neutral? Yes!

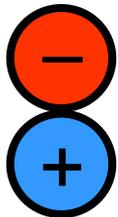


# Molecular Bonding and Spectra-Why molecules form

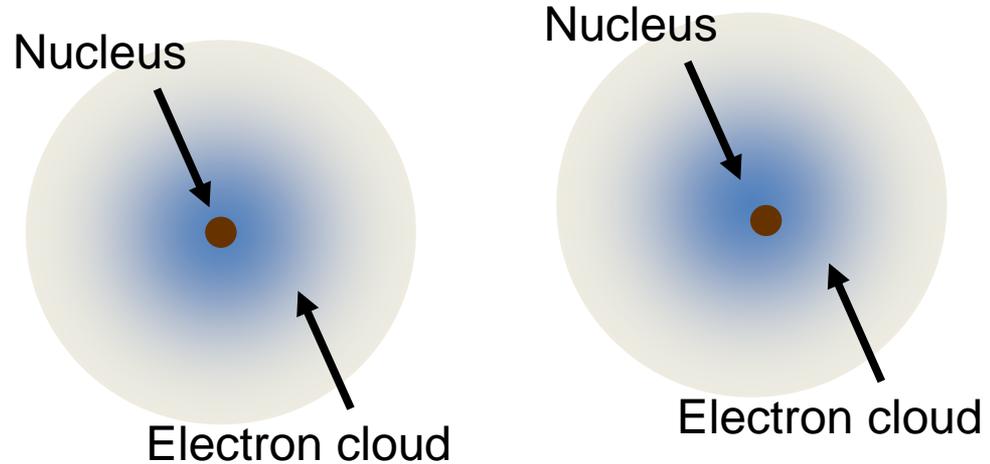
- Indeed, there is no attraction between spherically symmetrical molecules—the positive and negative charges both behave like point sources and so their fields cancel out perfectly!
- So how do molecules form?

Most atoms are not spherically symmetrical. For example, these two “Atoms” attract each other:

Atom #1



Atom #2

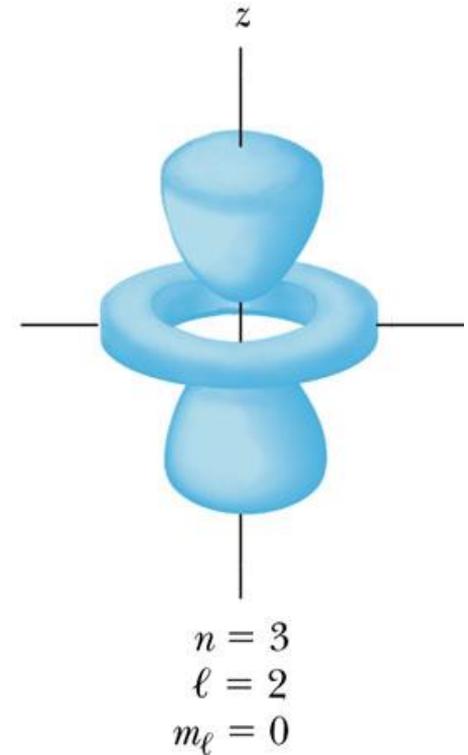
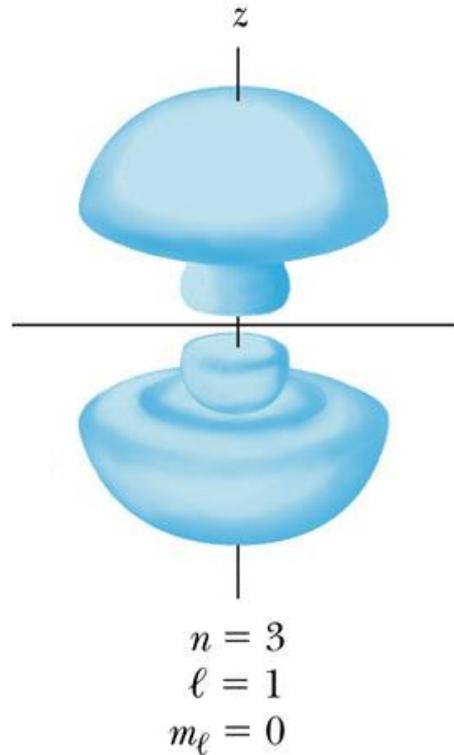
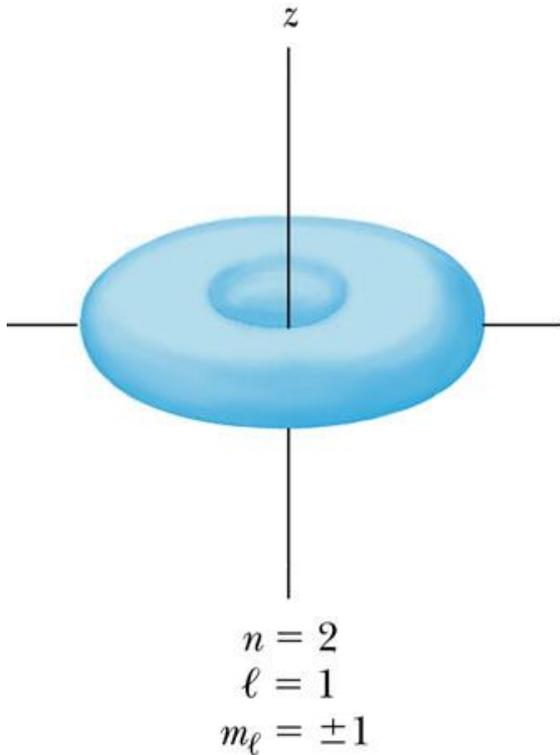


The **combination** of **attractive** and **repulsive** forces creates a stable molecular structure

Force is related to the potential energy surface,  $F = -dV/dr$ , where  $r$  is the position.

# Charge is distributed very unevenly in most atoms.

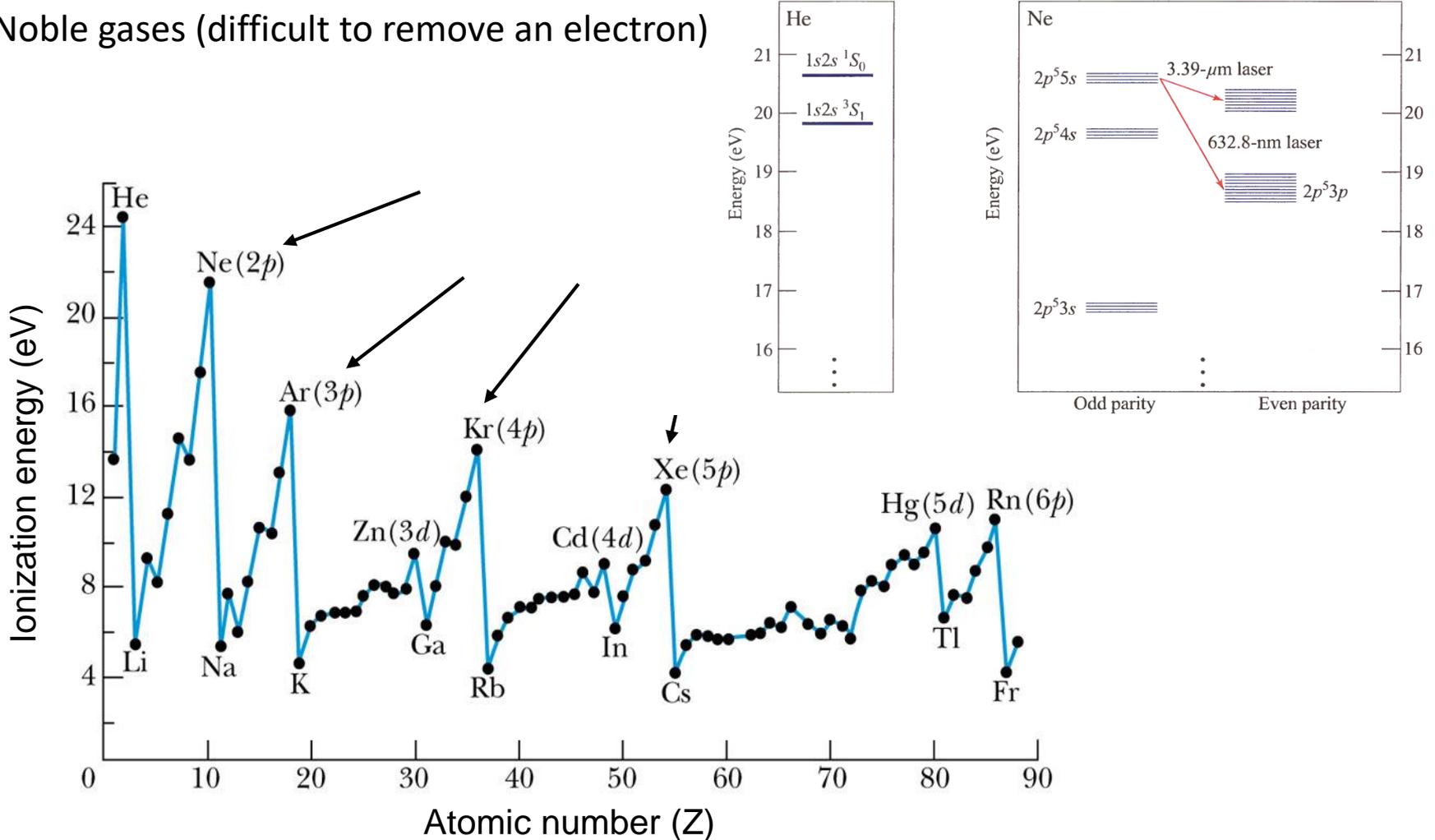
- The probability density for the hydrogen atom for three different electron states.



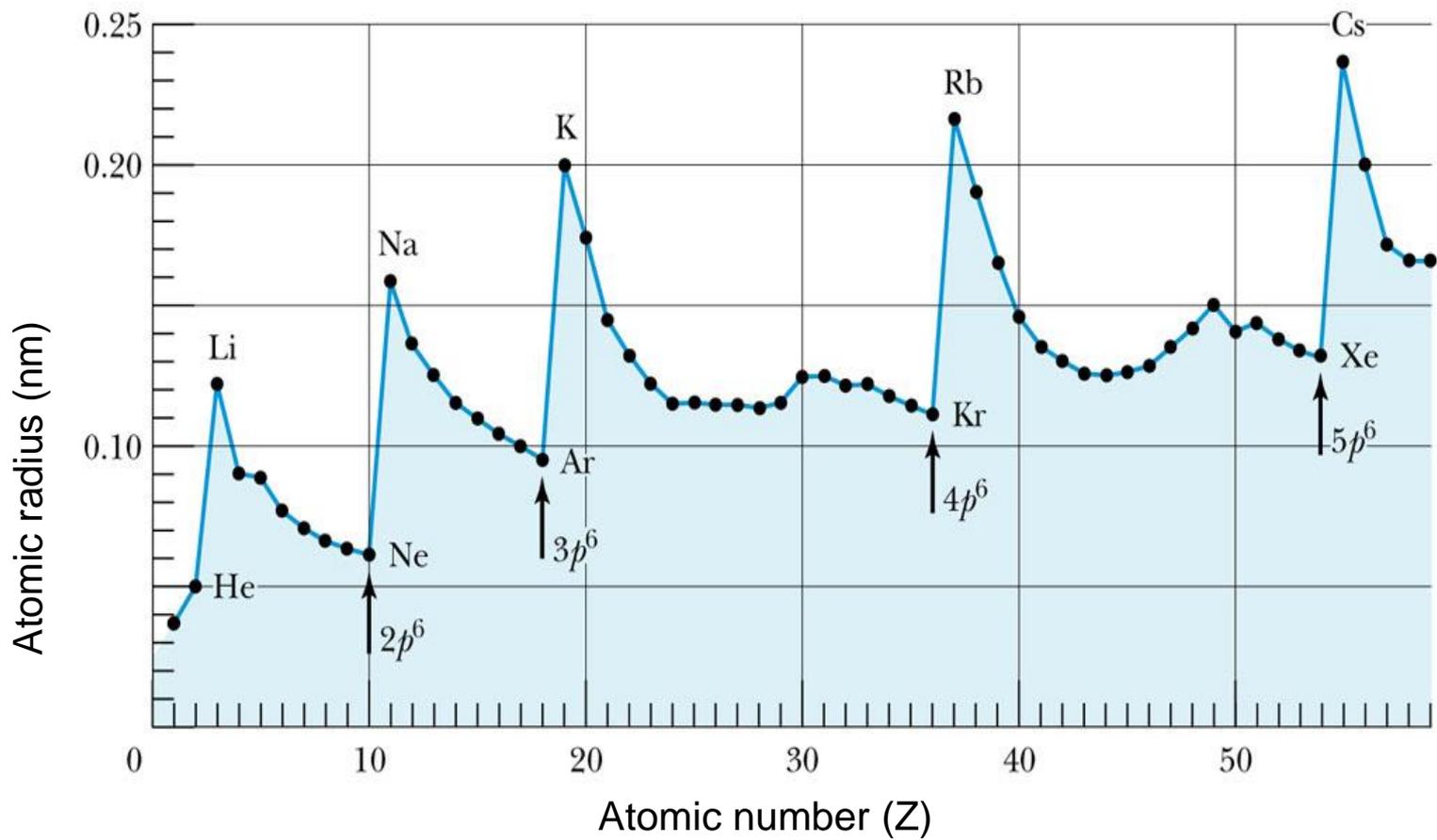
# Closed shells of electrons are spherically symmetrical

- Atoms with closed shells (noble gases) are the most difficult to ionize.

Noble gases (difficult to remove an electron)



- Atoms with closed shells (noble gases) also have the smallest atomic radii.

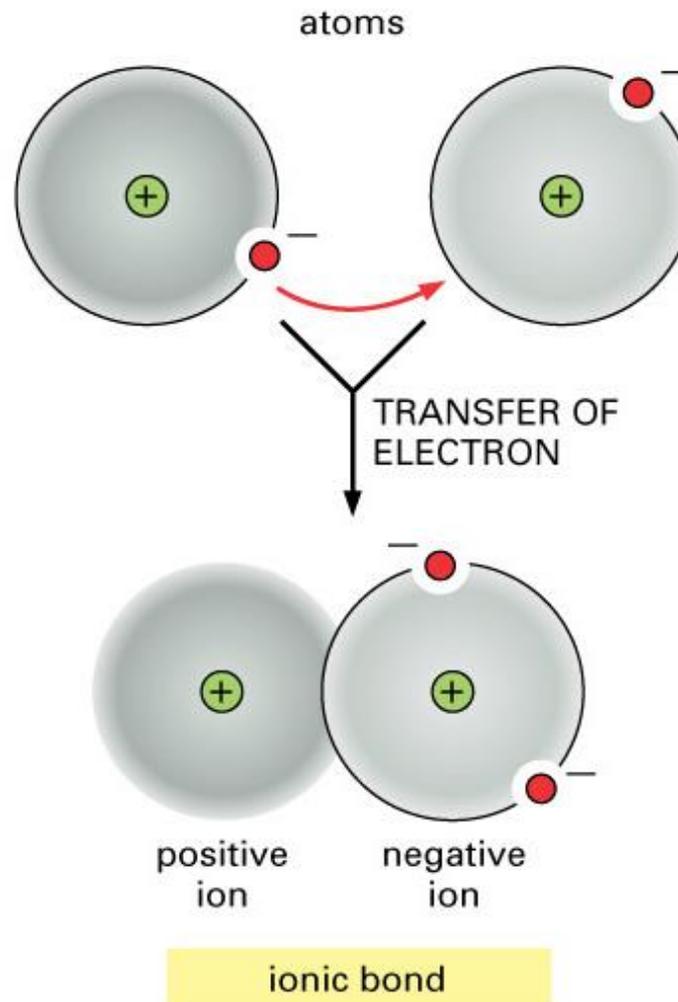
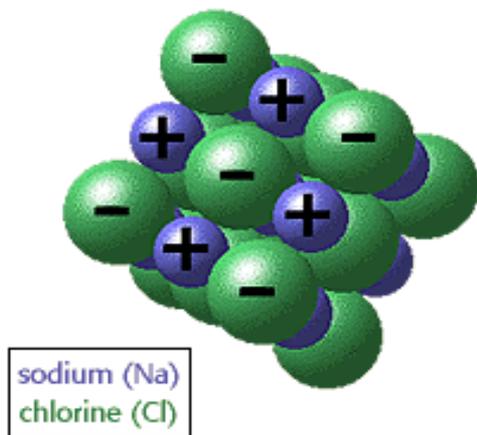


Noble gases do not form molecules (unless significantly perturbed).



# Ionic Bond

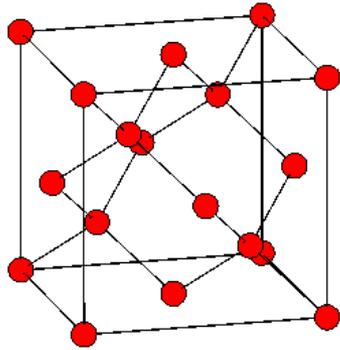
- An electropositive atom gives up an electron to an electronegative one.
- Example: Sodium ( $1s^2 2s^2 2p^6 3s^1$ ) readily gives up its 3s electron to become  $\text{Na}^+$ , while chlorine ( $1s^2 2s^2 2p^6 3s^2 3p^5$ ) easily gains an electron to become  $\text{Cl}^-$ .



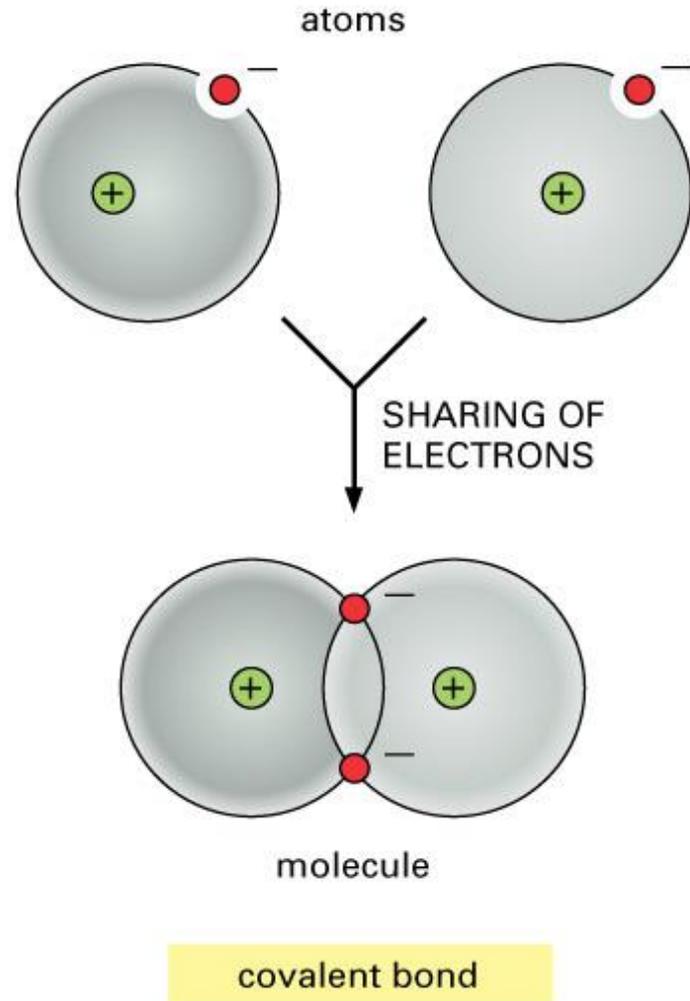
787 kJ/mol

# Covalent Bond

- Two electronegative atoms share one or more electrons.
- Example: Diatomic molecules formed by the combination of two identical atoms tend to be covalent.
- Larger molecules are formed with covalent bonds.

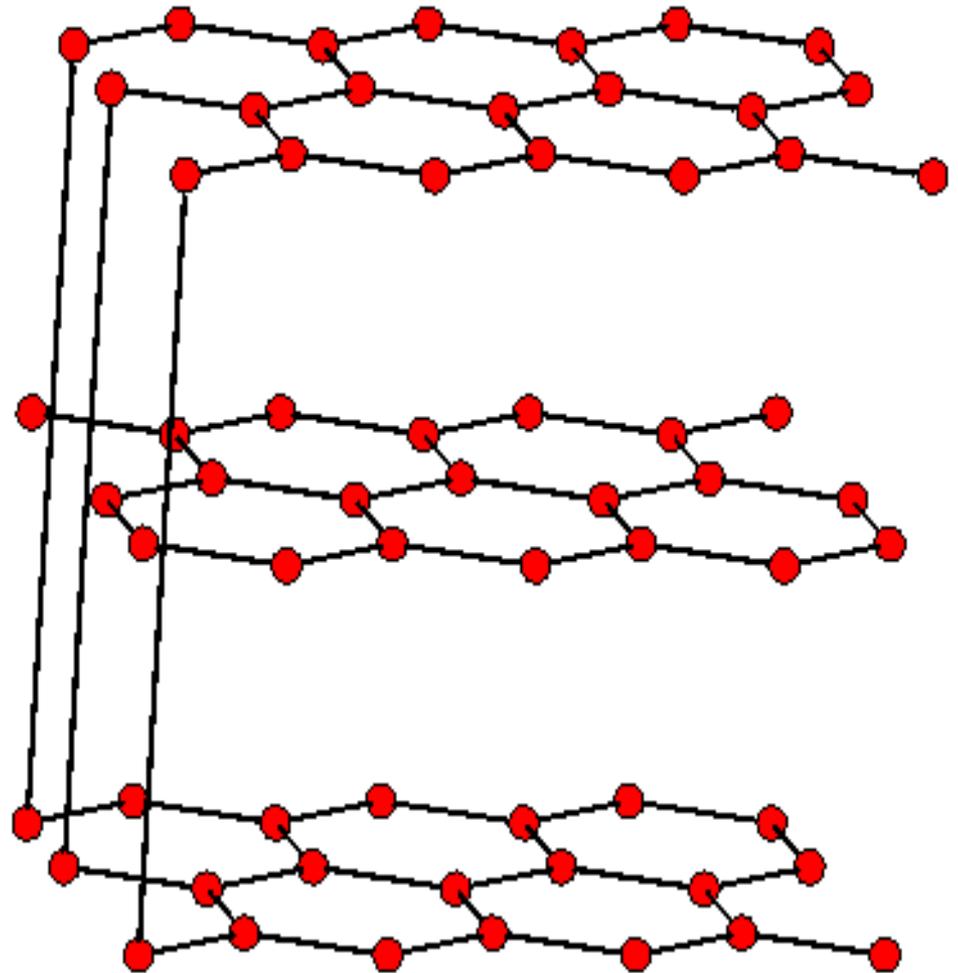
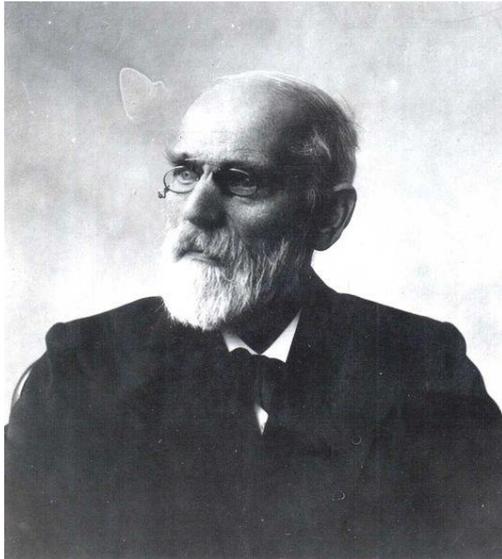


Diamond



# Van der Waals bonds

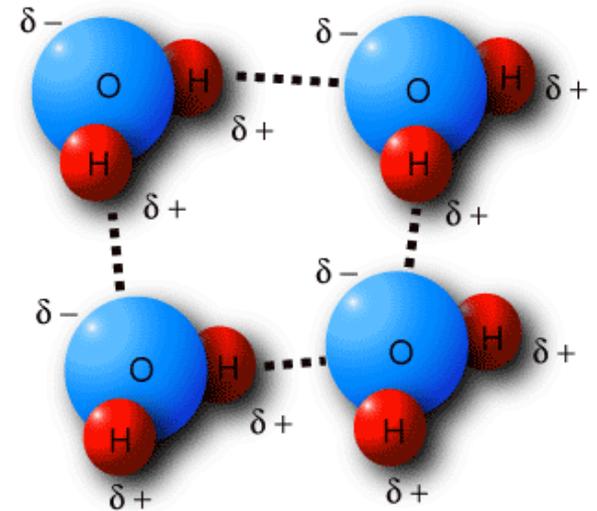
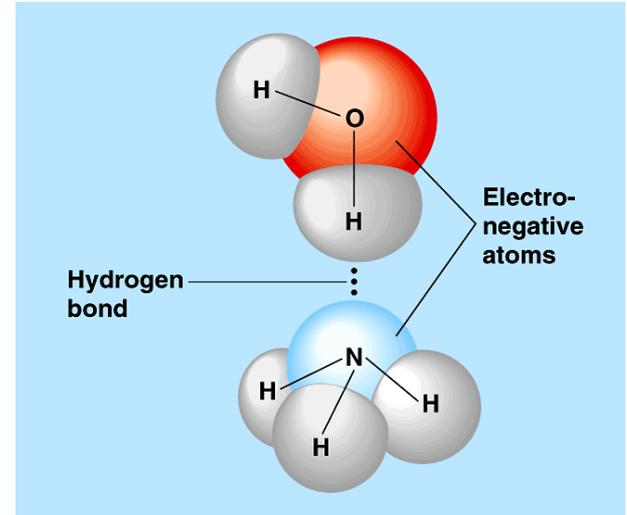
- A weak bond found mostly in liquids and solids at low temperature.
- Example: in graphite, the van der Waals bond holds together adjacent sheets of carbon atoms. As a result, one layer of atoms slides over the next layer with little friction. The graphite in a pencil slides easily over paper.



Johannes Diderik van der Waals (1837 – 1923)

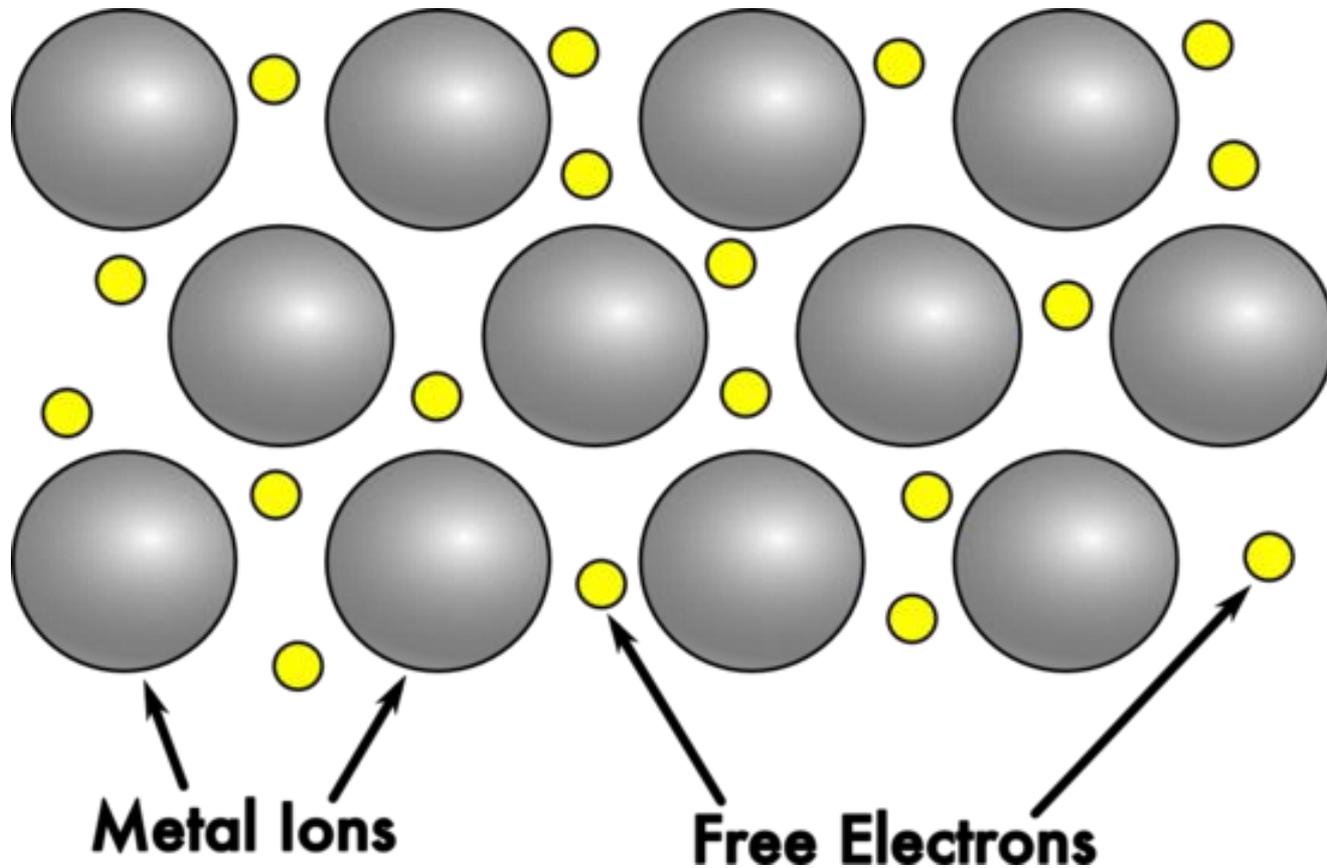
# Hydrogen bond

- If a hydrogen atom is covalently bonded to an electronegative atom, the H can simultaneously bond essentially covalently to another molecule.
- The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals bond, but weaker than covalent or ionic bonds.



# Metallic Bonds

- In metals, in which electrons are very weakly bound, valence electrons are essentially free and may be shared by a number of atoms. The Drude model for a metal: **a free-electron gas!**

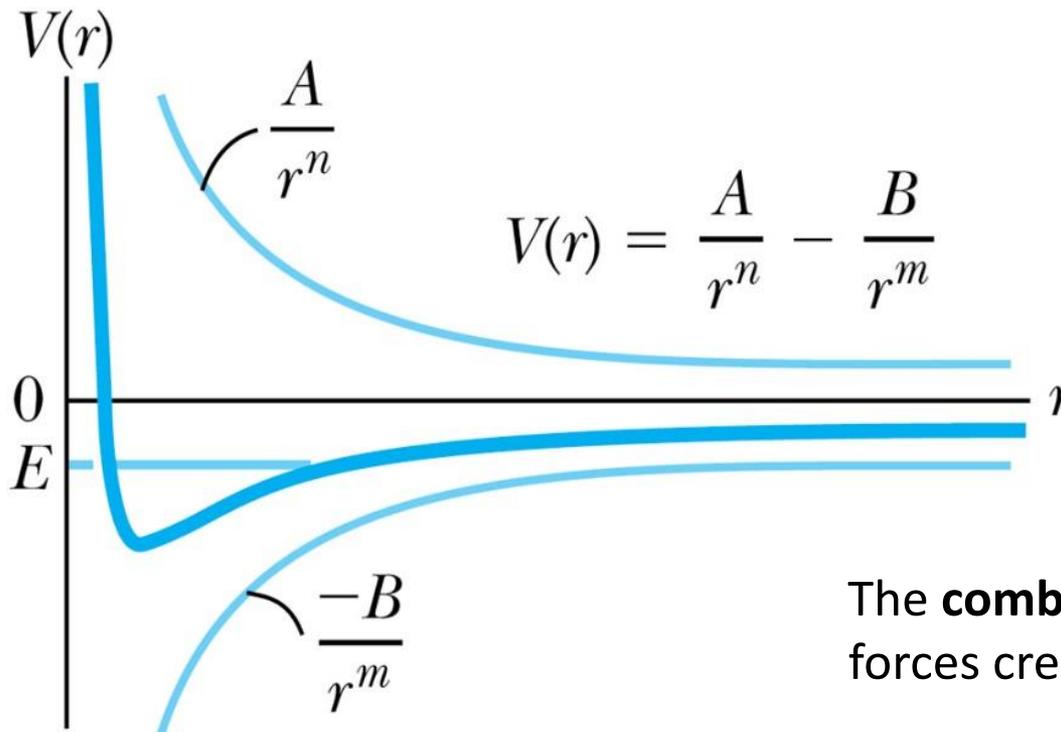


# Molecular Bonding and Spectra

- An approximation of the force felt by one atom in the vicinity of another atom is:

$$V = \frac{A}{r^n} - \frac{B}{r^m}$$

- where  $A$  and  $B$  are positive constants.
- Because of the complicated shielding effects of the various electron shells,  $n$  and  $m$  are not equal to 1

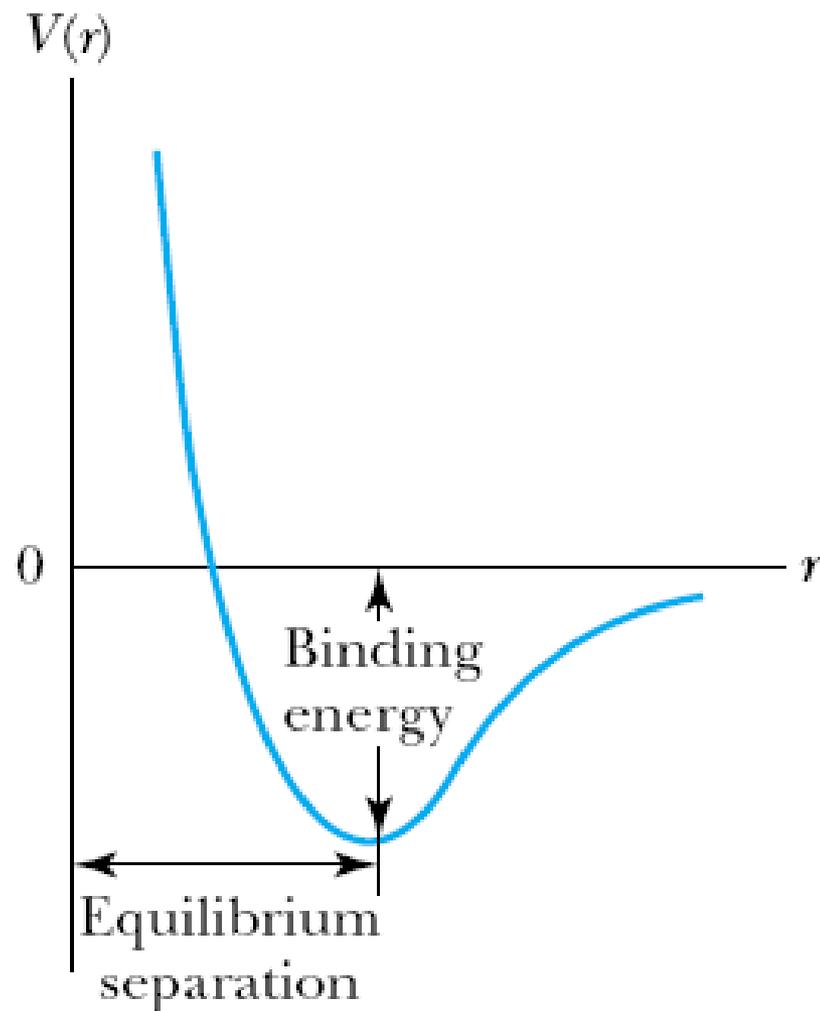


A stable equilibrium exists with total energy  $E < 0$ . The shape of the curve depends on the parameters  $A$ ,  $B$ ,  $n$ , and  $m$ . Also  $n > m$ .

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

# Molecular Bonding and Spectra

- A pair of atoms is joined.
- One would have to supply energy to raise the total energy of the system to zero in order to separate the molecule into two neutral atoms.
- The corresponding value of  $r$  of a minimum value is an **equilibrium separation**. The amount of energy to separate the two atoms completely is the **binding energy** which is roughly equal to the depth of the potential well



Vibrations are excited thermally, so the exact level of  $E$  depends on temperature.

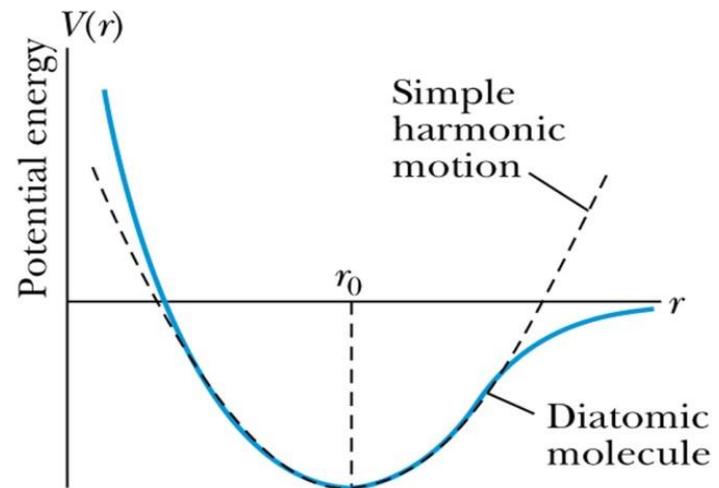
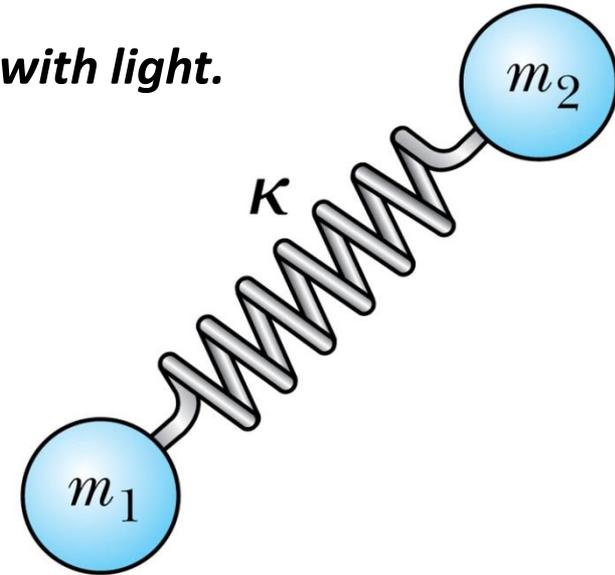
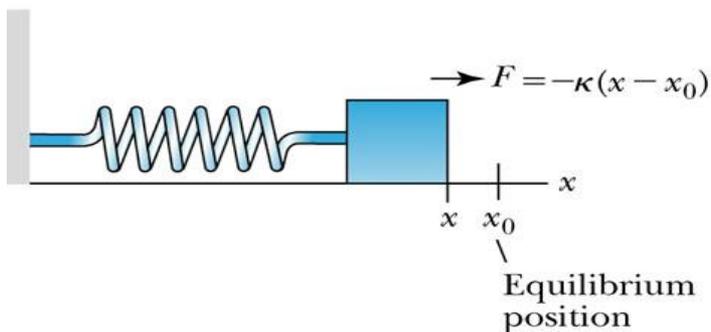
# Vibrational States

- A vibrational energy mode can also be excited.
- Thermal excitation of a vibrational mode can occur.
- ***It is also possible to stimulate vibrations in molecules with light.***

Assume that the two atoms are point masses connected by a massless spring with simple harmonic motion.

## Vibrational motion: a simple harmonic oscillator

The simple harmonic oscillator accurately describes a diatomic molecule, as well as more complex molecules.



# Vibrational States

- The energy levels are those of a quantum-mechanical oscillator

$$E_{\text{vibr}} = (n + \frac{1}{2}) \hbar \omega$$

$$\omega = \sqrt{\kappa / M_r}$$

$$m_{\text{red}} = \mu = \frac{1}{\frac{1}{m_1} + \frac{1}{m_2}} = \frac{m_1 m_2}{m_1 + m_2}$$

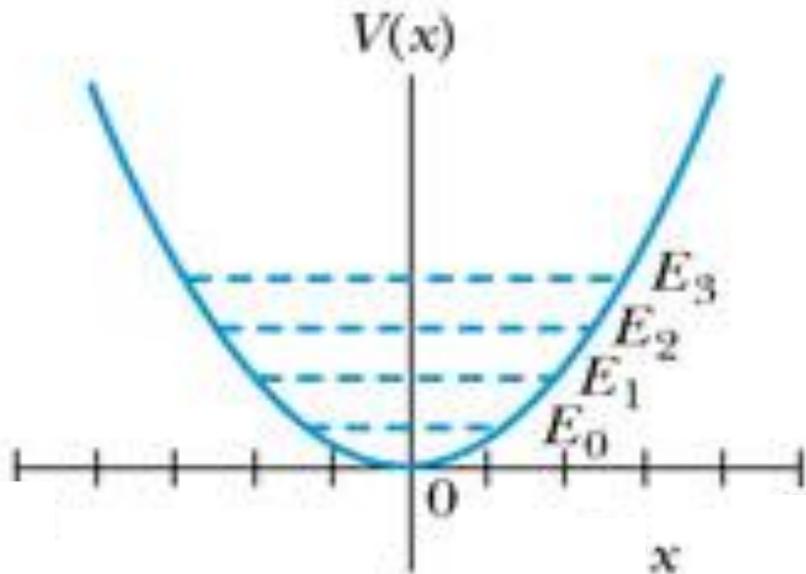
$n$  is called the **vibrational quantum number**. Don't confuse it for  $n$ , the **principal quantum number of the electronic state**.

Vibrational-transition selection rule:

$$\Delta n = \pm 1$$

The only spectral line is  $\omega$ !

However, deviations from a perfect parabolic potential allow other transitions, called **overtones**, but they're much weaker.



# Vibrational States

- The energy levels are those of a quantum-mechanical oscillator

$$E_{vibr} = (n + \frac{1}{2}) \hbar \omega$$

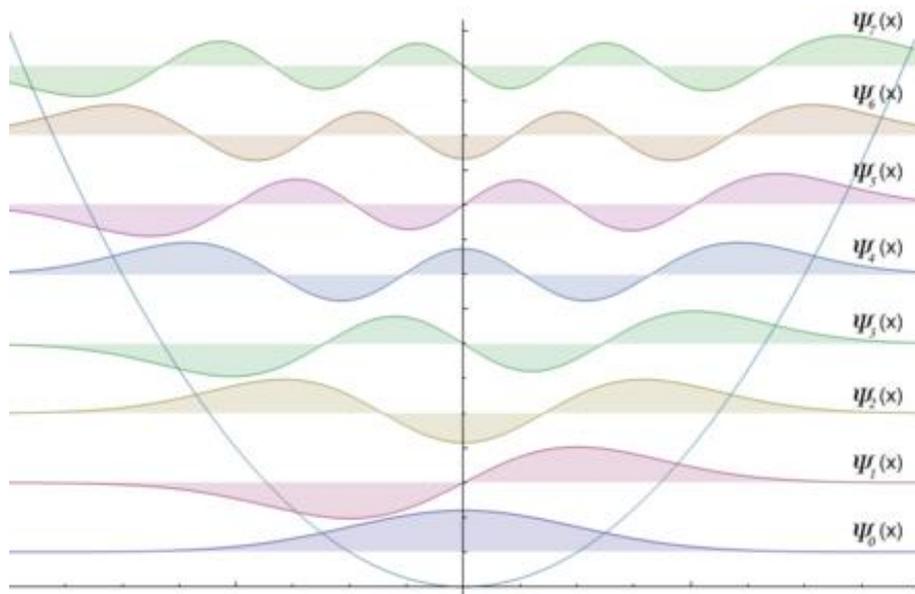
$$\omega = \sqrt{\kappa / M_r}$$

$$m_{red} = \mu = \frac{1}{\frac{1}{m_1} + \frac{1}{m_2}} = \frac{m_1 m_2}{m_1 + m_2}$$

$n$  is called the **vibrational quantum number**. Don't confuse it for  $n$ , the **principal quantum number of the electronic state**.

Vibrational-transition selection rule:

$$\Delta n = \pm 1$$

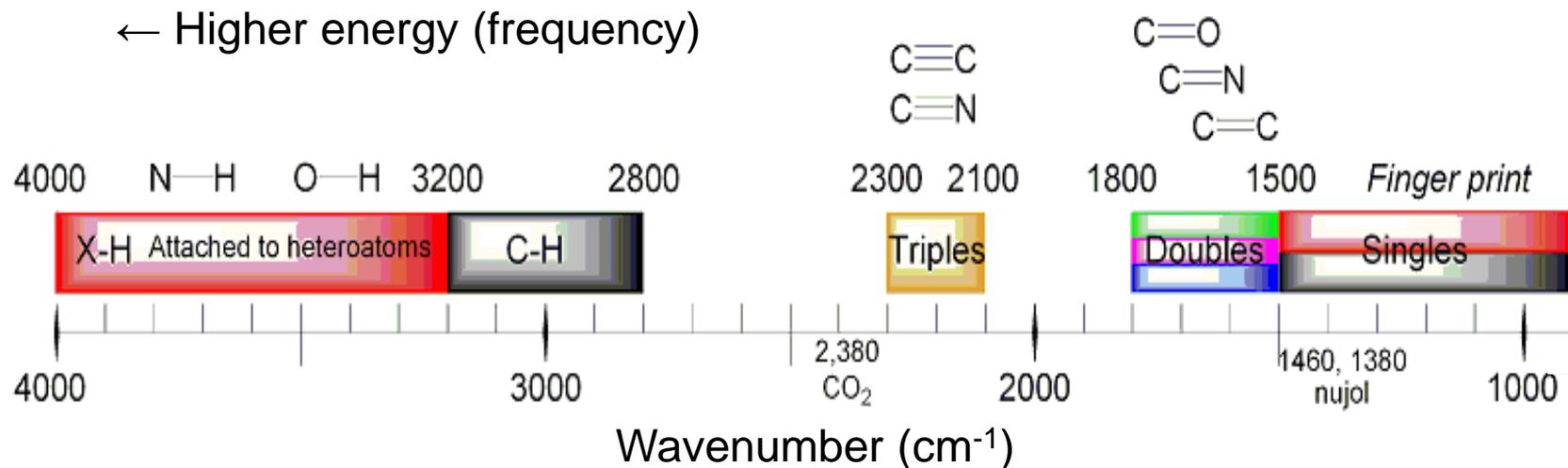


The only spectral line is  $\omega$ !

However, deviations from a perfect parabolic potential allow other transitions, called **overtones**, but they're much weaker.

# Vibrational frequencies for various bonds

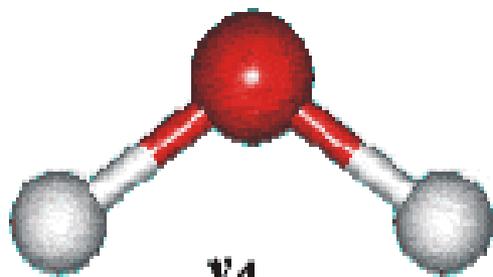
- Different bonds have different vibrational frequencies (which are also affected by other nearby atoms).



Notice that bonds containing Hydrogen vibrate faster because H is lighter.

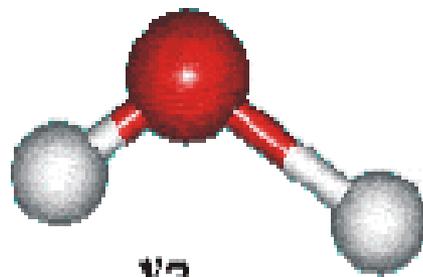
Unlike the energy levels of the hydrogen atom and the rotating diatomic molecule, the vibrational energy levels of the diatomic molecule **are equally spaced**. In practice, however, the potential-energy curves for most molecules become anharmonic as the energy increases, resulting in a diminution of energy-level separations

# Water vibrations-vibrating triatomic molecules



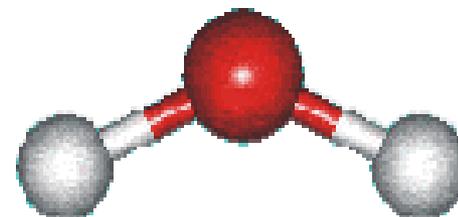
$\nu_1$

symmetric stretch



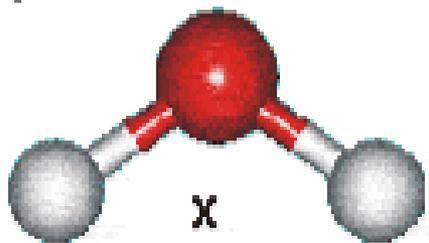
$\nu_3$

asymmetric stretch

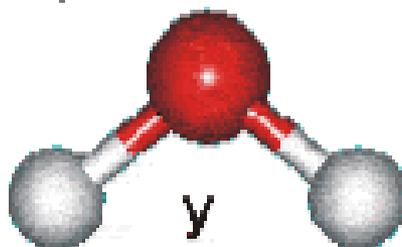


$\nu_2$

bend

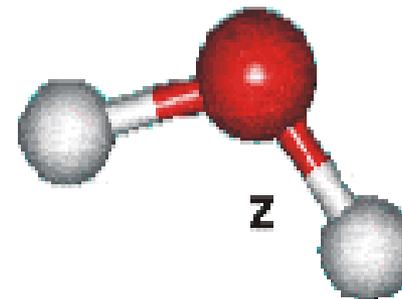


x



y

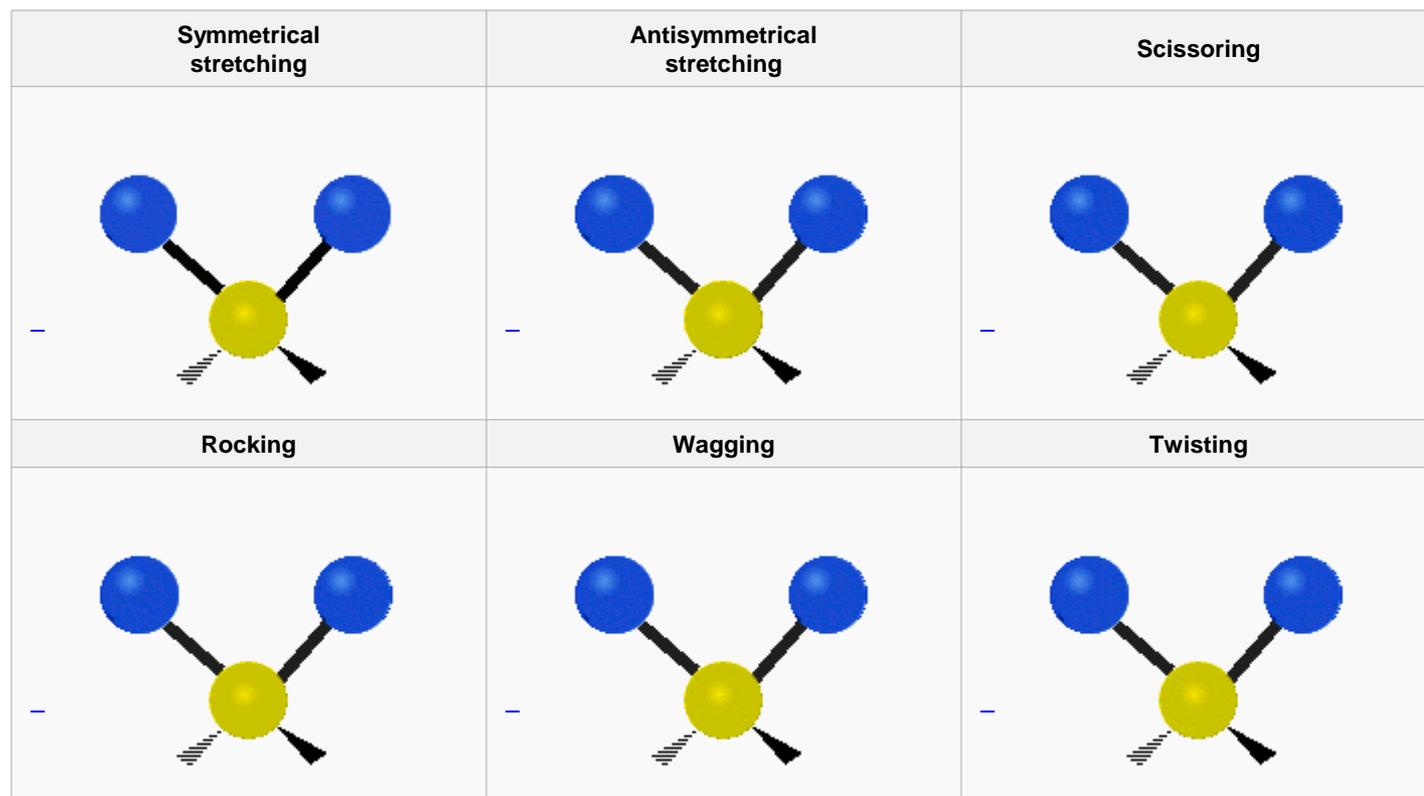
librations



z

# Carbon-Hydrogen-vibration-vibrating triatomic molecules

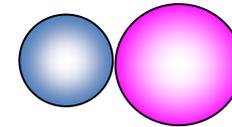
- CH<sub>2</sub>-Carbon-Hydrogen bonds are important in the chemistry of life-laser medium



As with diatomic molecules, each vibrational level is split into many closely spaced rotational levels

# Rotational states

- Consider diatomic molecules



- A diatomic molecule may be thought of as two atoms held together with a massless, rigid rod (*rigid rotator model*).

- In a purely rotational system, the kinetic energy is expressed in terms of the angular momentum  $L$  and rotational inertia  $I$ .

$$E_{rot} = \frac{L^2}{2I}$$

- $L$  is quantized

$$L = \sqrt{\ell(\ell + 1)} \hbar$$

- The energy levels are

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

- $E_{rot}$  varies only as a function of the quantum number  $\ell$ .

# Rotational states

- The energy separations of rotational energy levels typically lie in the range  $10^{-4}$ – $10^{-2}$  eV, corresponding to photons in the **microwave and far-infrared regions of the spectrum**.
- The energy spacing between successive rotational energy levels **increases with increasing quantum rotational number**, in contrast to the spacing between successive electronic energy levels of the hydrogen atom, **which decrease with increasing quantum number**.
- Diatomic molecules with identical nuclei (such as  $N_2$ ) have no permanent electric dipole moment; they therefore do not exhibit pure rotational spectra.

# Vibration and Rotation Combined

- It's possible to excite rotational and vibrational modes simultaneously.
- Total energy of a simple vibration-rotation system:

$$E = E_{rot} + E_{vibr} = \frac{\hbar^2 \ell(\ell + 1)}{2I} + \left( n + \frac{1}{2} \right) \hbar \omega$$

- Vibrational energies are spaced at regular intervals.

- Transitions from  $\ell + 1$  to  $\ell$  :

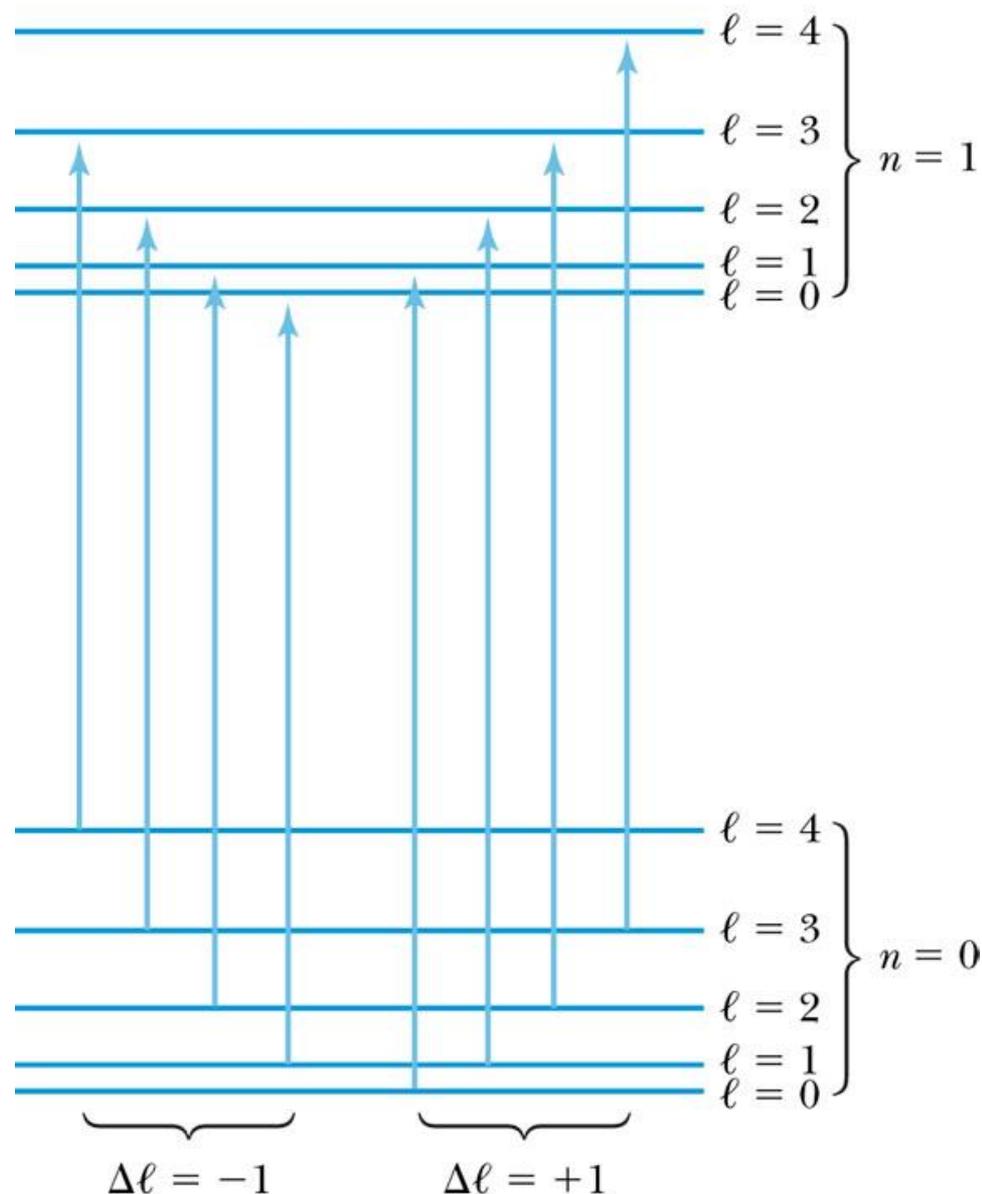
$$E_{ph} = \frac{\hbar^2}{2I} [(\ell + 1)(\ell + 2) - \ell(\ell + 1)]$$

- Photons will have energies at regular intervals (plus the vibrational energy difference):

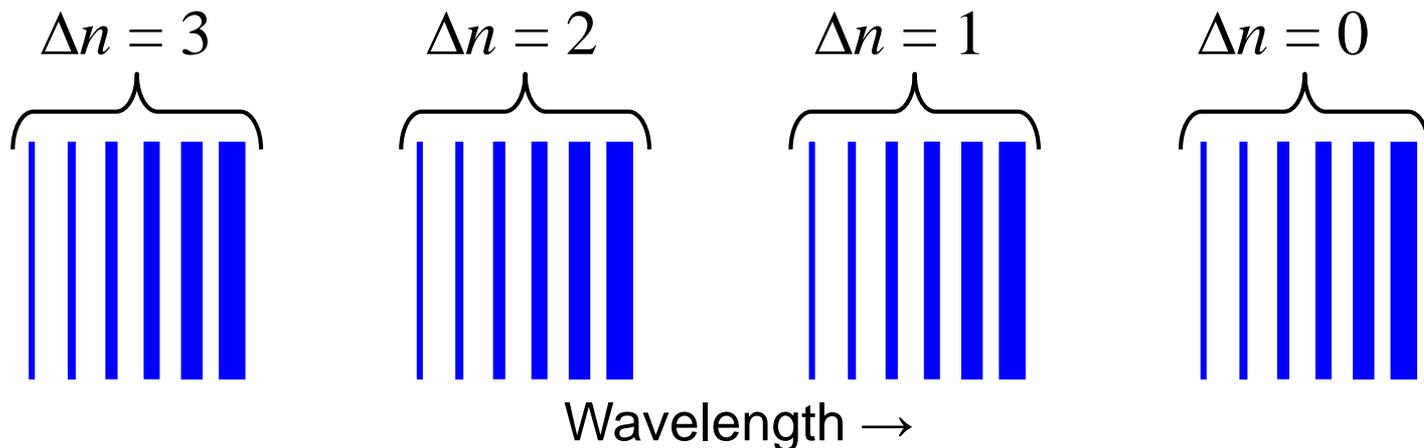
$$= \frac{\hbar^2}{2I} [\ell^2 + 3\ell + 2 - \ell^2 - \ell] = \frac{\hbar^2}{I} (\ell + 1)$$

# Vibration and Rotation Combined

- $\Delta E$  increases linearly with  $\ell$ .
- Many transitions are forbidden by the selection rules that requires  $\Delta\ell = \pm 1$  and  $\Delta n = \pm 1$
- The emission (and absorption) spectrum spacing varies with  $\ell$ .
- The higher the starting energy level, the greater the photon energy.
- Vibrational energies are greater than rotational energies. For a diatomic molecule, this energy difference results in band structure.
- The line strengths depend on populations of the states and the vibrational selection rules, however.

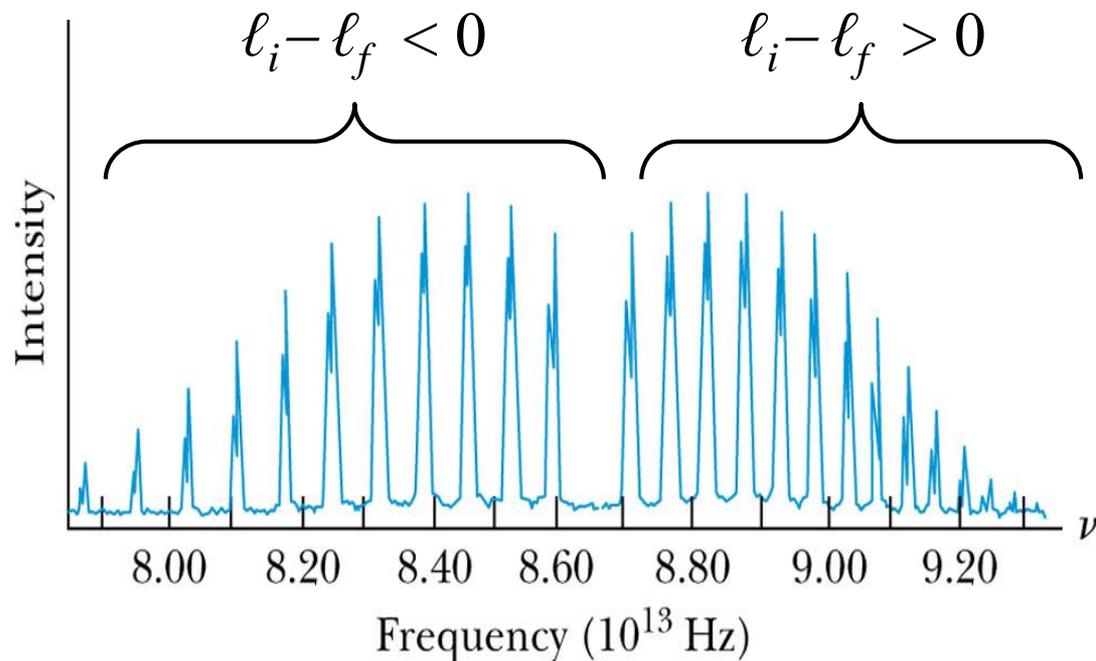


# Vibration and Rotation Combined



- In the absorption spectrum of HCl, the spacing between the peaks can be used to compute the rotational inertia  $I$ .
- The missing peak in the center
- corresponds to the forbidden
- $\Delta \ell = 0$  transition.

$$n_i - n_f = 1$$

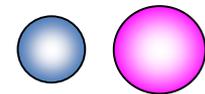
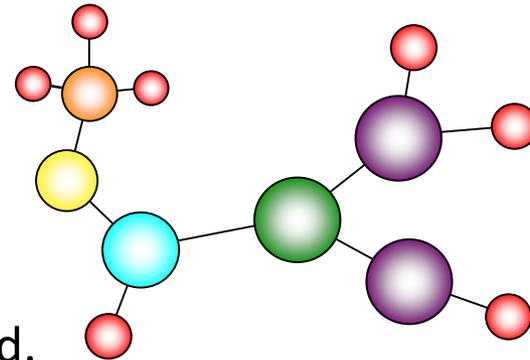
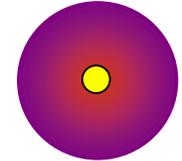


# Motion frequencies in atoms and molecules

- Electrons vibrate in their motion around nuclei
- High frequency:  $\sim 10^{14} - 10^{17}$  cycles per second.

- Nuclei in molecules vibrate with respect to each other
- Intermediate frequency:  $\sim 10^{11} - 10^{13}$  cycles per second.

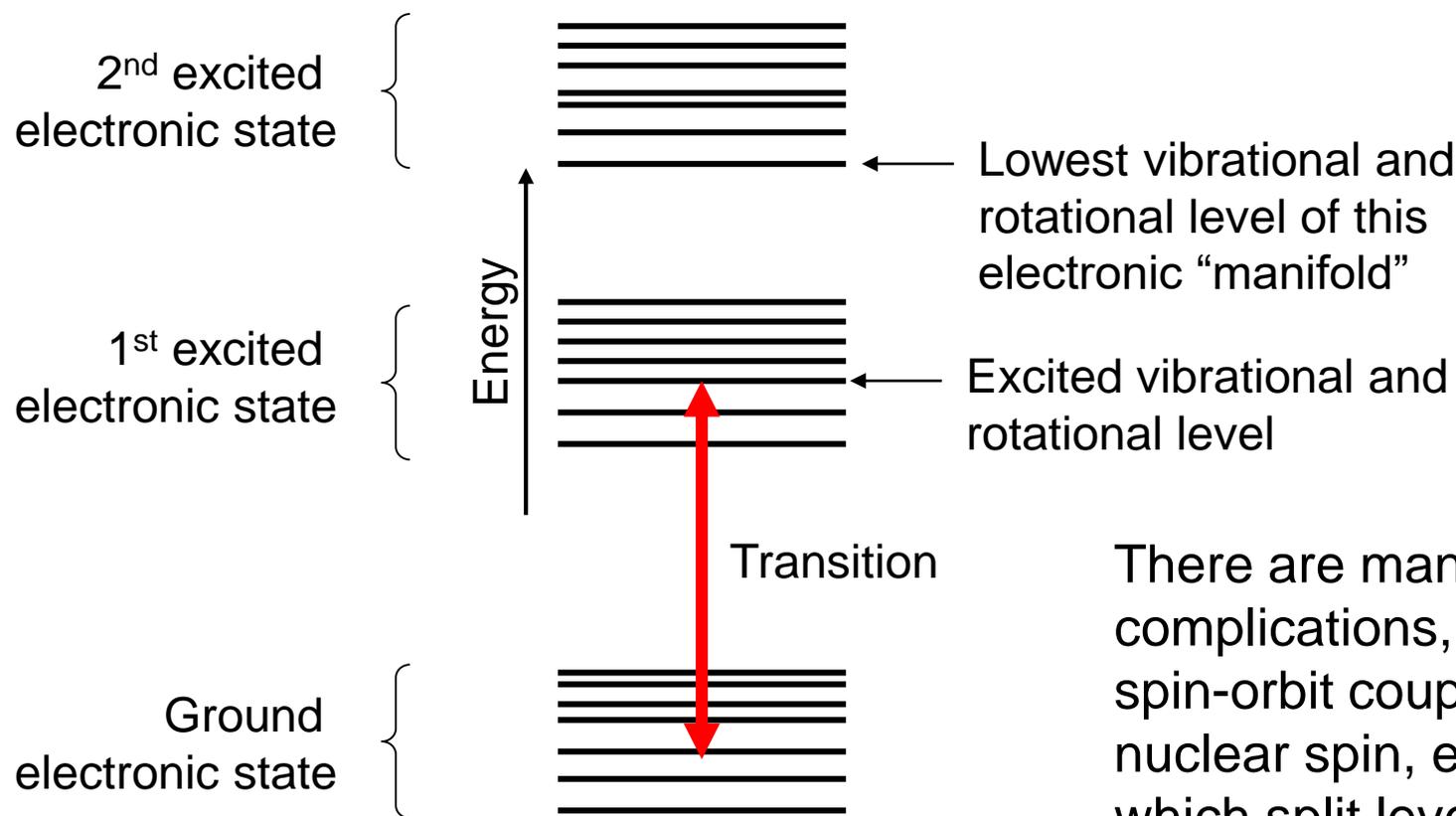
- Nuclei in molecules rotate
- Low frequency:  $\sim 10^9 - 10^{10}$  cycles per second.



# Including electronic energy levels

- A typical large molecule's energy levels

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$



There are many other complications, such as spin-orbit coupling, nuclear spin, etc., which split levels.

As a result, molecules generally have **very complex spectra**.

# Studying Vibrations and Rotations

- **Fourier transform infrared (FTIR) spectroscopy**
- The Fourier transform of the output intensity vs. delay of a Michelson Interferometer is the spectrum

