Molecular and Supramolecular Photochemistry

Modern Molecular Photochemistry of Organic Molecules
Or
Principles of Photochemistry

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Chapters 1 & 2

Photochemistry

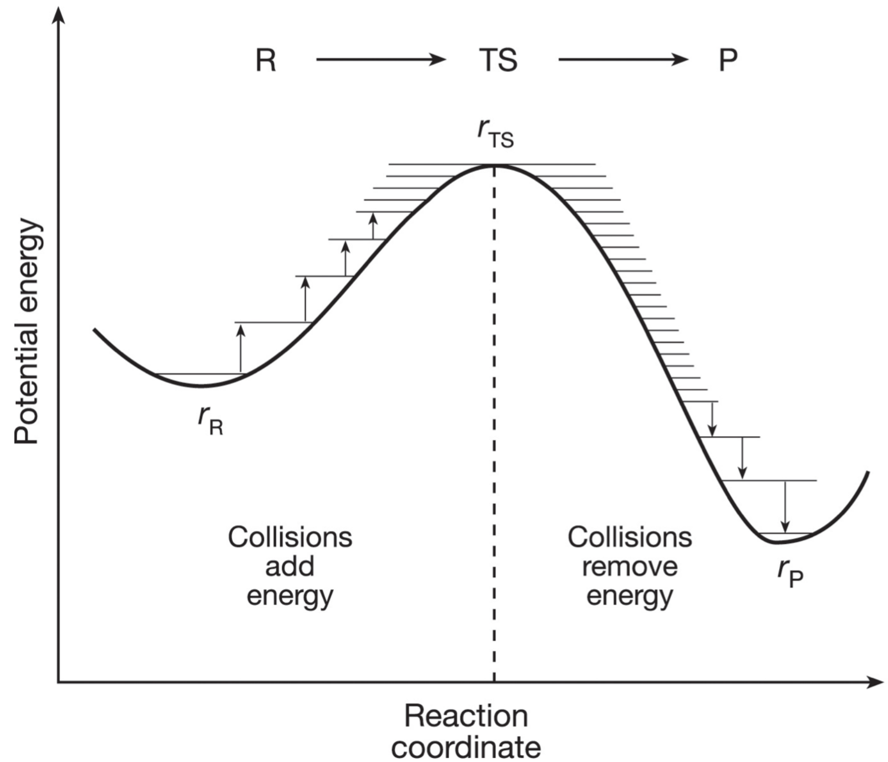
Interaction of Light with Matter (Molecules)

- *Organic Photochemistry*
- *Inorganic Photochemistry*
- *Photobiology*

What is the difference between thermochemistry and photochemistry?

- **Mode of activation**
  - Activated by collisions (thermo)
  - Activated by light (photo)
- **Selectivity in activation**
  - Entire molecule gets activated
  - Only the chromophore that absorbs the light gets activated
- **Energy distribution**
  - Energy used for vibrational/rotational transition
  - Energy used for electronic transition only

Visualization of Thermal Reactions



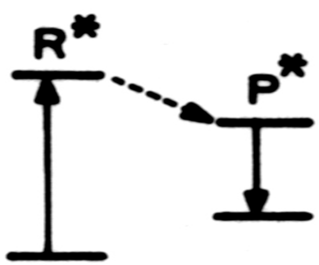
- Transition state connects a single reactant to a single product (intermediate) and it is a saddle point along the reaction course.
- Collisions are a reservoir of continuous energy (~ 0.6 kcal/mol per impact).
- Collisions can add or remove energy from a system.
- Concerned with a single surface.

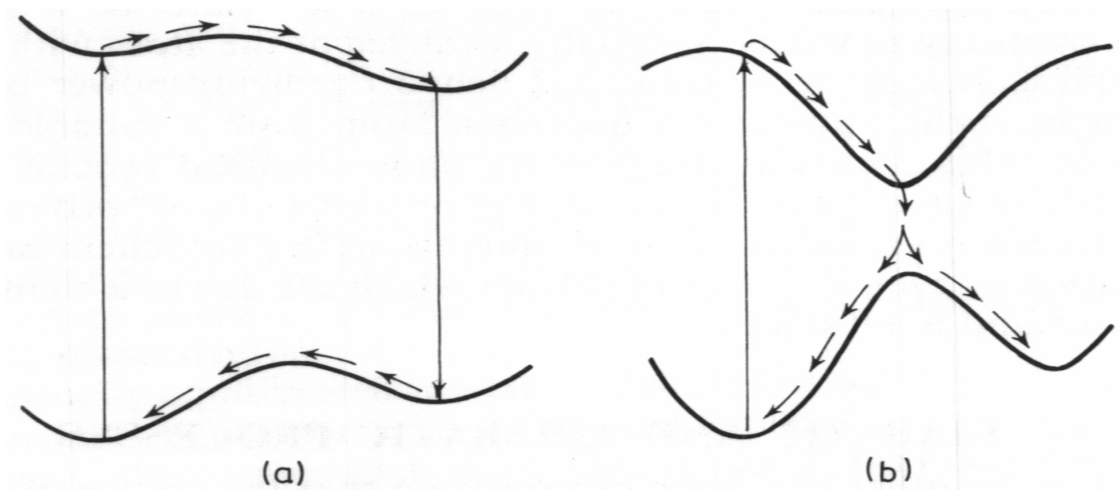
Visualization of Photochemical Reactions

We need to deal with two surfaces (ground and excited state.

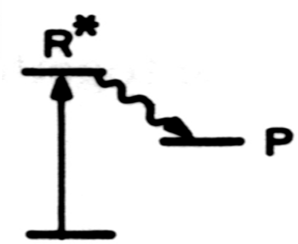
Adiabatic

Diabatic



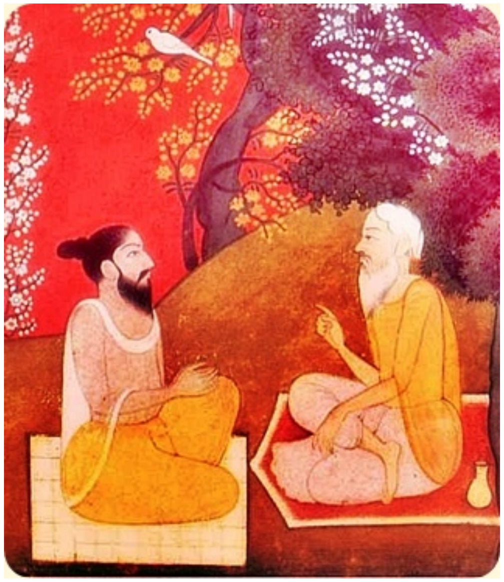


Pathways of photochemical reactions: (a) adiabatic, (b) diabatic.



Photochemistry starts with interaction of a Photon with a Molecule

- What is a photon?
- What is a molecule?
- How do they interact?
- What are the consequences of interaction?



The Basic Laws of Photochemistry

Grotthuss-Draper law

The First Law of Photochemistry: <u>light must be absorbed for photochemistry to occur</u>.

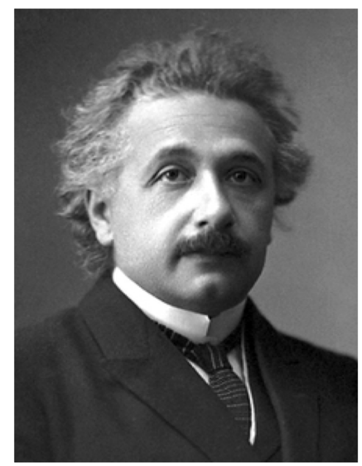
Grotthus

Drapper

Stark-Einstein law

The Second Law of Photochemistry: for <u>each photon</u> of light absorbed by a chemical system, <u>only one molecule</u> is activated for a photochemical reaction.

Stark



Einstein

The Light Paradigm (500 BC-1850 AD)

500 BC

2018 AD

55 BC
Lucretius

1000

1500 1700

Newton
(1643-1727)

Particles!

Waves!

Maxwell
(1831-1879)

…but then came the 1900’s - new people, tools, and paradigms!

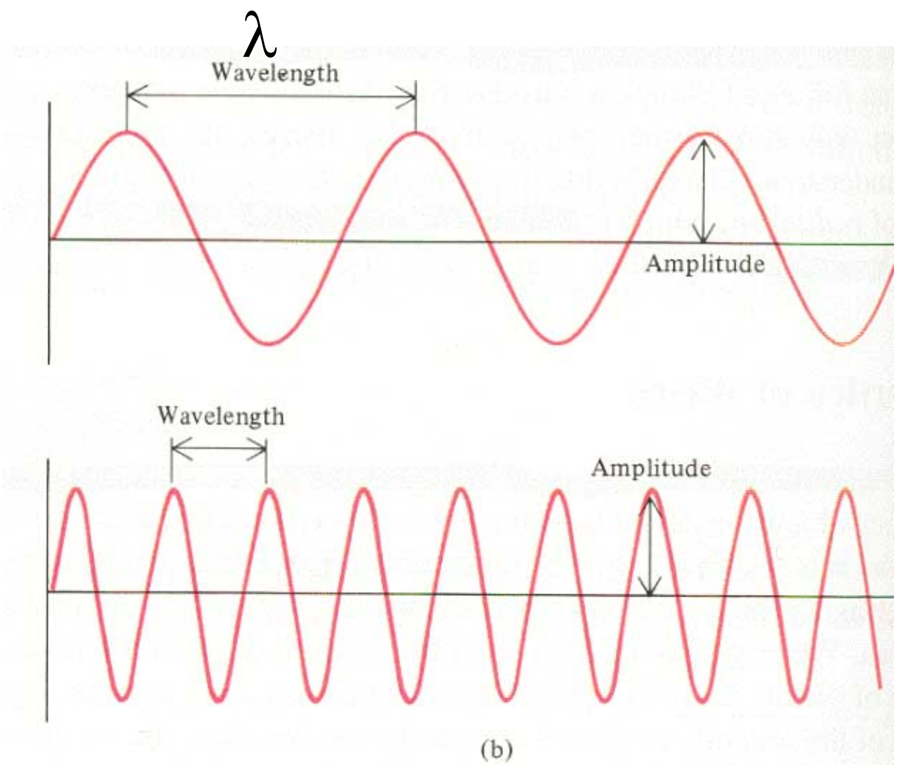
James Clerk Maxwell
1831-1879

Paradigm 1800s: Light consists of waves (energy propagated by waves): Energy is spread over space like a liquid.

Maxwell's theory is called the ***classical*** theory of light.

Key equations:
$c = \lambda\nu$;   [λ (Gk lambda), ν(Gk nu)]
c = speed of light wave wave propagation
λ = wavelength, ν = frequency

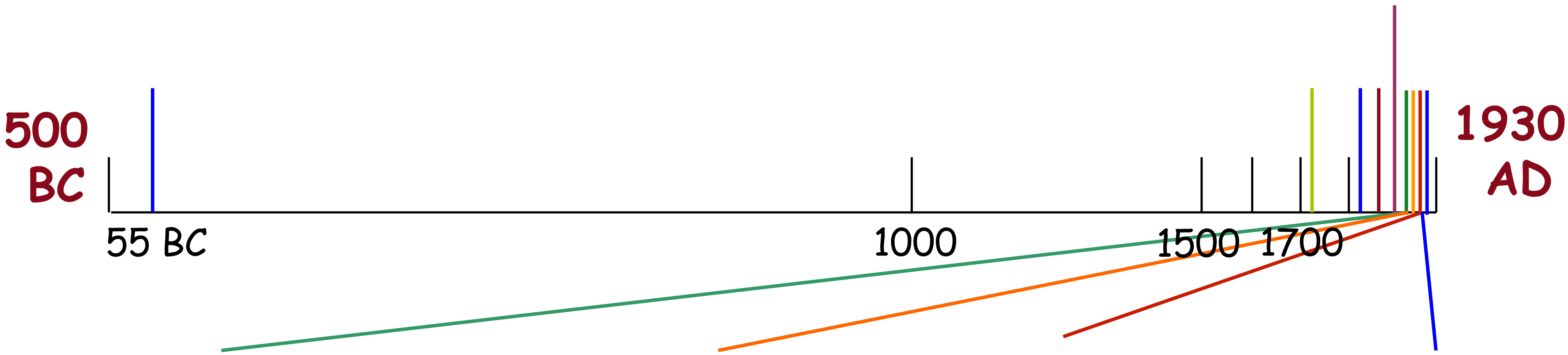
Classical: Energy carried by a light wave is proportional to the *amplitude* of the wave.



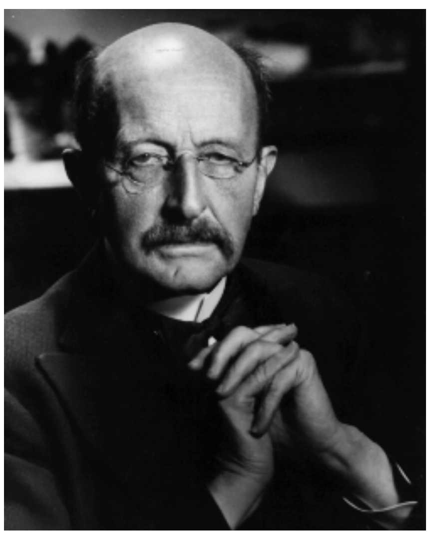
Low Frequency

High Frequency

The Light Paradigm (1850 AD-1930 AD)

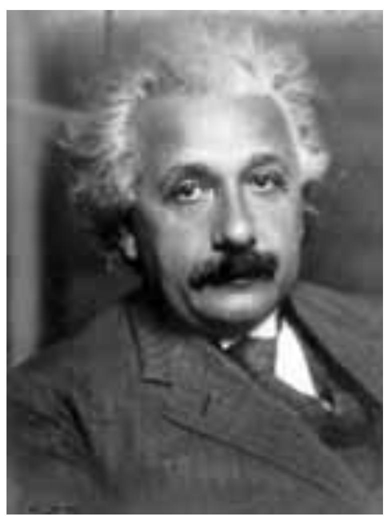


Max Planck (1918)



$E = h\nu$, quanta

Albert Einstein (1921)



$E = h\nu$, photons

Niels Bohr (1922)

$E_2 - E_1 = h\nu$, transitions

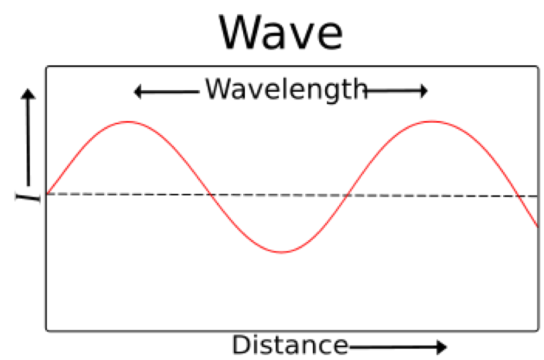
De Broglie (1929)

$E = h\nu = mc^2$

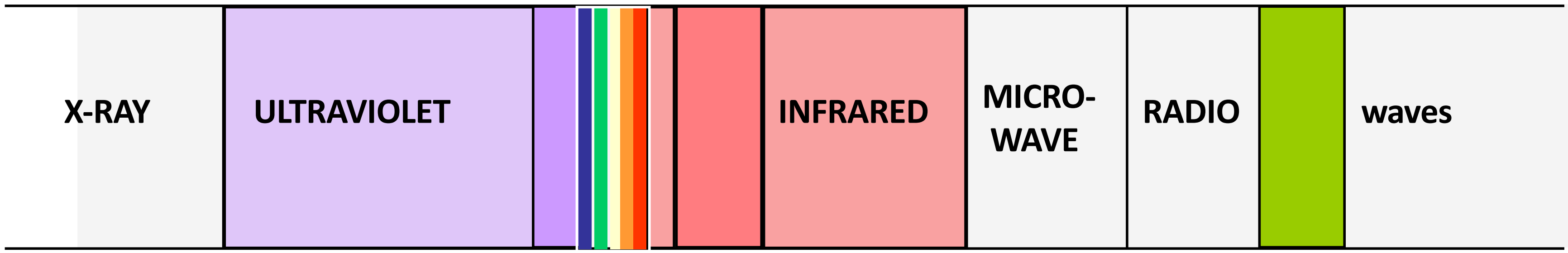
What is a photon?

Photon (Light) has dual characteristics: a particle and a wave

Wavelength	λ	c/ν
Wavenumber:	υ	$1/\lambda$
Frequency:	ν	c/λ
Energy	$h\nu$	hc/λ
Einstein:	$Nh\nu$	Mole of photons (one Avagadro number of photons)
Velocity:	186,281 miles/sec; 2.9979×10^{10} cm/sec	
Momentum:	E/c	
Mass:	Momentum/c (no real mass)	
Charge:	0 (no charge)	
Spin	$1\hbar$	



The Range of Electromagnetic Radiation (Light)



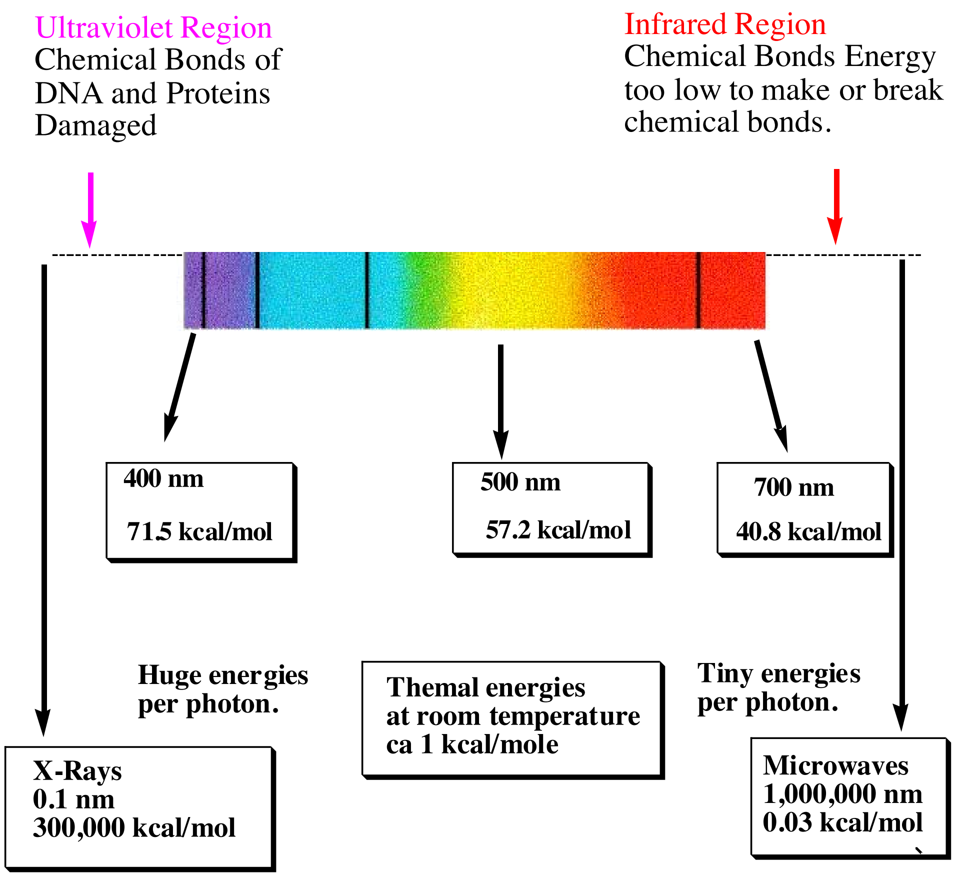
REGION	ENERGY TRANSITIONS
X-ray	Ionization
UV/Visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radio Frequency (NMR)	Nuclear and Electronic Spin

Light and Energy Scales

$$E\ (\text{kcal mol}^{-1}) = [2.86 \times 10^{4}\ \text{kcal mol}^{-1}\ \text{nm}]/\lambda\ \text{nm}$$

$$E\ (\text{kcal mol}^{-1}\ \text{nm}) = 2.86 \times 10^{4}/700\ \text{nm} = 40.8\ \text{kcal mol}^{-1}$$

$$E\ (\text{kcal mol}^{-1}\ \text{nm}) = 2.86 \times 10^{4}/200\ \text{nm} = 143\ \text{kcal mol}^{-1}$$



What is a matter, a material and a molecule? Early paradigms

Lucretius: ca 99-55 BC

All *matter* consists of tiny fundamental building blocks called ***atoms***

"All nature consists of twain of things: of *atoms* and of the void in which they're set."

"DE RERUM NATURA"

John Dalton 1766-1844

All matter is composed of small indivisible particles termed *atoms*. Atoms of a given element possess unique characteristics and weight.

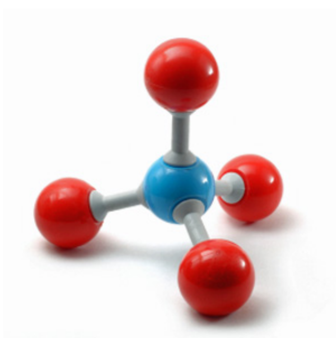
"A New System of Chemical Philosophy"

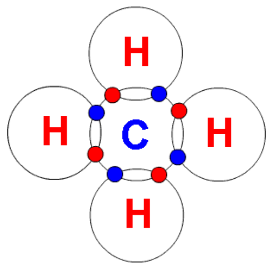
Paradigm: Matter consists of tiny particles called atoms.

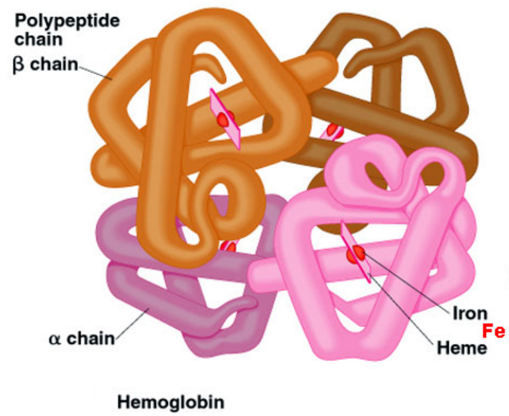
What is a matter or material?

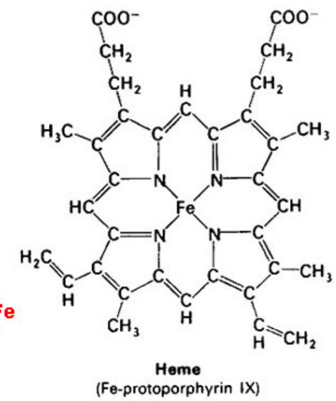
- **A Matter is a collection of molecules**
- **A Molecule is a collection of atoms**
- **An Atom is a collection of nuclei and electrons**
- **The fundamental components of matter and molecules are nuclei and electrons**
- **To understand a matter and a molecule one needs to know the location and energies of nuclei and electrons.**

Molecule: a collection of atoms (nuclei and electrons) is defined by Ψ









$$H\Psi = E\Psi$$

Operator

Eigenvalue

What is Ψ ?

Ψ defines a molecule in terms of nuclei and electrons

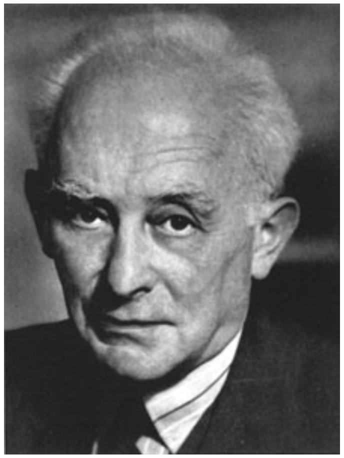
Ψ is made of three parts

$$\Psi \quad = \quad \Psi_o \quad \chi \quad S$$

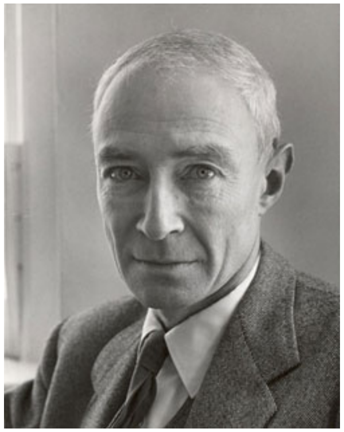
Electronic Nuclear Spin

The three parts are interconnected. So it is hard to define a molecule precisely in terms of Ψ

Born – Oppenheimer Approximation



Born



Oppenheimer

- Electronic motion faster than nuclear motion (vibration).
- Weak magnetic-electronic interactions separate spin motion from electronic and nuclear motion.

$$\Psi = \Psi_o \quad \chi \quad S$$

Electronic Nuclear Spin

Time scale matter

Electron

- It has dual wave and particle properties, just like a photon
- Negatively charged, does not change with energy
- Electric charge oscillates with time
- It has spin of 1/2 $\hbar$
- It is a small magnet
- Coupled with protons and neutrons it holds atoms, molecules and everything in the world
- It is small, radius of 0.00028 nm.

Born – Oppenheimer Approximation

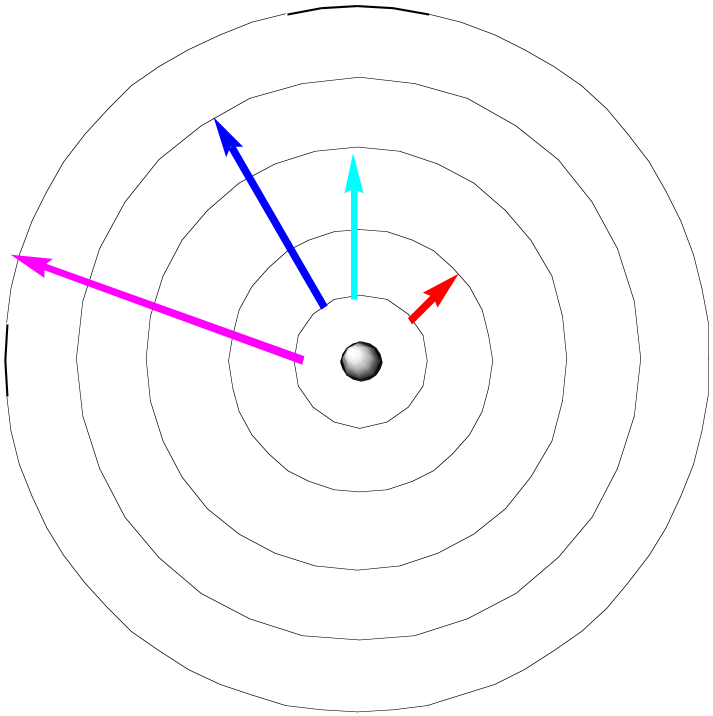
- Electronic motion and nuclear motion can be separated (Born-Oppenheimer approximation)
- To understand molecules, first focus on the location and energies of electrons
- Understand: Ψ_o(electronic) independent of χ and S

Where are the electrons in atoms and molecules?

Niels Bohr
Nobel Prize 1922

"the structure of atoms and the radiation emanating from them"

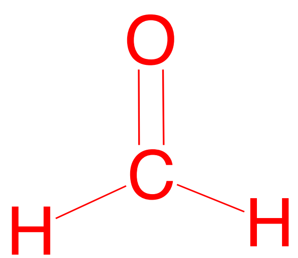
Atomic orbitals: s, p, d, f



Viewing electrons in atoms and molecules

Atoms: Electrons are present in atomic orbitals (Bohr)

Molecules: Electrons are present in molecular orbitals



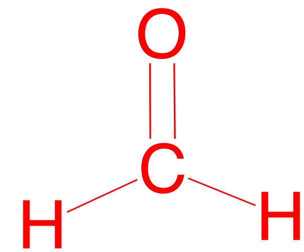
Inner orbitals

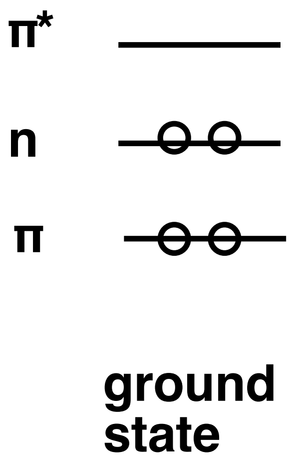
Bonding orbitals

Frontier orbitals

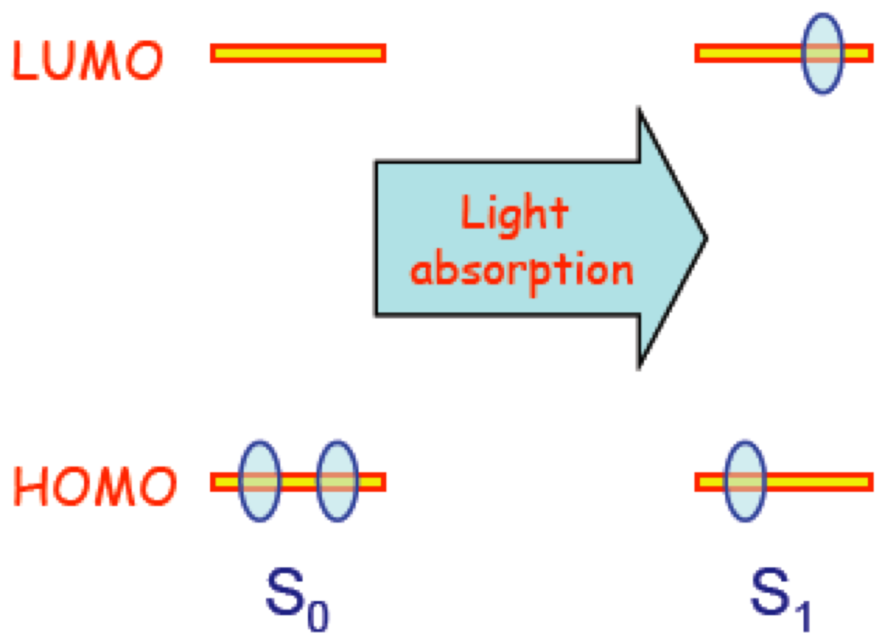
$$\Psi_0(H_2C{=}O) = (1s_O)^2(1s_C)^2(2s_O)^2(\sigma_{CH})^2(\sigma'_{CH})^2(\sigma_{CO})^2(\pi_{CO})^2(n_O)^2 \; (n_o)^2$$

Types of transitions in formaldehyde





Light absorption and electron movement



Excited state energies

The energy required to produce an electronically excited state

$$R\ (E_1) + h\nu \rightarrow R^*\ (E_2)$$

is obtained by inspecting the absorption spectrum of the molecule.

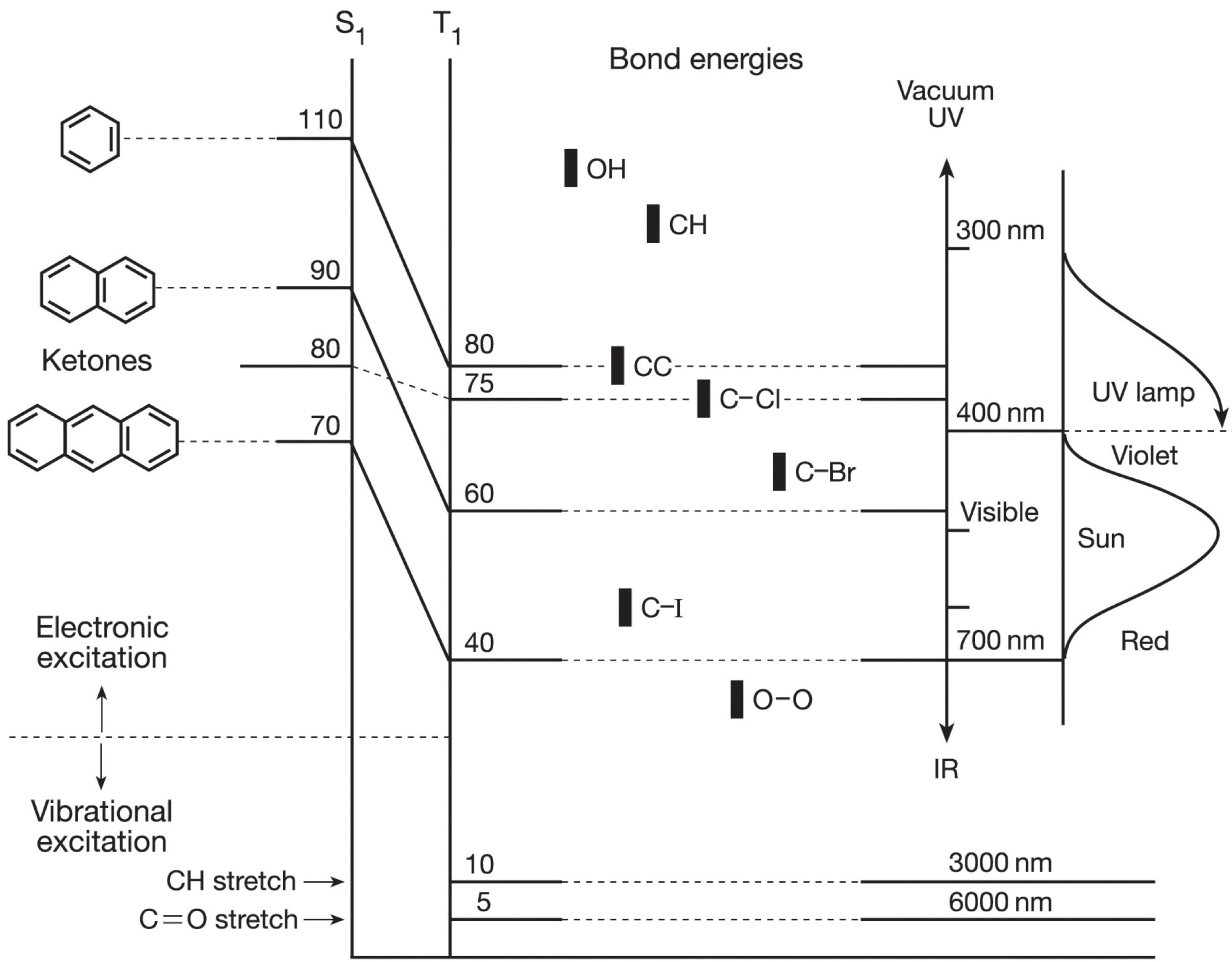
$$\Delta E = |E_2 - E_1| = |E_2(^*\mathrm{R}) - E_1(\mathrm{R})| = h\nu = hc/\lambda$$

h is Planck's constant (1.58×10^{-34} cal s)

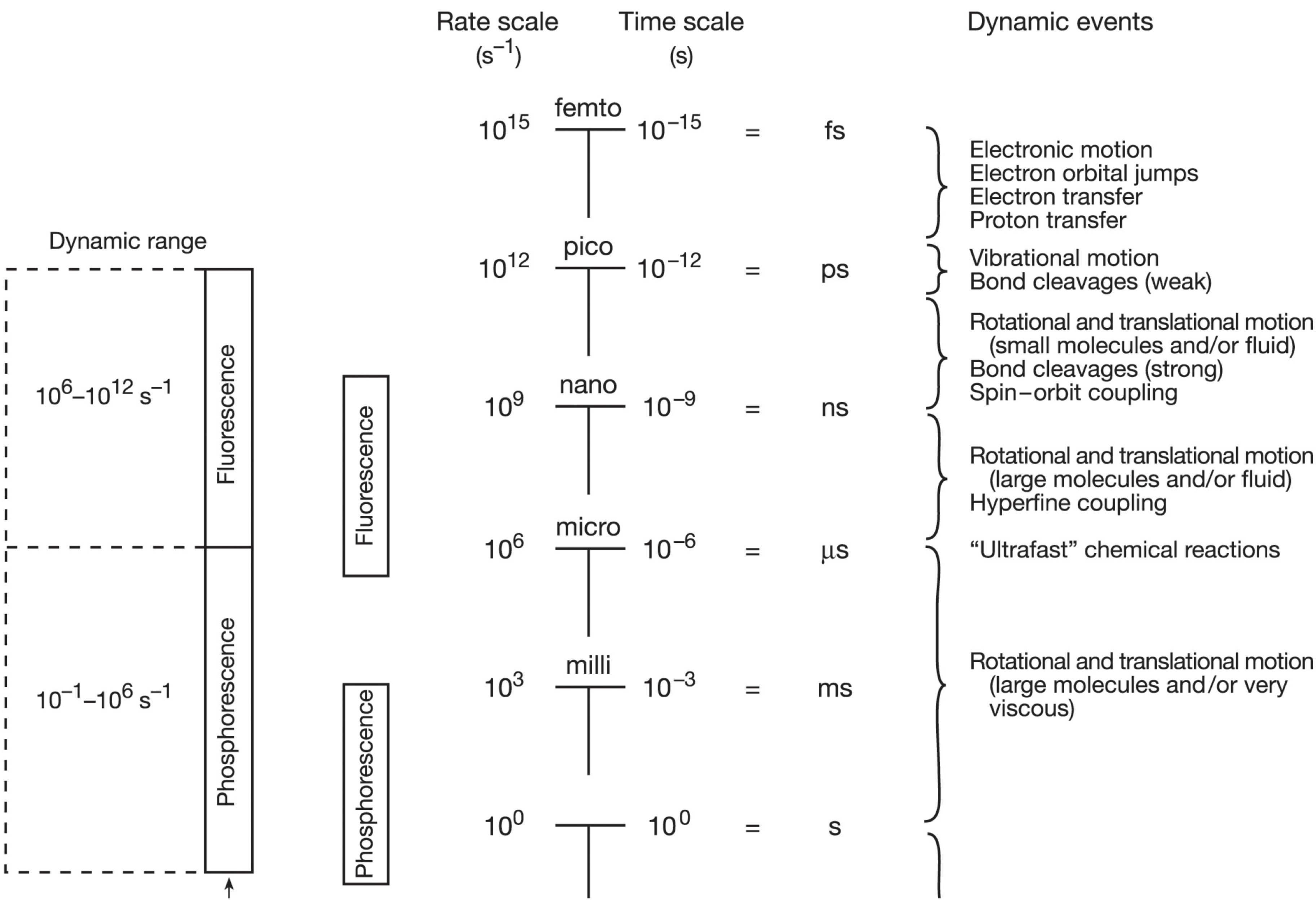
λ is the wavelength at which absorption occurs (commonly given in units of nanometers, nm),

c is the speed of light (3×10^{8} cm s^{-1})

Excitation energy, bond energy and radiation wavelength



Time scales



Rate scale (s^{-1})
Time scale (s)
Dynamic events
femto
10^{15}
10^{-15} = fs
pico
10^{12}
10^{-12} = ps
nano
10^{9}
10^{-9} = ns
micro
10^{6}
10^{-6} = µs
milli
10^{3}
10^{-3} = ms
10^{0}
10^{0} = s
Electronic motion
Electron orbital jumps
Electron transfer
Proton transfer
Vibrational motion
Bond cleavages (weak)
Rotational and translational motion (small molecules and/or fluid)
Bond cleavages (strong)
Spin–orbit coupling
Rotational and translational motion (large molecules and/or fluid)
Hyperfine coupling
"Ultrafast" chemical reactions
Rotational and translational motion (large molecules and/or very viscous)
Dynamic range
10^{6}–10^{12} s^{-1}
10^{-1}–10^{6} s^{-1}
Fluorescence
Phosphorescence
Fluorescence
Phosphorescence

Nobels in Photochemistry

Development of Flash Photolysis and Femtosecond Chemistry

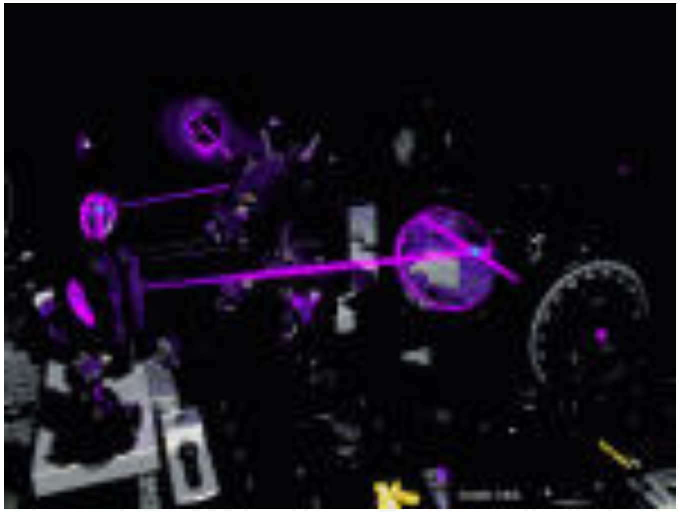
Norrish

Porter

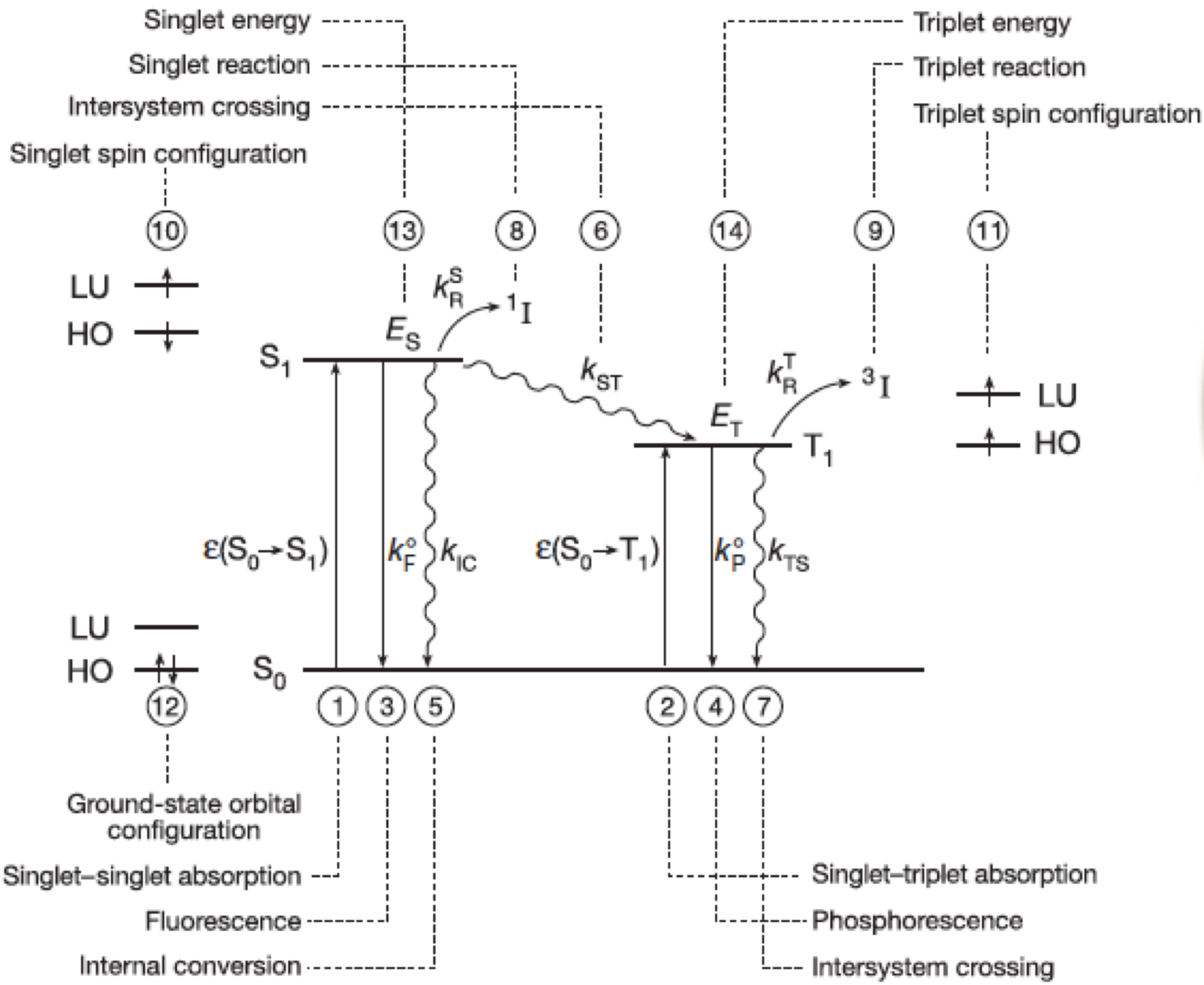
Zewail

The Nobel Prize in Chemistry 1967

The Nobel Prize in Chemistry 1999



Jablonski Diagram



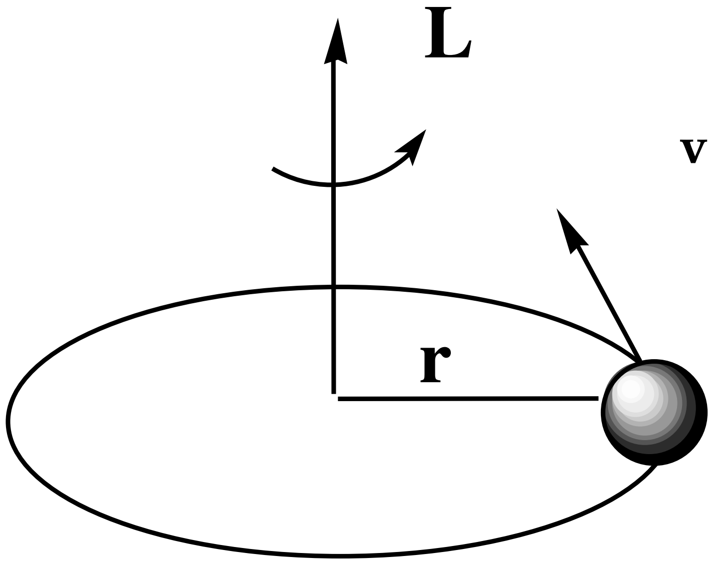
Alexander Jablonski
(1898-1980)

Visualization of Spin Chemistry

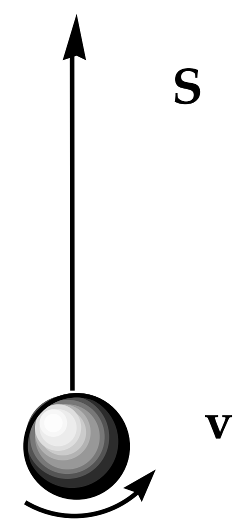
- Quantum mechanics requires mathematics for a quantitative treatment
- Much of the mathematics of quantum mechanics can be visualized in terms of pictures that capture the qualitative aspects of the phenomena under consideration
- Visualizations are incomplete, but it is important to note "correct" mathematical representations fail for complex systems as molecules

Electron spin and orbital angular momenta

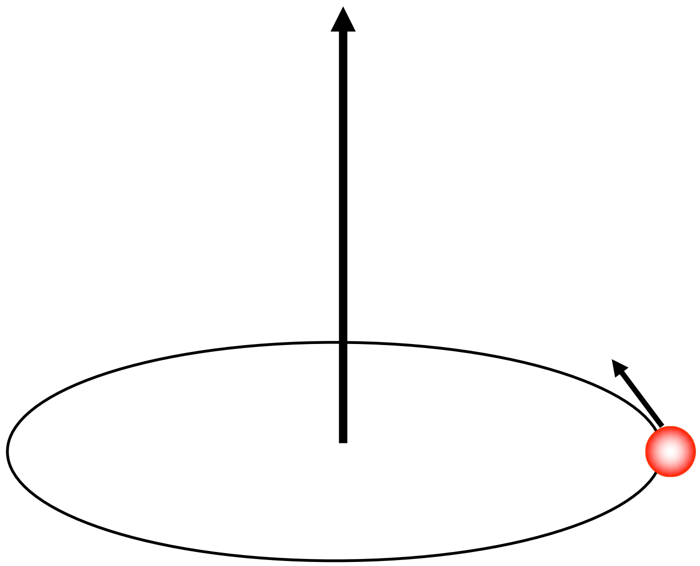
orbitral angular
momentum vector, **L**



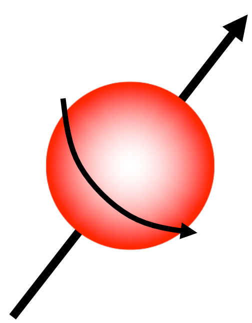
spin angular
momentum vector, **S**



Spin

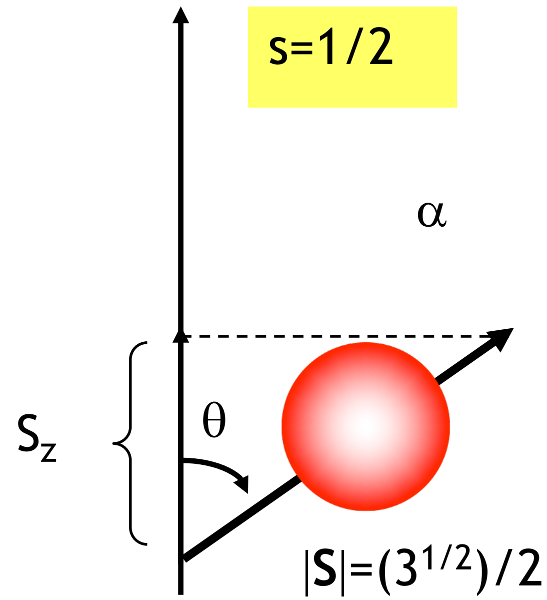


- Quantum particles possess an intrinsic angular momentum called spin which is not associated to a rotation about an axis, although we can visualize it as if it was generated by a rotation of the particle about its own axis



- Classically angular momentum is a property of a macroscopic object which is in rotation about an axis s=1/2

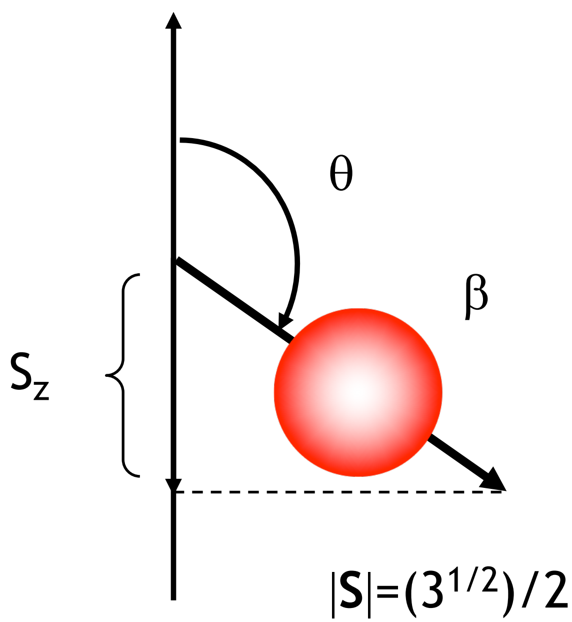
Spin multiplicity= 2S+1 = 2



In particular for

$S=1/2 \rightarrow |\mathbf{S}|=(3^{1/2})/2$

$\theta=55^o$ for $M_s= 1/2$



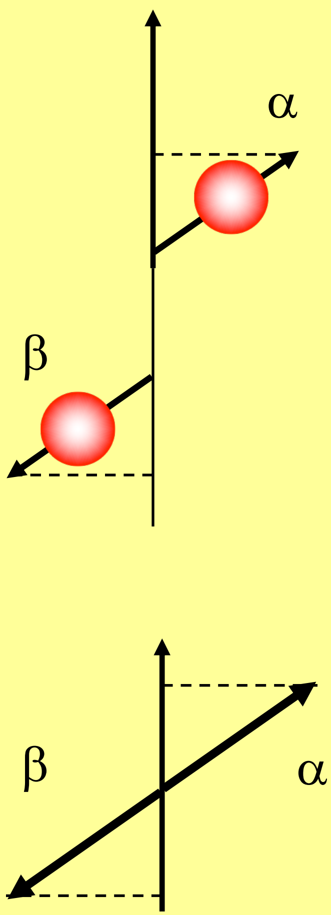
$\theta=125^o$ for $M_s=-1/2$

Two spins of ½: S = 0

Spin multiplicity = 2S+1 = 1

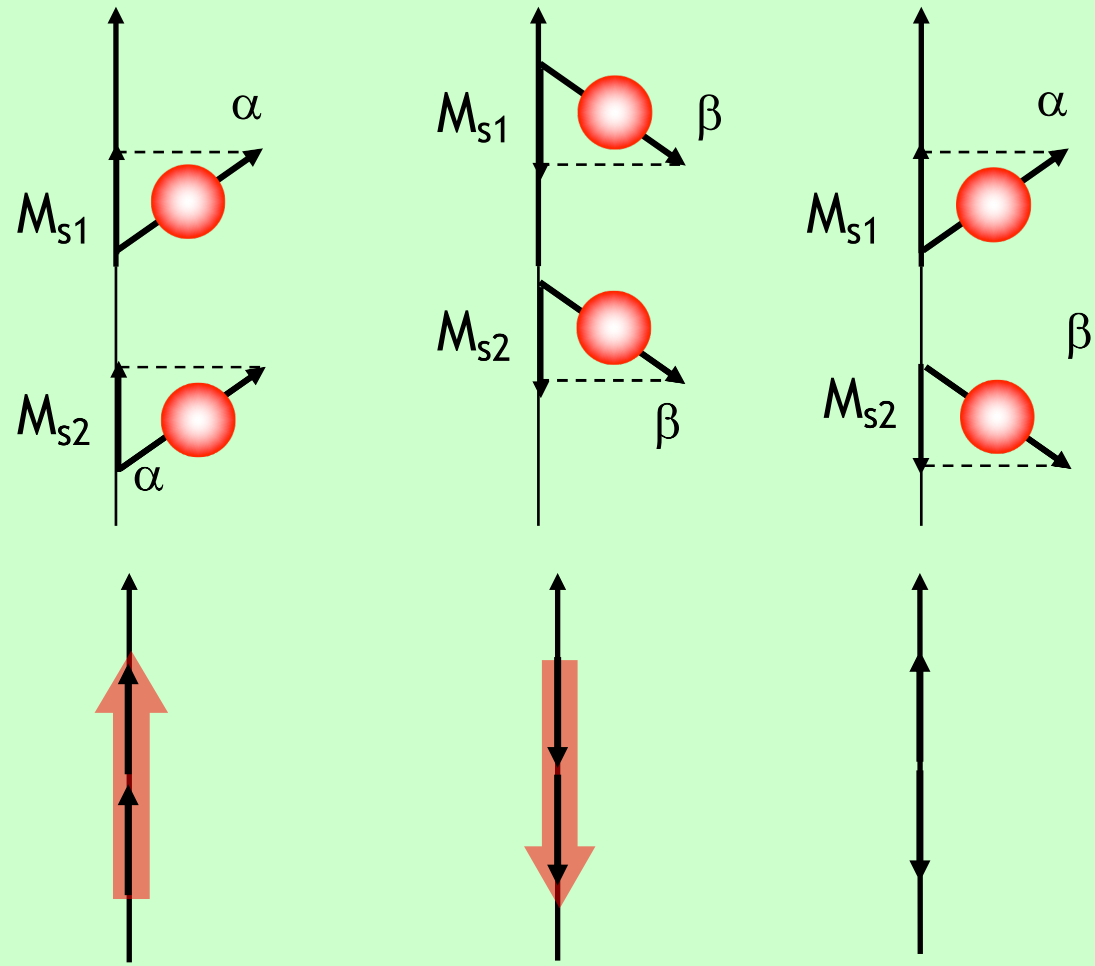
Two spins of ½: S = 1

Spin multiplicity= 2S+1 = 3



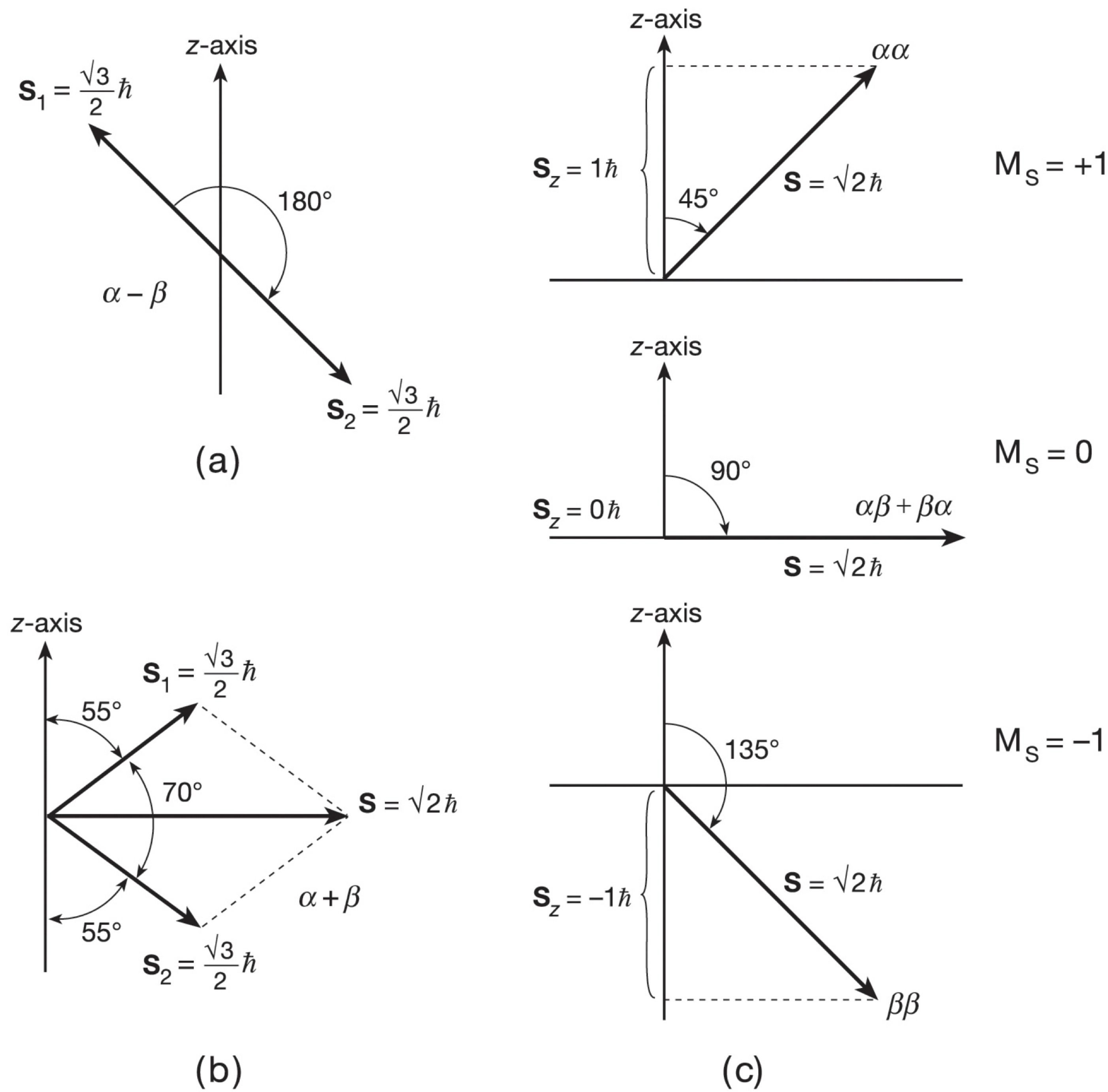
M_S=0

αβ−βα



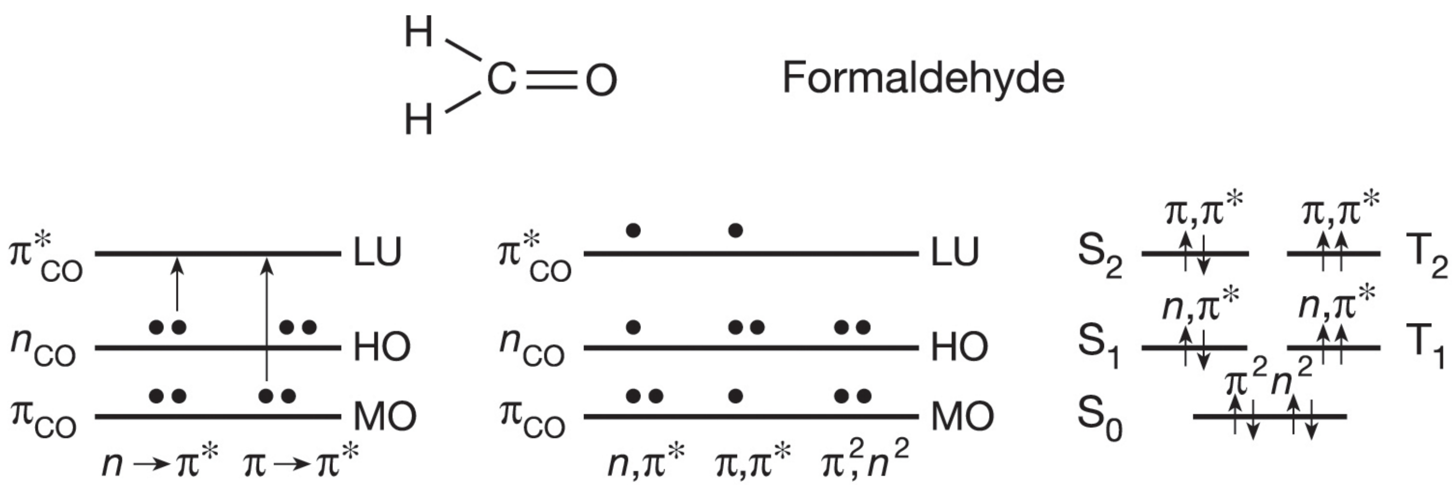
M_S=1 M_S=-1 M_S=0

αα ββ αβ+βα

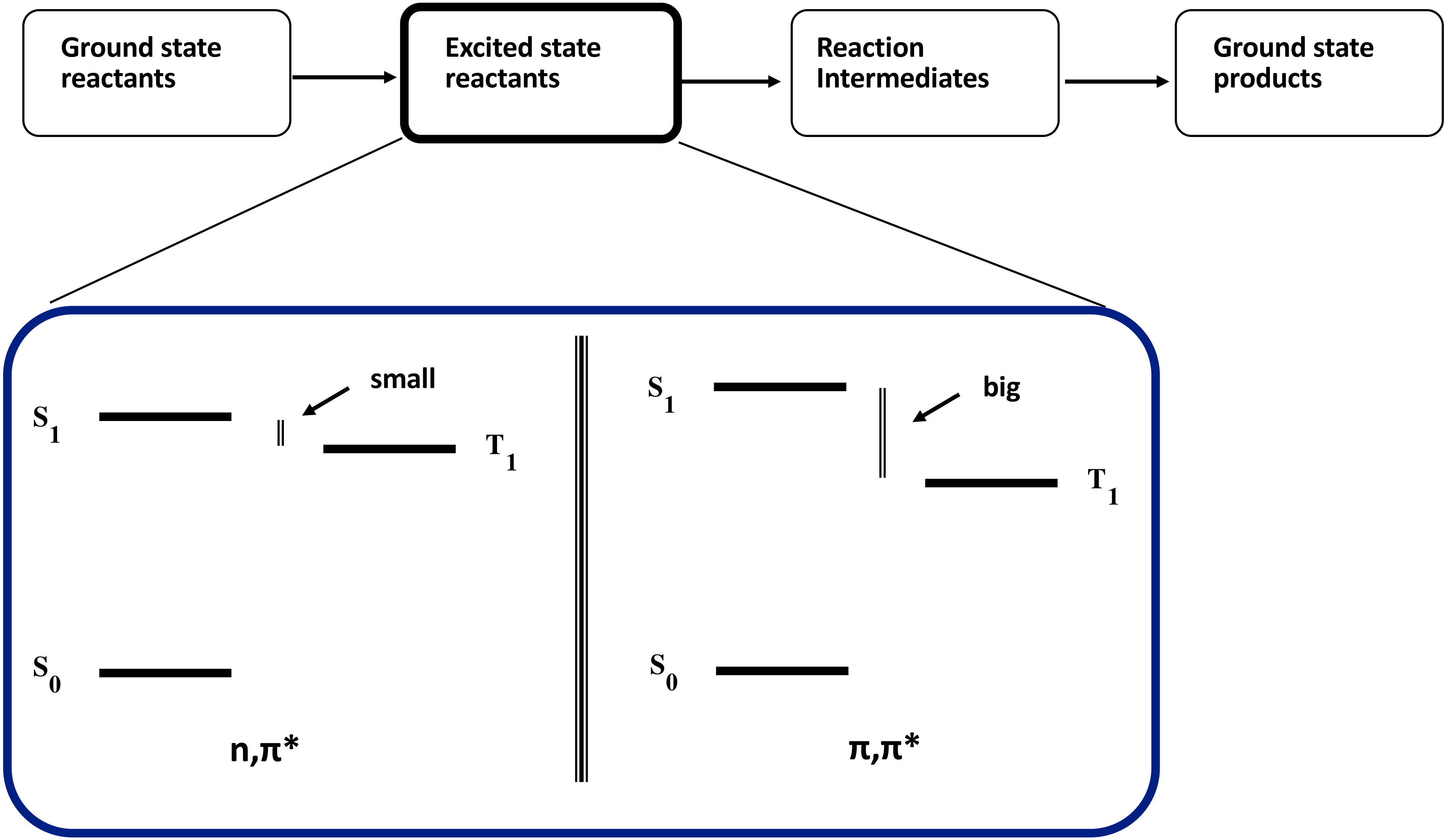


z-axis
S1 = √3/2 ħ
180°
α − β
S2 = √3/2 ħ
(a)
z-axis
S1 = √3/2 ħ
55°
70°
S = √2 ħ
α + β
55°
S2 = √3/2 ħ
(b)
z-axis
αα
Sz = 1ħ
45°
S = √2 ħ
MS = +1
z-axis
90°
Sz = 0ħ
αβ + βα
S = √2 ħ
MS = 0
z-axis
135°
MS = −1
S = √2 ħ
Sz = −1ħ
ββ
(c)

Electronic and Spin Configuration of States



S_1-T_1 energy gap



Why triplets are lower in energy than singlets?

What controls the singlet-triplet energy gap?

$$E_S = E_0(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*)$$

$$E_T = E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*)$$

$$\Delta E_{ST} = E_S - E_T = E_0(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*) - [E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*)]$$

$$\Delta E_{ST} = E_S - E_T = 2J(n,\pi^*)$$

$$J(n,\pi^*) = \langle n\phi(1)\pi^*(2)|e^2/r_{12}|\ n\phi(2)\pi^*(1)\rangle$$

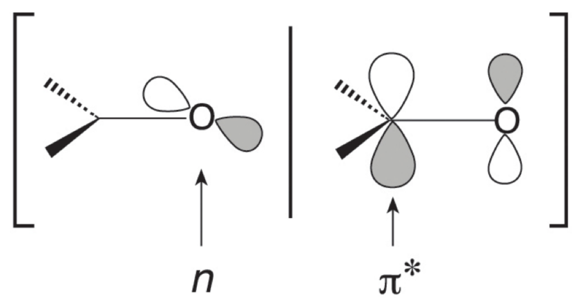
$$J(n,\pi^*) \sim e^2/r_{12} \langle\ n\phi(1)\pi^*(2)|n\phi(2)\pi^*(1) \sim\ \langle\ \phi(1)|\phi(2)\ \rangle$$

overlap integral controls the gap

$$J(n,\pi^*) = \langle n(1)\pi^*(2)|e^2/r_{12}|n(2)\pi^*(1)\rangle$$

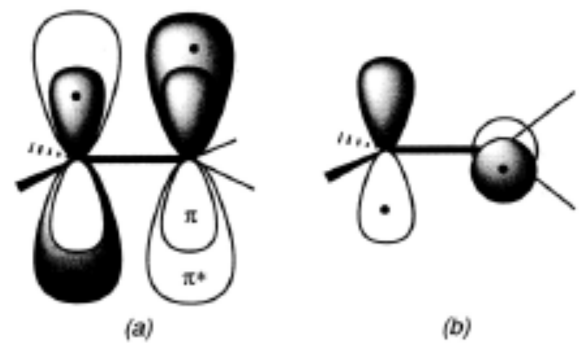
$$J(n,\pi^*) \sim e^2/r_{12}\langle n(1)\pi^*(2)|n(2)\pi^*(1) \sim \langle n|\pi^*\rangle$$

$J_{n,\pi^*} \longrightarrow$

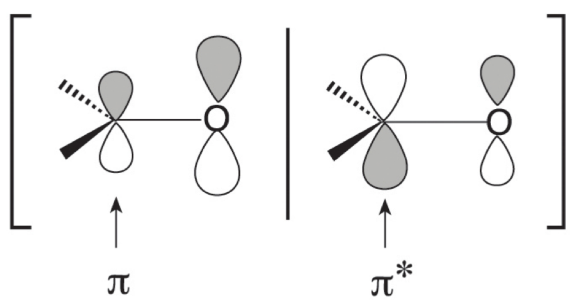


Small orbital overlap between n and π^*

$\langle n|\pi^*\rangle$ Small



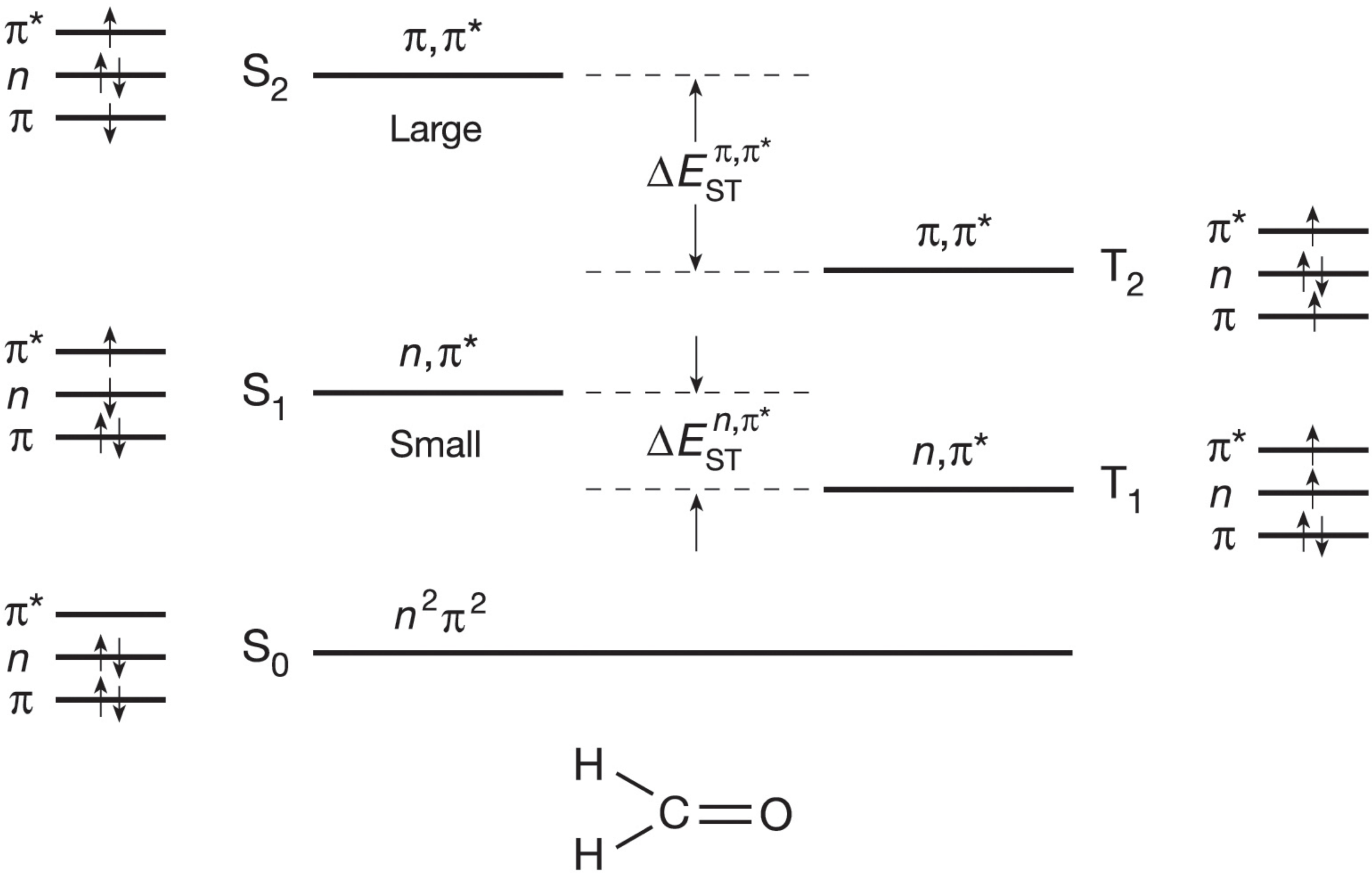
$J_{\pi,\pi^*} \longrightarrow$



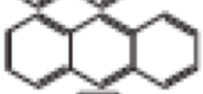
Large orbital overlap between π and π^*

$\langle \pi|\pi^*\rangle$ Large

Energies of singlet and triplet states



S_1-T_1 energy gap: Examples

Molecule	Configuration of S_1 and T_1	ΔE_{ST} (kcal mol^{-1})
$CH_2{=}CH_2$	π,π^*	~ 70
$CH_2{=}CH{-}CH{=}CH_2$	π,π^*	~ 60
$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$	π,π^*	~ 48
	π,π^*	25[a] (52)[b]
	π,π^*	31[a] (38)[b]
	π,π^*	~ 34
	π,π^*	30
$CH_2{=}O$	n,π^*	10
$(CH_3)_2C{=}O$	n,π^*	7
$(C_6H_5)_2C{=}O$	n,π^*	5

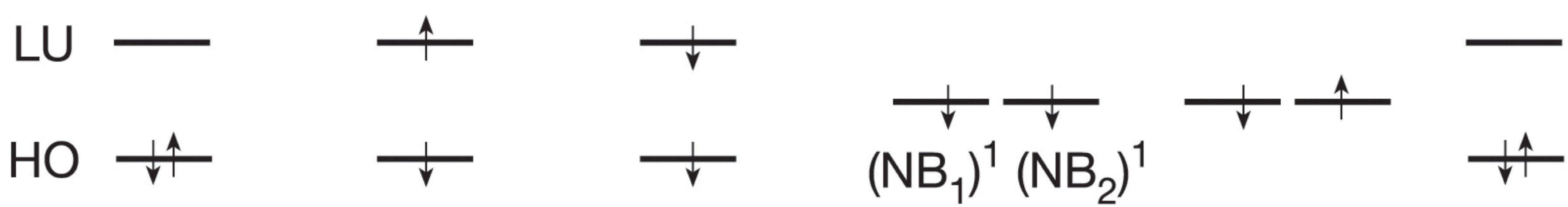
a. ΔE_{ST} between states of different orbital symmetry.
b. ΔE_{ST} between states of the same orbital symmetry.

Singlet States, Triplet States, Diradicals, and Zwitterions: Key Structures Along a Photochemical Pathway from *R to P

$$R \xrightarrow{h\nu} P$$

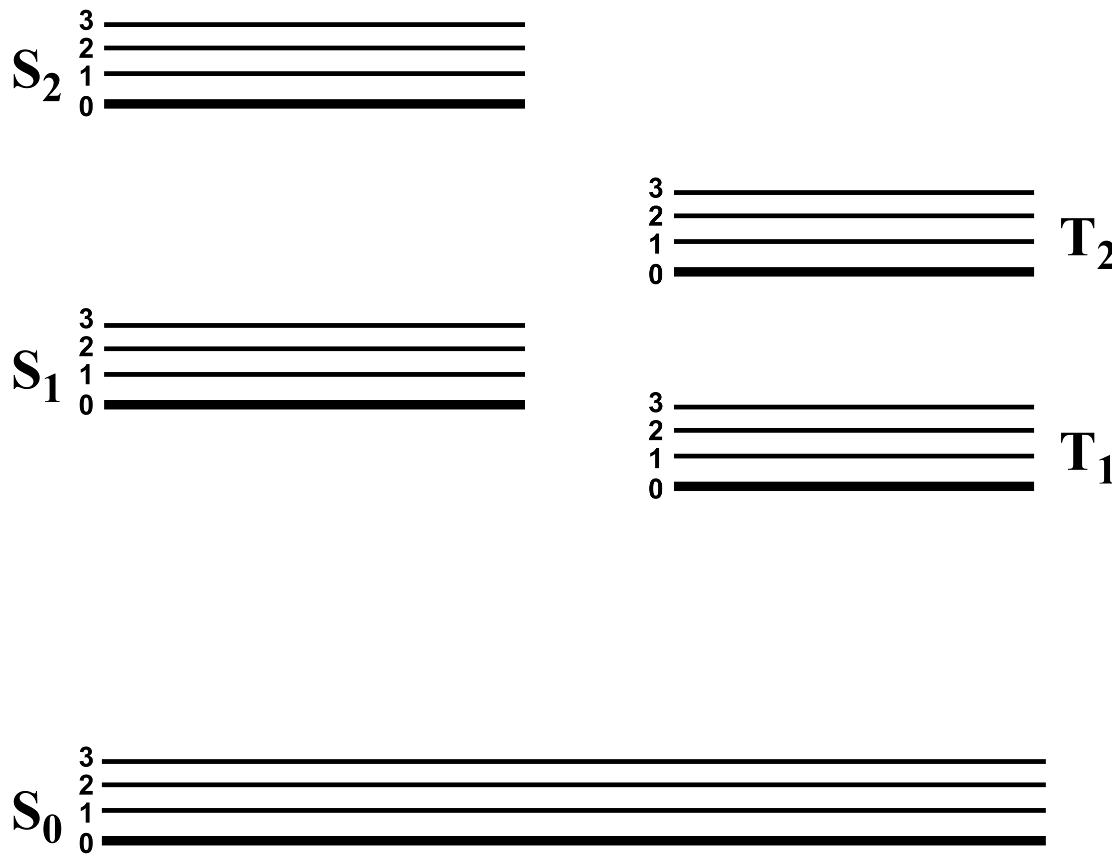
$$R \xrightarrow{h\nu} {}^*R \longrightarrow I \longrightarrow P$$

$$R \xrightarrow{h\nu} {}^{1*}R \xrightarrow{ISC} {}^{3*}R \longrightarrow {}^{3}I \xrightarrow{ISC} {}^{1}I \longrightarrow P$$



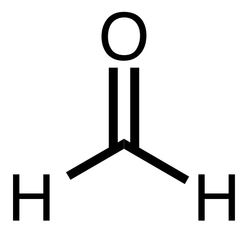
$$R(S_0) \longrightarrow {}^{1*}R(S_1) \longrightarrow {}^{3*}R(T_1) \longrightarrow {}^{3}I(D) \longrightarrow {}^{1}I(D) \longrightarrow P(S_0)$$

Energy level diagram of molecules



Formaldehyde

CH_2O



$$H\Psi = E\Psi$$

$$\Psi \quad = \quad \Psi_o \quad \chi \quad S$$

$$\Psi_0(H_2C{=}O) = (1s_O)^2(1s_C)^2(2s_O)^2(\sigma_{CH})^2(\sigma'_{CH})^2(\sigma_{CO})^2(\pi_{CO})^2(n_O)^2 \; (n_o)^2$$

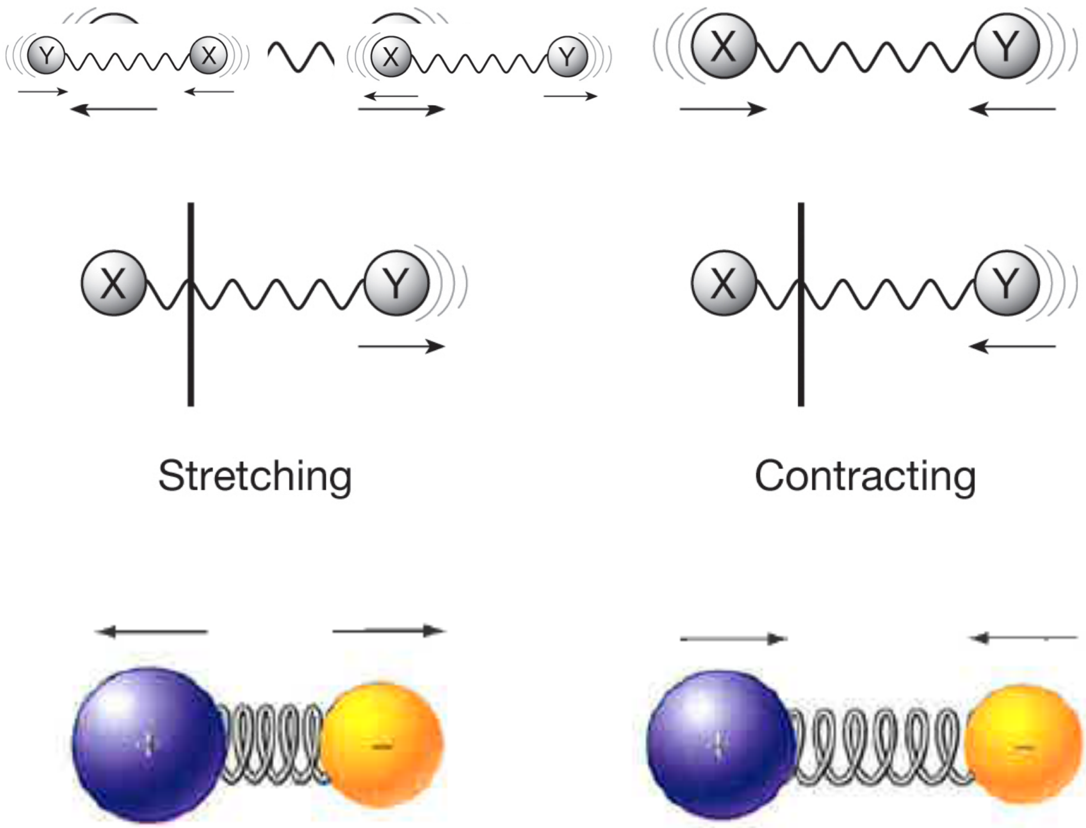
Born-Oppenheimer Approximation

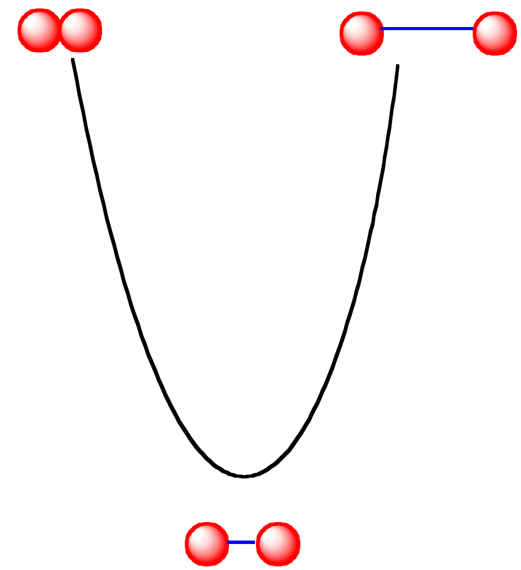
Motions of electrons in orbitals are much more rapid than nuclear vibrational motions

$$\Psi \quad \sim \quad \Psi_0 \, \chi \, \mathbf{S}$$

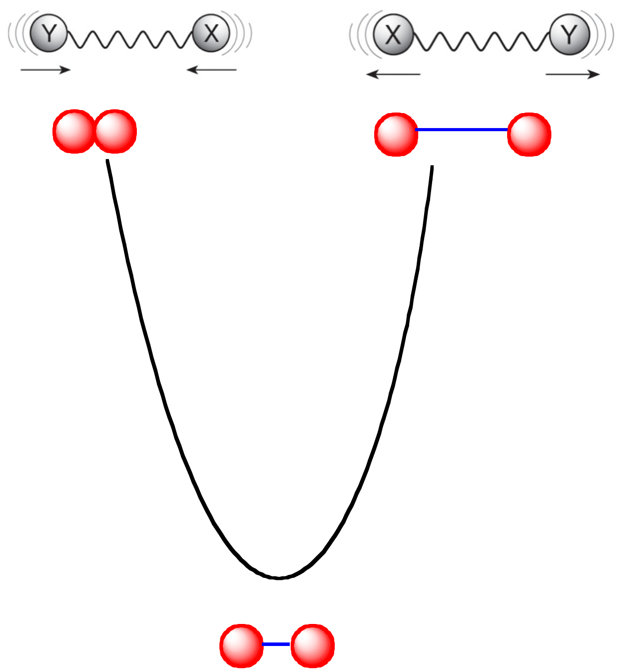
"true" molecular wavefunction **(electronic)(nuclei)(spin)**

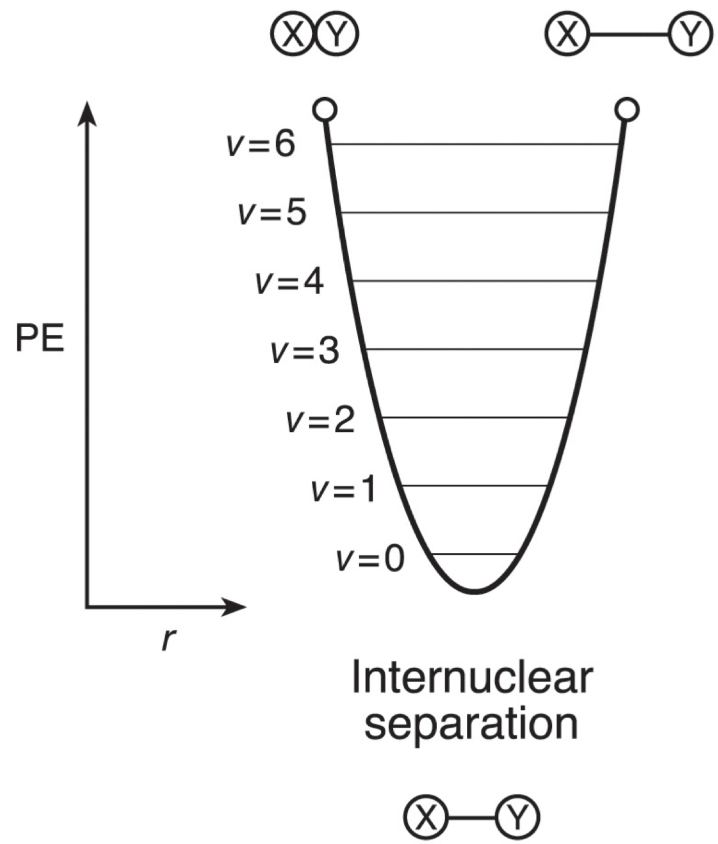
A Model for Vibrational Wavefunctions
The Classical Harmonic Oscillator





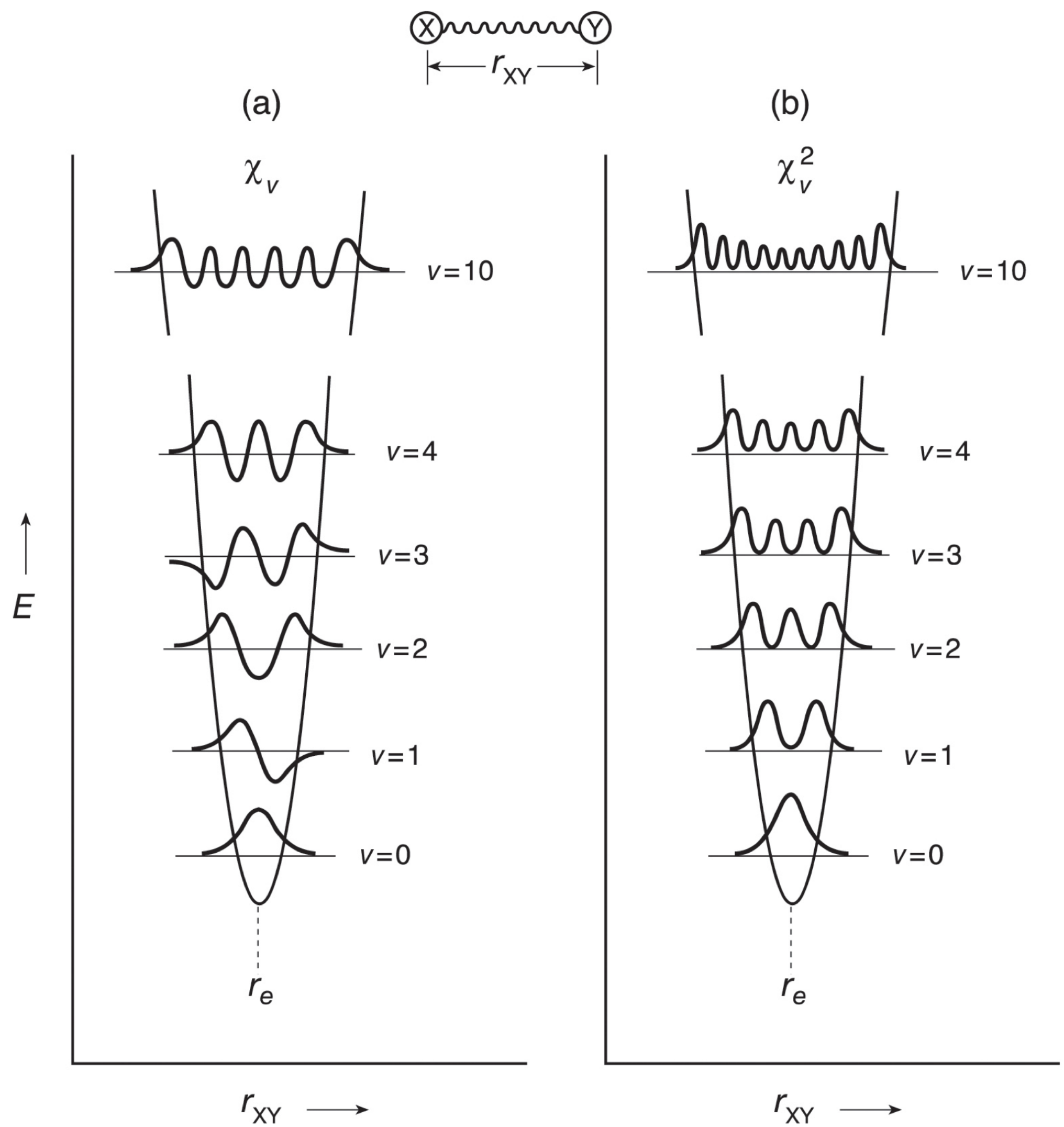
Independent of number of atoms we think in terms of two dimensional drawings



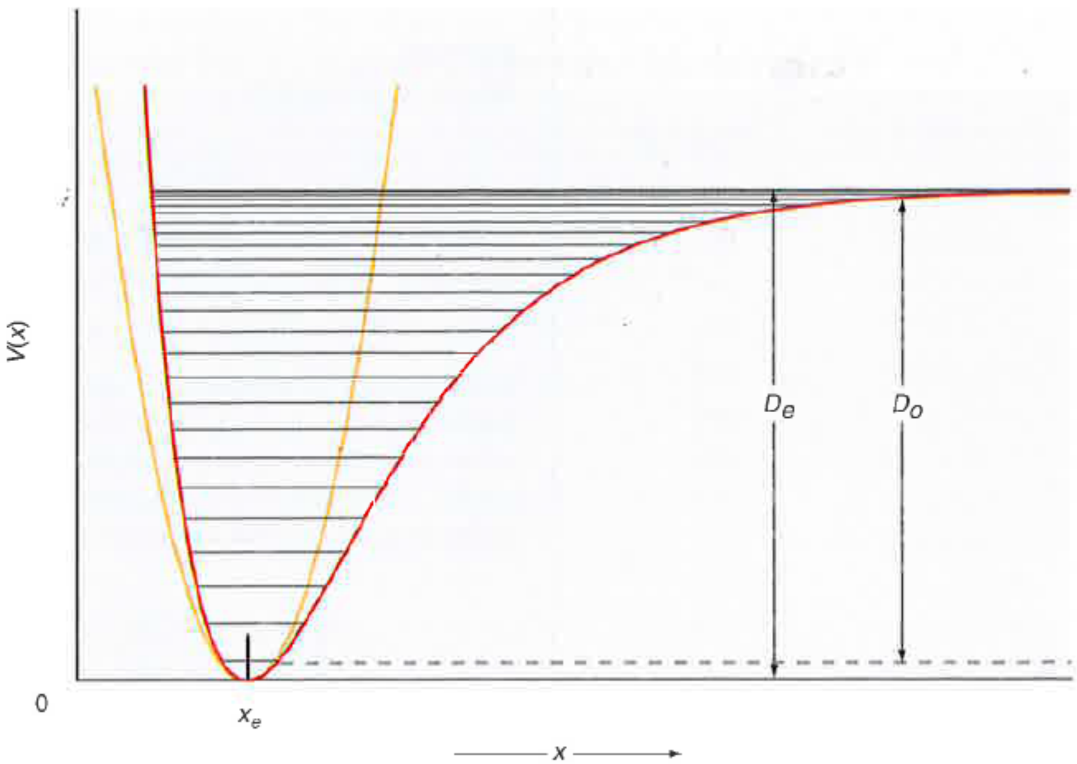


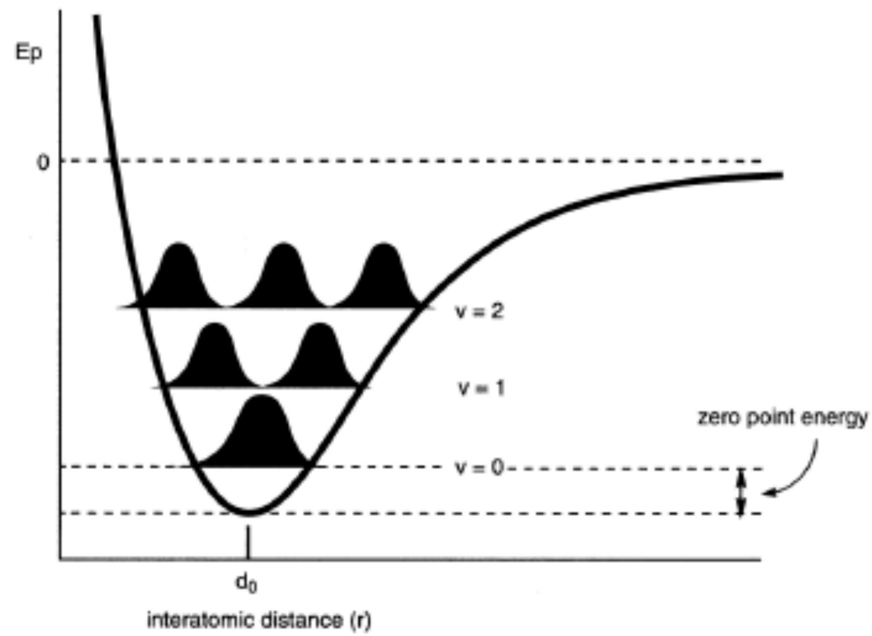
Quantized Harmonic Oscillator

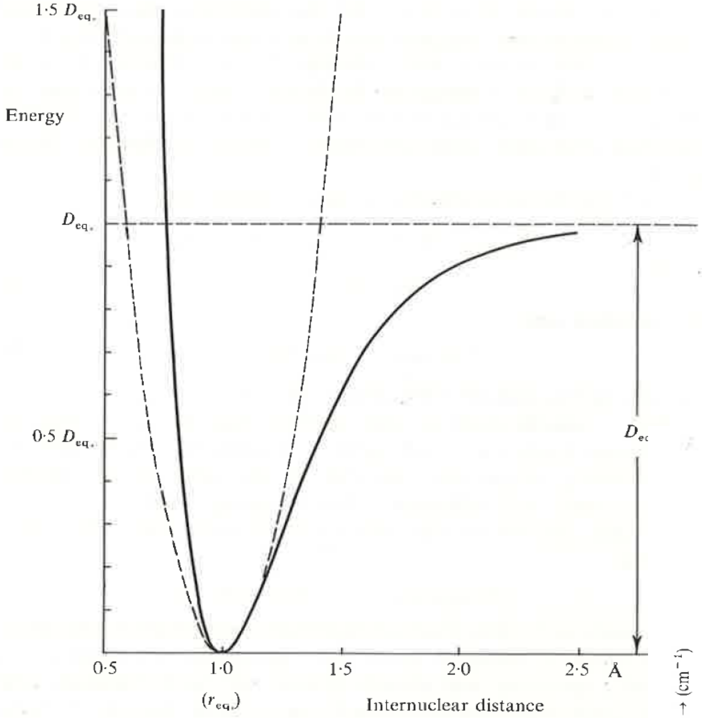
The Quantum Mechanical Version of the Classical Harmonic Oscillator



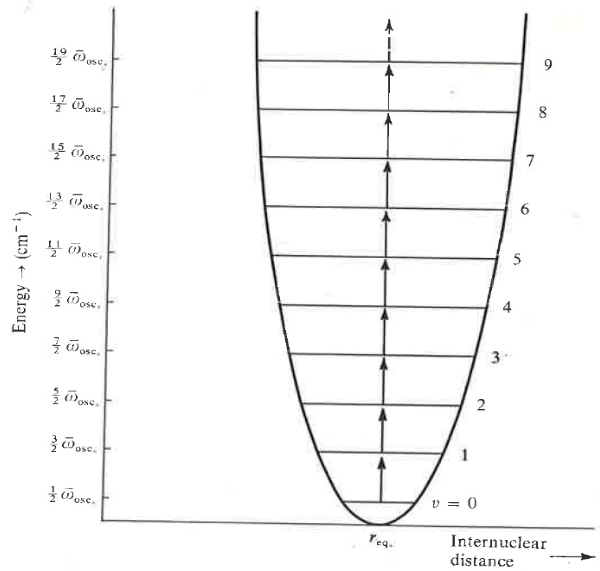
Harmonic and Anharmonic Oscillator



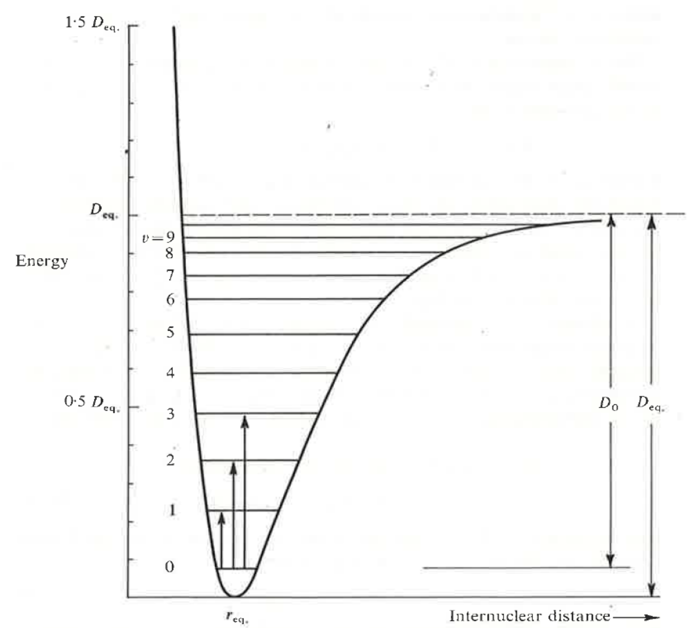




1·5 $D_{eq.}$
Energy
$D_{eq.}$
0·5 $D_{eq.}$
D_{eq}
0·5
1·0
1·5
2·0
2·5 Å
($r_{eq.}$)
Internuclear distance

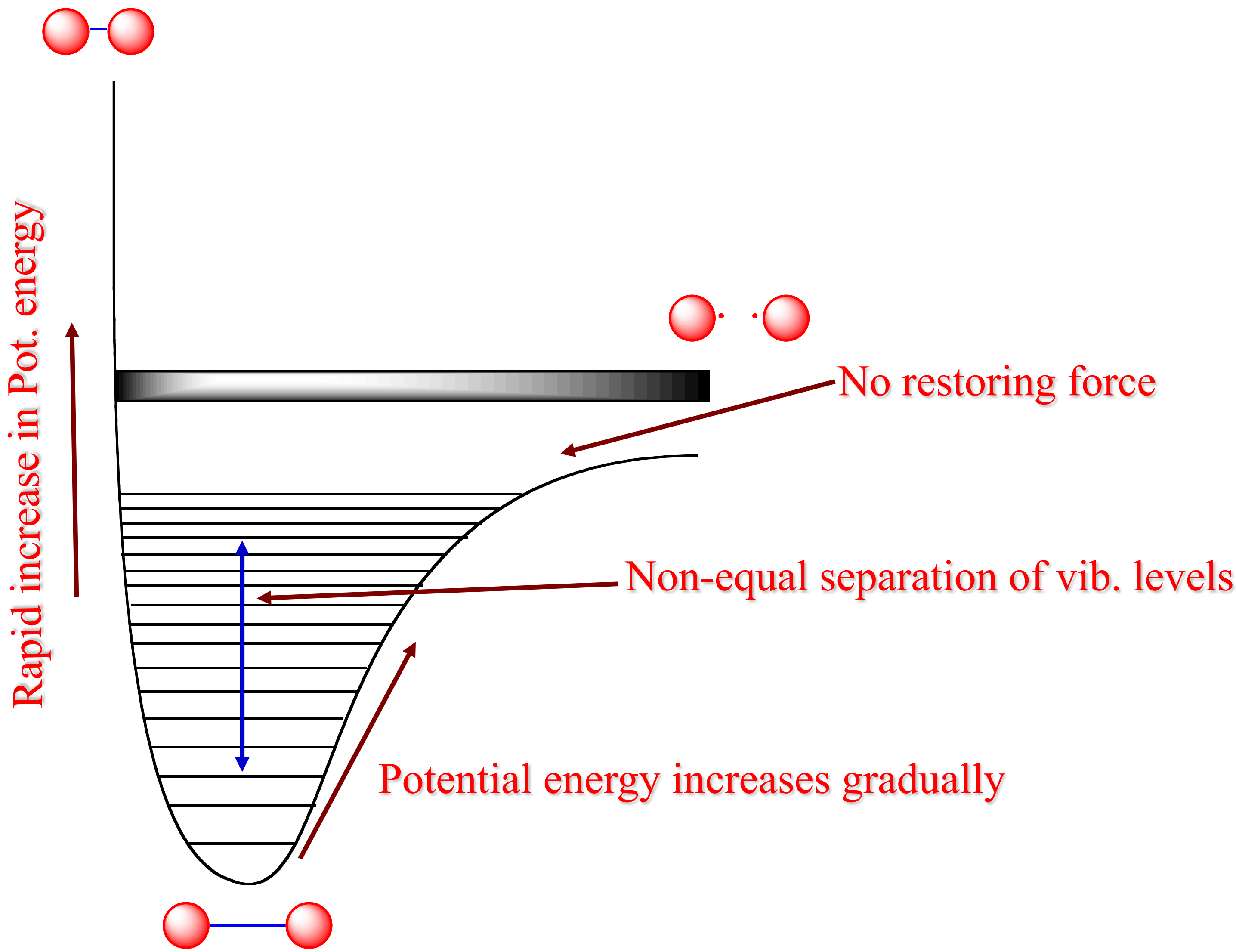


Energy → (cm^{-1})
$\frac{19}{2}\bar{\omega}_{osc.}$
$\frac{17}{2}\bar{\omega}_{osc.}$
$\frac{15}{2}\bar{\omega}_{osc.}$
$\frac{13}{2}\bar{\omega}_{osc.}$
$\frac{11}{2}\bar{\omega}_{osc.}$
$\frac{9}{2}\bar{\omega}_{osc.}$
$\frac{7}{2}\bar{\omega}_{osc.}$
$\frac{5}{2}\bar{\omega}_{osc.}$
$\frac{3}{2}\bar{\omega}_{osc.}$
$\frac{1}{2}\bar{\omega}_{osc.}$
9
8
7
6
5
4
3
2
1
$v = 0$
$r_{eq.}$
Internuclear distance

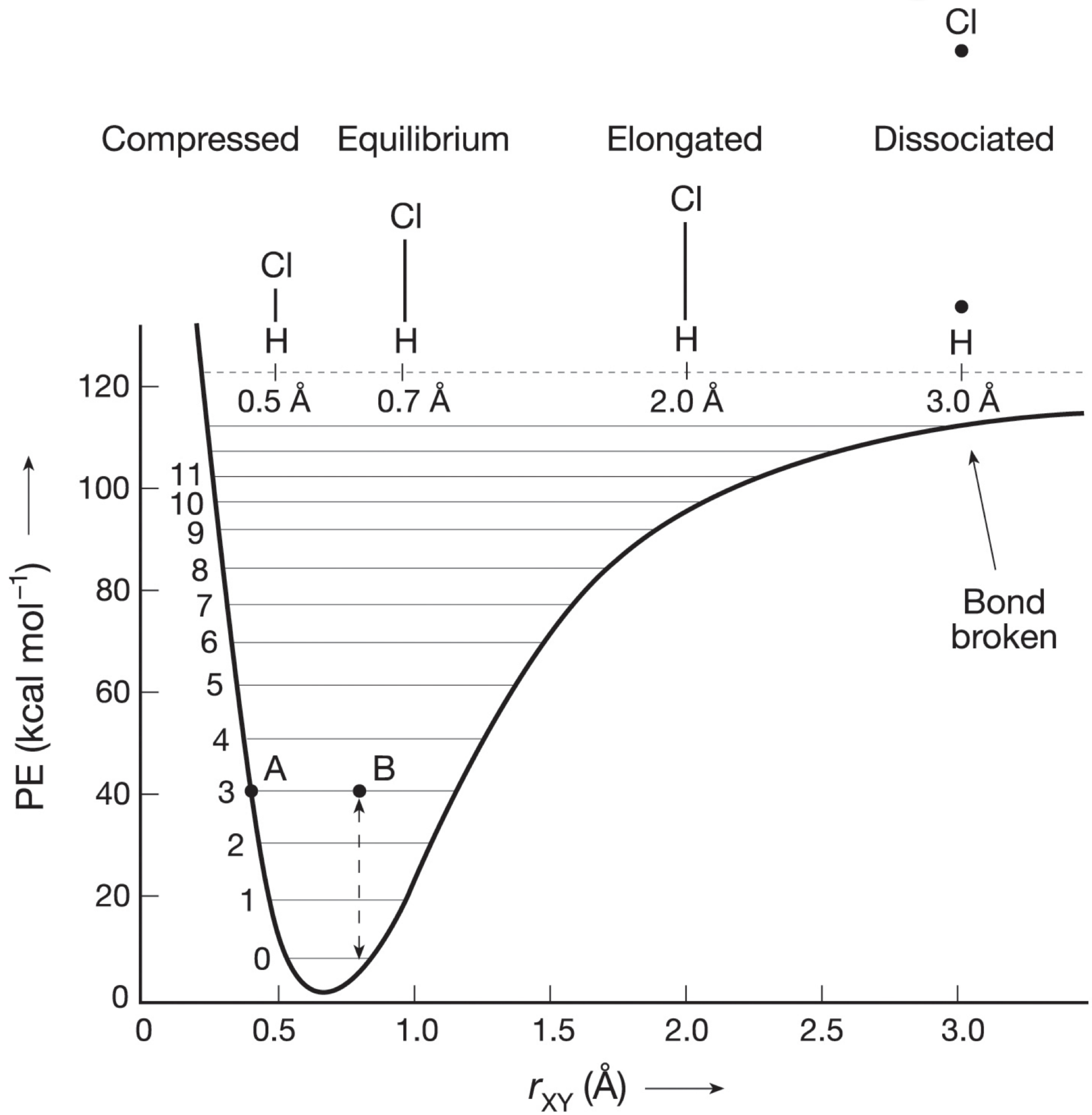


1·5 $D_{eq.}$
$D_{eq.}$
Energy
0·5 $D_{eq.}$
$v = 9$
8
7
6
5
4
3
2
1
0
D_0
$D_{eq.}$
$r_{eq.}$
Internuclear distance

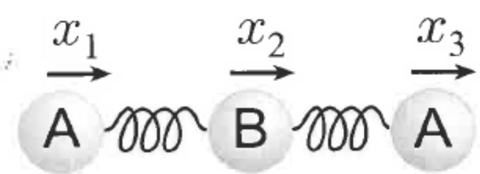
The Anharmonic Oscillator

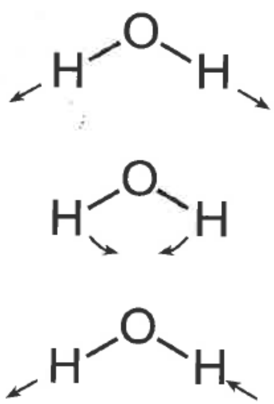


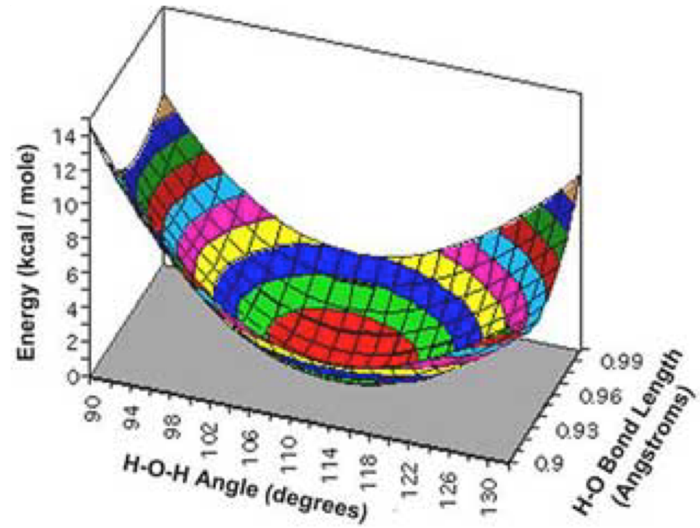
The Anharmonic Oscillator: e.g., HCl



Representation of Polyatomic Molecules







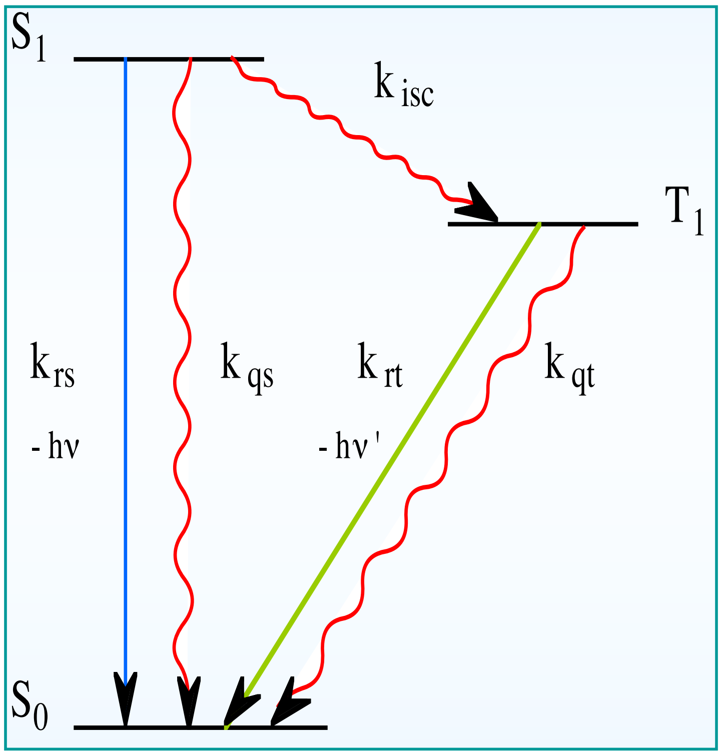
Water

To represent molecules with more than three atoms one needs 3N–6 space

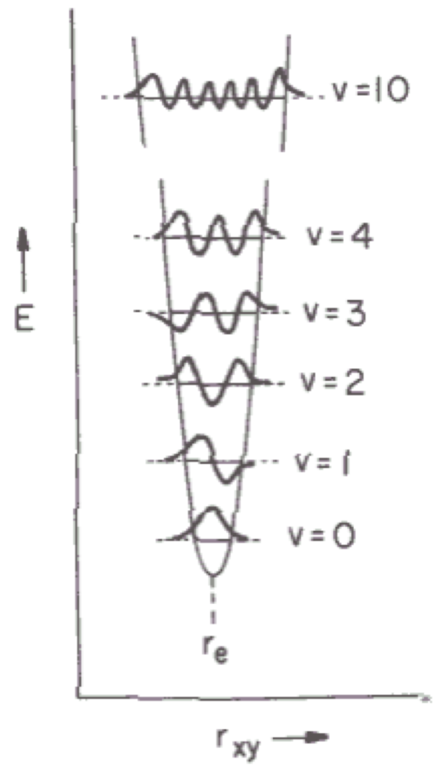
Polyatomic molecules are represented in two or three dimensional space.

What may appear to be a minimum, barrier or saddle point in one subspace may turn out to be nothing of the kind when viewed in another cross section

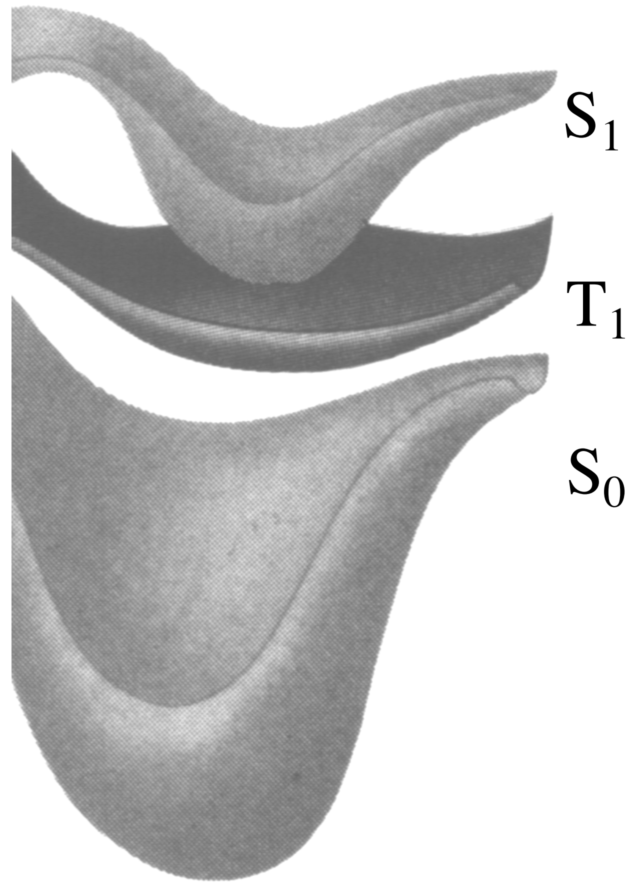
Visualizing molecules in ground and excited states



Molecule represented
in one dimension



Molecule represented
in two dimensions



Molecule represented
in three dimensions