SRI AKILANDESWARI WOMEN’S COLLEGE

DEPARTMENT OF CHEMISTRY

TOPIC: PHOTOCHEMISTRY

CLASS: III – B.SC., CHEMISTRY

PREPARED BY:
MR. D. PRAKASH, ASSISTANT PROFESSOR,

DEPARTMENT OF CHEMISTRY.

Photochemistry

Lecture 1

Electronic excitation of atoms and molecules

What is Photochemistry about?

- Photochemistry is concerned with the changes in chemical and physical behaviour of molecules following absorption of one (or more) photons.
- Primarily consider absorption of visible/UV although IR absorption may also change chemical behaviour
  - Mainly concerned with electronic excitation, usually accompanied by some vibrational excitation (and rotational in gas phase) excitation.

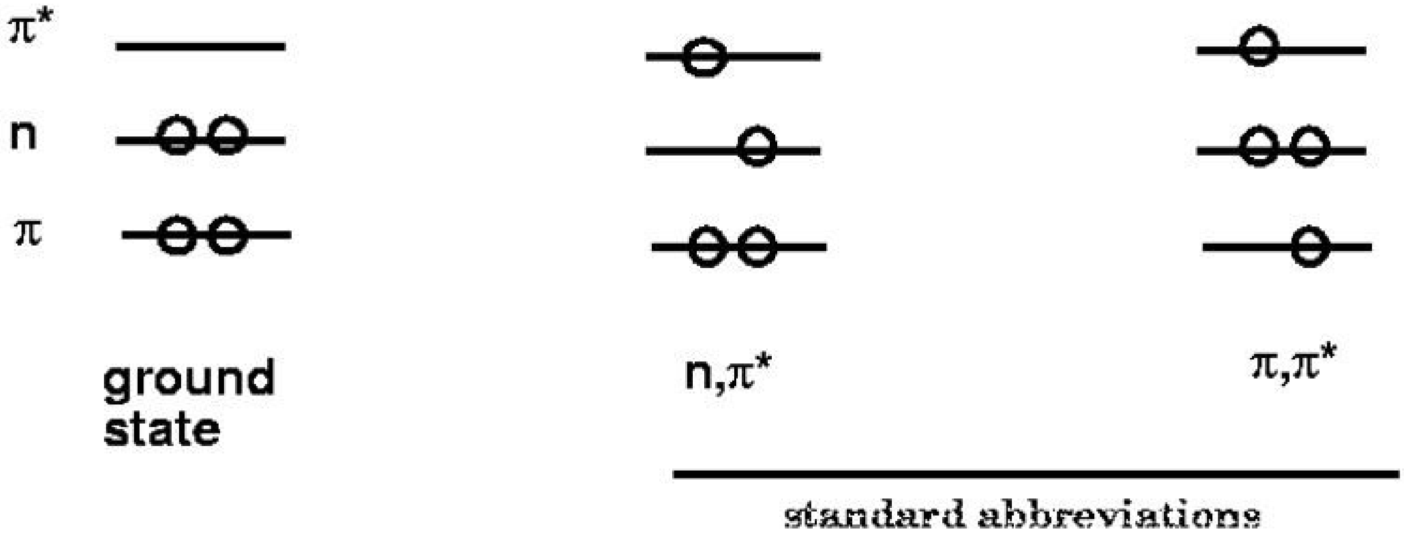
Chemistry of excited states

- Electronic excitation

⇒ change of molecular orbital occupancy
⇒ increased energy
⇒ change of bonding characteristics and possibly geometry
⇒ change of charge distribution
⇒ possible changes of resultant electron spin, orbital symmetry

⇒ Change of
  Lifetime
  Electron donating/accepting ability
  Acid/base characteristics
  Symmetry or energetic constraints on reaction

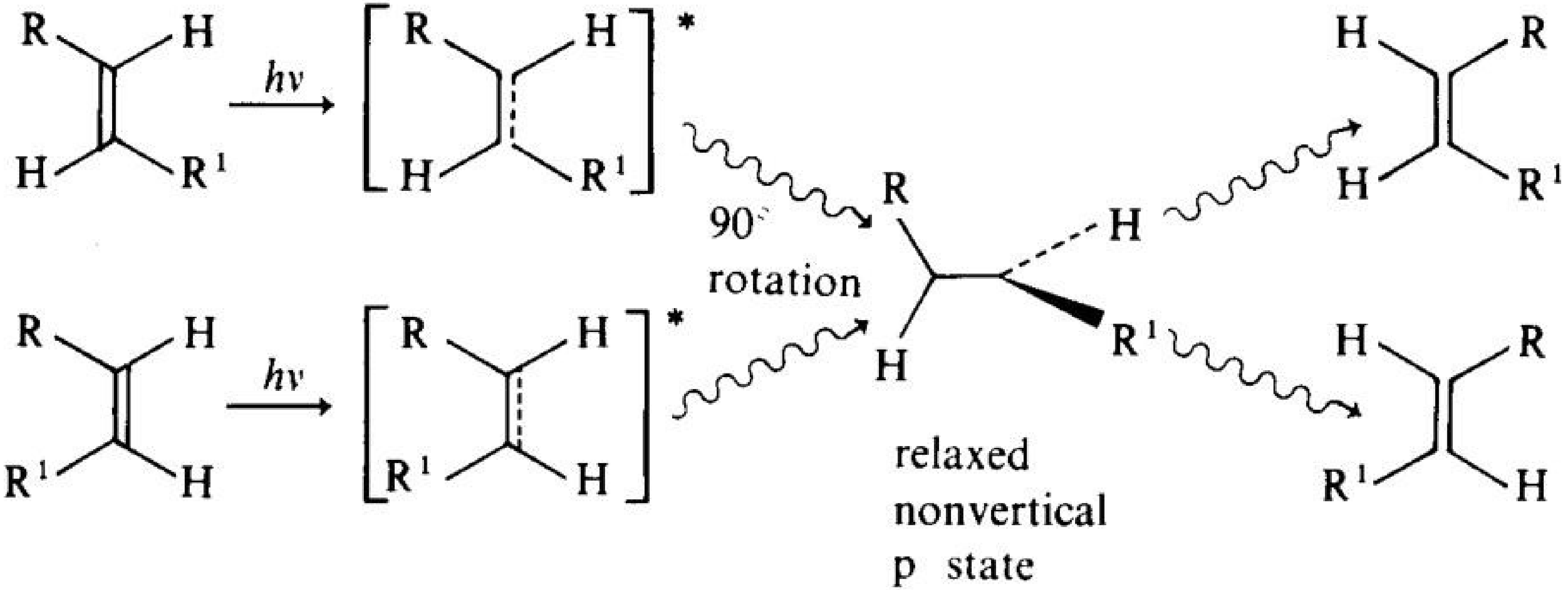
Excited states of formaldehyde



Resembles alkoxy radical

No free radical properties

Geometry change in alkene excited states



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Stability of electronically excited molecules

- Typically large molecules survive for « 1μs in the state to which they are excited.

- Decay processes:
  - Reaction (unimolecular or bimolecular)
  - Energy transfer (intramolecular or intermolecular)
  - Radiative (fluorescence/phosphorescence)

- Interplay between decay processes determines the chemistry

Processes for producing electronically excited atoms and molecules

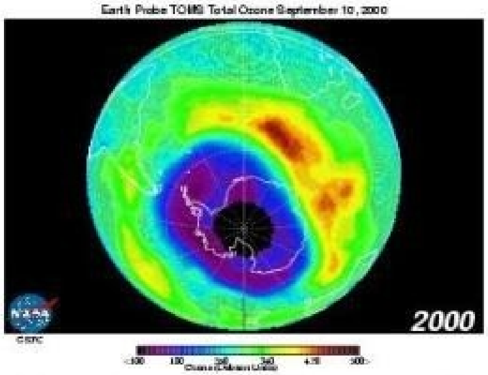
- Radiative excitation
- Electron impact excitation
- Collisional energy transfer
- Exothermic chemical processes (or reactions of excited species)

Significance of photochemical processes

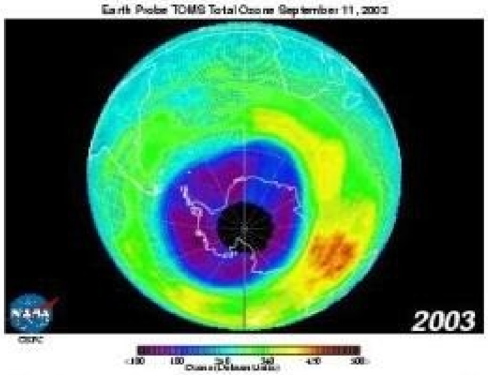
- Atmospheric and astrophysical chemistry
- Photosynthesis
- Lasers
- Solar energy
- Semiconductor etching
- Biological damage – skin cancer etc
- Vision
- New chemistry
- Chemical Dynamics

Ozone hole

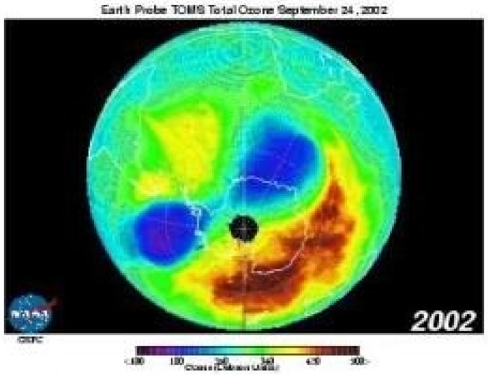
Second Largest Ozone Hole Area



Maximum Area = 11.5 million square miles

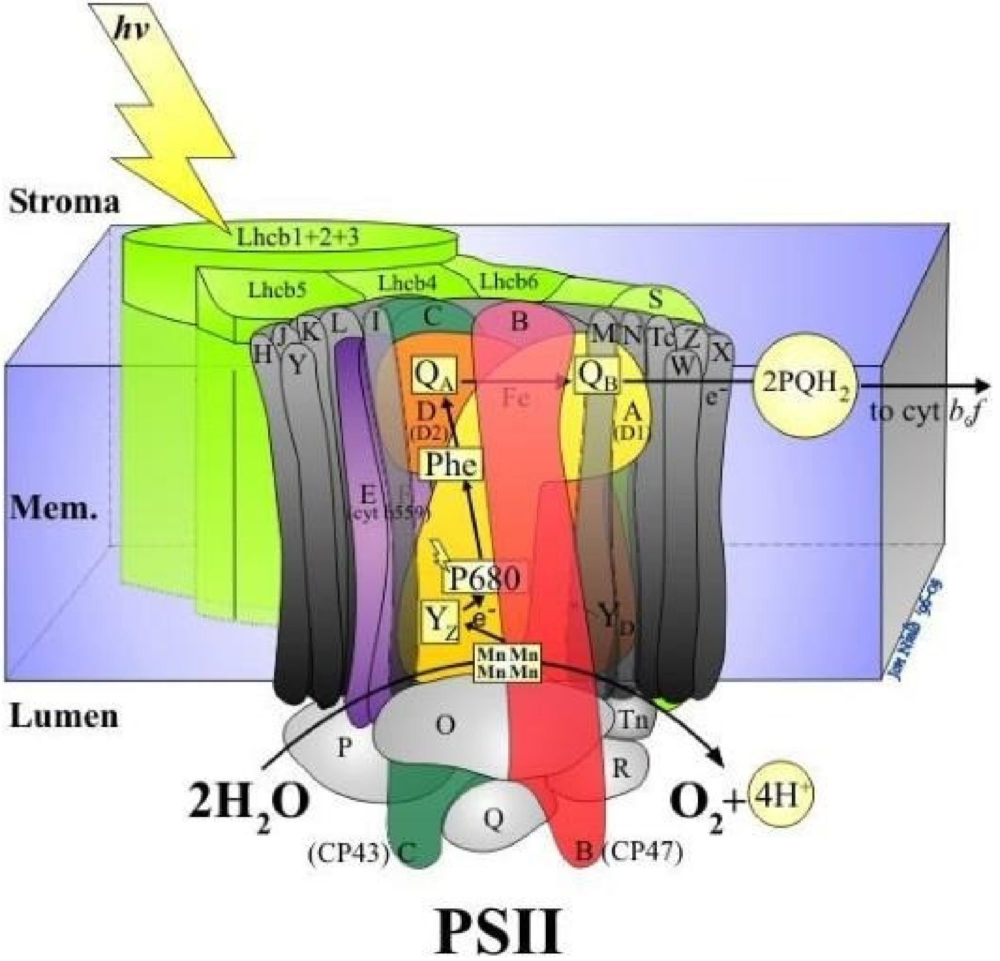


Maximum Area = 10.9 million square miles



Maximum Area = 8.1 million square miles

Photosynthesis –photosystem II



Semiconductor etching

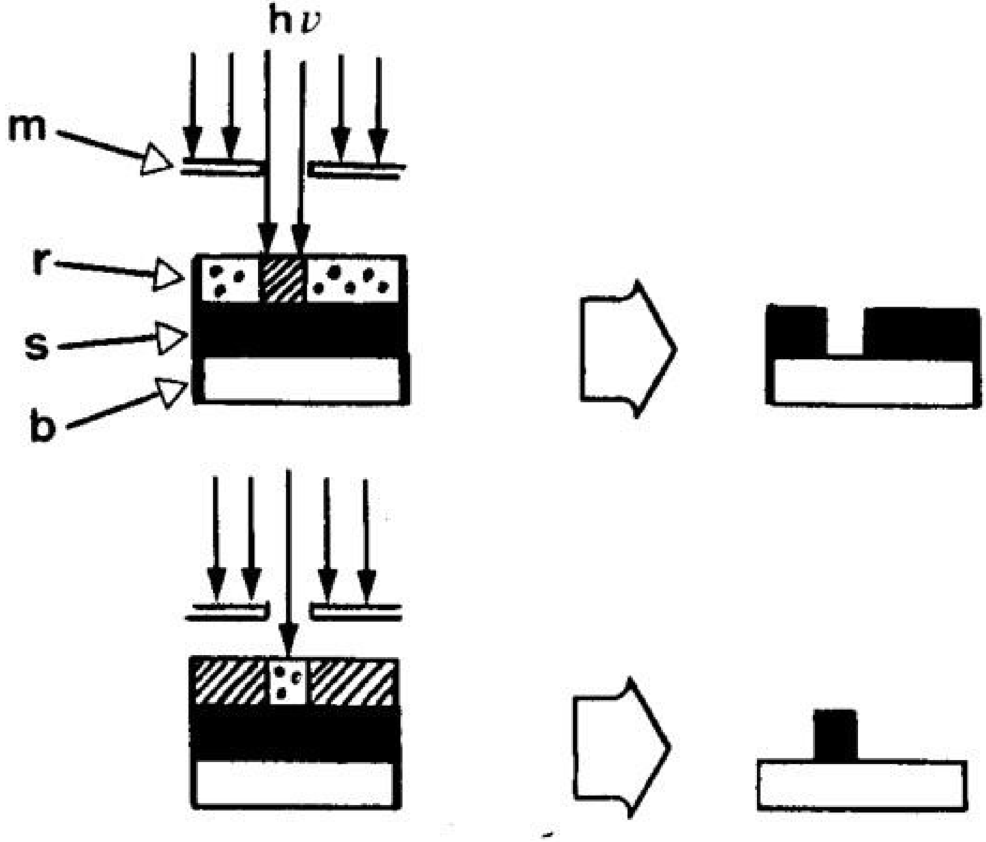


Figure 6.8 *Photo-resist technology. A metal substrate (s) deposited on an insulator base (b) is protected by the resist (r). Irradiation of the resist through a mask (m) results in photoinduced polymerization or polymer destruction*

Chemical dynamics

- A photodissociation process can be considered as half a collision:

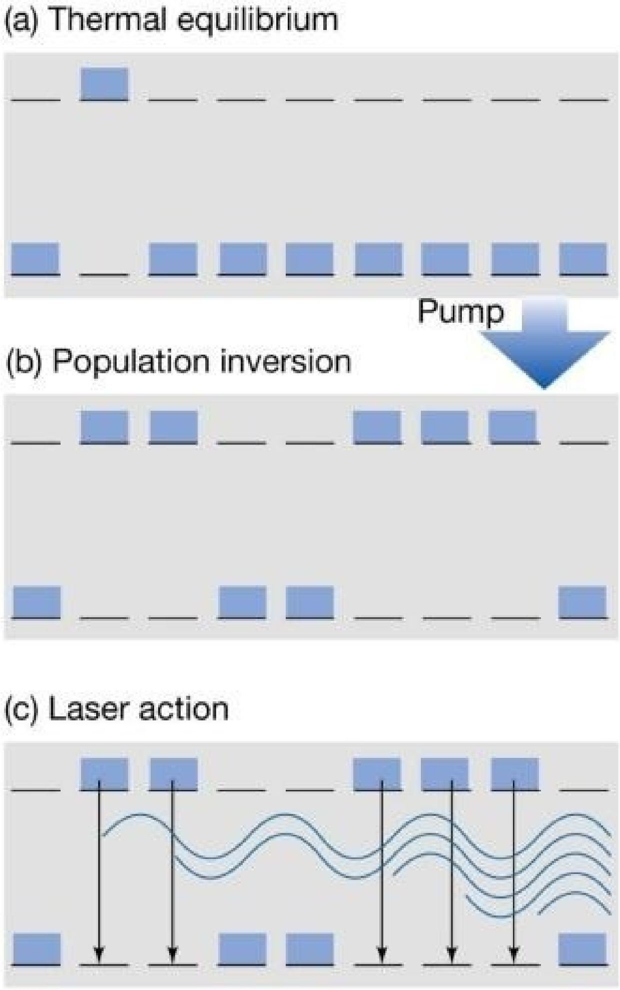
Bimolecular reaction (full collision)

$A + BC \rightarrow ABC^* \rightarrow AB + C$

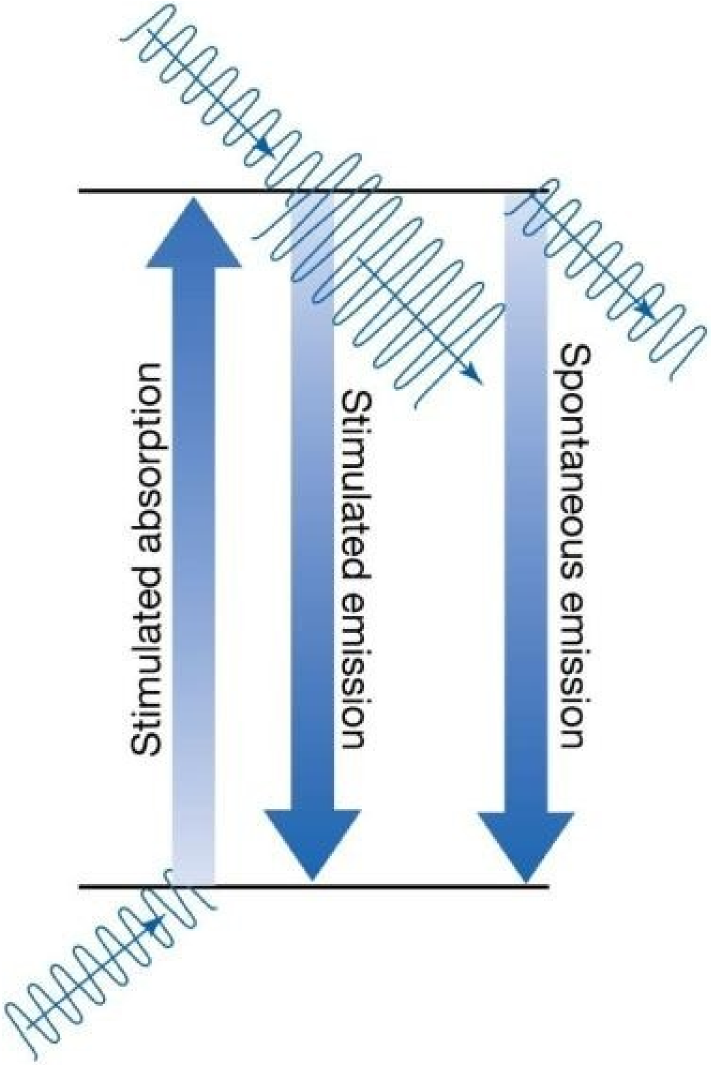
Photodissociation (half collision)

$$\begin{aligned} ABC + h\nu \rightarrow ABC^* &\rightarrow AB + C \\ &\rightarrow A + BC \end{aligned}$$

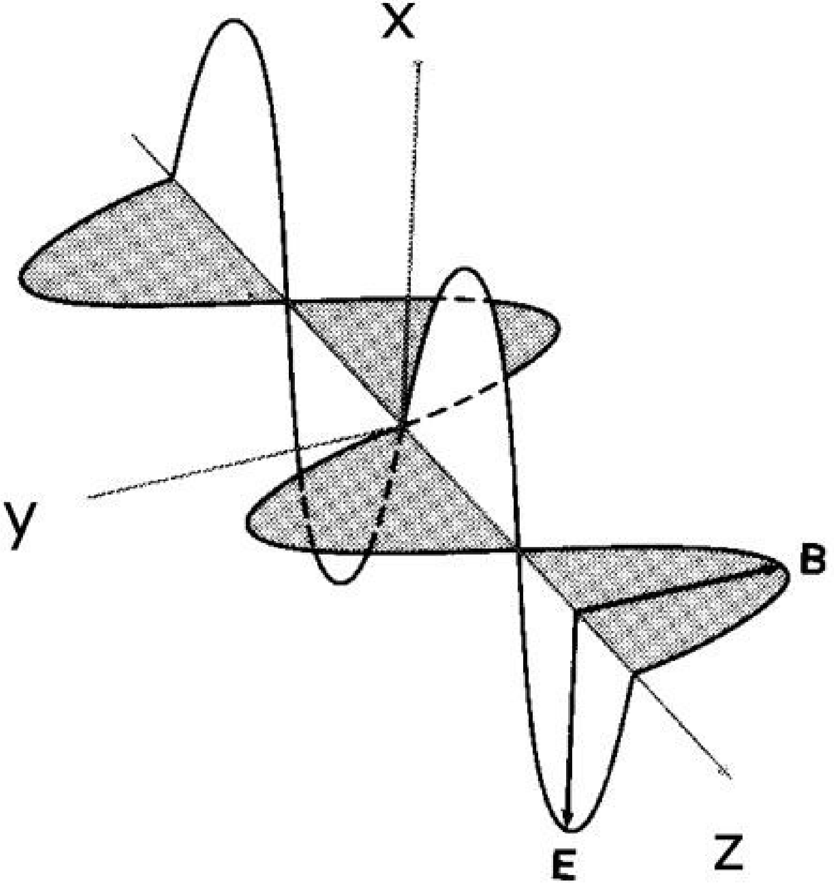
Lasers


(a) Thermal equilibrium
Pump
(b) Population inversion
(c) Laser action

Absorption and emission of radiation



Electromagnetic wave



Interaction of atoms and molecules with electromagnetic radiation

- Classical potential energy of electric dipole moment in an electric field

$$V = -\boldsymbol{\mu}.\mathbf{E}$$

- EM radiation is an oscillating electric (and magnetic field)

$$E(t) = E_0 \cos(\omega t)$$

- In quantum mechanics this adds an extra term to PE part of Hamiltonian

$$H = H_0 + H'$$

$$H' = -\boldsymbol{\mu}.\mathbf{E} = -\mu_x E_{0x} \cos \omega t$$

Transition probability

- Under the influence of a time-dependent Hamiltonian, the wavefunction evolves with time.

$$\Psi_i \xrightarrow{h\nu} a_i(t)\Psi_i + a_f(t)\Psi_f$$

- Probability that molecule is in state *f* after time *t* (see e.g., Atkins MQM Ch 6, or Gilbert and Baggott Ch 3)

$$P_f = \left|a_f\right|^2 \approx {E_{0x}}^2 \left|R_{if}\right|^2 t^2 / \hbar^2$$

- R_{if} is the transition moment and determines the selection rules.

$$R_{if} = \int \Psi_f^* \mu \Psi_i d\tau$$

Einstein transition probabilities

- Consider non-monochromatic radiation.
  - Radiation density ρ is energy of radiation field per unit energy interval per unit volume (energy = hν) - related to intensity I.

$$\rho(E)dE = \frac{I(E)dE}{c}$$

- Total rate of stimulated transition i → f for initial population N_i

$$W_{if} = N_i B_{if} \rho(E_{if}) \qquad B_{if} = \frac{R_{if}{}^2}{6\varepsilon_0 \hbar^2}$$

- Einstein identified additional mechanism of spontaneous emission (due to zero-point fluctuations of radiation field)

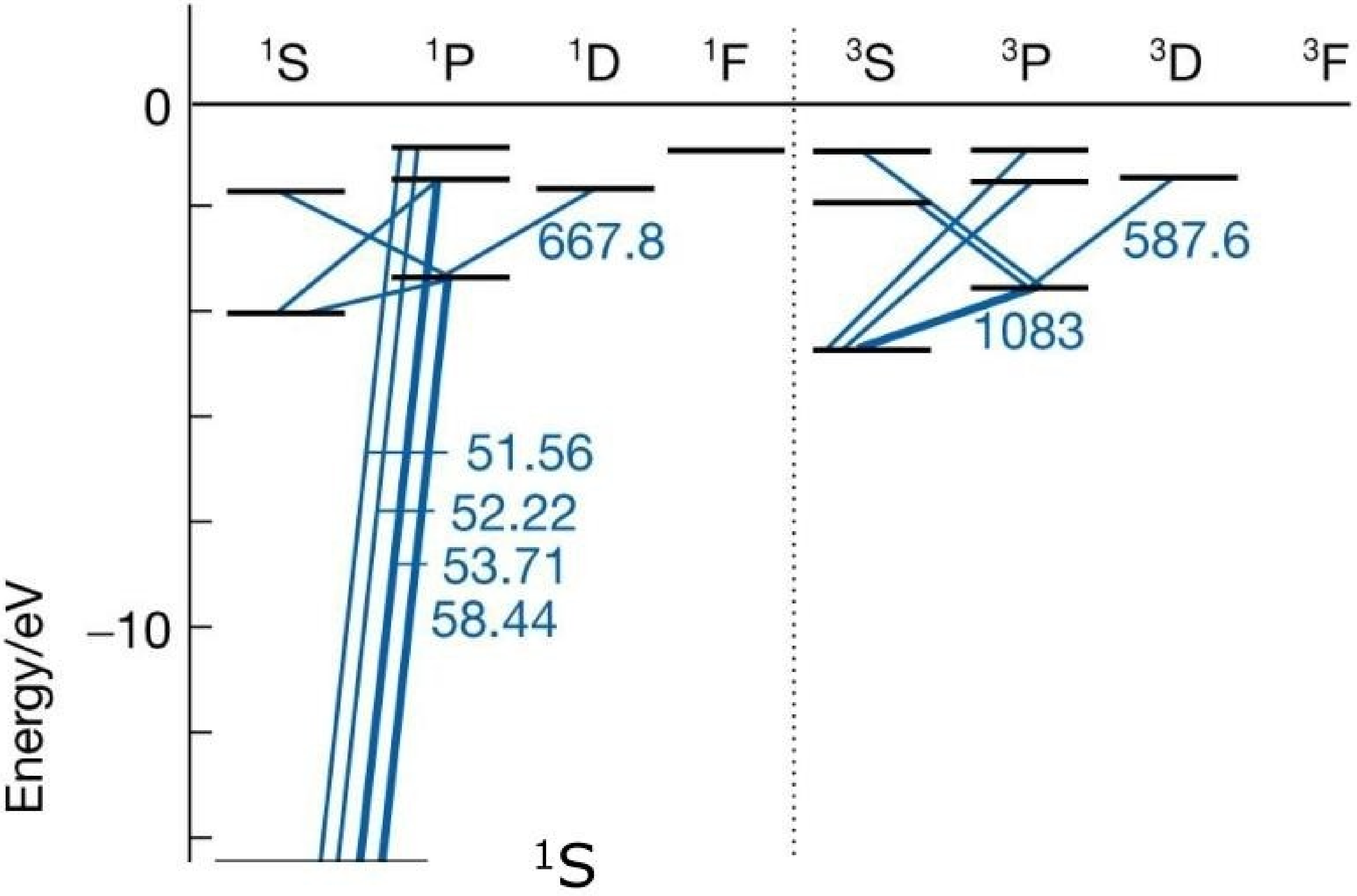
$$\frac{-dN_i}{dt} = N_i B_{if} \rho(E_{if}) - N_f B_{fi} \rho(E_{if}) - N_f A_{fi}$$

$$A_{fi} = \frac{8\pi h \nu_{fi}^3}{c^3} B_{fi} \qquad B_{fi} = B_{if}$$

Photoexcitation of atoms

- Selection rules (Russell-Saunders coupling)
- $\Delta\ell = \pm 1$ (for one-electron change)
- $\Delta L = 0, \pm 1$ (resultant orbital angular momentum)
- $\Delta S = 0$ (resultant spin angular momentum)
- $\Delta J = 0, \pm 1$, but not $0 \rightarrow 0$ (total angular momentum)

Helium atomic transitions



How well do these selection rules work?

- $\Delta\ell = \pm 1$ (for one-electron change) <u>strong rule</u> – combination of symmetry and angular momentum conservation
- Radiative lifetime of 1s2s ($^1S_0$) state of He is 20 ms, 1s2s ($^3S_1$) 8000 s (cf 1s2p($^1P_1$) state 0.5 ns)

- $\Delta J = 0, \pm 1$ (but not $0 \to 0$) <u>strong rule</u>
- conservation of angular momentum for one photon absorption
- Breaks down if J no longer well-defined
  - If electric or magnetic field present
  - If J is not the total angular momentum (nuclear spin coupling)

Weaker selection rules

- $\Delta S=0$
- $\Delta L=0,\pm 1$

- Transitions with e.g., $\Delta S=0$ or $\Delta L=2$ only forbidden insofar as S and L are well-defined quantum numbers.

These selection rules become progressively weaker as the atomic number increases and spin-orbit coupling gets stronger.

Spin Orbit Coupling

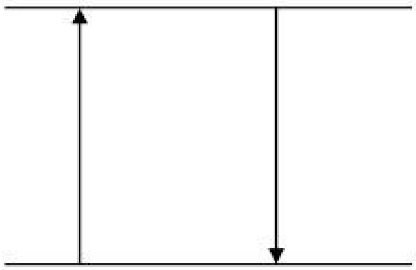
- The spin-orbit coupling part of the Hamiltonian operator leads to
  - Splitting of terms such as ^3P (J = 1,2,3)
  - A perturbation between terms such as ^1P and ^3P arising from the same configuration (subject to conservation of J)

    i.e., between $^1P_1$ and $^3P_1$
- The interaction between terms such as $^3P_1$ and $^1P_1$ causes a mixing of the wavefunctions such that the nominal triplet state has a little singlet character and vice versa.

$$\Psi = c_1\psi(^1P_1) + c_3\psi(^3P_1)$$

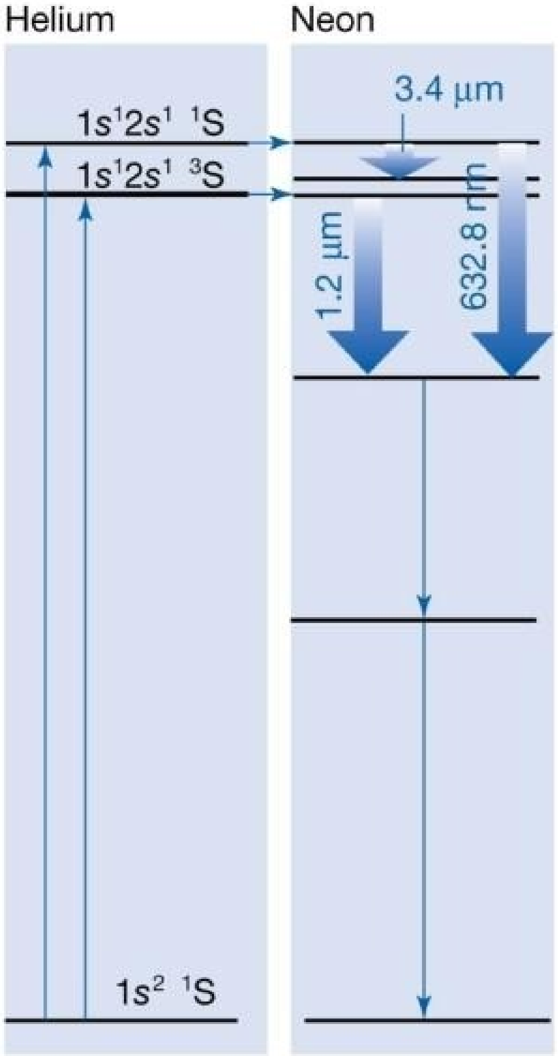
- Spin-orbit coupling becomes stronger as Z increases – more singlet-triplet mixing, breakdown of $\Delta S = 0$ selection rule.

Fates of excited atoms



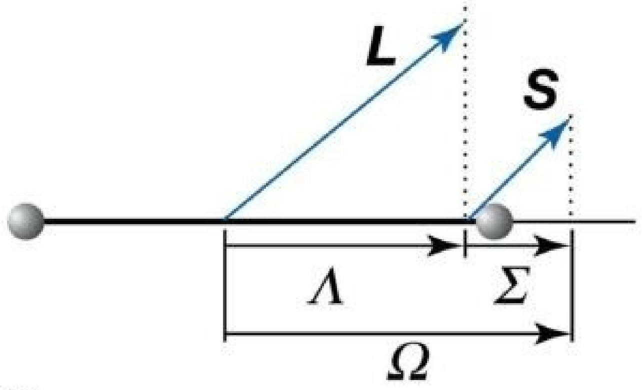
- Resonance fluorescence (spontaneous emission)
- Collisional deactivation
  - e.g., HeNe laser
- Bimolecular reaction
  - e.g., different chemical behaviour of $O(^1D)$ versus $O(^3P)$

Collisional deactivation in HeNe laser



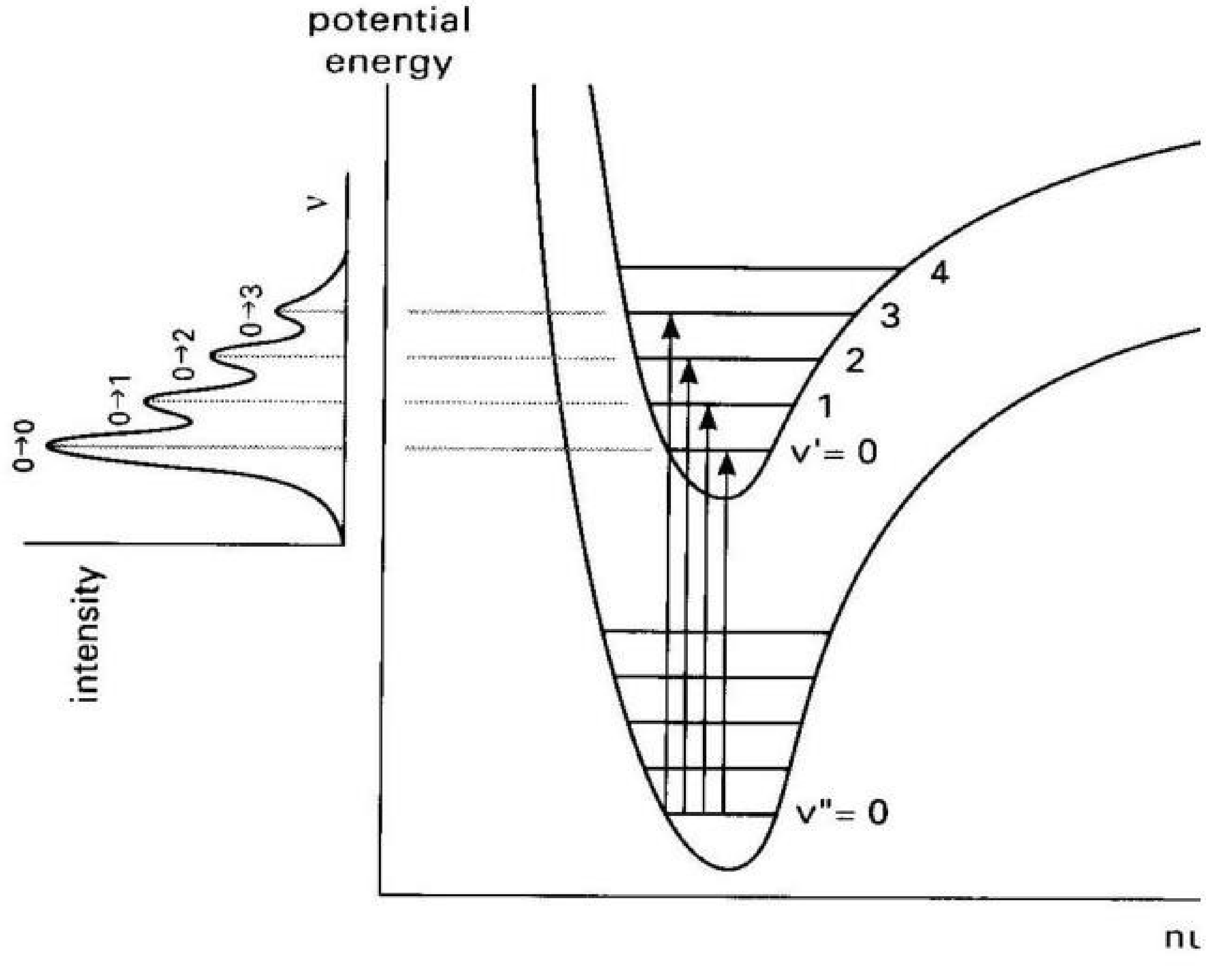
Electronic excitation of diatomic (and linear) molecules

- Total orbital angular momentum L no longer well defined, only its component along internuclear axis , Λ.

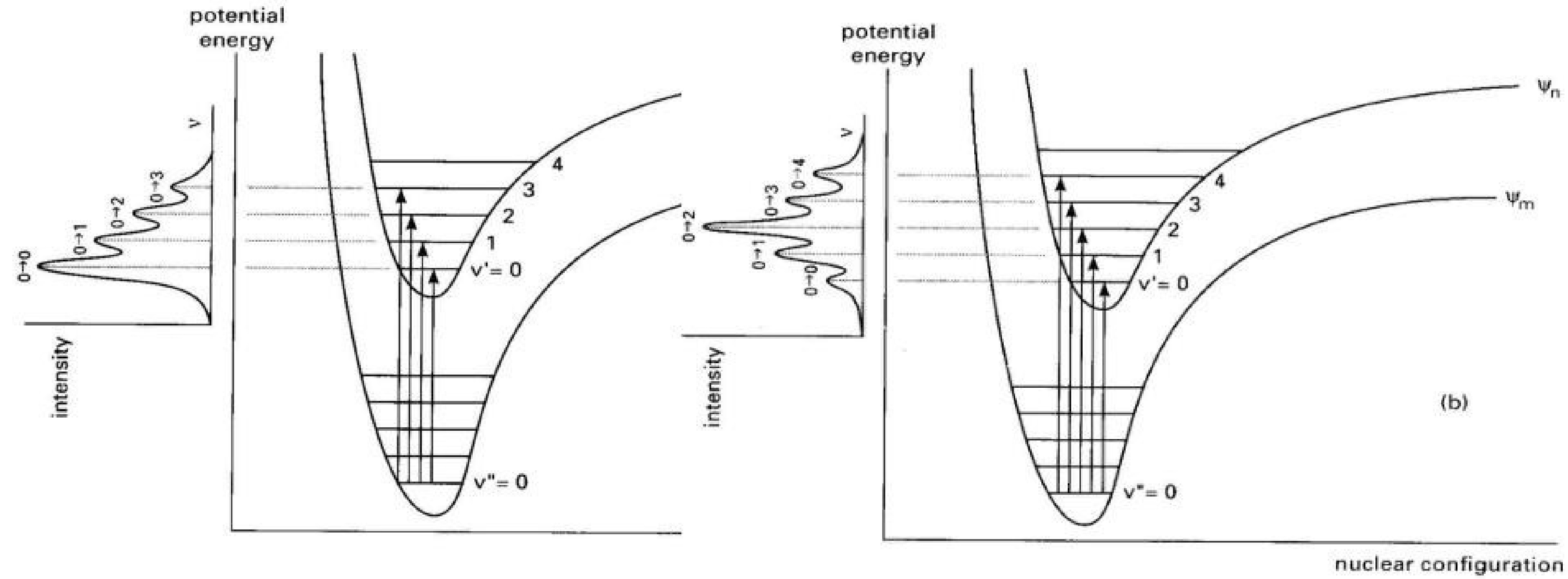


- Selection rules
- ΔΛ= 0 (parallel) or ±1 (perpendicular)
- ΔS =0
- ΔJ = ±1 (parallel) or 0 and ±1 (perpendicular)
  - J is the total (rotational + orbital) angular momentum

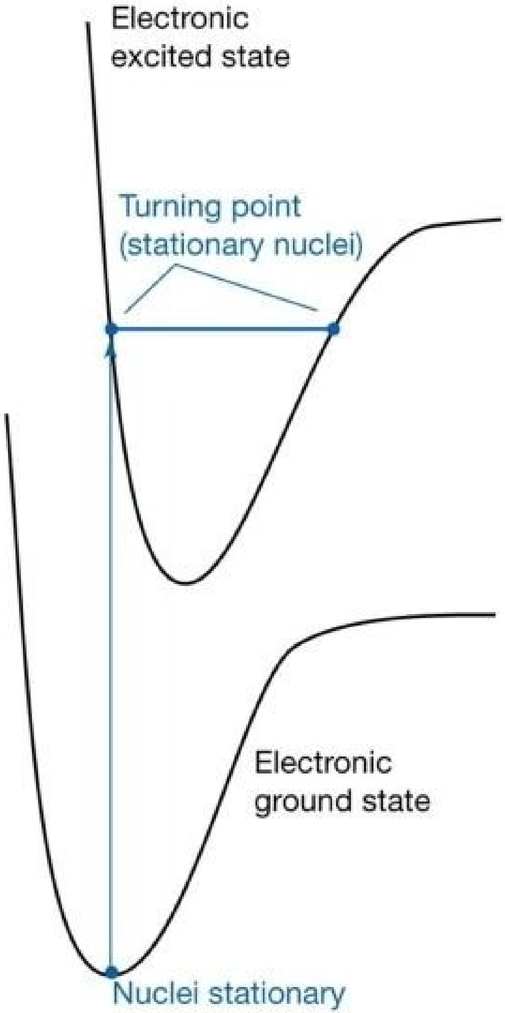
Combined electronic and vibrational excitation



Intensities of vibrational bands in electronic spectra



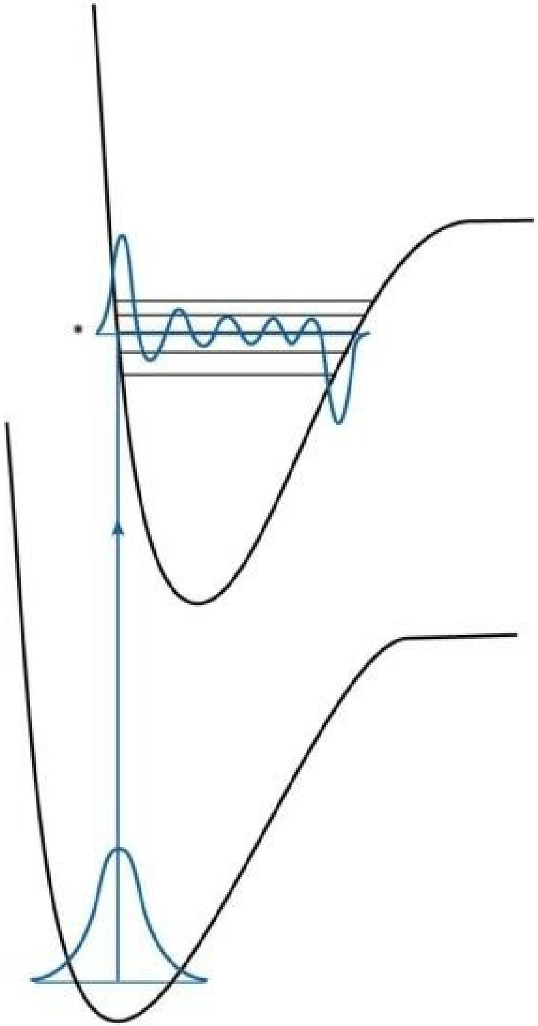
Vibrational excitation: Classical Franck-Condon Principle



Transition takes place with nuclei stationary

Most probable vibrational change depends on where vertical line from ground state hits upper curve

Quantum Franck Condon Principle



Overlap of vibrational wavefunctions determines transition probability

$$\Psi = \psi_{el}(r;R)\psi_{vib}(R)$$

$$R_{fi} = \langle f|\mu|i\rangle = \mu_{fi}{}^{e} S(v_f, v_i)$$

$$\boxed{S(v_f, v_i) = \int \psi_f(R)\psi_i(R)dR}$$

$$\mu_{if}{}^{e} = \int \psi^{*}_{el;f}\,\mu\,\psi_{el;i}\,d\tau$$

Fates of excited states of diatomics molecules

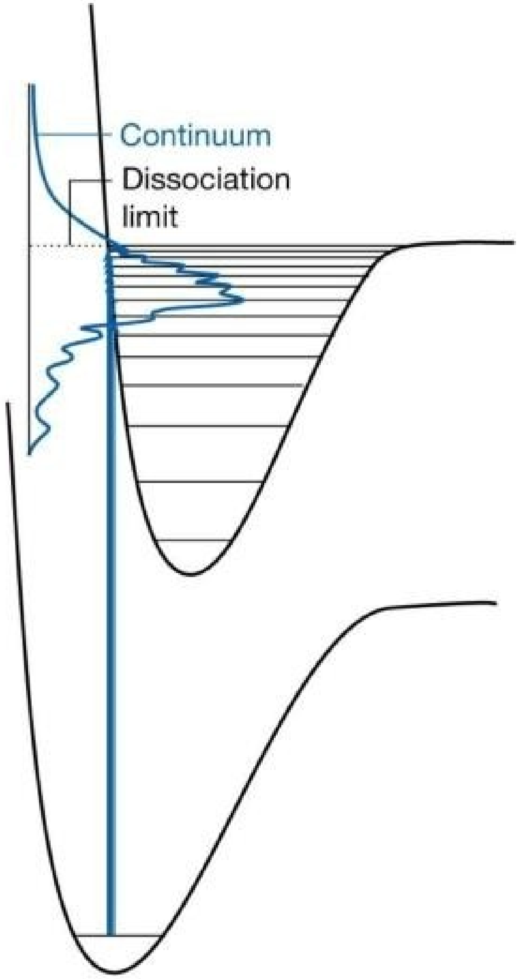
- Fluorescence – final vibrational level determined by Franck-Condon principle
- Collisional deactivation
- Bimolecular Reaction
- Dissociation (direct or predissociation)

Collisional processes

- Collisions may be reactive or just inelastic (or elastic)
- Inelastic collisions result in energy transfer without change of chemical identity
- Energy transfer subject to conservation of energy (and momentum)
- Categorised according to degrees of freedom involved
  - V-T initial vibrational energy converted to translation
  - E-T electronic energy converted to translation
  - E-V, V-V, V-R etc etc

Translation is a lower-grade form of energy; specificity of excitation lost - quenching

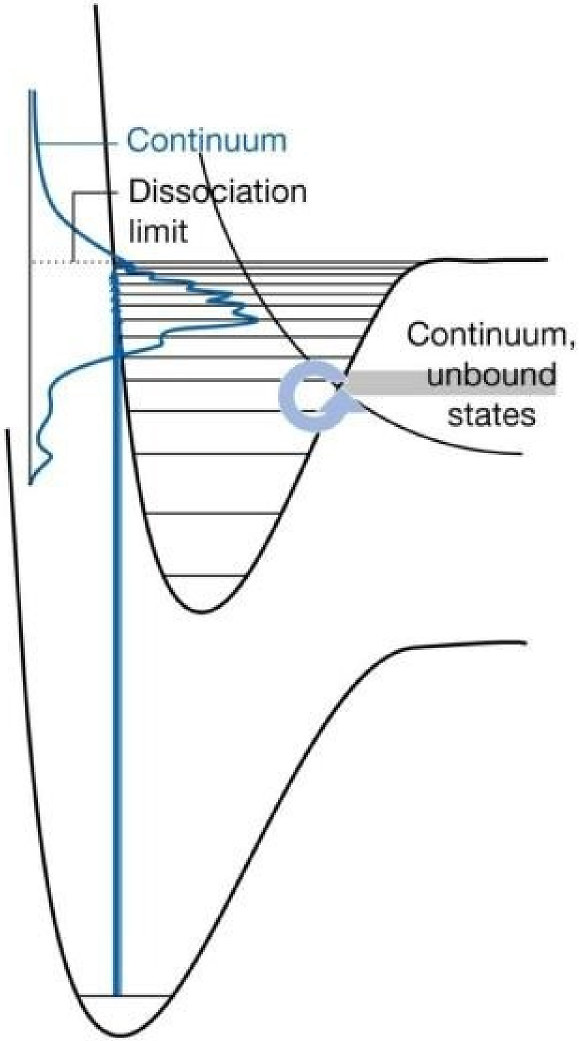
Direct Dissociation



Large change of geometry could mean that vertical excitation is above dissociation energy for excited state.

Could produce electronically excited products

Predissociation



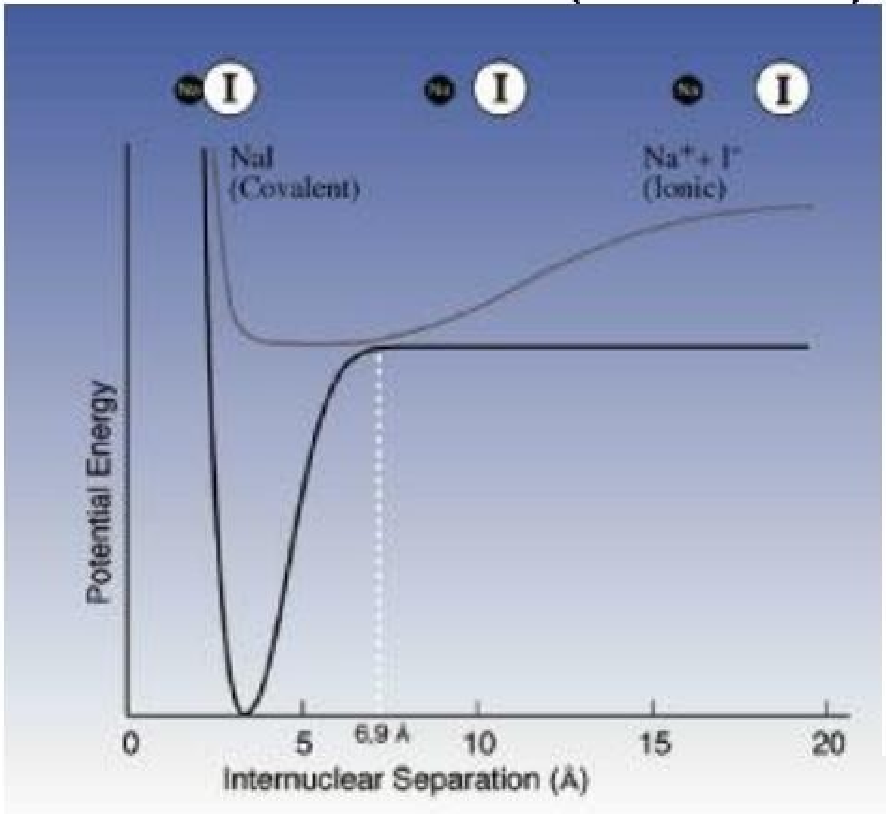
Potential energy curve crossing between bound and dissociative electronic states.

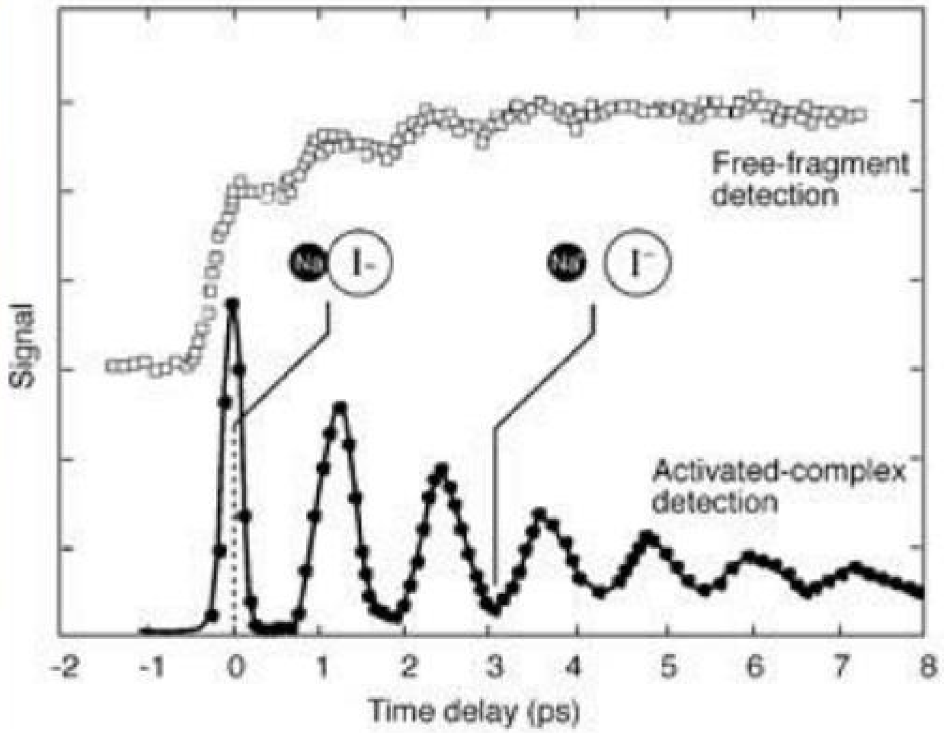
Femtosecond studies of simple dissociation processes.

- Pulses of light as short as a few fs (10^{-15}s) routinely created with certain types of laser
- Frequency bandwidth of pulse broadens as pulse duration shortens
- 10 fs pulse has a bandwidth of $\approx 10^3$ cm^{-1}
- cf typical vibrational frequencies

$$\Delta E \Delta t \approx \hbar / 2$$

Femtosecond laser studies of NaI dissociation (Zewail)





Short pulse creates synchronous motion of NaI molecules – observe Na fragments increasing for each vibrational period (see lecture 8)