

Electronic Spectroscopy

- Using light absorption to change charge distribution of electrons about molecule
- This is a lot of energy – often can break bonds.

Types of electronic transitions:

Organics: Involving π , σ , n electrons

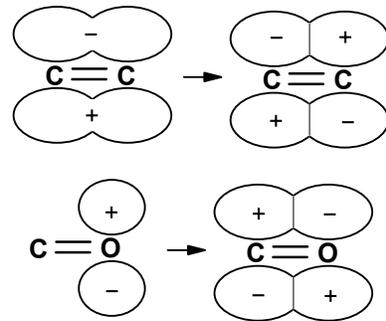
Saturated compounds

$\sigma \rightarrow \sigma^*$ (<150 nm), $n \rightarrow \sigma^*$ (<250 nm):
deep UV

Double bonds/unsaturated systems—

less energy to π^*

$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions : UV and
visible (200-700 nm)



Inorganics: Additionally, transitions between d orbitals split by presence of ligand field. Usually in visible.

d-d transition

Charge transfer transition: Electron moves between ligand and metal.
One must act as donor and other as acceptor



Electronic Spectra *(We will work with examples from diatomics)*

- At equilibrium, molecule is in ground electronic state \rightarrow lowest energy electronic state and typically in $v=0$.
- Transitions to higher lying electronic states are accompanied by changes in v , J .
- Excitation is accompanied by vibrational excitation, feels restoring force in excited state.

Quantitative information is in the shape of potential energy curves.

Excited state surfaces:

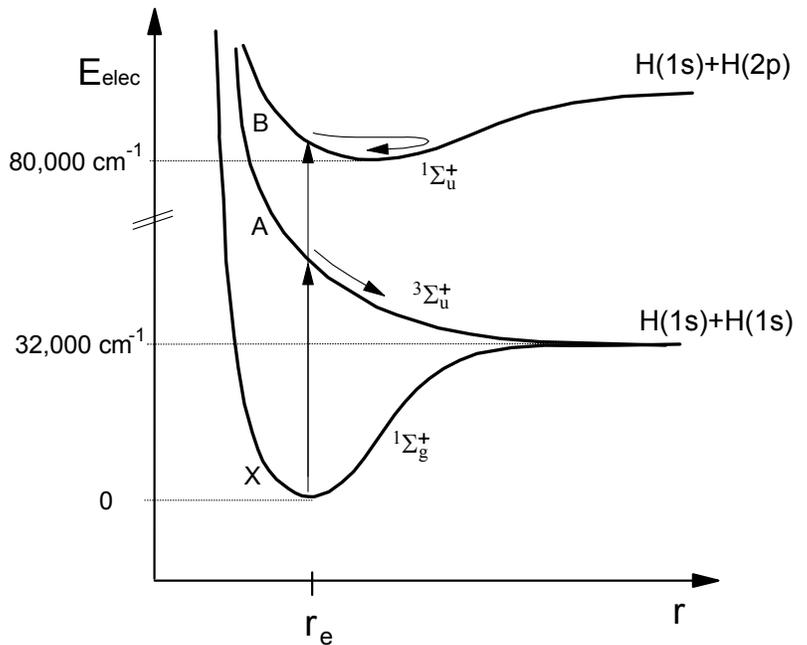
1) **Unbound or repulsive state**
(antibonding) → dissociates into atoms

(A state of H₂)

2) **Bound state**—bonding orbitals—has stable minimum

Excitation to bound state (usually leads to large nuclear displacement)

(B state of H₂)



(For diatomics: ground state = X; excited states = A, B, C . . .)

Franck-Condon principle (vertical transitions):

- Electrons respond much faster than nuclear motion, therefore an excitation proceeds without a change to the nuclear geometry.
- Light will be resonant with electronic energy gap at equilibrium nuclear geometry.

Selection Rules — Even for diatomics, this gets complicated.

- Conservation of nuclear/spin/total angular momentum makes it tough to predict precisely for larger molecules.
- Again absorption requires $\frac{\partial \mu}{\partial q} \neq 0$ → change of parity: $u \leftrightarrow g$.

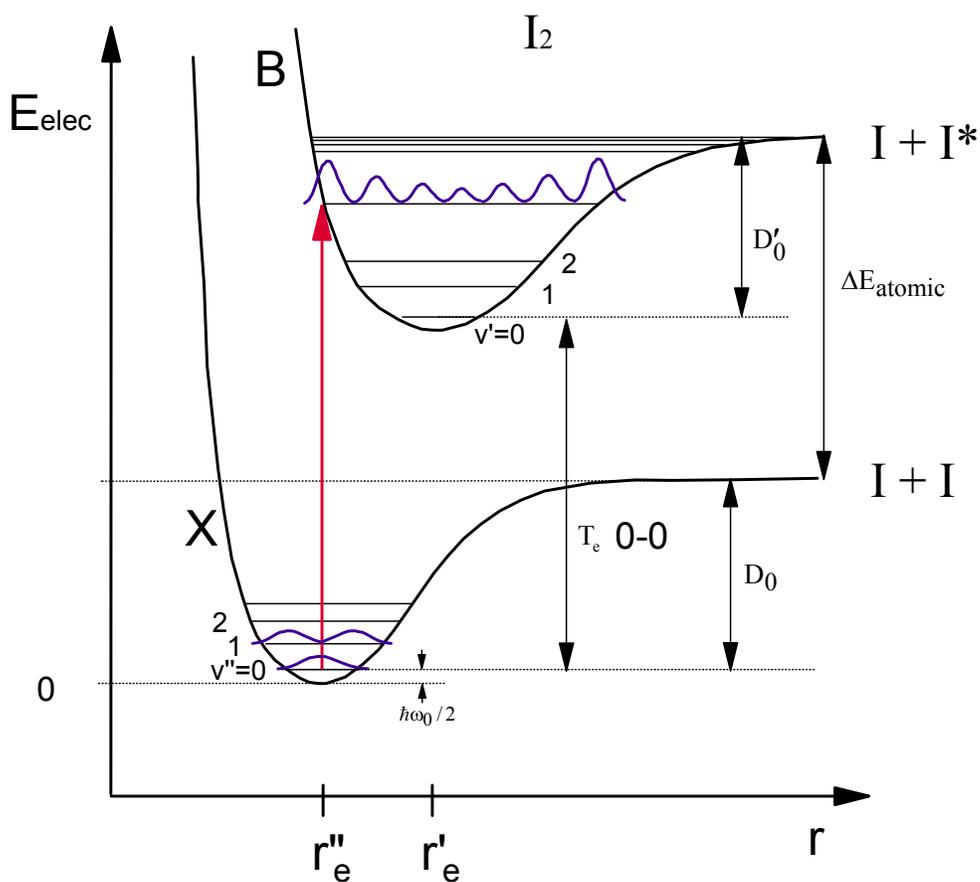
- For transitions between initial and final vibrational states, the probability of excitation is given by the Franck-Condon overlap integral

$$P_{i \rightarrow f} = \left| \int \psi_{\text{final}}^* \hat{\mu} \psi_{\text{initial}} d\mathbf{R} \right|^2 \quad \Psi_{\text{final}}^* = \psi_{e'}^* \psi_{v'}^* \dots \quad \Psi_{\text{initial}} = \psi_{e''} \psi_{v''} \dots$$

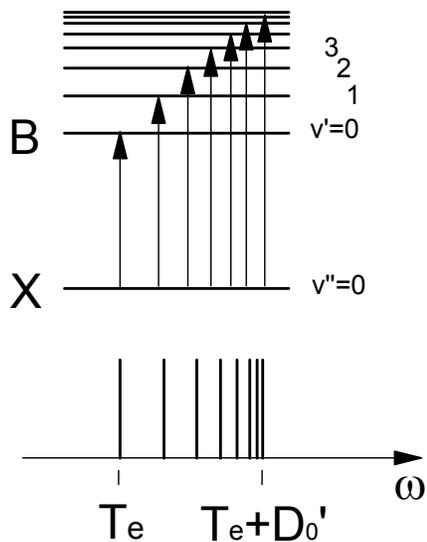
\mathbf{R} specifies the electronic and nuclear coordinates.

If $\hat{\mu}$ doesn't depend much on nuclear geometry, then

$$P_{i \rightarrow f} \propto \left| \int \psi_{v'}^*(r) \psi_{v''}(r) dr \right|^2 \quad \text{Franck-Condon Factor}$$



- Excited state is anharmonic. Vibrational spacing Δv will decrease for higher excitation.
- The electronic spectrum will be a converging series of lines:



From 0-0 transition and convergence limit \rightarrow get D_0'

Since

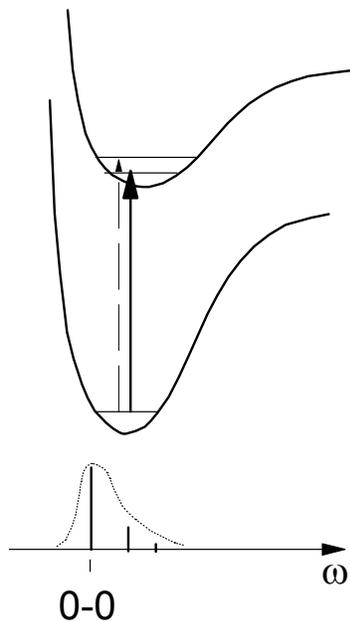
$$T_e + D_0' = D_0 + \Delta E_{atomic}$$

if you know ΔE_{atomic} , you can get D_0

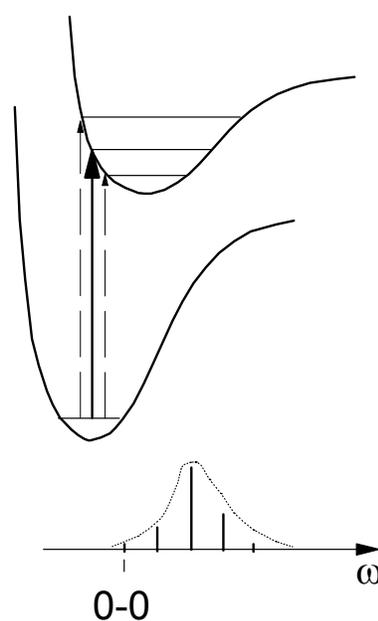
Intensities: Dictated by Franck-Condon factor.

- Most probably excitation is to classical turning point.
- So the intensities tell us about $r_e'' - r_e'$: the displacement.

small displacement



large displacement



Position of peak absorption related to displacement

Relaxation of Electronic States

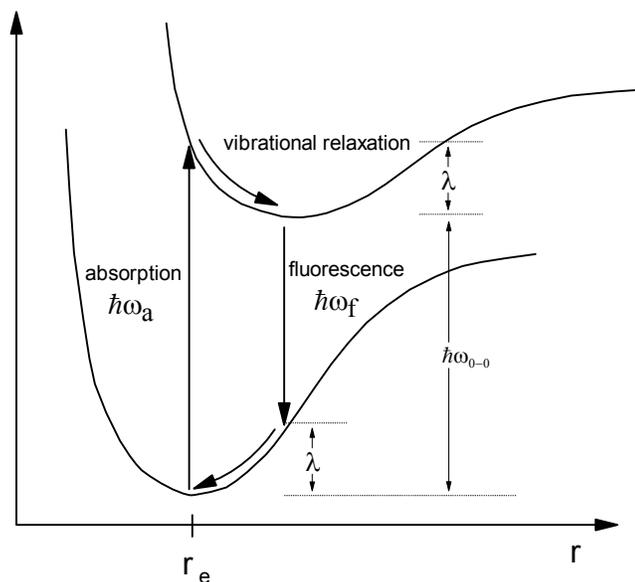
Typically when we electronically excite a molecule, there is a displacement of charge and a new equilibrium nuclear separation.

→ Leads to vibrational excitation also. The system vibrationally relaxes— nonradiatively.

The energy dissipated is λ (reorganization energy).

Now, there is a huge amount of energy to release out to the ground state

→ Most probable way is **fluorescence**.



In gas phase: vibrational relaxation (T_1) $\sim 10^{-12} - 10^{-11}$ s 1–10ps for large molecules

fluorescence (T_1) $\sim 1-10$ ns

In solutions: dephasing, T_2^* fast $\sim 10^{-14}$ s 10–20 fs
 fluctuations of solvent
 vibrational relaxation $\sim 1-10$ ps
 fluorescence $\sim 1-10$ ns

Fluorescence is always red-shifted relative to absorption.

