

5.33 Lecture Notes: Electronic Spectroscopy

Electronic Spectroscopy: Using light absorption to change charge distribution of electrons about molecule (a lot of energy: often can break bonds)

At equilibrium, molecule is in ground electronic state → lowest energy electronic state and typically in $v=0$.

Transitions to higher lying electronic states are accompanied by changes in v , J .

Selection Rules — Even for diatomics, this gets complicated

→ conservation of nuclear/spin/total angular momentum.
(In larger molecules: tough to predict.)

Again absorption requires $\frac{\partial \mu}{\partial q} \neq 0$

→ change of parity: $u \leftrightarrow g$, change of inversion symmetry to orbitals.

Types of electronic transitions:

Organics: Involving π , σ , n electrons

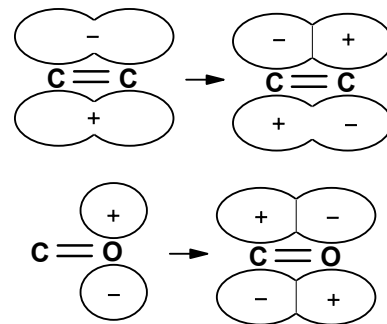
Saturated compounds

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

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.

d-d transition

Charge transfer transition: Electron moves between ligand and metal.

One must act as donor and other as acceptor



Electronic Spectra of Diatomics

- Electronic absorption also carries vibrational and rotational structure.
- Typically in a ground electronic state with $v=0$, you have transitions to excited electronic state with change in v .
- Excitation is accompanied by vibrational excitation, feels restoring force in excited state.

Electronic transitions: Franck Condon principle (vertical transitions):

Electrons respond much faster than nuclear motion, therefore an excitation proceeds without a change to the nuclear geometry.

Excited state surfaces:

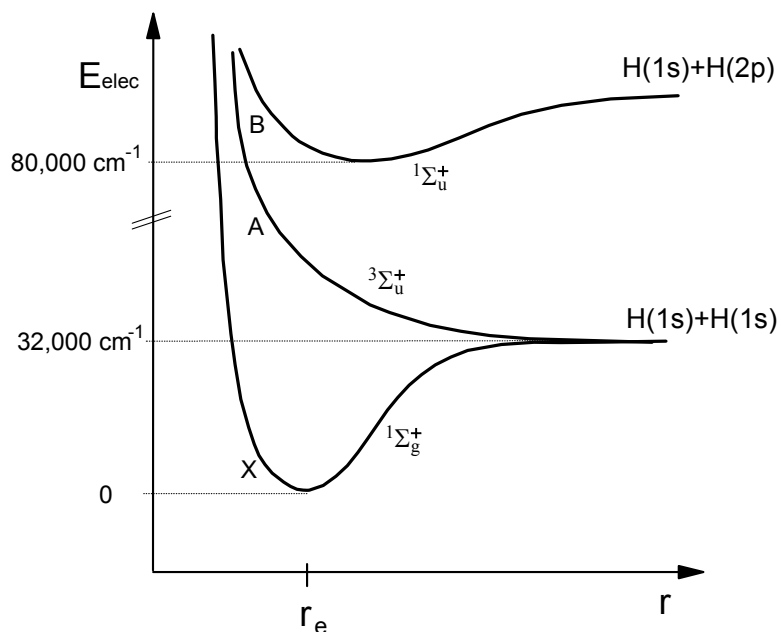
- 1) **Unbound or repulsive state**
(antibonding) \rightarrow dissociates into atoms

(A state of H_2)

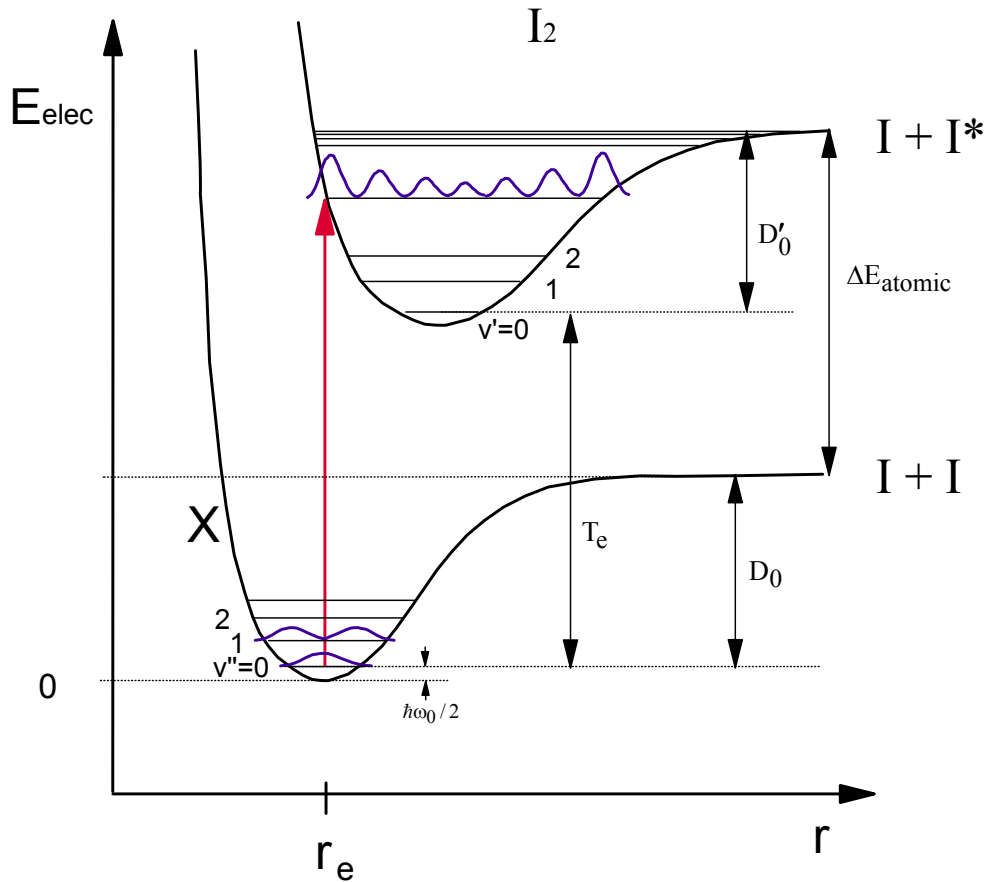
- 2) **Bound state**—bonding orbitals—has stable minimum

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

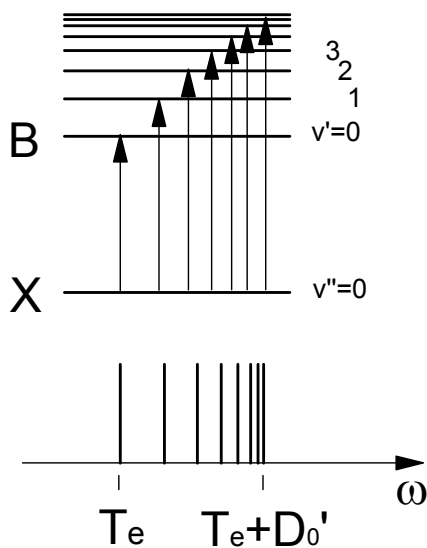
(B state of H_2)



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



Excited state is anharmonic—surface must allow for dissociation of atoms, thus vibrational spacing Δv will decrease for higher excitation.



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: Transition probabilities dictated by Franck-Condon principle

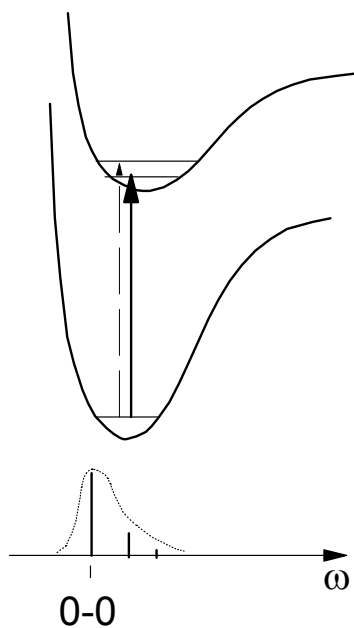
Most probably excitation is to classical turning point.

The “selection rule” is the Franck-Condon overlap integral

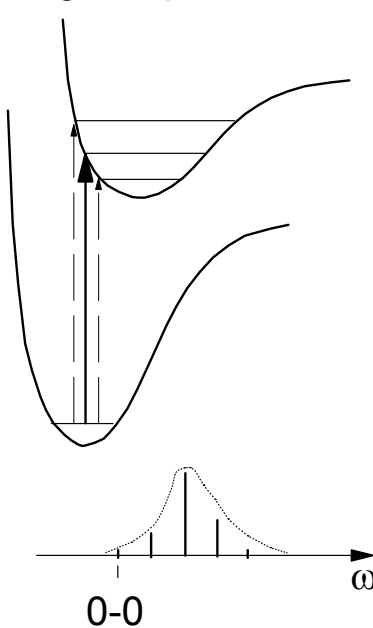
$$\rightarrow \int \psi_{v'}^*(R) \psi_{v''}(R) dR$$

...so the intensities tell us about r_e vs. r_e' : the displacement.

small displacement



large displacement



Position of peak
absorption
gives
displacement

Relaxation of Electronic States (Bound States)

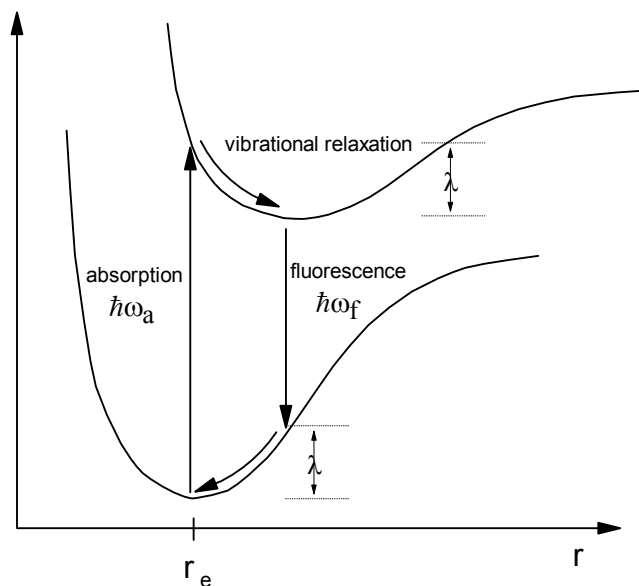
Typically when we electronically excite a molecule, there is a displacement of charge and a new equilibrium nuclear separation.

→ 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) $\sim 10^{-11} - 10^{-10}$ s 1 – 10 ps

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

In solutions: dephasing, T_2^* fast $\sim 10^{-14}$ s 10 – 20 fs

fluctuations of solvent

vib. relax. $\sim 1-10$ ps

fluorescence $\sim 1-10$ ns

Fluorescence is always red-shifted relative to absorption.

