

## 5.33 Lecture Notes: Electronic Spectroscopy

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**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.

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### Types of electronic transitions:

**Organics:** Involving  $\pi$ ,  $\sigma$ ,  $n$  electrons

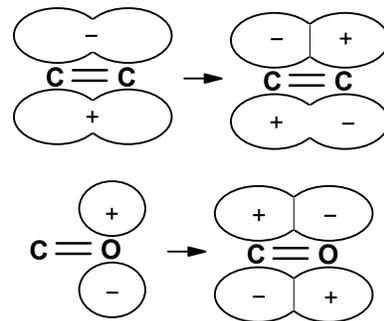
**Saturated compounds**

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

**Double bonds/unsaturated systems**—

less energy to  $\pi^*$

$\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  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:

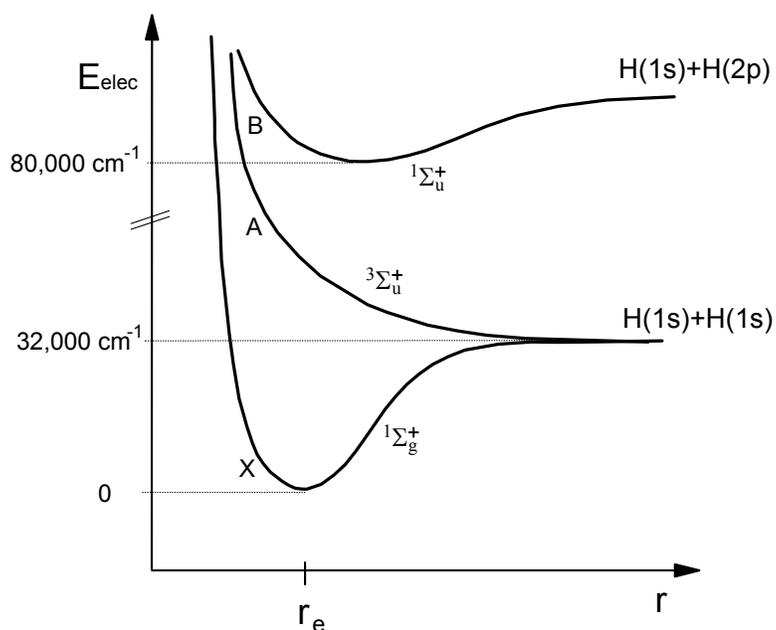
- 1) **Unbound or repulsive state**  
(antibonding)  $\rightarrow$  dissociates into atoms

(A state of  $H_2$ )

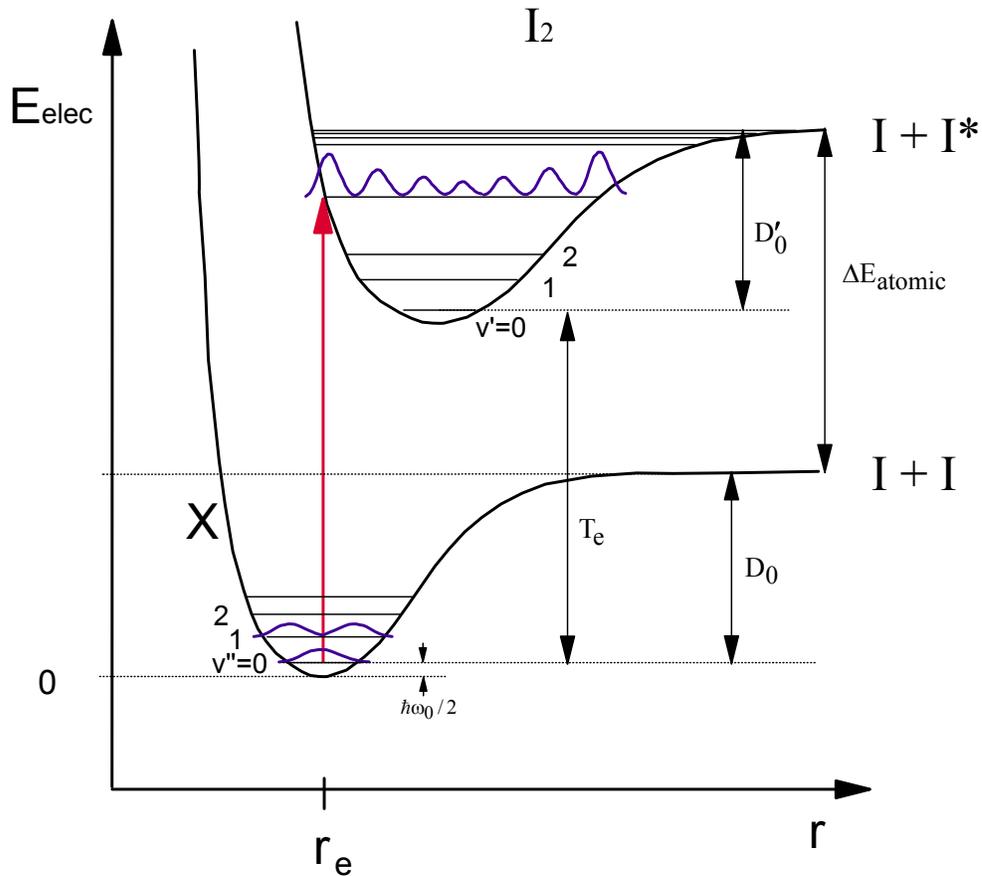
- 2) **Bound state**—bonding orbitals—has stable minimum

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

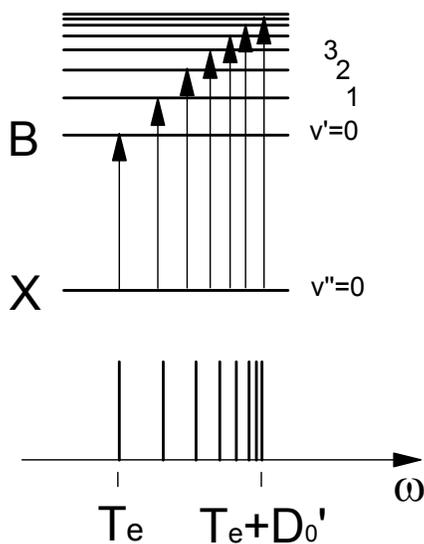
(B state of  $H_2$ )



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



Excited state is anharmonic—surface must allow for dissociation of atoms, thus vibrational spacing  $\Delta v$  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  $\Delta E_{atomic}$  you can get  $D_0$

**Intensities:** Transition probabilities dictated by Franck-Condon principle

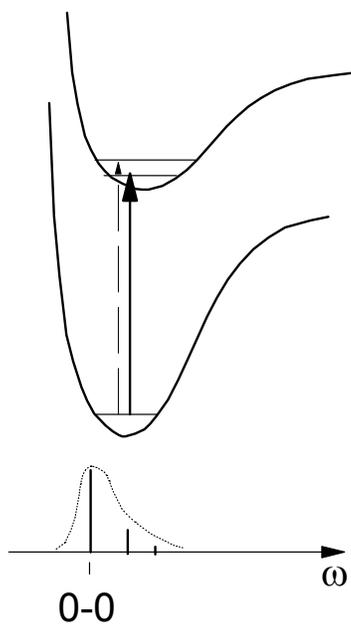
Most probably excitation is to classical turning point.

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

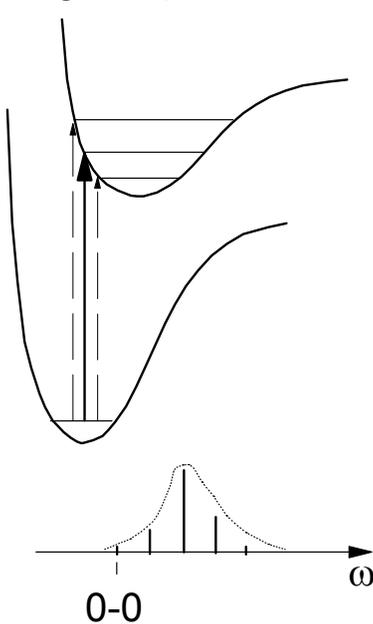
$$\rightarrow \int \psi_{v'}^*(R) \psi_{v''}(R) dR$$

...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)

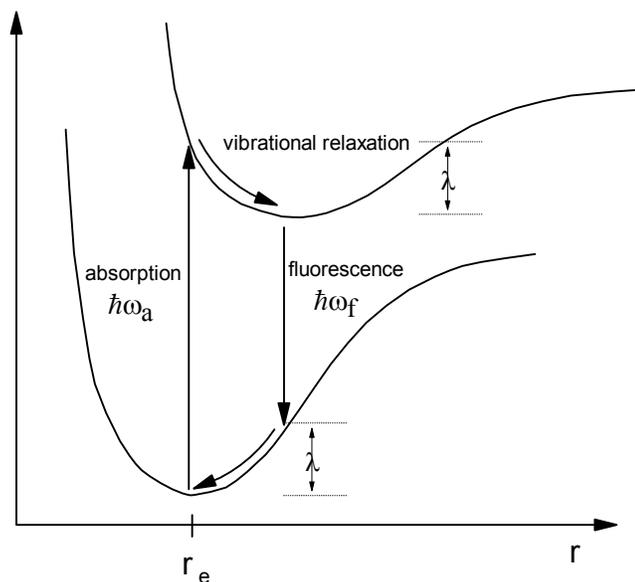
Typically when we electronically excite a molecule, there is a displacement of charge and a new equilibrium nuclear separation.

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

The energy dissipated is  $\lambda$  (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.

