Atomic and Molecular Physics

By

Prof. S. Arumugan
Department of Physics
Bharathidasan University
Trichy – 24.

Electronic spectroscopy of diatomics

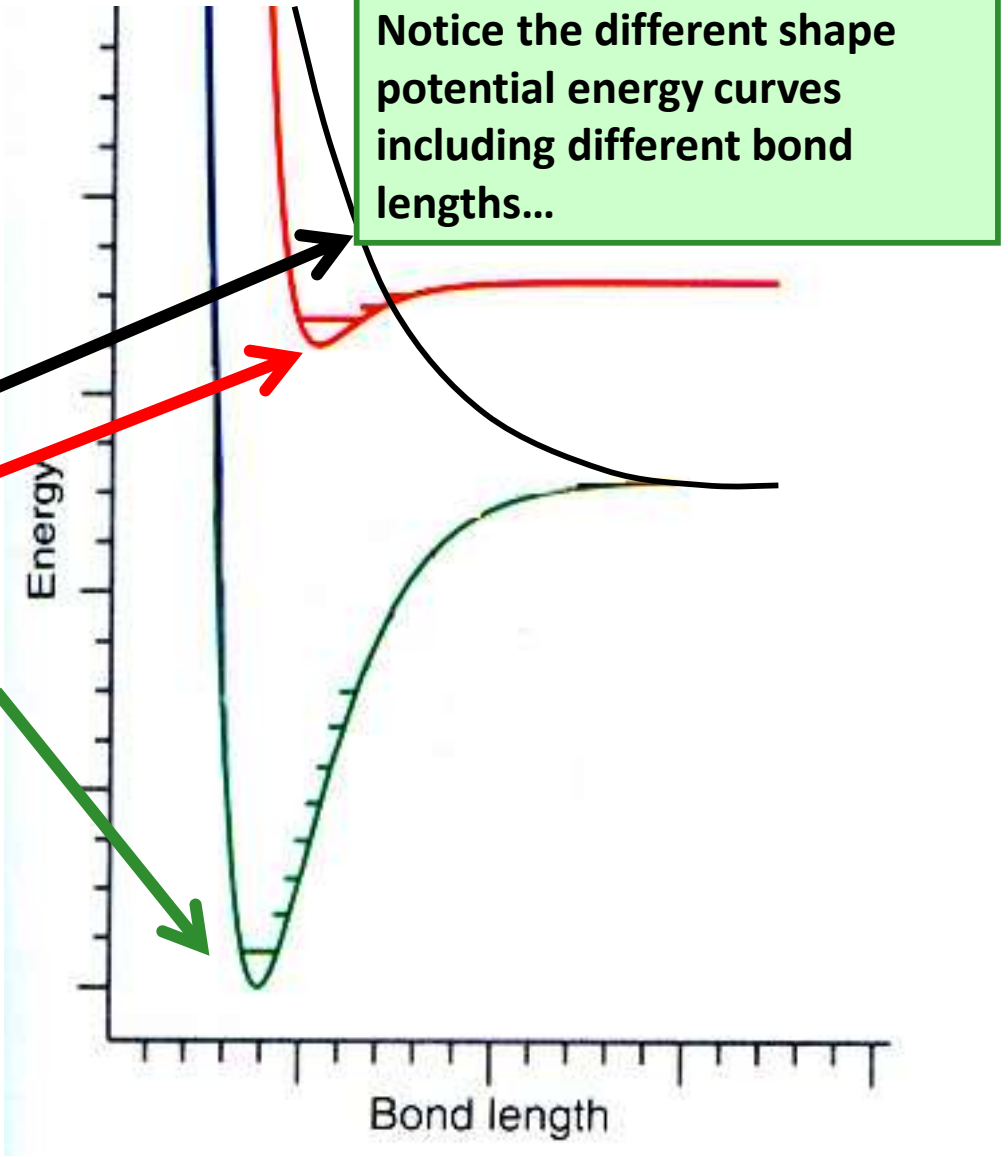
Depicting other electronic states

Excited Electronic States

1. Unbound
2. Bound

Ground Electronic State

There is an infinite number of excited states, so we only draw the ones relevant to the problem at hand.

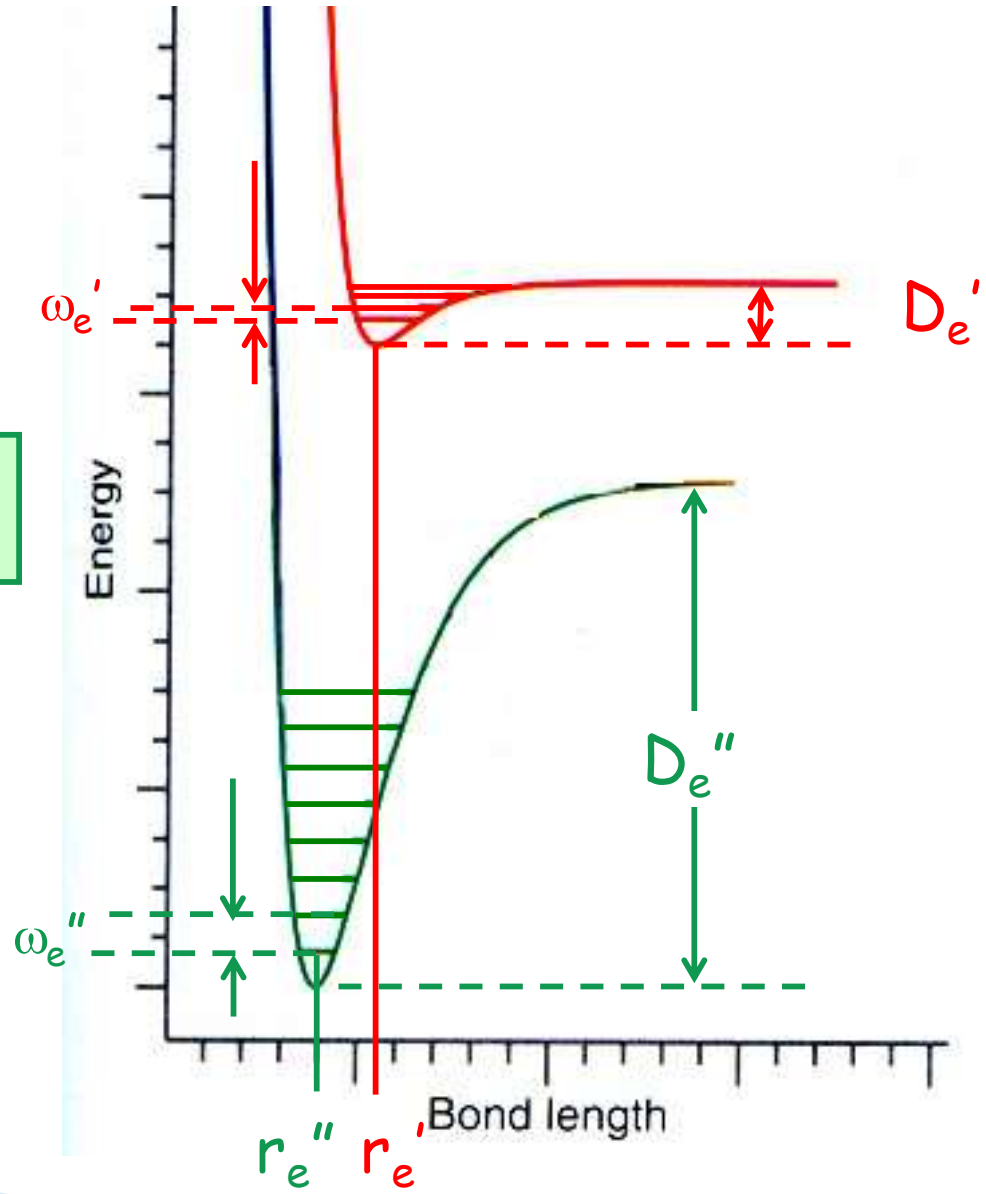


Each electronic state has its own set of vibrational states.

Note that each electronic state has its own set of vibrational parameters, including:

- bond length, r_e
- dissociation energy, D_e
- vibrational frequency, w_e

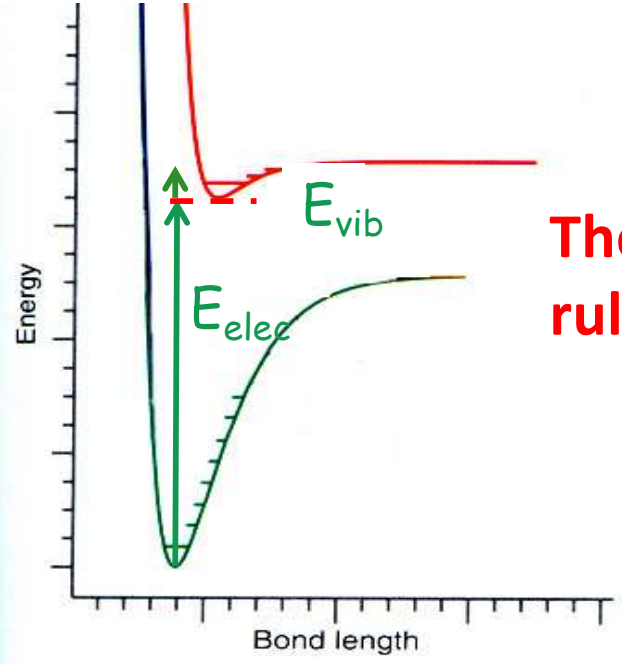
Notice: single prime (′) = upper state
double prime (″) = lower state



The Born-Oppenheimer Approximation

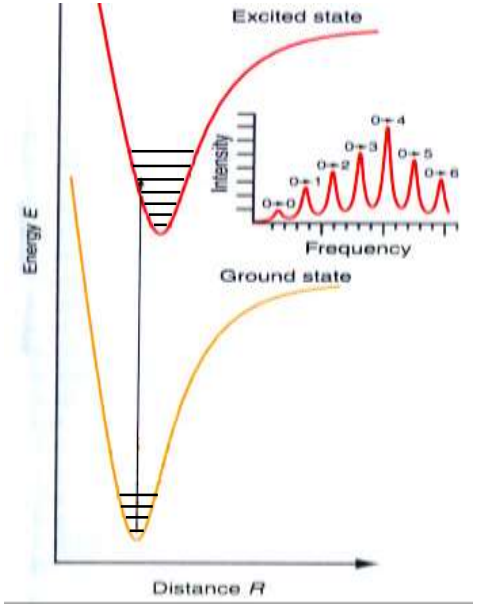
The total energy of the molecule is the sum of electronic and vibrational energies:

$$E_{tot} = E_{elec} + E_{vib}$$



Electronic Absorption

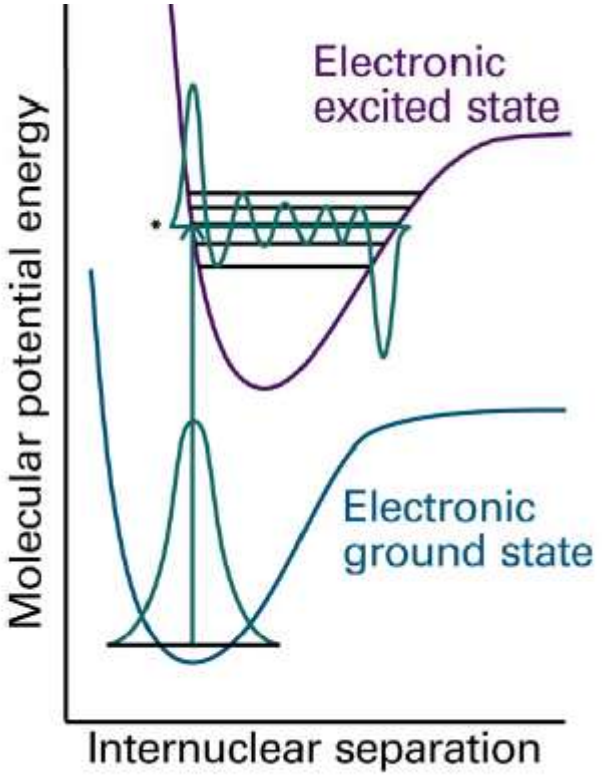
There are no vibrational selection rules, so any Δv is possible.



The Franck-Condon Principle

Assumption: electronic transitions take place on such a short timescale that the nuclei remain frozen (*R* unchanged) during the transition.

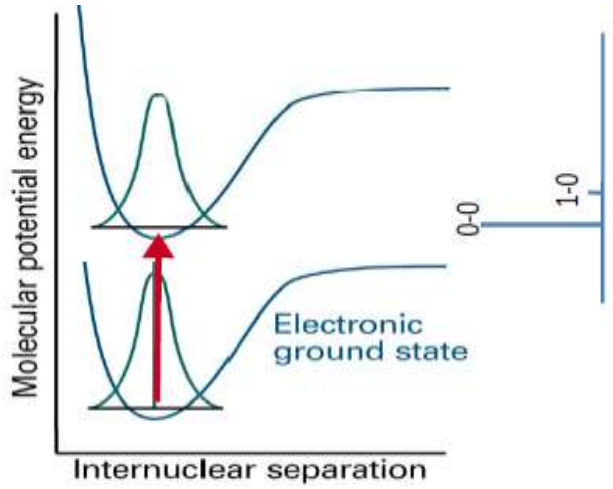
- **We talk of "vertical transitions" between potential energy curves.**
- **There is no selection rule governing the allowed vibrational changes accompanying an electronic transition.**
- **Instead, the probability of undertaking a v' → v' transition is governed by Franck-Cond factors (the overlap of the two vibrational wavefunctions).**



Vibrational Structure: Franck-Condon factors

The overlap of the function is governed by nature of electronic states involved

If the bonding nature of two states are similar

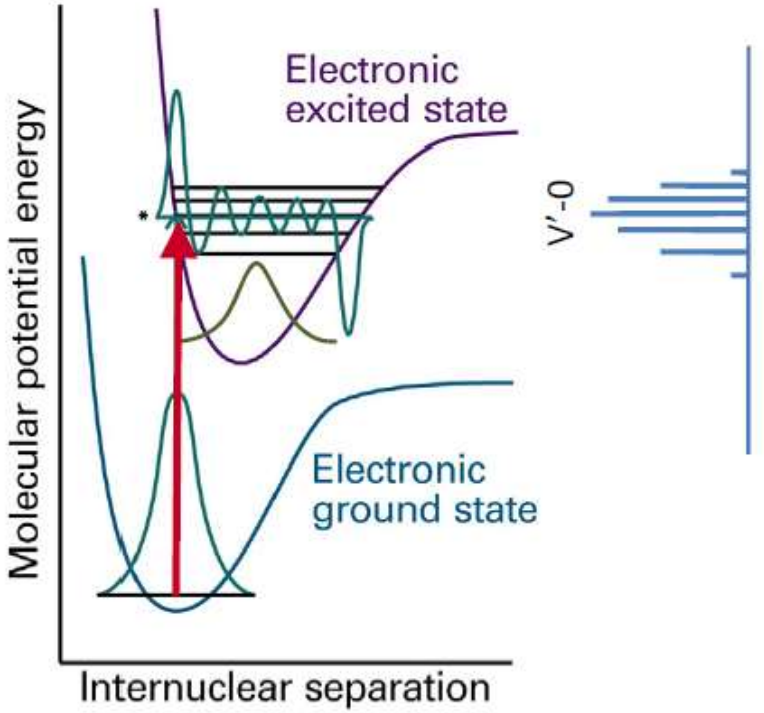


$R_e' \sim R_e''$

Best overlap ($v' = 0$) – ($v'' = 0$)

"Short progression"

If the bonding character of the two states is different



$R_e' \neq R_e''$

Best overlap ($v' > 0$) – ($v'' = 0$)

"Long progression"