5. Electronic Spectroscopy

15 September 2023 08:05

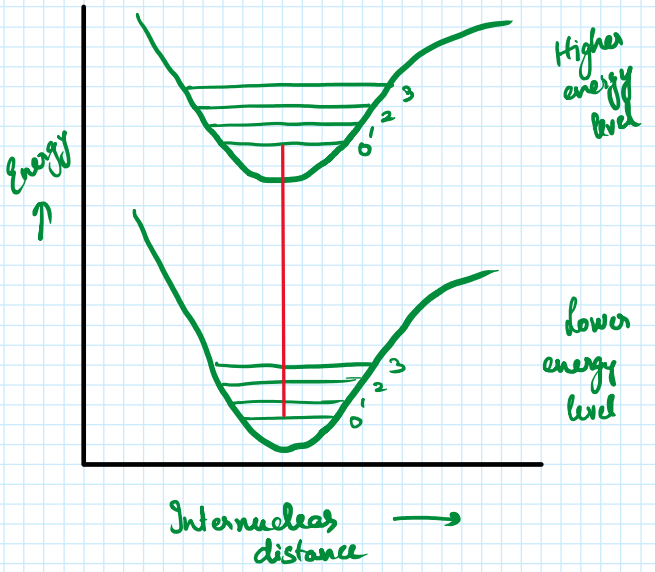
ELECTRONIC SPECTROSCOPY

- Study of electronic transition
- NO selection rule
- Transition from HOMO → LUMO
- Homodiatomic and heterodiatomic both give electronic spectra

BORN-OPPENHEIMER APPROXIMATION

$$\Delta E_{total} = \Delta E_{rot} + \Delta E_{vib} + \Delta E_{elect} \quad cm^{-1}$$

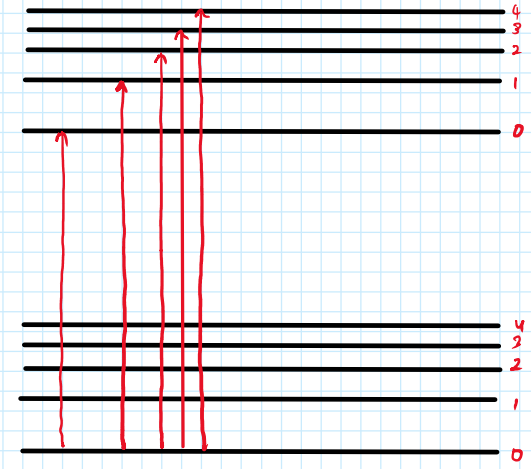
VIBRATIONAL COARSE STRUCTURE



E', r', v'

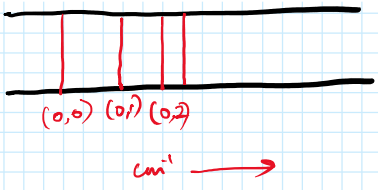
E'', r'', v''

E - energy
r - internuclear distance
v - quantum number ?



v' - Higher energy level

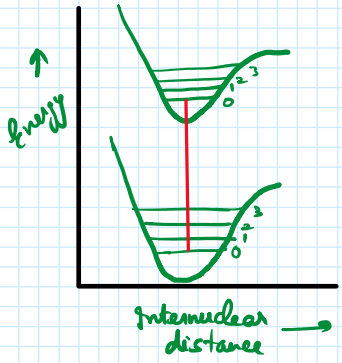
v'' - Lower energy level

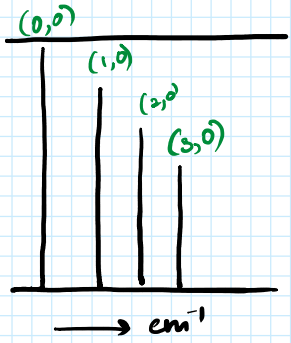


FRANCK - CONDON PRINCIPLE

An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

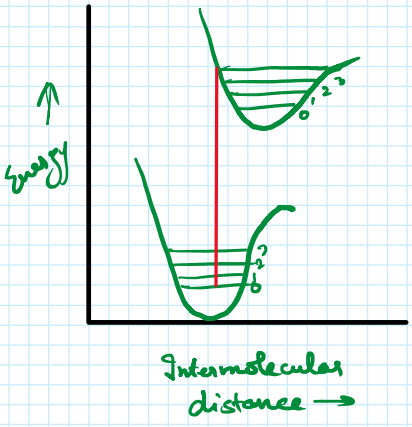
① When $r'' = r'$

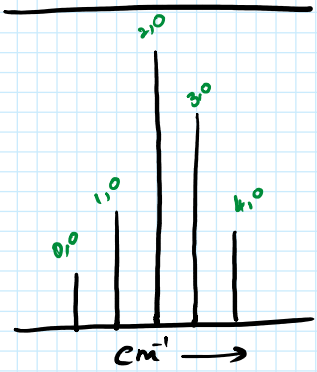




$v''-0 \rightarrow v'-0 \rightarrow 0,0$

② When $r'' < r'$

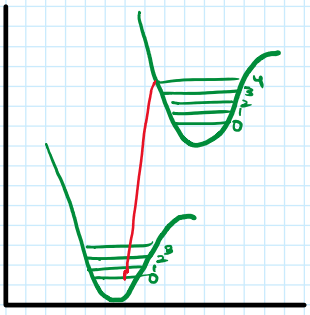


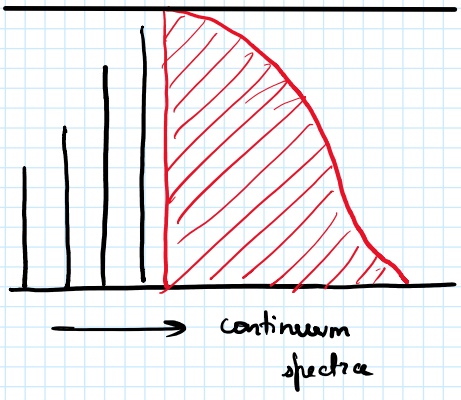


$v''-0 \rightarrow v'-2 \rightarrow 2,0$

$v''-0 \rightarrow v'-3 \rightarrow 3,0$

③ $r'' << r'$





$v''-0 \rightarrow v'-4 \rightarrow$ Continuum spectra

(energy is not quantized)

Molecule $\xrightarrow{\text{dissociates}}$ atoms $\xrightarrow{\text{gaining K.E.}}$ energy is not quantized $\xrightarrow{\text{gives}}$ continuum spectrum

- Vertical line indicates energy transition
- Higher energy levels are crowded

WHY?

Anti-bonding nature, "k" value is less