ENGINEERING CHEMISTRY

Department of Science and Humanities

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Class content:

- ***Electronic spectroscopy***
- ***Born – Oppenheimer Approximation***

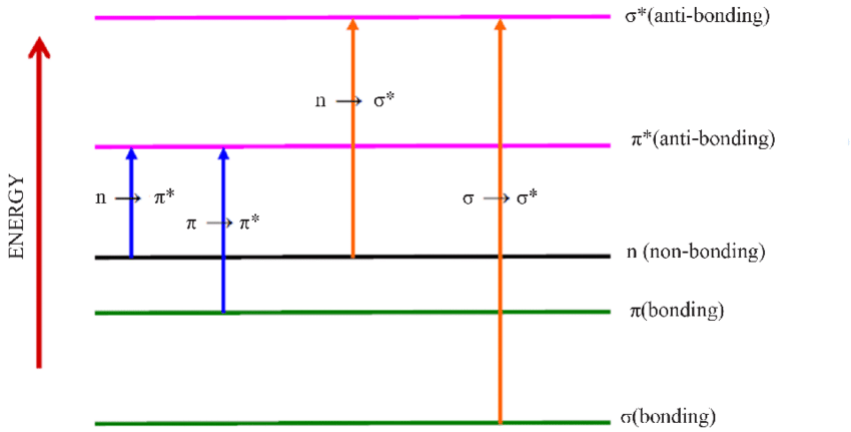
ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Electronic spectroscopy

Electronic transitions :

•**Highest Occupied Molecular Orbitals** (HOMO) → **Lowest Unoccupied Molecular Orbitals**(LUMO)



•Transitions in **UV-Visible region**

• σ → σ* , π → π* , n → π*

• If transitions in visible region **colour** can be seen

• Electron redistribution causes **change in electric field**

• **All molecules** can undergo electronic transitions

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Electronic spectroscopy

Born-Oppenheimer approximation

According to Born-Oppenheimer approximation, the **total energy** of a molecule is the sum of translational, rotational, vibrational and electronic energies, i.e. $E_{Total} = E_t + E_r + E_v + E_e$

which implies that the electronic, vibrational and rotational energies of a molecule are **completely independent** of each other.

The change in total energy of the molecule is given by

$$\Delta E_{Total} = \Delta E_{Rot} + \Delta E_{Vib} + \Delta E_{Electronic}$$ in Joules

$$\Delta \varepsilon_{Total} = \Delta \varepsilon_{Rot} + \Delta \varepsilon_{Vib} + \Delta \varepsilon_{Electronic}$$ in cm^{-1}

The approximate orders of magnitude are

$$\Delta \varepsilon_{Rot} \times 10^6 \simeq \Delta \varepsilon_{Vib} \times 10^3 \simeq \Delta \varepsilon_{Electronic}$$

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

- Electronic transitions involve **electronic redistribution** hence electrostatic forces experienced by the molecule which **vibrates in response** and this in turn **affects rotation** of the molecule
- Electronic transitions are accompanied by vibrational and rotational changes. Hence vibrational changes will produce **"coarse structure"** and rotational changes will produce **"fine structure"** in the electronic spectra of molecules
- Information about vibrational and rotational structure of **homonuclear molecules** like H_2, N_2 which are inactive in IR and Microwave region can be obtained from their electronic spectra

THANK YOU

Department of Science and Humanities