UNIT – V

Electronic Spectra of Diatomic Molecules

Electronic spectra of a molecule arise → when the electrons of a molecule are excited to higher energy states. The energy involved is generally large → usually found in visible and ultraviolet region. Electronic spectra arise due to changes in the arrangement of molecular electrons.

Electronic transition → result of change in electronic energy.

A small change in electronic energy → accompanied by large change in the vibrational energy of the molecule.

Vibrational energy changes → Vibrational transitions (group of bands)

Small change in vibrational energy → accompanied by a large change in the rotational energy of the molecule.

These rotational energy changes → Rotational transitions (series of lines in each band)

So called fine structure of each band

The Born - Oppenheimer Approximation

As a first approach to the electronic spectra of diatomic molecule → we may use Born-Oppenheimer approximation.

$$E_{total} = E_{electronic} + E_{vibration} + E_{rotation} \quad (1)$$

⇒ electronic, vibrational and rotational energies of a molecule are completely independent of each other → However, we see later that this approximation is invalid ⇐

but up to what extent?

A change in the total energy of a molecule may be written

$$\Delta E_{total} = \Delta E_{elec.} + \Delta E_{vib.} + \Delta E_{rot} \quad \text{Joule}$$

or

$$\Delta \varepsilon_{total} = \Delta E_{ele.} + \Delta \varepsilon_{vib.} + \Delta \varepsilon_{rot.} \quad \text{cm}^{-1} \qquad -(2)$$

The approximate orders of magnitude of these changes are:

$$\Delta \varepsilon_{ele.} \simeq \Delta \varepsilon_{vib.} \times 10^{3} \simeq \Delta \varepsilon_{rot.} \times 10^{6} \qquad -(3)$$

i.e. Vibrational changes will produce a 'coarse structure' and rotational changes a 'fine structure' on the spectra of electronic transitions.

Pure rotation spectra → shown only by molecules possessing a permanent electric dipole moment

Vibrational spectra → require a change of dipole during the motion

Electronic spectra → Given by all molecules, since changes in the electron distribution in a molecule are always accompanied by a dipole change.

⇒ Homonuclear molecule (such as H_2 or N_2) which show no rotation or vibration-rotation spectra

→ give an electronic spectrum and show vibrational and rotational structure in their spectra from which rotational constants and bond vibration frequencies may be derived.

Initially we ignore rotational fine structure and discuss the appearance of the vibrational coarse structure of spectra.

Vibrational Coarse Structure: Progressions

Ignoring Rotational changes, eq^n(1) can be written as

$$E_{total} = E_{elec.} + E_{vib.} \quad \text{Joules}$$

or

$$\varepsilon_{total} = \varepsilon_{elec.} + \varepsilon_{vib.} \quad cm^{-1} \quad -(4)$$

$$\Rightarrow \varepsilon_{total} = \varepsilon_{elec.} + (v+\tfrac{1}{2})\bar{\omega}_e - x_e(v+\tfrac{1}{2})^2\bar{\omega}_e \quad cm^{-1} \quad -(5)$$

$$(v = 0, 1, 2, \ldots)$$

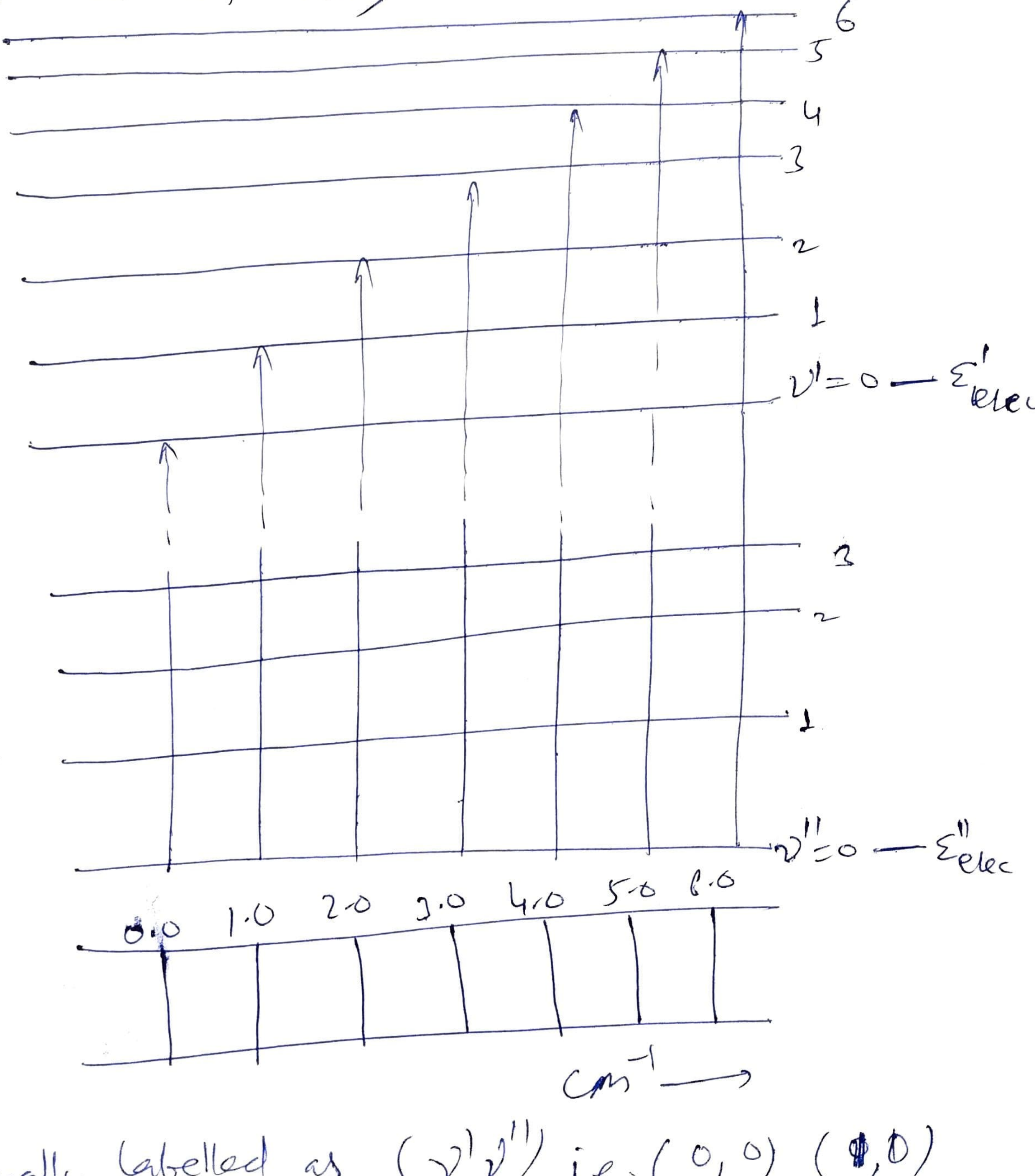
We show energy levels of this eq^n in following figure for two arbitrary values of $\varepsilon_{elec.}$

The lowest states → v'', ε''_{elec}

Upper state → v', ε'_{elec}

Spacing between the upper vibrational levels are smaller than that between the lower → an excited electronic state usually corresponds to a weaker bond in the molecule and hence a smaller vibrational wavenumber $\bar{\omega}_e$.

Essentially no selection rule for v when a molecule undergoes an electronic transition, i.e. every transition $v'' \to v'$ has some probability. and many spectral lines would be expected. If the absorption spectrum is considered from the electronic ground state → virtually all the molecules exist in the lowest vibrational state, i.e. $v''=0$ so the transitions observed with considerable intensity are as follows;



Vibrational 'coarse' Structure of the band formed during electronic absorption from the ground ($v''=0$) state to a higher state

Conventionally labelled as (v', v'') i.e. (0,0) (1,0) (2,0) (3,0)..etc. Such a set of transitions are called a band and ~~more~~ particularly v' progressions.

lines in a band crowd together more closely at high frequencies; → consequence of the anharmonicity of the upper state vibration which causes the excited vibrational levels to converge.

From eqⁿ (5), we have

$$\Delta \varepsilon_{total} = \Delta \varepsilon_{elec} + \Delta \varepsilon_{vib}$$

$$\therefore \bar{\nu}_{spec} = (\varepsilon' - \varepsilon'') + \left\{ (v'+\tfrac{1}{2})\bar{\omega}_e' - x_e'(v'+\tfrac{1}{2})^2 \bar{\omega}_e' \right\} - \left\{ (v''+\tfrac{1}{2})\bar{\omega}_e - x_e''(v''+\tfrac{1}{2})^2 \bar{\omega}_e'' \right\} \text{ cm}^{-1} \quad \text{—(6)}$$

and, provided, some half dozen lines can be observed in the band, values of $\bar{\omega}_e'$, x_e', $\bar{\omega}_e''$ and x_e'' as well as separation between electronic states, $(\varepsilon' - \varepsilon'')$ can be calculated.

Observation of band spectrum → leads to values of vibrational frequency and anharmonicity constant in the ground state ($\bar{\omega}_e''$ and x_e'') as well as in the excited state ($\bar{\omega}_e'$ and x_e').

This is very valuable as such excited states maybe extremely & unstable. Band spectrum can tell us a great deal about the bond strength of such species.

Molecules normally have many excited electronic energy levels → whole absorption spectrum of a diatomic molecule will be more complicated than above figure.