Electronic Spectroscopic of molecules

In atomic spectra, when electrons of an atom are excited to higher energy states, the radiations that are absorbed in this process appear as the absorption spectra of atoms. In a similar way, electronic spectra of molecules arise when the electrons of a molecule are excited to higher energy states. The energy involved in this process is generally large and electronic spectra of molecules are ~~usually~~ usually found in visible and ultra-violet regions. Therefore, electronic spectra arise due to ~~the~~ changes in the arrangement of molecular electrons. We shall discuss the electronic spectra of diatomic molecules.

The electronic transition is the result of change in electronic energy. A small change in the electronic energy will be accompanied by a large change in the vibrational ~~rotational~~ energy of the molecule.

These vibrational energy changes give rise to vibrational transitions which form a group of various bands. Further a small change in the vibrational energy will be accompanied by a large change in the rotational energy of the molecule

These rotational energy changes give rise to rotational transitions forming a series of lines in each vibrational band — the so called the fine structure of each band.

Sailent Features of Molecular Electronic Spectra

(1) It appears in the visible and ultraviolet regions.

2) It involves a change in all the three electronic, vibrational and rotational energies of the molecule.

3. They are studied both in emission and absorption, and the bands show a fine structure usually more complicated than in vibrational - rotational bands. The tendency of head formation is much stronger and the bands may be degraded either towards the red or towards the violet.

4. All molecules exhibit electronic spectra. Homonuclear molecules such as H_2, N_2, O_2 which neither give rotational nor rotational-vibrational spectra (as they do not possess permanent dipole moment) exhibit electronic spectra. The reason is that the instantaneous dipole moment changes during the redistribution of electronic charge which accompanies the electronic transition.

Electronic spectra of diatomic molecule

Formation of Electronic Spectra: Electronic Transition

Let us consider the case of a diatomic molecule. If one of its atom is excited (i.e. its valence electron is pushed into an orbital farther from the nucleus) then the molecule is said to be excited. There are various possible electron arrangements for a given molecule ~~they~~ form a pattern of allowed electronic states for the molecule. For each of the electronic state the internuclear separation varies and hence the potential energy differ.

Each electronic state is characterized by
(i) minimum
(ii) an equilibrium internuclear distance re, at which minimum occurs

(iii) a dissociation limit, De

(iv) a set of discrete vibrational levels and sets of discrete rotational levels.

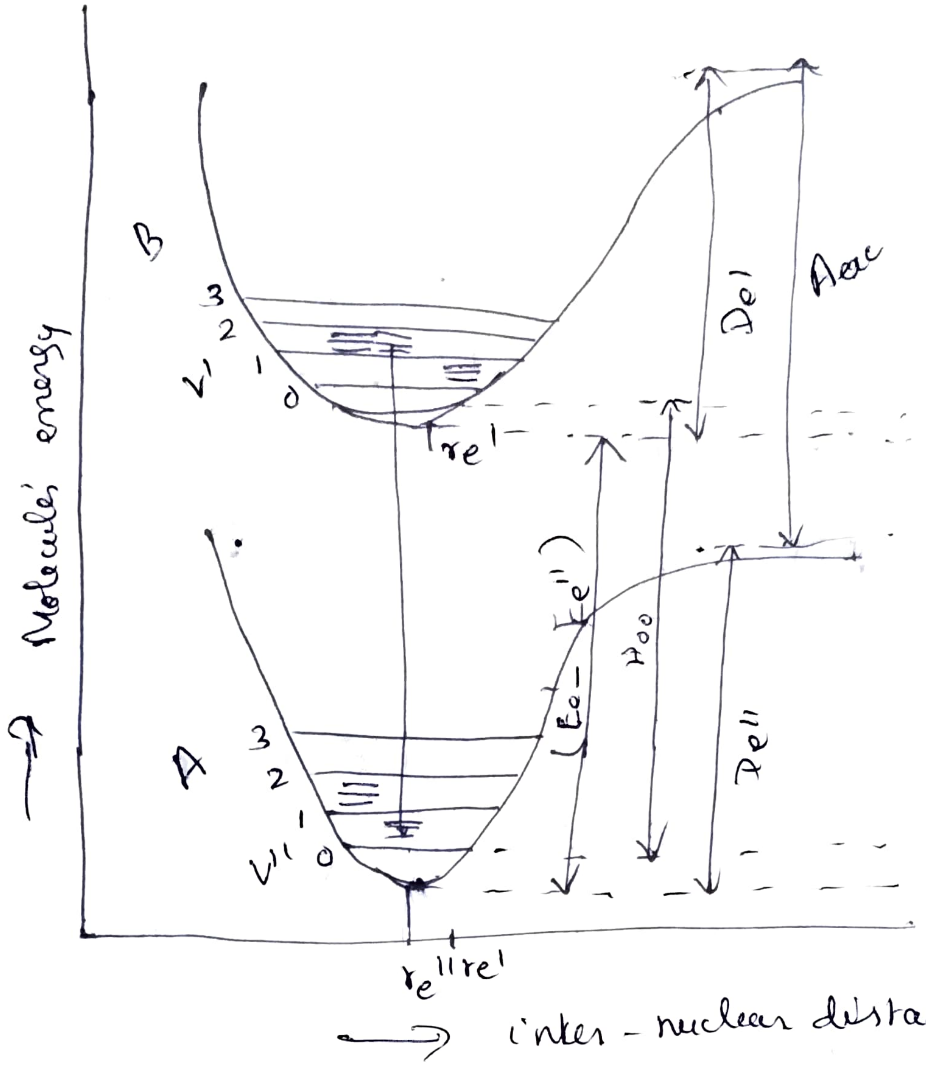

Fig: Potential energy curve for a diatomic molecule

The lower curve A represents ground state
The upper curve B represents excited electronic state.

Ee' and Ee'' represents the electronic energies of the molecule in upper and lower states

For each electronic state there are a number of vibrational state which in turn accompanied by rotational levels.

Thus a single electronic transition in a molecule gives rise to a band system. The bands of the system which correspond to the same upper vibrational state (v') but different lower vibrational levels (v'') are said to be v'' progression, while the the bands which correspond to same lower vibrational level v'' but different upper vibrational levels (v') form a v' progression.

~~The total~~

The total energy of the molecule in the given quantum state is the sum of the electronic energy E_e, vibrational energy E_v and the rotational energy E_r: thus

$$E = E_e + E_v + E_r$$

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_r \quad \text{ergs}$$

$$\frac{\Delta E}{hc} = \frac{\Delta E_e}{hc} + \frac{\Delta E_v}{hc} + \frac{\Delta E_r}{hc} \text{ cm}^{-1}$$

The approximate orders of magnitude of these changes are

$$\frac{\Delta E_e}{hc} \approx \frac{\Delta E_v}{hc} \times 10^3 \text{ cm}^{-1}$$

$$\approx \frac{\Delta E_r}{hc} \times 10^6 \text{ cm}^{-1}$$

which clearly shows vibrational energy changes will produce a coarse structure and rotational changes a fine structure in the spectra of electronic transition.

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Franck - Condon principle

The propability of transition between two given vibration levels of two electronic states A and B is determined by Frank - Condon principle. The principle suggests that :

(i) The observed transitions between two states start from extreme positions of vibrational levels.

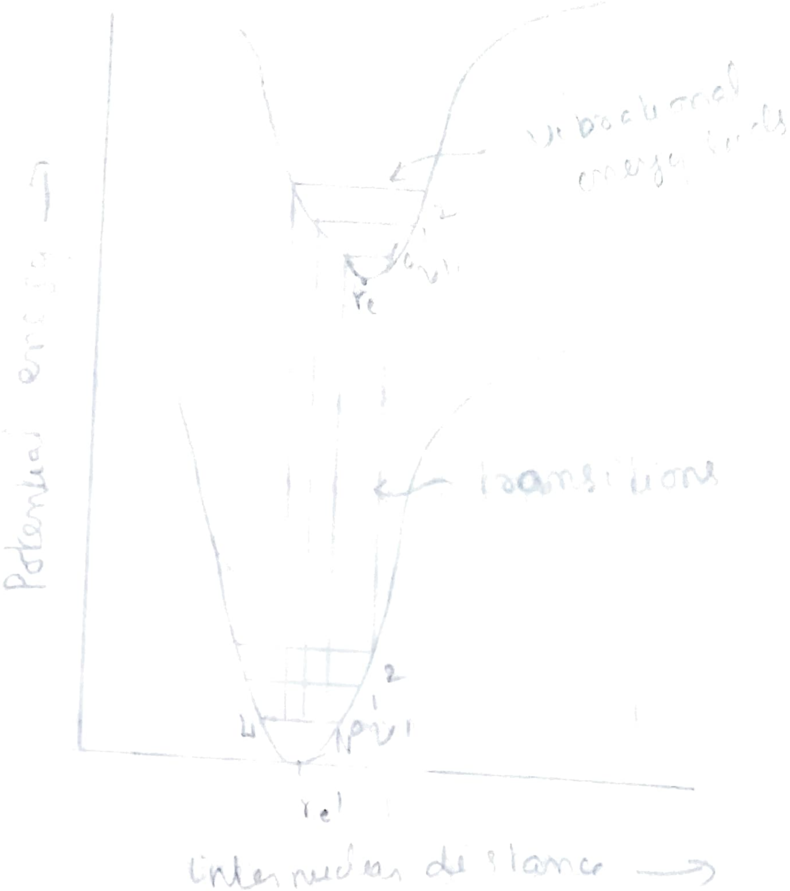
(ii) They should be represented by vertical lines

The principle stems from the idea that electrons move and rearrange themselves much faster than the nuclei of molecules. For example if one calculates the time for an electron to circle a hydrogen nuclear (10^{-16} sec) then it comes out to be a thousand times shorter than the typical period of vibration of molecule (10^{-13} sec). It means an electronic configuration will change in a time so short that the nuclei will not change their positions. Franck condon principle states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

As the internuclear distance of a vibrating molecule, in the coarse of transition between two electronic states, does not change appreciably, such a transition should then be represented by a vertical line

Further, Franck - Condon principle states that transitions from one state to another are most propable when nuclei are in their mean positions. for example, at L and N for the level LN.

Franck Condon principle states that "An electronic transition in a molecule takes place so much rapidly than in a vibration transition, the internuclear distance can be regarded as fixed and velocity is nearly the same before and after the transition.



This is because the nuclei spend at these positions the longest time on account of vibrational kinetic energy being zero there; also quantum mechanically, square of the vibrational configuration is greatest at the extreme positions implying that the propability of finding the nuclei is greatest there. However for the lowest vibrational level (v=0), quantum mechanics predicts that the most propable position for the nuclei to remain in, corresponds to equilibrium position (i.e. minima of the curve, re). Thus the most propable internuclear distance for, the vibrational levels other than v=0, corresponds to the extreme positions and to mid position for v=0

It means transition would start from extreme positions for levels other than $v = 0$ as for the latter they would start from the mid-point. Since these transitions are most probable, the corresponding vibrational bands will be more intense.

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Franck-Condon principle states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition

A diatomic molecule can execute rotations and vibrations quite independently - Born-Oppenheimer approximation

The electrons move faster than nuclei; thus the nuclei feel the P.E of the averaged electronic distribution. This forms the basis of Born-Oppenheimer approximation.

Definition of predissociation: the transition without emission of radiation of a molecule from a stable excited state to an unstable excited state that leads to dissociation

Dissociation and Predissociation - If excitation transfers a molecule in a state containing more energy than the separated components (atoms or molecules), dissociation takes place. Predissociation can be usually explained as a result of internal conversion from an excited state A into a dissociate state B.

~~If a number~~

Predissociation

If a large number of vibrational transitions are observed for a particular molecule, it sometimes happens that the vibrational and rotational structure are quite distinct within a progression for large and small changes in the vibrational quantum number, but either the rotational structure is burred or a complete continuum is observed for intermediate changes. A continuum at high wavenumber would correspond to ordinary dissociation but the central continuum at energies well below the true dissociation limit is refered to as predissociation