



6.1 ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

6.1.1 The Born–Oppenheimer Approximation

As a first approach to the electronic spectra of diatomic molecules we may use the Born–Oppenheimer approximation previously mentioned in Sec. 3.2; in the present context this may be written:

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}} \quad (6.1)$$

which implies that the electronic, vibrational, and rotational energies of a molecule are completely independent of each other. We shall see later to what extent this approximation is invalid. A change in the total energy of a molecule may then be written:

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

or

$$\Delta \varepsilon_{\text{total}} = \Delta \varepsilon_{\text{elec.}} + \Delta \varepsilon_{\text{vib.}} + \Delta \varepsilon_{\text{rot.}} \quad \text{cm}^{-1} \quad (6.2)$$

The approximate orders of magnitude of these changes are:

$$\Delta \varepsilon_{\text{elec.}} \approx \Delta \varepsilon_{\text{vib.}} \times 10^3 \approx \Delta \varepsilon_{\text{rot.}} \times 10^6 \quad (6.3)$$

vibrational changes will produce a 'coarse structure' and rotational changes a 'fine structure' on the spectra of electronic transitions. We should also note that whereas pure rotation spectra (Chapter 2) are shown only by molecules possessing a permanent electric dipole moment, and vibrational spectra (Chapter 3) require a change of dipole during the motion, electronic spectra are given by *all* molecules since changes in the electron distribution in a molecule are always accompanied by a dipole change. This means that homonuclear molecules (for example, H_2 or N_2), which show no rotation or vibration-rotation spectra, *do* give an electronic spectrum and show vibrational and rotational structure in their spectra from which rotational constants and bond vibration frequencies may be derived.

vibrational changes → coarse structure
rotational changes → fine structure



Vibrational Coarse Structure: Progressions

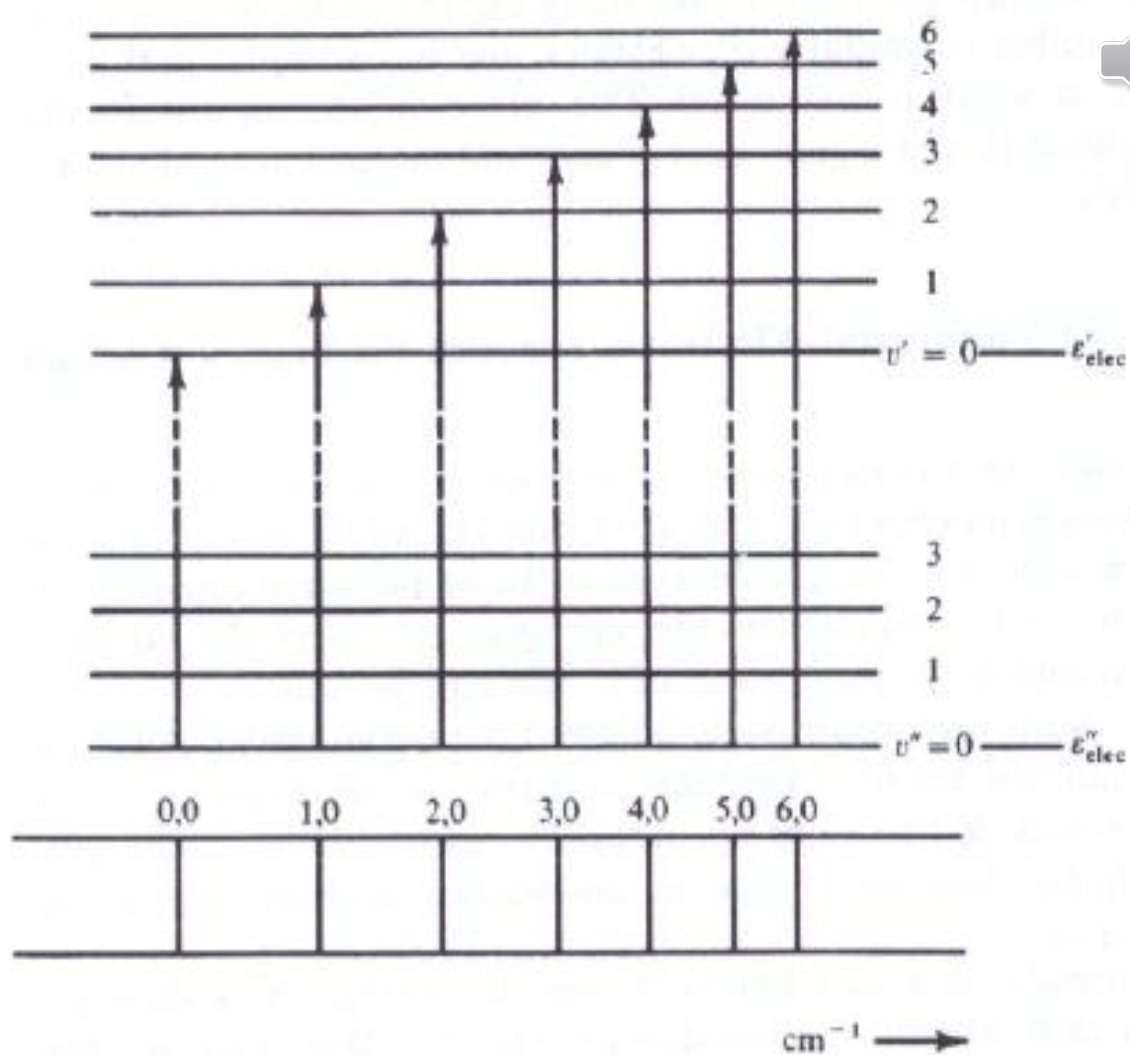


Figure 6.1 The vibrational 'coarse' structure of the band formed during electronic absorption from the ground ($v'' = 0$) state to a higher state.

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

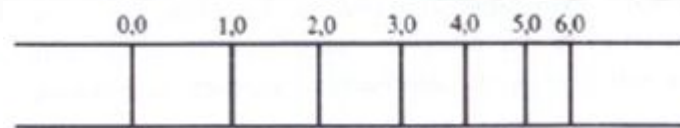
$$E_{\text{total}} = E_{\text{elec}} + E_{\text{vib}} \quad \text{cm}^{-1}$$

$$E_{\text{total}} = E_{\text{elec}} + (v + 1/2) \bar{\omega}_e - x_e (v + 1/2)^2 \bar{\omega}_e \quad \text{cm}^{-1}$$

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

- lower state is distinguished by double prime.
- spacing between the upper energy levels is deliberately shown to be rather smaller than the lower, since an excited electronic state usually corresponds to a weaker bond in the molecule and hence a smaller vibrational wavenumber, $\bar{\omega}_e$.

There is essentially no selection rule for v when a molecule undergoes an electronic transition, i.e., every transition $v'' \rightarrow v'$ has some probability, and a great many spectral lines would, therefore, be expected. However, the situation is considerably simplified if the *absorption* spectrum is considered from the electronic ground state. In this case, as we have seen in Sec. 3.1.3, virtually all the molecules exist in the lowest vibrational state, that is, $v'' = 0$, and so the only transitions to be observed with appreciable intensity are those indicated in Fig. 6.1. These are conventionally labelled according to their (v', v'') numbers (note: upper state *first*), that is, $(0, 0)$, $(1, 0)$, $(2, 0)$, etc. Such a set of transitions is called a *band* since, under low resolution, each line of the set appears somewhat broad and diffuse, and is more particularly called a v' *progression*, since the value of v' increases by unity for each line in the set. The diagram shows that the lines in a band crowd together more closely at high frequencies; this is a direct consequence of the anharmonicity of the upper state vibration which causes the excited vibrational levels to converge.



Intensity of Vibronic Spectrum

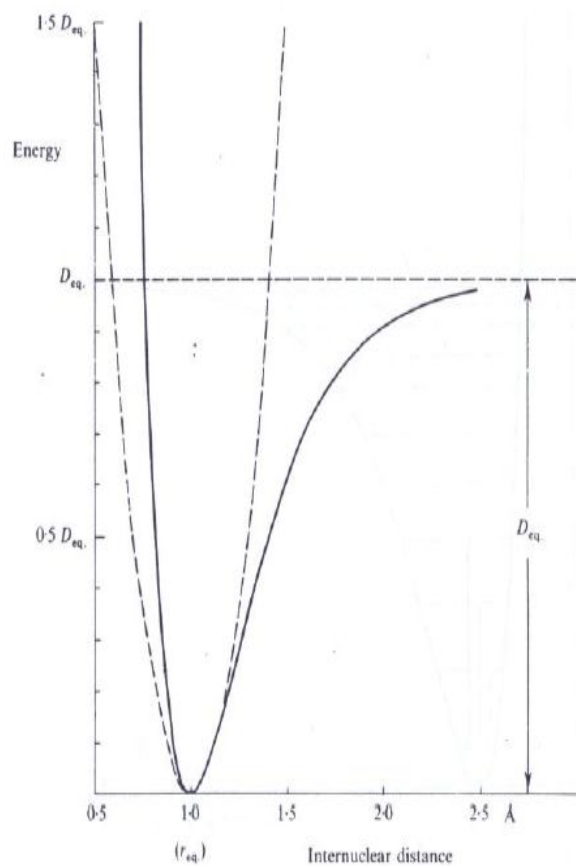
6.1.3 Intensity of Vibrational–Electronic Spectra: the Franck–Condon Principle

Although quantum mechanics imposes no restrictions on the change in the vibrational quantum number during an electronic transition, the vibrational lines in a progression are not all observed to be of the same intensity. In some spectra the (0, 0) transition is the strongest, in others the intensity increases to a maximum at some value of v' , while in yet others only a few vibrational lines with high v' are seen, followed by a continuum. All these types of spectrum are readily explicable in terms of the *Franck–Condon principle* which states that *an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.*

The Franck-Condon principle states that since the time required for a molecule to execute a vibration (about 10^{-12} sec) is much longer than that required for transition of electrons (about 10^{-15} sec.), during electronic transitions the nuclei do not appreciably alter their positions. This means that the internuclear distance remains unaltered during the transition.

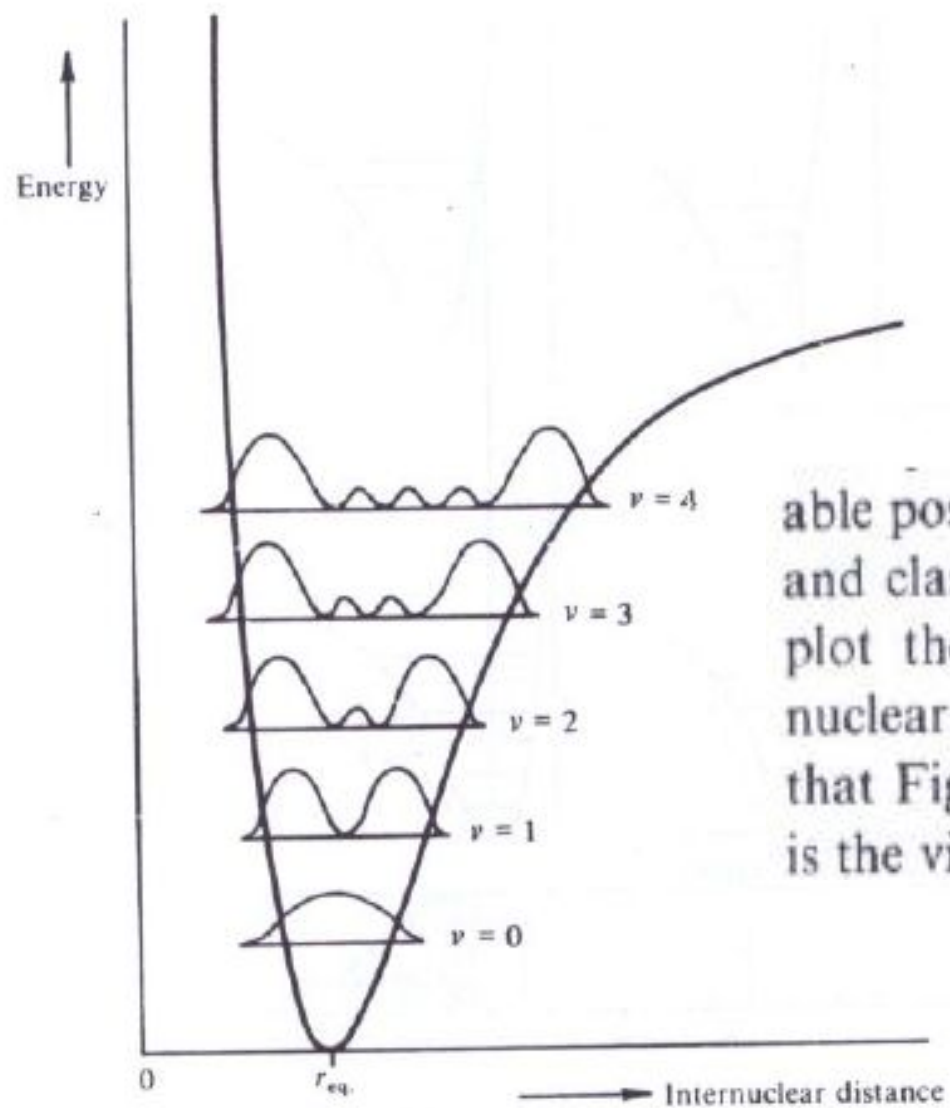


A very useful guiding principle for investigating the vibrational structure of electronic spectra is provided by the well known **Franck-Condon principle** which states that *an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition*. This principle is, to a first approximation, true since the electrons move so much faster than the nuclei that during the electronic transition the nuclei do not change their position. Hence, *an electronic transition may be represented by a vertical line on a plot of potential energy versus the internuclear distance*.



Classical theory would suggest that the oscillating atom would spend most of its time *on* the curve at the turning point of its motion, since it is moving most slowly there; quantum theory, while agreeing with this view for high values of the vibrational quantum number, shows that for $v = 0$ the atom is most likely to be found at the *centre* of its motion, i.e., at the equilibrium internuclear distance r_{eq} .





For $v = 1, 2, 3, \dots$ the most probable positions steadily approach the extremities until, for high v , the quantal and classical pictures merge. This behaviour is shown in Fig. 6.2 where we plot the probability distribution in each vibrational state against internuclear distance. Those who have studied quantum mechanics will realize that Fig. 6.2 shows the variation of ψ^2 with internuclear distance, where ψ is the vibrational wave function.



Figure 6.2 The probability distribution for a diatomic molecule according to the quantum theory. The nuclei are most likely to be found at distances apart given by the maxima of the curve for each vibrational state.

If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable with respect to dissociation into its atoms, then we can represent the upper state by a Morse curve similar in outline to that of the ground electronic state. There will probably (but not necessarily) be differences in such parameters as vibrational frequency, equilibrium internuclear distance, or dissociation energy between the two states, but this simply means that we should consider each excited molecule as a new, but rather similar, molecule with a different, but also rather similar, Morse curve.

Before the absorption the molecule is in the ground vibrational state of the ground electronic state. The nuclei are located at the equilibrium separation R_e . When the transition occurs, the molecule is excited to the state represented by the upper curve. According to the Franck Condon principle the nuclear framework remains constant during the excitation, and so we may represent this transition by a vertical line



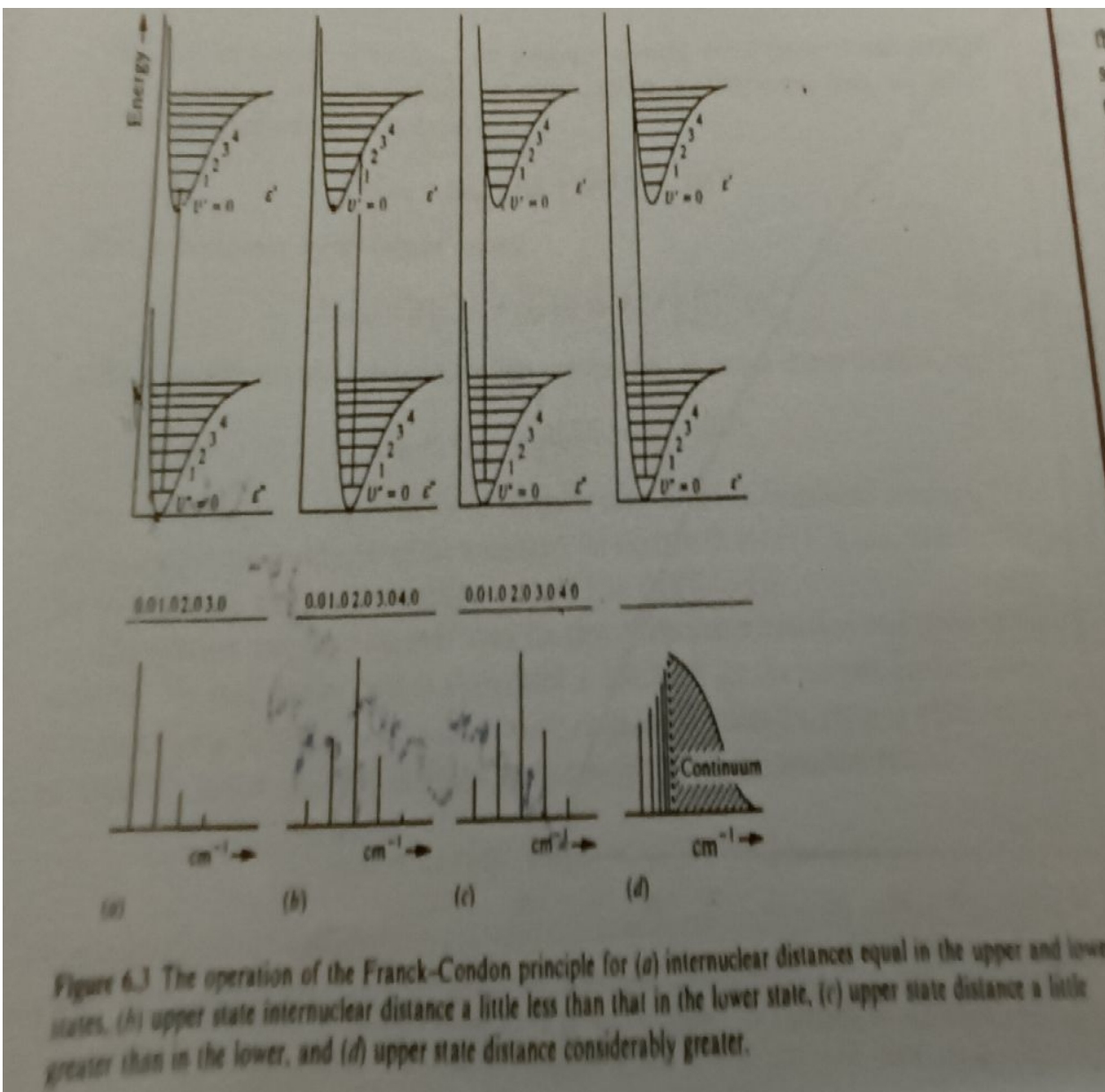


Figure 6.3 The operation of the Franck-Condon principle for (a) internuclear distances equal in the upper and lower states, (b) upper state internuclear distance a little less than that in the lower state, (c) upper state distance a little greater than in the lower, and (d) upper state distance considerably greater.

- It is not sure if the σ_{eq} of the excited state is equal to the σ_{eq} of the ground state.

• This leads to four different possibilities.

Possibility 1 $\rightarrow \sigma_{eq} \text{ of } v'' = \sigma_{eq} \text{ of } v'$

Possibility 2 $\rightarrow \sigma_{eq} \text{ of } v'' > \sigma_{eq} \text{ of } v'$

Possibility 3 $\rightarrow \sigma_{eq} \text{ of } v'' < \sigma_{eq} \text{ of } v'$

Possibility 4 $\rightarrow \sigma_{eq} \text{ of } v'' \ll \sigma_{eq} \text{ of } v'$



Figure 6.3 shows three possibilities. In (a) we show the upper electronic state having the same equilibrium internuclear distance as the lower. Now the Franck–Condon principle suggests that a transition occurs *vertically* on this diagram, since the internuclear distance does not change, and so if we consider the molecule to be initially in the ground state both electronically (ε'') and vibrationally ($v'' = 0$), then the most probable transition is that indicated by the vertical line in Fig. 6.3(a). Thus the strongest spectral line of the $v'' = 0$ progression will be the (0, 0). However, the quantum theory only says that the *probability* of finding the oscillating atom is greatest at the equilibrium distance in the $v = 0$ state—it allows some, although small, chance of the atom being near the extremities of its vibrational motion. Hence there is some chance of the transition starting from the ends of the $v'' = 0$ state and finishing in the $v' = 1, 2$, etc., states. The (1, 0), (2, 0), etc., lines diminish rapidly in intensity, however, as shown at the foot of Fig. 6.3(a).



In Fig. 6.3(b) we show the case where the excited electronic state has a *slightly* greater internuclear separation than the ground state. Now a vertical transition from the $v'' = 0$ level will most likely occur into the upper vibrational state $v' = 2$, transitions to lower and higher v' states being less likely; in general the upper state most probably reached will depend on the difference between the equilibrium separations in the lower and upper states. In Fig. 6.3(c) the upper state separation is drawn as *considerably* greater than that in the lower state and we see that, firstly, the vibrational level to which a transition takes place has a high v' value. Further, transitions can now occur to a state where the excited molecule has energy in excess of its own dissociation energy. From such states the molecule will dissociate without any vibrations and, since the atoms which are formed may take up any value of kinetic energy, the transitions are not quantized and a continuum results. This is shown at the foot of the figure.

Case 1: Fig. 7.5 a shows the near ultraviolet spectrum of CN^- radical. The potential energy minima lie very nearly one above the other. The 0–0 band has maximum intensity. 1–0, 2–0, 3–0 bands decrease in intensity. The equilibrium bond lengths (R_e, R'_e) and vibrational wavenumbers (ω, ω') for the 0–0 band for CN^- radical are given below:

$$R'_e = 0.11506 \text{ nm}, \quad \omega' = 2164.1 \text{ cm}^{-1}$$

$$R_e = 0.11718 \text{ nm}, \quad \omega = 2068.7 \text{ cm}^{-1}$$

Case 2 : Fig. 7.5 b shows the spectrum of CO. The minimum of the upper potential energy lies at a moderately greater R_e value (0.01–0.02 nm) than the lower potential energy. The 0–3 band has maximum intensity and other bands on both sides have decreased intensity. The equilibrium bond lengths and vibrational wave numbers are given below:

$$R'_e = 0.1235 \text{ nm}, \quad \omega' = 1515.6 \text{ cm}^{-1}$$

$$R_e = 0.1128 \text{ nm}, \quad \omega = 2170.2 \text{ cm}^{-1}$$

Case 3 : The minimum of the upper potential energy curve lies at a considerable distance away from that of the lower potential energy curve in the spectrum of I_2 (Fig. 7.5 c). In this case, transition takes place to a very high vibrational level in the upper state, which corresponds to the continuum level. The continuum level has very high energy and the molecule undergoes dissociation. The 0 – 0 band is absent in this spectrum.



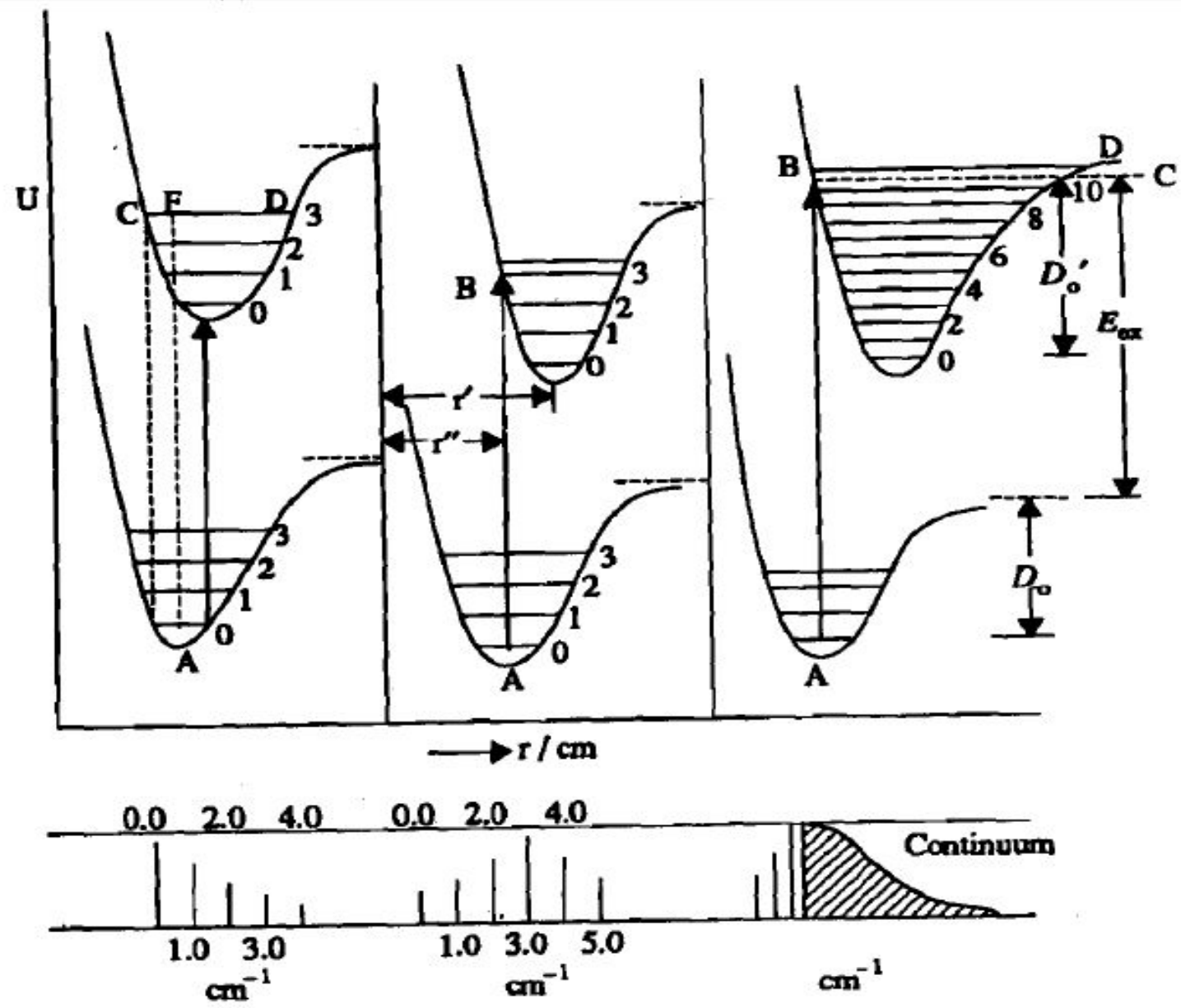


Fig. 7.5 : Application of Franck-Condon principle to the spectra of (a) CN^- radical (b) CO molecule (c) I_2 molecule.



Electronic Spectra of Polyatomic Molecules

The electronic spectra of polyatomic molecules show greater degree of complexity. The vibrational structure and the rotational fine structure of electronic spectra can only be observed in the gaseous states of small molecules. In solution, the rotational energy levels are not well defined; moreover, large molecules have very high moments of inertia. Hence, the rotational fine structure is totally wiped out in solution. Even vibrational transitions are broad, as shown by the Franck-Condon principle. Thus, the electronic spectra of molecules in solution appear as large unresolved bands rather than as sharp peaks. This is a characteristic feature of electronic spectra in condensed media and must be borne in mind. It also follows that if the rotational and vibrational structure of an electronic band can be fully resolved in the gaseous state, considerable information can be obtained from the electronic spectrum.

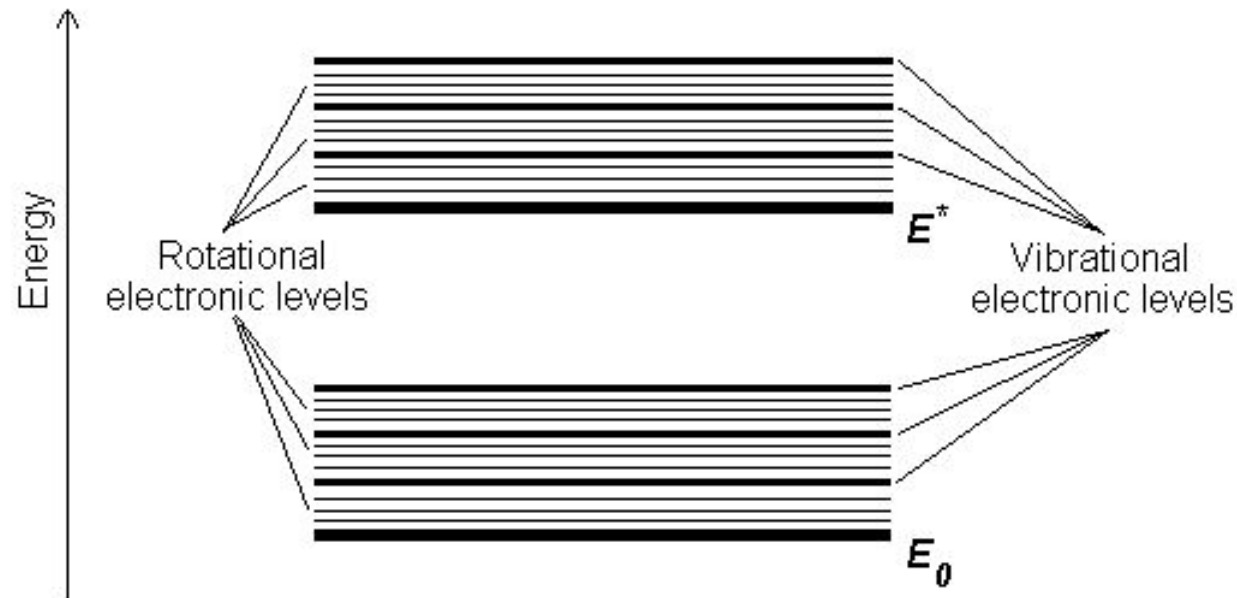
Organic compounds, particularly those containing groups like $C=C$, $C=O$, $-N=N-$ and extensively conjugated systems, form a special class of polyatomic molecules whose electronic spectra are amenable to simple interpretation even though the investigation of their detailed spectral features may require knowledge of quantum mechanics and group theory. On the basis of the molecular orbital theory (MOT), the electrons can be classified as σ , π or n (non-bonding) depending upon the MOs they occupy. For organic carbonyl compounds, the electronic transitions involve promotion of the electrons in n , σ and π orbitals in the ground state to σ^* and π^* ABMOs in the excited state (Fig. 33). In other words, only the transitions of the type $\sigma^* \leftarrow \sigma$, $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ are allowed. Since electrons in the n orbitals are not involved in bond formation, there are no ABMOs associated with them.

Electronic transitions

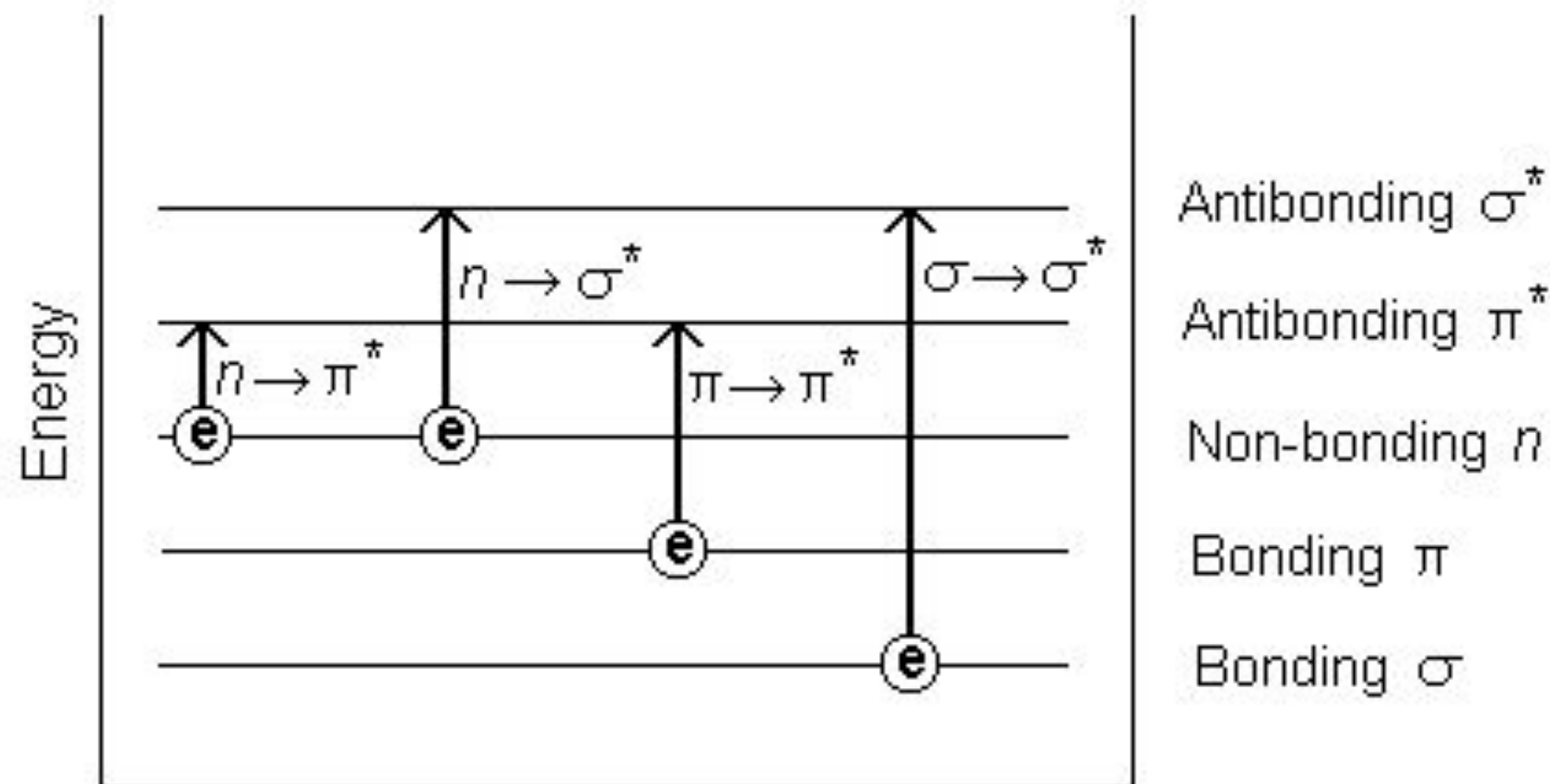
The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered;

1. Transitions involving π , σ , and n electrons
2. Transitions involving charge-transfer electrons
3. Transitions involving d and f electrons

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level.



Possible *electronic* transitions of π , σ , and n electrons are;



$\sigma \rightarrow \sigma^*$ Transitions

An electron in a bonding σ orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

$n \rightarrow \sigma^*$ Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Most absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons.