

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.*

We have already seen in Chapter 3 how the energy of a diatomic molecule varies with internuclear distance (cf. Fig. 3.3). We recall that this figure, the Morse curve, represents the energy when one atom is considered fixed on the $r = 0$ axis and the other is allowed to oscillate between the

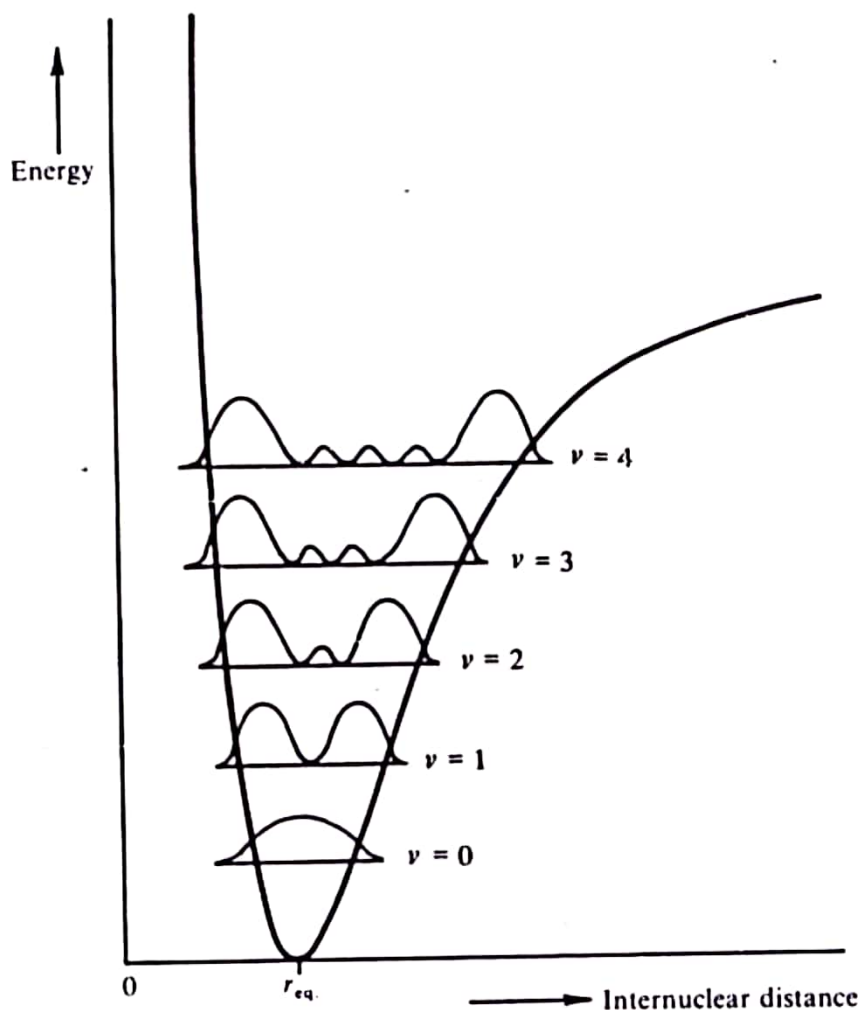


Figure 6.2 The probability distribution for a diatomic molecule according to the quantum theory. The nuclei are most likely to be found at distances apart given by the maxima of the curve for each vibrational state.

limits of the curve. 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.

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

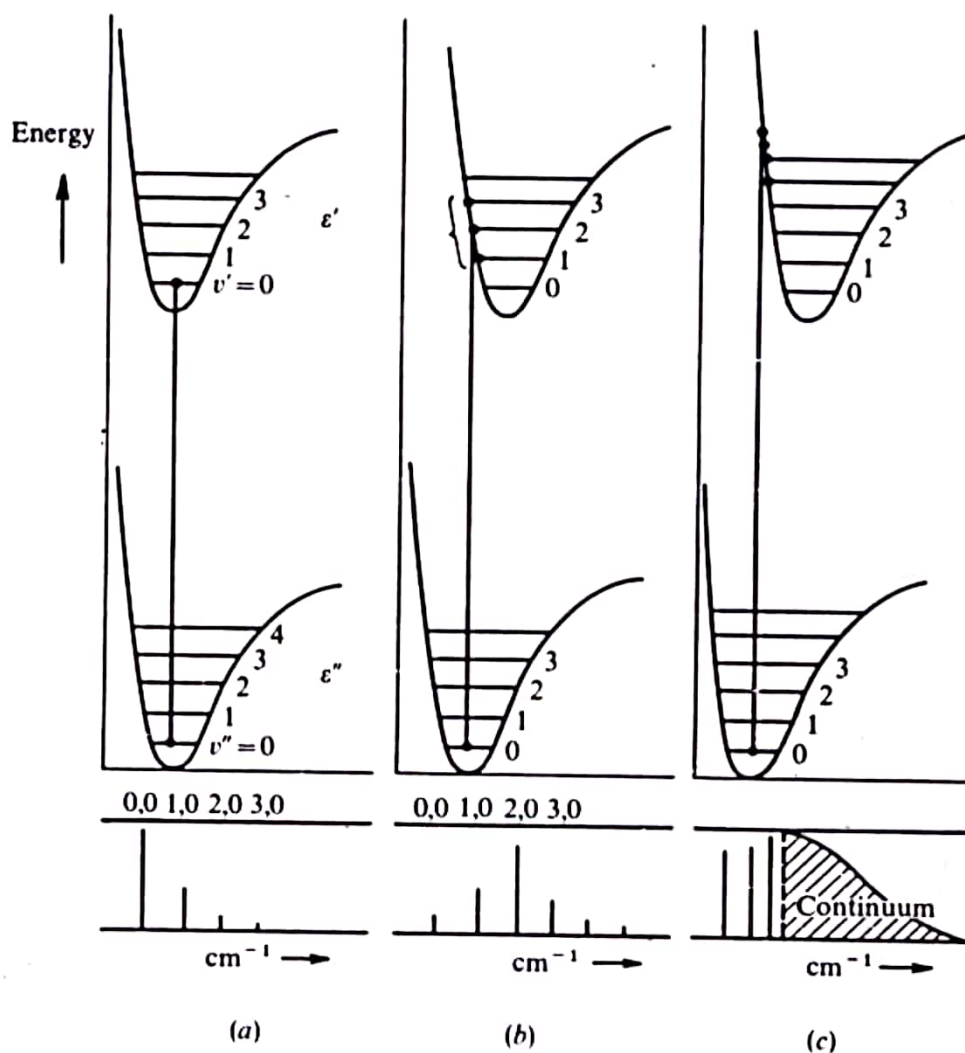


Figure 6.3 The operation of the Franck–Condon principle for (a) internuclear distances equal in upper and lower states, (b) upper-state internuclear distance a little greater than that in the lower state, and (c) upper-state distance considerably greater.

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.

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. We consider the phenomenon of dissociation more fully in the next section.

The situation is rather more complex for emission spectra and for absorption from an excited vibrational state, for now transitions take place from *both ends* of the vibrational limits with equal probability; hence each progression will show two maxima which will coincide only if the equilibrium separations are the same in both states.