

The Franck–Condon principle

In 1925, before the development of the Schrödinger equation, Franck put forward qualitative arguments to explain the various types of intensity distributions found in vibronic transitions. His conclusions were based on an appreciation of the fact that an electronic transition in a molecule takes place much more rapidly than a vibrational transition so that, in a vibronic transition, the nuclei have very nearly the same position and velocity before and after the transition.

Possible consequences of this are illustrated in Figure 7.20(a), which shows potential curves for the lower state, which is the ground state if we are considering an absorption process, and the upper state. The curves have been drawn so that $r'_e > r''_e$. When the lower state is the ground state this is very often the case since the electron promotion involved is often from a bonding orbital to an orbital which is less bonding, or even antibonding. For example, in nitrogen, promotion of an electron from the $\sigma_g 2p$ to the $\pi_g^* 2p$ orbital (Figure 7.14) gives two states,¹¹ $a^1\Pi_g$ and $B^3\Pi_g$, in which r_e is 1.2203 Å and 1.2126 Å, respectively, considerably increased from 1.0977 Å in the $X^1\Sigma_g^+$ ground state.

In absorption, from point A of the ground state in Figure 7.20(a) (zero-point energy can be neglected in considering Franck's semi-classical arguments) the transition will be to point B of the upper state. The requirement that the nuclei have the same position before and after the transition means that the transition is between points which lie on a vertical line in the figure: this means that r remains constant and such a transition is often referred to as a vertical transition. The second requirement, that the nuclei have the same velocity before and after the transition, means that a transition from A, where the nuclei are stationary, must go to B, as this is the classical turning point of a vibration, where the nuclei are also stationary. A transition from A to C is highly improbable because, although the nuclei are stationary at A and C, there is a large change of r . An A to D transition is also unlikely because, although r is unchanged, the nuclei are in motion at the point D.

Figure 7.20(b) illustrates the case where $r'_e \simeq r''_e$. An example of such a transition is the $D^1\Sigma_u^+ - X^1\Sigma_g^+$ Mulliken band system of C_2 (see Table 7.6 and Figure 7.17). The value of r_e is 1.2380 Å in the D state and 1.2425 Å in the X state. Here the most probable transition is from A to B with no vibrational energy in the upper state. The transition from A to C

¹¹ Unfortunately, in N_2 as in I_2 , the conventional labelling of states in footnote 7 on page 236 is not adhered to.

maintains the value of r but the nuclear velocities are increased due to their having kinetic energy equivalent to the distance BC.

In 1928, Condon treated the intensities of vibronic transitions quantum mechanically.

The intensity of a vibronic transition is proportional to the square of the transition moment R_{ev} , which is given by (see Equation 2.13)

$$R_{ev} = \int \psi'_{ev}{}^* \boldsymbol{\mu} \psi''_{ev} d\tau_{ev} \quad (7.84)$$

where $\boldsymbol{\mu}$ is the electric dipole moment operator and ψ'_{ev} and ψ''_{ev} are the vibronic wave functions of the upper and lower states, respectively. The integration is over electronic and vibrational coordinates. Assuming that the Born–Oppenheimer approximation (see Section 1.3.4) holds, ψ_{ev} can be factorized into $\psi_e \psi_v$. Then Equation (7.84) becomes

$$R_{ev} = \iint \psi'_e{}^* \psi'_v{}^* \boldsymbol{\mu} \psi''_e \psi''_v d\tau_e dr \quad (7.85)$$

First we integrate over electron coordinates τ_e , giving

$$R_{ev} = \int \psi'_v{}^* R_e \psi''_v dr \quad (7.86)$$

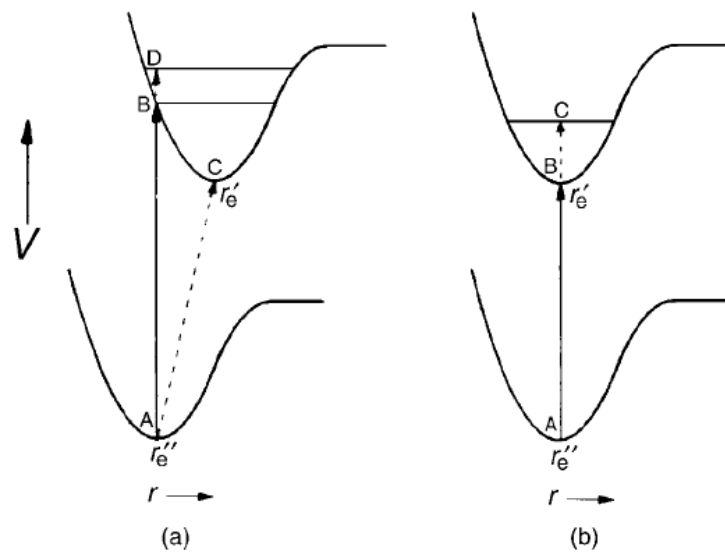


Figure 7.20 Illustration of the Franck principle for (a) $r'_e > r''_e$ and (b) $r'_e \simeq r''_e$. The vibronic transition B–A is the most probable in both cases

where r is the internuclear distance and \mathbf{R}_e is the electronic transition moment given by

$$\mathbf{R}_e = \int \psi_e'^* \boldsymbol{\mu} \psi_e'' d\tau_e \quad (7.87)$$

Our ability to do the integration to give Equation (7.86) is a consequence of the Born–Oppenheimer approximation which assumes that the nuclei can be regarded as stationary in relation to the much more fast-moving electrons. This approximation also allows us to take \mathbf{R}_e outside the integral in Equation (7.86), regarding it as a constant, independent of r , which is good enough for our purposes here. Thus we have

$$\mathbf{R}_{ev} = \mathbf{R}_e \int \psi_v'^* \psi_v'' dr \quad (7.88)$$

The quantity $\int \psi_v'^* \psi_v'' dr$ is called the vibrational overlap integral, as it is a measure of the degree to which the two vibrational wave functions overlap. Its square is known as the Franck–Condon factor to which the intensity of the vibronic transition is proportional. In carrying out the integration the requirement that r remain constant during the transition is necessarily taken into account.

The classical turning point of a vibration, where nuclear velocities are zero, is replaced in quantum mechanics by a maximum, or minimum, in ψ_v near to this turning point. As is illustrated in Figure 1.13 the larger is v the closer is the maximum, or minimum, in ψ_v to the classical turning point.

Figure 7.21 illustrates a particular case where the maximum of the $v' = 4$ wave function near to the classical turning point is vertically above that of the $v'' = 0$ wave function. The maximum contribution to the vibrational overlap integral is indicated by the solid line, but appreciable contributions extend to values of r within the dashed lines. Clearly, overlap integrals for v' close to four are also appreciable and give an intensity distribution in the $v'' = 0$ progression like that in Figure 7.22(b).

If $r_e' \gg r_e''$ there may be appreciable intensity involving the continuum of vibrational levels above the dissociation limit. This results in a $v'' = 0$ progression like that in Figure 7.22(c) where the intensity maximum is at a high value of v ; or it may be in the continuum. An example of this is the $B^3\Pi_{0_u^+} - X^1\Sigma_g^+$ transition of iodine. In the B and X states r_e is 3.025 Å and 2.666 Å, respectively, leading to the broad intensity maximum close to the continuum, as observed in Figure 7.19.

Figure 7.22(a) shows the intensity maximum at $v' = 0$ for the case when $r_e' \simeq r_e''$. The intensity usually falls off rapidly in such a case.

Occasionally, we encounter a case where $r_e' < r_e''$. When the lower state is the ground state this is unusual but it can happen when the electron promotion is from an antibonding to a non-bonding or bonding orbital. The situation is more likely to arise in a transition between two excited states. Qualitatively, the situation is similar to that in Figure 7.21 except that the upper potential curve is displaced to low r so that the right-hand maximum of, for example, $v' = 4$ is above the $v'' = 0$ maximum. The result is, again, an intensity distribution like that in Figure 7.22(b) so that an observation of a long $v'' = 0$ progression with an intensity

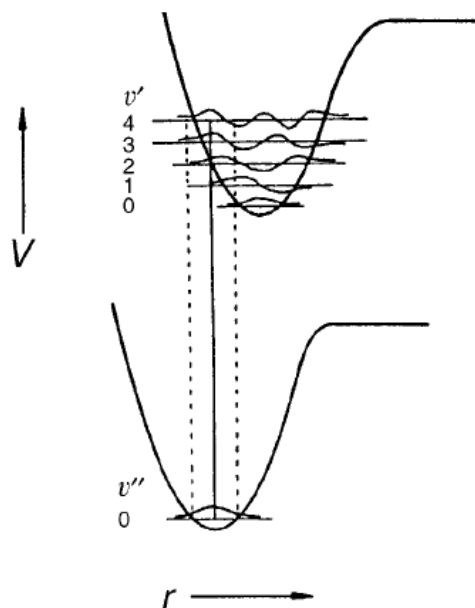


Figure 7.21 Franck–Condon principle applied to a case in which $r'_e > r''_e$ and the 4–0 transition is the most probable

maximum at $v' > 0$ indicates qualitatively an appreciable change in r_e from the lower to the upper state but does not indicate the sign of the change. This would be true, even quantitatively, if the molecule behaved as a harmonic oscillator but, because of anharmonicity, the intensity distribution along the progression is slightly different for $r'_e > r''_e$ than for $r'_e < r''_e$.

In the case where $r'_e > r''_e$ there is, when anharmonicity is taken into account, a relatively steep part of the excited state potential curve above $v'' = 0$, giving a relatively broad

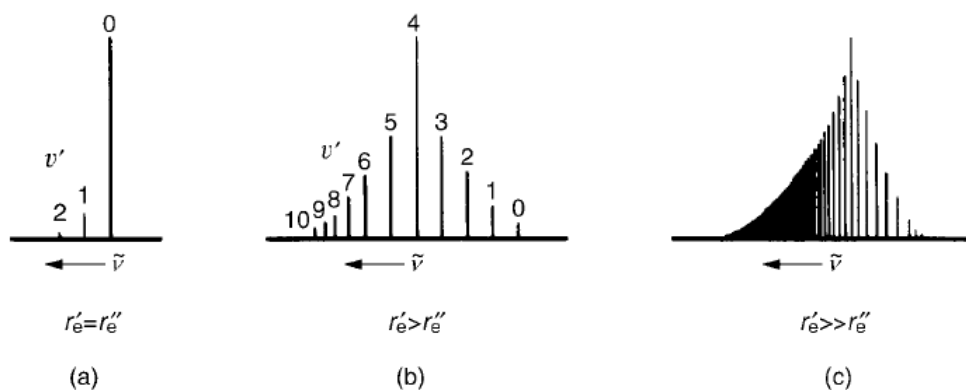


Figure 7.22 Typical vibrational progression intensity distributions

maximum in the progression intensity. For $r'_e < r''_e$, there is a shallower part of the excited state potential curve above $v'' = 0$ and a sharper intensity maximum results.

Accurate intensity measurements have been made in many cases and calculations of $r'_e - r''_e$ made, including the effects of anharmonicity and even allowing for breakdown of the Born–Oppenheimer approximation.