

Franck-Condon Principle

Since the nuclei are so much more massive than the electrons, an electronic transition takes place faster than the nuclei can respond. Then, after the transition, electron density is rapidly built up in new regions of the molecule, and the stationary nuclei, suddenly, experience a new force field. Then the nuclei start to oscillate from their original separation, therefore, the stationary equilibrium separation of the nuclei in the initial electronic state becomes the turning point, which corresponds to the point of a vibration where the nuclei are classically stationary, in the final electronic state.

Quantum Mechanically, this allows us to calculate the intensities of the transitions to different vibrational levels of the electronically excited molecule and, then, to account for the shape of the absorption band.

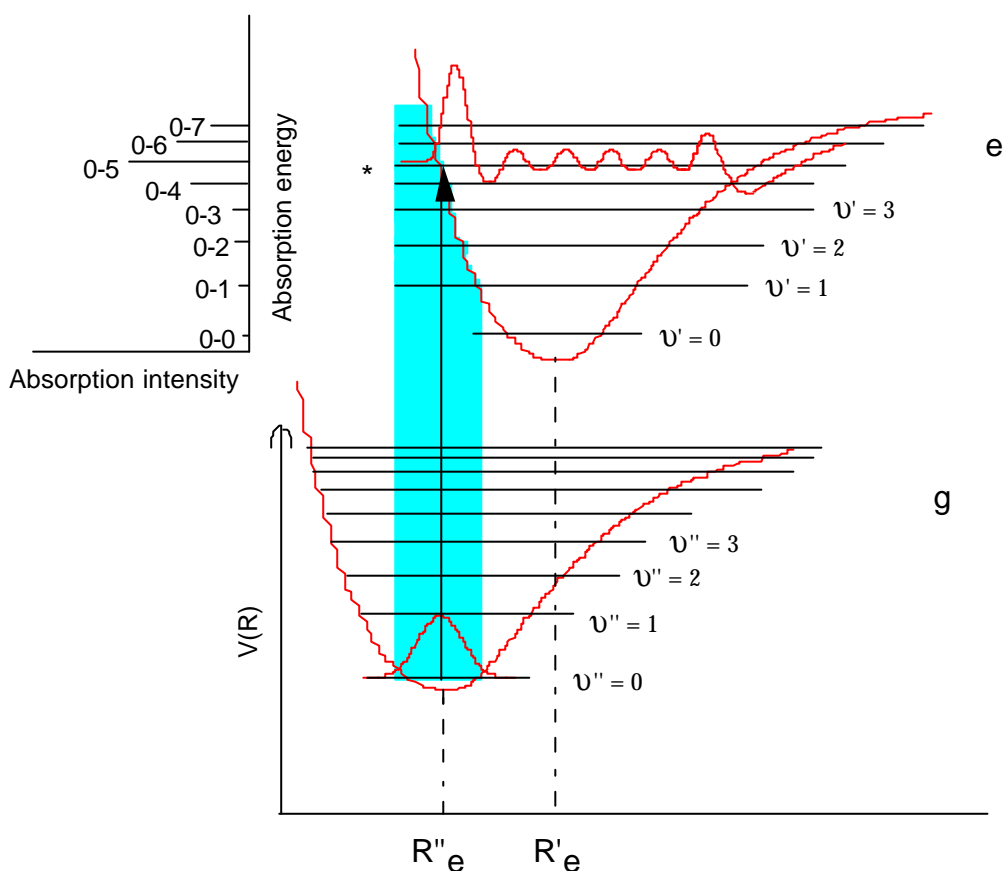


Fig 14. The form of the vibrational wavefunction shows that the most probable location of the nuclei is at their equilibrium separation, R_e for $V=0$.

The electronic transition, hence, is most likely to take place when the nuclei have this separation. The nuclear framework remains constant during this excitation, and the electronic transition occurs without change of nuclear geometry along the vertical transition. The level marked with * is the one in which the nuclei are most probably at the initial separation, R_e , because the vibrational wavefunction has the maximum

amplitude there, and so this is the most probable level for the termination of the transition.

The Franck-Condon Principle for absorption

“The electron jump in a molecule takes place so rapidly in comparison to the vibrational motion that immediately afterwards the nuclei still have very nearly the same relative position and velocity as before the jump”.

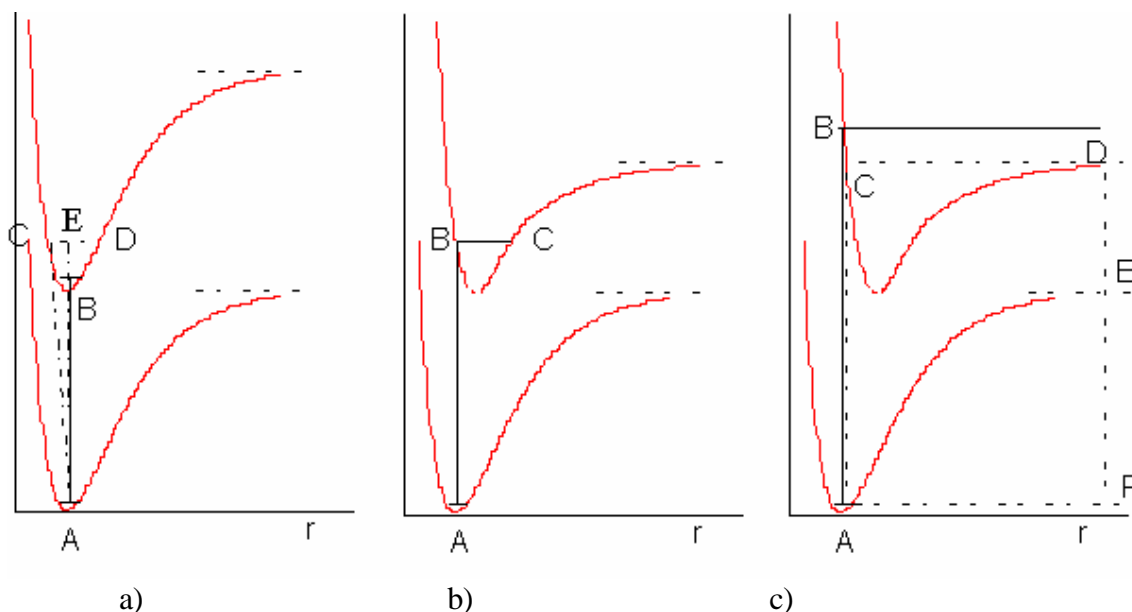


Fig 15. Potential curves explaining the intensity distribution in absorption according to the Franck-Condon principle. In c), AC gives the energy of the dissociation limit, EF the dissociation energy of the ground state, and DE the excitation energy of the dissociation products.

The potential curves of the two electronic states (in a)) have been so chosen that their minima lie very nearly one above the other (equal internuclear distance). In absorption, the molecule is initially at the minimum of the lower potential curve, if we disregard the zero point vibration. Due to the Franck-Condon principle a transition between the lowest levels in the ground and upper state will have only small changes in position and momentum. However, a transition into a high vibrational state, CD, would be possible only when, at the moment of the electronic jump, either the position (transition from A to C) or the velocity (transition from A to E) or both alter to an appreciable extent. At the point E the molecule has the amount of kinetic EB. Only at the turning point C or D are the velocity and the kinetic energy zero, as the initial state at A. Hence, following the Franck-Condon principle a transition from $v'=0$ to such a high vibrational level is forbidden or at least highly improbable. For the level $v'=1$, the necessary alteration of the position or the velocity during the electron jump is comparatively small.

In b), the minimum of the upper potential curve lies at a somewhat greater r value than of the lower. Therefore the transition between the minima of the two electronic states is no longer the most probable, since the internuclear distance must alter somewhat in

such a transition. The most probable transition is from A to B. For this transition there is no change in the internuclear distance at the moment of the jump and no change of the velocity. Hence, after the transition, the two nuclei still have their old distance from each other and the same relative velocity. But now, the equilibrium internuclear distance has a different value in the new electronic state, the nuclei start to vibrate between B and C. The vibrational levels whose left turning points lie in the neighbourhood of B are the upper levels of the most intense bands. For still higher vibrational levels an appreciable change of the internuclear distance or velocity must take place, as a result of which the intensity of the bands decrease again with increasing v' .

In c) the minimum of the upper potential curve lies at a still greater internuclear distance. The Franck-Condon principle is strictly fulfilled for the transition AB. However, the point B on the upper potential curve lies above the asymptote of this curve and therefore corresponds to the continuous region of the vibrational spectrum of the upper state.

Therefore, it can be said that in absorption the most intense transition from $v''=0$ is always that corresponding to a transition from the minimum of the lower potential curve vertically upward.

The Franck-Condon Principle for Emission

According to the Franck-Condon principle, the variation of intensity in a band progression with $v'=0$ in emission corresponds exactly to that of a progression with $v''=0$ in absorption. But, actually, there are some differences: There is an intensity maximum at v'' value that is determined by the relative position of the minima of the two potential curves and their shape.

However, the intensity distribution is different for band progressions in emission having v' different to zero.

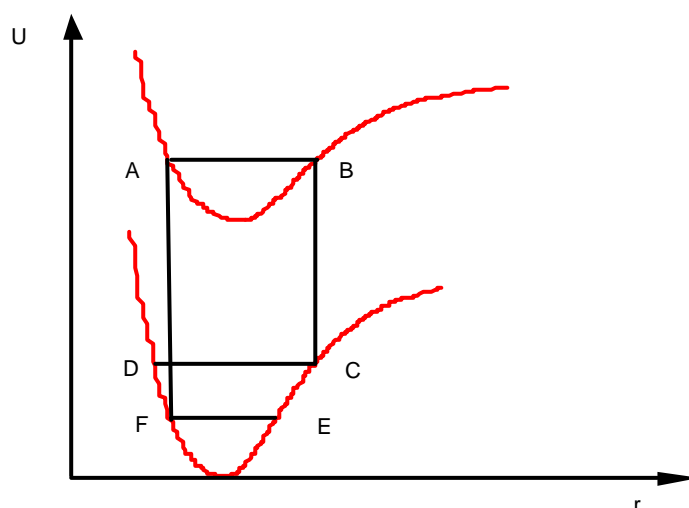


Fig 16. During the vibration in the upper state the molecule is on line AB and when it emits, if the molecule is at B, and if there is to be no change in position and velocity, immediately after the jump the molecule take place over C, at the turning point for the new vibrational motion CD, but the electron can jump from A to F, and form the left

turning point of the new vibrational motion EF. Therefore, we can see that there are two v'' values for which the probability of the transition from a given v' is a maximum; that is, there are two intensity maxima to be expected in a v'' -progression, one at small v'' and a second at large v'' .

The quantitative basis of the Frank-Condon principle is the transition dipole moment integral. In order to deal with the vibronic transitions, we have to consider the total electronic and vibrational wavefunctions of the initial and final states. In terms of the Born-Oppenheimer approximation, these can be approximated as a product of electronic and vibrational wavefunctions. Then, for an electronic state, ϵ , and vibrational state, v , the transition dipole moment for the excitation $\epsilon', v' \leftarrow \epsilon, v$ is therefore approximately:

$$\mu = -e \int \{\Psi_{\epsilon'}(r) \Psi_{v'}(R)\}^* r \{\Psi_{\epsilon}(r) \Psi_v(R)\} d\tau_{\text{elec}} d\tau_{\text{nuc}} \quad (50)$$

$$= -e \int \Psi_{\epsilon'}^*(r) r \Psi_{\epsilon}(r) d\tau_{\text{elec}} \int \Psi_{v'}^*(R) \Psi_v(R) d\tau_{\text{nuc}} \quad (51)$$

Where r stands for the electronic coordinates and R for the nuclear coordinates.

The second integral is the overlap integral, $S_{v',v}$ between the initial and final vibrational state wavefunctions. Since the intensity of a transition depends on the square of the transition dipole moment, the vibronic transition intensity depends on $S_{v',v}^2$, which is known as the Franck-Condon factor for the $\epsilon', v' \leftarrow \epsilon, v$ transition: $\int \Psi_{v'}^* \Psi_v d\tau$

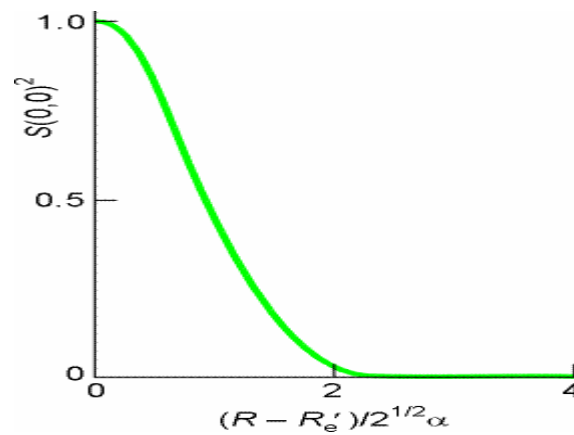


Fig 17. The variation of the Franck-Condon factor as the difference between the bond lengths of the lower and upper vibrational states increases.