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Franck condon principle in spectroscopy

 The Franck-Condon Principle explains vibronic transitions by saying that molecules don't change much when they electronically transition because nuclei are more massive and electronic transitions happen faster. This principle involves a vertical transition from ground to excited state and can be calculated using overlap integrals like \(S_{v',v}\). The probability of a vibrational transition can be calculated at a fixed nuclear position, and this change in vibration is maintained during a state termed the rapid electronic excitation. The resulting Coulombic forces produce an equilibrium, which can be mapped by drawing a vertical line from the minimum of the lower curve to the intersection of the higher electronic state. This procedure is termed a vertical transition and relates to the Franck-Condon Principle, which explains the relative intensities of vibronic transitions by relating the probability of a vibrational transition to the overlap of the vibrational wave functions. The Franck-Condon Principle states that the probability of a vibrational transition occurring is weighted by the Franck-Condon overlap integral. Within the Franck-Condon approximation, the nuclei are considered "fixed" during electronic transitions, and electronic transitions can be considered vertical transitions on electronic potential energy curves. The principle has both Classical and Quantum applications. Classically, the Franck-Condon principle is an approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck-Condon state, and the transition involved, a vertical transition. In the quantum mechanical formulation, the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states involved in the transition. The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic and nuclear wave functions given the total wavefunction. The transition operator, , can be separated from the nuclear components, allowing calculation of the probability of the transition occurring. If the nuclear overlap integral is zero for this transition, then the transition will not be observed. The nuclear overlap integral, denoted as S_{00}, can be calculated using the following formula: S_{00} = \sqrt{\dfrac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR where α is a constant related to the mass and spring constant of the system, Re is the equilibrium bond length in the ground electronic state, and Qe is the equilibrium bond length in the excited electronic state. The formula can be simplified by completing the square inside the integral, which results in: S_{00} = e^{-\alpha(R_e-Q_e)^2/4} This simplification shows that the nuclear overlap integral depends only on the difference between the equilibrium bond lengths in the ground and excited states. Similarly, the overlap of the zeroth level vibration in the ground state with the first excited vibrational level of the excited state can be calculated using: S_{01} = \sqrt{\dfrac{2\alpha^2}{\pi}} e^{-\alpha(R_e-Q_e)^2/4} \int_{-\infty}^{\infty} (R-Q_e) e^{-\alpha \{R- 1/2 (R_e+Q_e)\}^2} The integral can be simplified using the same method as before, resulting in: S_{01} = \sqrt{\dfrac{\alpha^2}{2}} (R_e-Q_e) e^{-\alpha(R_e-Q_e)^2/4} This shows that the overlap of the zeroth level vibration with the first excited vibrational level depends on the difference between the equilibrium bond lengths and the square root of the product of α and the mass. The same procedure can be applied to calculate the overlap of the zeroth level in the ground state with all higher vibrational levels, resulting in a progression of transitions between different levels each separated by a specific energy. The FC factor's significance can be understood by examining a ground and excited state potential energy surface at T = 0 Kelvin. Two states separated by 8,000 cm-1 in energy are considered, with the wavenumber of the vibrational mode being 1,000 cm-1. The bond length increases due to an electron's removal from a bonding orbital and placement in an anti-bonding orbital upon electronic excitation. A "stick" spectrum is generated based on this model for the Franck-Condon factor, where each vibrational transition is infinitely narrow and occurs only when E = hu exactly. However, a more realistic picture of the absorption spectrum is achieved by adding Gaussians to the stick spectrum. The nuclear displacement between the ground and excited state determines the shape of the absorption spectrum. For smaller displacements (S = ½), the zero-zero or v = 0 vibrational transition becomes much larger, while for larger displacements (S = 2), there is decreased overlap with higher vibrational levels achieving maximum intensity. The absorption spectra displayed have identical integrated intensities but exhibit distinct shapes due to varying degrees of displacement in the excited state potential energy surface. This is evident in Figure \(\PageIndex{8}\), which illustrates stick spectra dressed with Gaussians for harmonic oscillator systems across a range of displacements. The relative vibronic band intensities can provide insight into whether there has been a displacement of the equilibrium nuclear coordinate accompanying a transition. An increase in bond length (\(Q_e > R_e\)) occurs when an electron is promoted from a bonding molecular orbital to a non-bonding or anti-bonding molecular orbital, resulting in lower bond order in the excited state compared to the ground state.

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