9.7: Vibronic Transitions

Just as rotational motion is important in understanding vibrational spectra, vibrational (as well as rotational) motion(s) are important in understanding electronic transition is molecules. Electronic transitions in which vibrational structure is resolved are sometimes referred to a **vibronic transition**. When rotation is thrown in to the mix, the term "**rovibronic transitions**" is sometimes used.

Vibronic transitions can be discussed in terms of the transition moment. Keeping in mind that the wavefunction for a vibronic state can be expressed as a product

$$\Psi_{tot} = \psi_{elec}\psi_{vib}$$

and that the transition moment is given by

$$\int \Psi_{tot}^{*} \vec{\mu}\, \Psi_{tot} d\tau$$

Substitution yields

$$\int \left(\psi_{elec}\psi_{vib}\right)^{*} \vec{\mu}\, \left(\psi_{elec}\psi_{vib}\right) d\tau$$

Since the dipole moment operator is a derivative operator, the chain rule must be employed, which yields

$$\int \psi_{elec}^{*}\psi_{elec} d\tau \int \psi_{vib}^{*}\vec{\mu}\psi_{vib} d\tau + \int \psi_{elec}^{*}\vec{\mu}\psi_{elec} d\tau \int \psi_{vib}^{*}\psi_{vib} d\tau$$

Since the electronic wavefunction must be orthogonal, the first term will vanish for transitions between two different electronic states. The second term however, does not vanish. In face, the magnitude of the $\int \psi_{vib}^{*}\psi_{vib} d\tau$ will be determined by the overlap of the two vibrational levels. (Note that since these represent vibrational wavefunctions in different electronic state, there is no reason for the wavefunctions to be orthogonal.)

Franck-Condon Factors

The intensity of a band in a vibronic transition will be governed by the magnitude of the Frank-Condon Factor for the band. The **Franck-Condon factor** (FCF) is defined by

$$FCF = \left[\int \psi_{vib}^{'}\psi_{vib}^{''} d\tau\right]^{2}$$

which is governed purely by the degree of overlap between the upper state vibrational wavefunction and that in the lower state. The overlap will be large for $\Delta v = 0$ if the potential energy functions of the upper and lower states are similar (similar ω_e, $\omega_e x_e$, r_e, etc.) and strong sequences will be observed in the spectrum. If, however, the equilibrium bond length changes significantly, the maximum Franck-Condon overlap will occur for combinations of v' and v" for which $\Delta v \neq 0$. In these cases, strong progressions will be observed.

The Franck-Condon principle is closely associated with the Born-Oppenheimer approximation. In cases where the Born-Oppenheimer breaks down, the Franck-Condon principle is compromised as well.