A. Electronic Absorption Spectroscopy

- Because of the relationship $\Delta E_{\text{elec}} \gg \Delta E_{\text{vib}} \gg \Delta E_{\text{rot}}$, much higher frequency radiation induces electronic transitions compared to vibrations or rotations. Irradiation of atoms and molecules with light in the UV-visible range produces electronic transitions.

- For a single electron molecule: $\Delta E_{\text{elec}} = \frac{m e^4}{8 \varepsilon_0^2 h^2} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$. In wave numbers this is $\nu_{\text{elec}} = \frac{\Delta E_{\text{elec}}}{h c} = \frac{m e^4}{8 \varepsilon_0^2 h^3 c} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$.

- In single electron atoms the transition moment can be calculated. Example appear in Homework set 4 and in chapter 19 problems 5 and 6.

- For molecular systems we will not calculate the transition moments explicitly. But we can outline the method for calculating such moments.

- For a molecule the dipole moment is

$$\mu = \mu_{\text{elec}} + \mu_{\text{nuc}} = -e \sum_i \vec{r}_i + e \sum_j Z_j \vec{R}_j$$

- $\mu_{\text{elec}} = -e \sum_i \vec{r}_i$ is the electronic contribution to the transition moment where $\vec{r}_i$ is the vector associated with the $i$ electronic coordinate.

- $\mu_{\text{nuc}} = e \sum_j Z_j \vec{R}_j$ is the nuclear contribution to the dipole moment where $\vec{R}_j$ is the vector associated with the $j$ nuclear coordinate.

- The energy associated with each energy level has an electronic and vibrational component:

$$E = E_{\text{elec}} + E_{\text{vib}}$$

- The wave function is a product of the electronic and vibrational wave functions: $\psi = \psi_{\text{elec}} \psi_{\text{vib}}$.

- If we assume the electronic and nuclear motions are correlated, it will be very hard to determine the value of the transition moment. However if we assume, using the Born-Oppenheimer Approximation that the nuclear coordinates are stationary relative to the electronic motions, the integrals can be separated, and the transition moment has the form
\[ U_{f \leftrightarrow i} = \int \psi_{\text{elec}, f}^* \psi_{\text{vib}, f} \left( \mu_{\text{elec}} + \mu_N \right) \psi_{\text{elec}, i} \psi_{\text{vib}, i} d\tau_{\text{elec}} d\tau_{\text{vib}} \]

\[ = \int \psi_{\text{elec}, f}^* \mu_{\text{elec}} \psi_{\text{elec}, f} d\tau_{\text{elec}} \times \int \psi_{\text{vib}, f} \psi_{\text{vib}, i} d\tau_{\text{vib}} + \int \psi_{\text{vib}, f} \mu_N \psi_{\text{vib}, i} d\tau_{\text{vib}} \times \int \psi_{\text{elec}, f}^* \psi_{\text{elec}, i} d\tau_{\text{elec}} \]

- Because \( \int \psi_{\text{elec}, f}^* \psi_{\text{elec}, f} d\tau_{\text{elec}} = 0 \) for \( f \neq i \), the transition moment reduces to

\[ U_{f \leftrightarrow i} = \int \psi_{\text{elec}, f}^* \mu_{\text{elec}} \psi_{\text{elec}, f} d\tau_{\text{elec}} \times \int \psi_{\text{vib}, f} \psi_{\text{vib}, i} d\tau_{\text{vib}} \]

- The electronic transition moment depends upon the transition moment integral \( \int \psi_{\text{elec}, f}^* \mu_{\text{elec}} \psi_{\text{elec}, f} d\tau_{\text{elec}} \) and the vibrational overlap integral \( \int \psi_{\text{vib}, f} \psi_{\text{vib}, i} d\tau_{\text{vib}} \).

- To evaluate the vibrational overlap integral we make the assumption that the internuclear distance does not change during an electronic transition. This assumption is called the Franck-Condon Principle.

- The two integrals \( \int \psi_{\text{vib}, f} \psi_{\text{vib}, i} d\tau_{\text{vib}} \) and \( \int \psi_{\text{elec}, f}^* \mu_{\text{elec}} \psi_{\text{elec}, f} d\tau_{\text{elec}} \) that determine whether the electronic transition occurs are called Franck-Condon factors.-The transition probability for an electronic transition goes like the product of the square of the Franck-Condon factors.

- \( \int \psi_{\text{vib}, f} \psi_{\text{vib}, i} d\tau_{\text{vib}} \) is called the vibrational overlap integral, because it expresses the degree to which the vibrational wave functions of the ground and excited states overlap.
In the figure above, an electronic transition is shown from the ground (g) electronic state to an excited (e) electronic state. Because $\Delta E_{\text{vib}}>kBT$, almost all the molecules are in the ground vibrational state in g. It is common that the excited state has a longer bond length $R_e'$ than the ground state, i.e. $R_e'>R_e''$. This causes the two energy level minima to be offset somewhat.

According to the Franck-Condon Principle, the internuclear distance will not change when a transition occurs. This means the electronic transition is represented by a vertical arrow, where the internuclear distances of g and e are the same.

Although the electronic transition originates in the ground vibrational state $v''=0$, (note notation change…the vibrational quantum number for the ground electronic state is $v''$), the transition can end in any of the vibrational states in the excited electronic state. This means the transition can go from $v''=0$ to $v'=0,1,2,3,4…$ The overlap integral can be estimated from the product of the intensity of the vibrational wave function at $R_e''$ and the intensity of the vibrational wave function for $v'$ at $R_e''$.

Therefore the electronic transition will have vibrational fine structure, composed of all the vibrational transitions from $v''=0$ to the various values of $v'$. From the graph above the overlap integral is largest for the transition from $v''=0$ to $v'=4$.

Transitional frequencies for the fine structure depends upon our model for the vibrational transition. Assume the energy of the vibration is that of an anharmonic oscillator such that

$$E'_v = \hbar \omega' \left( v' + \frac{1}{2} \right) - \left( \frac{\hbar \omega'}{4D_e'} \right)^2 \left( v' + \frac{1}{2} \right)^2$$

The transition energy change is

$$\Delta E = \Delta E_{\text{elec}} + \Delta E_{v'\rightarrow v''}$$

$$= \Delta E_{\text{elec}} + \hbar \omega' \left( v' + \frac{1}{2} \right) - \left( \frac{\hbar \omega'}{4D_e'} \right)^2 \left( v' + \frac{1}{2} \right)^2 - \left[ \hbar \omega'' \left( v'' + \frac{1}{2} \right) - \left( \frac{\hbar \omega''}{4D_e''} \right)^2 \left( v'' + \frac{1}{2} \right)^2 \right]$$

$$= \Delta E_{\text{elec}} + \hbar \omega' \left( v' + \frac{1}{2} \right) - \hbar \omega'' \left( v'' + \frac{1}{2} \right) - \left( \frac{\hbar \omega'}{4D_e'} \right)^2 \left( v' + \frac{1}{2} \right)^2 + \left( \frac{\hbar \omega''}{4D_e''} \right)^2 \left( v'' + \frac{1}{2} \right)^2$$

B. Dissociation
- It may occur that an electronic absorption occurs to a state that has more energy than is required for dissociation. See figure below.

- In this case a continuum of absorption states is encountered. Therefore at low frequencies, discrete absorption transitions are observed while at higher frequencies a broad continuum of absorption transitions is observed. This can be observed in the figure above and in Figure 19.10 in the textbook.

- Although electronic absorption spectra show some resolution of vibrational transitions for small molecules in the gas phase, for large polyatomic molecules in the gas phase and for molecules in solution, and especially solution of large macromolecules like proteins and DNA, the electronic absorption spectrum is essentially unresolved. See for example Figure 19.11.

- For solutions of DNA the extinction coefficient $\varepsilon$ in Beer’s Law $A = \varepsilon bc$ is sensitive to DNA composition. This fact will be demonstrated in chapter 19 homework problems 19.10, for example.