University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2012

Lecture 17 2/27/12

A. Electronic Absorption Spectroscopy

- Because of the relationship $\Delta E_{elec} \gg \Delta E_{vib} \gg \Delta E_{rot}$, much higher frequency radiation indices 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: $\Delta E_{elec} = \dfrac{me^4}{8\varepsilon_0^2 h^2}\left(\dfrac{1}{n_f^2} - \dfrac{1}{n_i^2}\right)$. In wave numbers this is $\bar{\nu}_{elec} = \dfrac{\Delta E_{elec}}{hc} = \dfrac{me^4}{8\varepsilon_0^2 h^3 c}\left(\dfrac{1}{n_f^2} - \dfrac{1}{n_i^2}\right)$.
- 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
$$\vec{\mu} = \vec{\mu}_e + \vec{\mu}_N = -e\sum_i \vec{r}_i + e\sum_j Z_j \vec{R}_j$$
- $\vec{\mu}_e = -e\sum_i \vec{r}_i$ is the electronic contribution to the transition moment where $\vec{r}_i$ is the vector associated with the i electronic coordinate.
- $\vec{\mu}_N = e\sum_j Z_j \vec{R}_j$ 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:
$$E = E_{elec} + E_{vib}$$
- The wave function is a product of the electronic and vibrational wave functions: $\psi = \psi_{elec}\psi_{vib}$.
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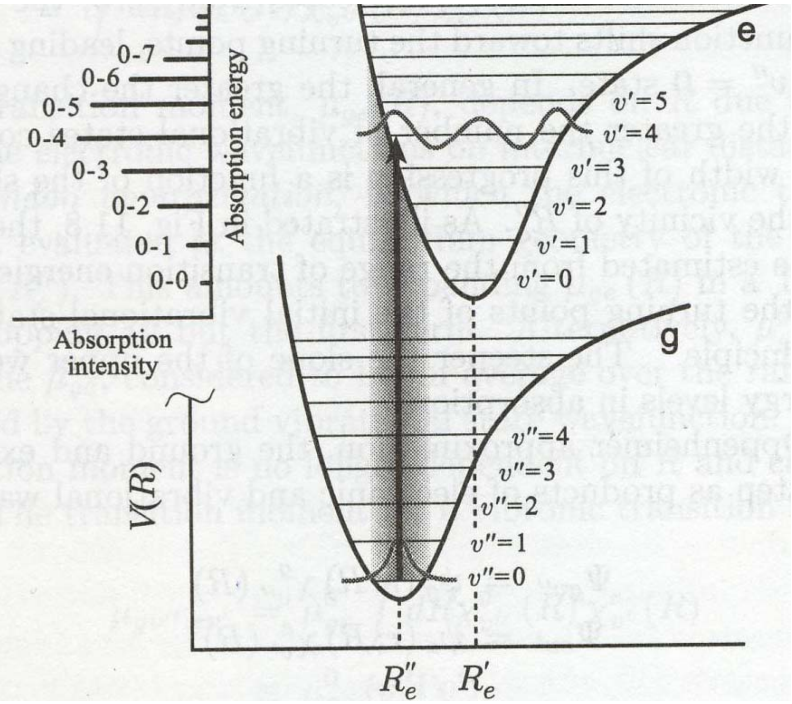
- If we assume the electronic and nuclear motions are correlated, it will be very hard to determine the value of the transition moment. However if we assume, using the Born-Oppenheimer Approximation that the nuclear coordinates are stationary relative to the electronic motions, the integrals can be separated, and the transition moment has the form

$$U_{f\leftarrow i}=\int\int\psi^{*}_{elec,f}\psi_{vib,f}\left(\vec{\mu}_{elec}+\vec{\mu}_{N}\right)\psi_{elec,i}\psi_{vib,i}d\tau_{elec}d\tau_{vib}$$
$$=\int\psi^{*}_{elec,f}\vec{\mu}_{elec}\psi_{elec,i}d\tau_{elec}\times\int\psi_{vib,f}\psi_{vib,i}d\tau_{vib}+\int\psi_{vib,f}\vec{\mu}_{N}\psi_{vib,i}d\tau_{vib}\times\int\psi^{*}_{elec,f}\psi_{elec,i}d\tau_{elec}$$

- Because $\int\psi^{*}_{elec,f}\psi_{elec,i}d\tau_{elec}=0$ for f≠i, the transition moment reduces to
$$U_{f\leftarrow i}=\int\psi^{*}_{elec,f}\vec{\mu}_{elec}\psi_{elec,i}d\tau_{elec}\times\int\psi_{vib,f}\psi_{vib,i}d\tau_{vib}$$
- The electronic transition moment depends upon the transition moment integral $\int\psi^{*}_{elec,f}\vec{\mu}_{elec}\psi_{elec,i}d\tau_{elec}$ and the vibrational overlap integral $\int\psi_{vib,f}\psi_{vib,i}d\tau_{vib}$.
- 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 $\int\psi_{vib,f}\psi_{vib,i}d\tau_{vib}$ and $\int\psi^{*}_{elec,f}\vec{\mu}_{elec}\psi_{elec,i}d\tau_{elec}$ 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.
- $\int\psi_{vib,f}\psi_{vib,i}d\tau_{vib}$ 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 $\Delta E_{vib} >> k_B T$, 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 v”=0 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

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

- The transition energy change is

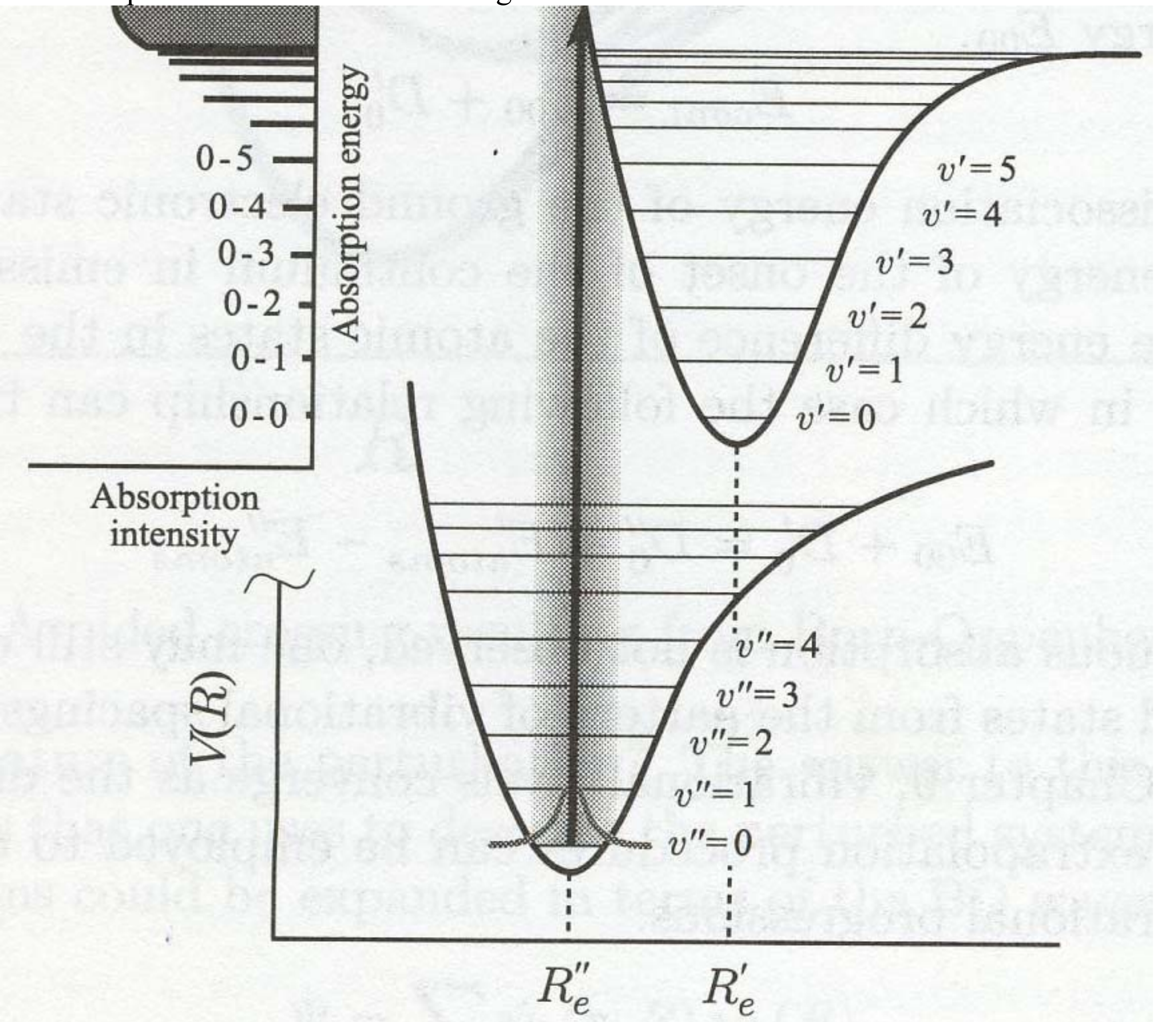
$$\Delta E = \Delta E_{elec} + \Delta E_{v' \leftarrow v''}$$

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

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

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.



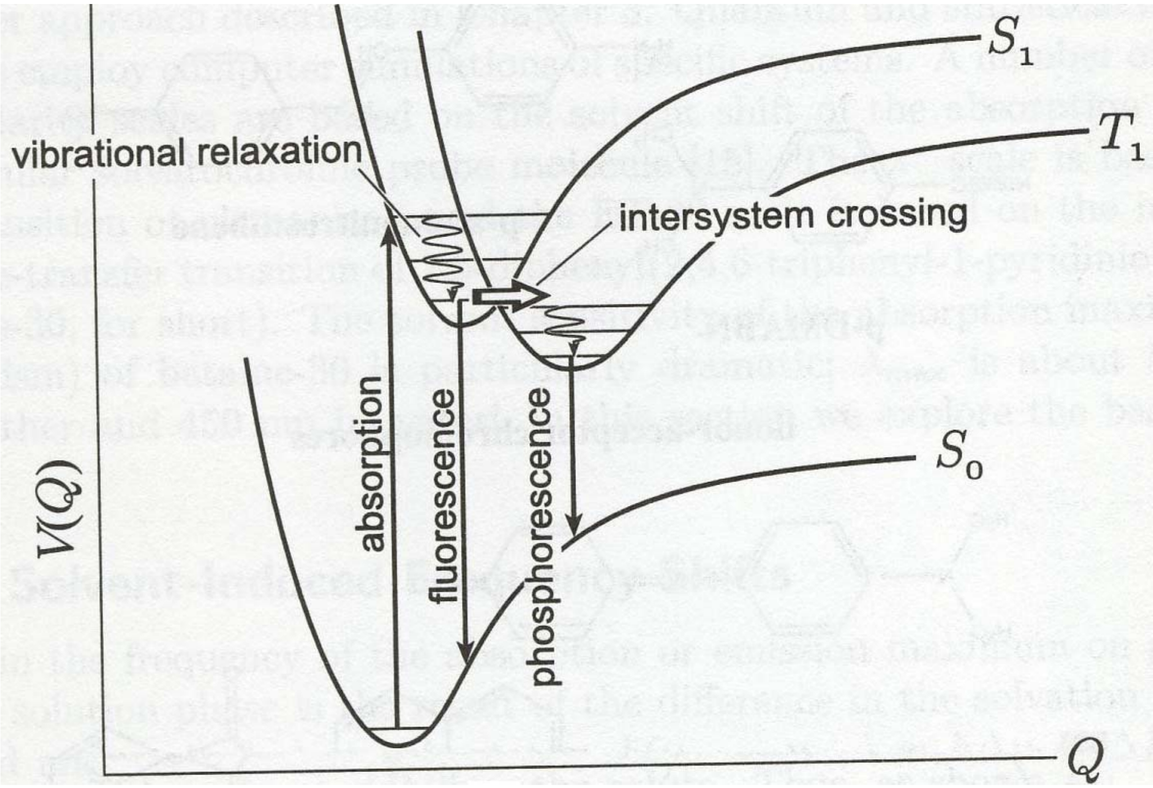
- In this case a continuum of absorption states is encountered. Therefore at low frequencies, discrete absorption transitions are observed while at higher frequencies a broad continuum of absorption transitions is observed. This can be observed in the figure above and in Figure 19.10 in the text book.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

C. Fluorescence: Introduction

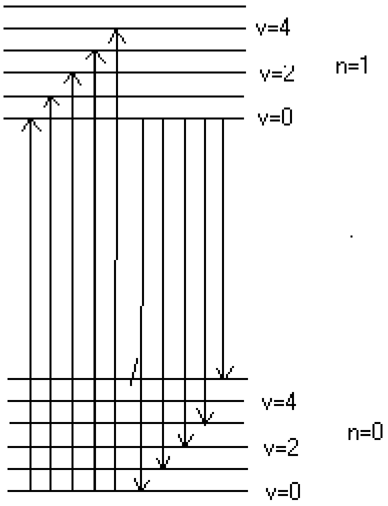
- Thus far we have only considered absorption processes. If resonant absorption occurs, a system will eventually return to the ground state.

There are a number of pathways that can be followed to return to the ground state. Important mechanisms whereby a system can return to the ground state include radiationless transfers (molecular collisions) fluorescent emission, and phosphorescence.

- Fluorescence is the emission of radiation that causes a transition from an excited state to the ground state, without a change in the electron spin multiplicity. Ground states usually are electronic singlet states in the sense that electrons with opposite spin angular momenta are paired. The ground state has no net spin angular momentum.
- Suppose a system is irradiated at n=(E_1-E_0)/h, thus inducing a transition from the electronic n=0 state to the n=1 state. Suppose the system is also in the vibrational ground state (v=0). See diagram.
- Resonant irradiation induces an absorptive transition from n=0 and v=0 to n=1, v=0,1,2,3…
    i. Absorptive transition to the excited state occurs in about 10^{-15} sec.
    ii. Electrons possess an angular moment not associated with their orbital moment, but rather associated with internal motions. This is called spin angular momentum and classically can be imagined as arising from the rotational motion of the electron.
    iii. Electron spin angular momentum is "up" (m=1/2) or "down" (m=-1/2), with reference to an external magnetic field. If all electrons are paired (N_2 in its ground state) in a molecular energy state its net spin S=0, and the molecule is said to be diamagnetic.
    iv. If there are two unpaired electrons in a molecule, S=1 and the state is called a triplet state. If a molecule has unpaired electrons in its ground state (e.g. O_2) it is called paramagnetic.
    v. In atomic spectroscopy, only transitions between singlet states are allowed. In molecular electronic spectroscopy, transitions between singlet and triplet states are weakly allowed, meaning the transition intensities are weak.



- Another way to represent absorption/fluorescence are Jablonski diagrams which have the general appearance:
- Jablonski diagrams can also include inter-system crossing and phosphorescent transitions.



- Suppose a molecule absorbs UV-Vis radiation and a transition occurs between a ground singlet state (S_0) and an excited singlet state (S_1). Once in the excited state, the molecule can rapidly relax to the vibrational ground state through radiationless transitions in a time on the order of a vibrational period…which is less than about 10^{-12} sec.
- Once in the ground vibrational state, molecules requires about 10^{-9} sec to return to the electronic ground state.
- Because of the loss of energy in the excited state through radiationless transitions, fluorescence occurs at longer wavelengths than the corresponding absorption.As shown below, the fluorescence spectrum is nearly the mirror image of the absorption spectrum, shifted to a longer wavelength.
- Besides fluorescing, an electron in the lowest vibrational state of S_1 can also cross over to an excited triplet state (T_1), by a process called inter-system crossing. Inter-system crossing occurs at a very low rate because the S_1 and T_1 states differ in total spin.
- The rate of inter-system crossing will be maximized if the singlet and triplet states have similar geometry. This being the case, if a vibrational state within the excited triplet state has about the same energy as the ground vibrational state of S_1, intersystem crossing can occur.
- Once in T_1, the electron will decay rapidly to the ground vibrational state of T_1 and then will decay to S_0 in a process called phosphorescence. Because it is spin-forbidden, phosphorescence takes a lot longer than fluorescence…about 10^{-6} s.
- Another pathway to exit the excited singlet state occurs if there is overlap between a vibrational state of S_1 and a high vibrational state of S_0. In this case rapid vibrational relaxation directly between S_1 and S_0 is called internal conversion. Once in a high vibrational state of S_0, the system relaxes to the ground vibrational state. Internal conversion can also occur between T_1 and S_0.