14.1 Organic Molecular Absorption Spectra

- the multiplicities of electronic states involved in absorption are singlets
- absorption is mostly due to electrons being promoted from $\pi$ to $\pi^*$-orbitals
- thermal population of rotational levels broadens absorption bands
- vibrational energy can be added to a molecule during an electronic transition
- energy state diagrams are used to show the origin of absorption spectra
Consider two electrons paired in an orbital, and their possible transitions to an empty orbital.

- the ground state has all electrons in the lowest energy orbital
- organic compounds almost always have paired spins, thus their ground state is almost always a singlet
- singlet-triplet transitions are optically forbidden - light cannot both promote an electron to a new orbital and change its spin
- in an organic compound most absorption spectra are due to singlet-singlet electronic transitions

\[ S = \sum_{i} s_i \]
\[ M = 2|S| + 1 \]
Electronic Transitions in Ethylene

- Attention will be restricted to electrons involved with carbon-carbon bonding.
- The two sp² electrons form the σ-bond, while the two pz electrons form the π-bond.
- Absorption of a photon will promote one of the bonding electrons into an antibonding orbital, preserving electron spin.
- The wavelength of absorbed light will follow Planck's Law, \( E = \frac{hc}{\lambda} \).
- The transition energies are: \( \sigma \to \sigma^* > \sigma \to \pi^*, \pi \to \sigma^* > \pi \to \pi^* \).
- The π → π* transitions are of most interest since they give us information about the conjugated double bond structure of a molecule.
\( \pi \rightarrow \pi^* \) Transitions in Butadiene

- Each carbon atom has one electron in a \( p_z \)-orbital.
- The four \( p_z \) electrons create two bonding \( \pi \)-orbitals and two anti-bonding \( \pi^* \)-orbitals.
- \( \pi_2 \rightarrow \pi_2^* \) absorption is in the deep UV, it has an energy similar to that in ethylene.
- The longest wavelength absorption is due to the \( \pi_1 \rightarrow \pi_1^* \) transition.
- Intermediate wavelength absorption is due to \( \pi_2 \rightarrow \pi_1^* \) and \( \pi_1 \rightarrow \pi_2^* \) transitions.
- The long wavelength transition has an energy that decreases with the number of double bonds.
Rotational Broadening

- Boltzmann's constant is $0.695 \text{ cm}^{-1} \text{ K}^{-1}$
- $kT = \sim 200 \text{ cm}^{-1}$ at room temperature
- The spacing of molecular rotational levels is a few tenths of reciprocal centimeters
- Thermal energy populates many rotational levels giving molecules an internal source of energy
- Rotational energy available within a molecule can add to that of a photon, making a range of optical energy that can satisfy Planck's Law, $\Delta E = h\nu + E_{rot}$
- The graph shows the energy of thermally populated rotational levels; the distribution has a width of $\sim 500 \text{ cm}^{-1}$
- An electronic transition will be broadened by this width

500 nm transition will be 13 nm wide (493 - 506 nm)
400 nm transition will be 8 nm wide (396 - 404 nm)
300 nm transition will be 5 nm wide (297 - 302 nm)
Vibronic Transitions

- A simultaneous change in vibrational and electronic quantum numbers is called a vibronic transition.
- If the inter-nuclear distances are not affected when the electron changes orbitals AND the transition is symmetry allowed, the spectrum will have a single peak and, no or very weak, vibronic bands.
- If one or more vibrations have different equilibrium inter-nuclear coordinates, a vibronic sequence will appear in the spectrum - this is shown in (a) for a single vibrational mode (more than one can be affected).
- If the electronic transition is symmetry forbidden, vibronic bands will appear for those vibrations that deform the molecule into a shape which has an allowed transition (b).
- Symmetry allowed: $\varepsilon = 10^3 - 10^5 \text{ M}^{-1} \text{ cm}^{-1}$
- Symmetry forbidden: $\varepsilon \leq 10^2 \text{ M}^{-1} \text{ cm}^{-1}$
State Diagrams and Absorption Spectra

Absorption spectrum

- \( \pi_1 \rightarrow \pi_2^* \) with a change in internuclear distance
- Symmetry forbidden \( \pi_1 \rightarrow \pi_1^* \)
- \( \lambda_{\text{max}} \)
- Long wavelength absorption band
- Infrared absorption

State diagram

- Energy levels: 0, 1, 2, 3, \( S_0^* \), \( S_1^* \)
- Transitions: 0-0 transition
- Excited singlet states
- Ground state: \( S_0 \) v = 0
- \( \lambda_{\text{max}} = 0 \text{ cm}^{-1} \) (4 nm)
- Long wavelength absorption band

E (cm\(^{-1}\))

- 30000 (333 nm)
- 25000 (400 nm)
- 20000 (500 nm)
- 15000 (667 nm)
- 10000 (1 \( \mu \text{m} \))
- 5000 (2 \( \mu \text{m} \))
- 0 cm\(^{-1}\) (\( \infty \text{ nm} \))