Interlude on Spectroscopy

“interaction of radiation with matter”

- type of interaction depends on the energy of the radiation
- use of the full electromagnetic spectrum is possible
- interaction happens through absorption
- spectrum is a plot of the absorption as a function of the energy used

\[ A \]

\[ \lambda, \text{ wavelength} \quad \Rightarrow \text{UV/Vis} \]

\[ \tilde{\nu}, \text{ wavenumber} \quad \Rightarrow \text{IR} \]

\[ \nu, \text{ frequency} \quad \Rightarrow \text{NMR} \]
Electromagnetic spectrum

- High energy
- Low energy
- High frequency
- Low frequency
- Short wavelength
- Long wavelength

Frequency ($\nu$) in Hz

- $10^{19}$
- $10^{17}$
- $10^{15}$
- $10^{13}$
- $10^{10}$
- $10^5$

Wavelength ($\lambda$) in meters

- $10^{-6}$
- $10^{-4}$
- $10^{-1}$
- 0.4
- 0.8
- $10^2$
- $10^6$
- $10^{10}$

- Cosmic rays
- $\gamma$-rays
- X-rays
- Ultraviolet light
- Visible light
- Infrared radiation
- Microwaves
- Radio waves

- Ionization: $M + h\nu \rightarrow M^{++} + e^-$
- Electronic transitions: UV/Vis
- Molecular vibrations: IR
- Nuclear spin transitions: NMR
- Molecular rotations: microwave spectroscopy
Chapter 2. Ultraviolet (and visible) spectroscopy

electronic transitions

• which transitions?
  wavelength and intensity, $\lambda_{\text{max}}$ and $\varepsilon$

• what happens if we change the molecule?
  substituent effects on $\lambda_{\text{max}}$ and $\varepsilon$

• laws for the prediction of $\lambda_{\text{max}}$ in conjugated alkenes and ketones

Reading:
Pavia
Chapter 7
Don’t need 7.13, 7.14D and E, 7.15
1. General

• range of radiation: \( \approx 200 - 800 \) nm
• absorption leads to excitation of electrons

Question: How large is the energy gap needed (let’s say at 200 nm) and what does that imply for the population of the two states?

Planck’s law

\[
E = h \nu = h \frac{c}{\lambda} = 6.6 \cdot 10^{-34} \text{Js} \cdot \frac{3 \cdot 10^8 \text{m/s} \cdot 10^9 \text{nm/m}}{200 \text{nm}} = 9.9 \cdot 10^{-19} \text{J}
\]

Boltzmann distribution

\[
\frac{N_u}{N_l} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{9.9 \cdot 10^{-19}}{1.38 \cdot 10^{-23} J/K \cdot 298 K}} = 0 \quad \Rightarrow \text{read: “1 upper over all lower”: all molecules are in their electronic ground state}
\]
2. Nature of electronic excitations

A. Electronic states

• electronic levels for the lowest-energy transition are HOMO and LUMO

• $E$ is quantized: only a specific $\Delta E$ leads to this promotion
  ⇒ we should observe a line spectrum
  ⇒ true for an atom, but not for a molecule
  ⇒ a molecule vibrates and rotates
2. Nature of electronic excitations continued

A. Electronic states

• every electronic state possesses vibrational and rotational states

\[ \lambda: \text{nm} \quad \mu\text{m} \quad \text{cm} \]
2. Nature of electronic excitations continued

A. Electronic states

⇒ leads to line broadening: all $\Delta E$ are similar but slightly different

A

$\lambda_{\text{max}}$ $\lambda$

(wavelength for maximum absorption)

⇒

A

$\lambda_{\text{max}}$ $\lambda$

observed band due to poor resolution
2. Nature of electronic excitations continued

B. Molecular orbitals

- occupied MOs: \( n \) \( \sigma \) \( \pi \)
- unoccupied MOs: \( \sigma^* \) \( \pi^* \)

- general orbital diagram

possible transitions:
- \( n \to \pi^* \)
- \( n \to \sigma^* \)
- \( \pi \to \pi^* \)
- \( \pi \to \sigma^* \)
- \( \sigma \to \pi^* \)
- \( \sigma \to \sigma^* \)
3. Selection rules

• govern which transitions are allowed, which forbidden
• allowed transition is observed
• forbidden transition is either not observed or very weak

• the promoted electron does not change spin

• only one electron is excited
• transitions between orbitals of different symmetry are forbidden

⇒ $\pi \rightarrow \pi^*$ allowed
⇒ $n \rightarrow \pi^*$ forbidden, but observed
4. Chromophores

• group of atoms that makes an absorption possible (at least two)

important chromophores

\[ R_2C=O, R_2C=S, R_2C=N-R \]
\[ R-N=N-R \]
\[ R-NO_2 \]
\[ \text{R-} \overset{\text{O}}{\text{C=O}}, \overset{\text{O}}{\text{C}=\overset{\text{O}}{\text{C}},} \overset{\text{O}}{\text{C}=\overset{\text{NH}_2}{\text{C}}} \]

(aromatics in general)

less important chromophores

(first \( \lambda_{\text{max}} \) too small/short)

\[ R-OH, R-O-R, R-NH_2 \]
\[ R_2C=CR_2, R-C=\overset{\equiv}{\text{C}}-R, R-C=\overset{\equiv}{\text{N}} \]

see Table 7.3
4. Chromophores continued

• probably the best-studied chromophore is the carbonyl group

280–290 nm
but
forbidden, low intensity

180–190 nm
allowed, high intensity, but too short to be observed!
4. Chromophores continued

• “typical” UV-Vis spectrum of a carbonyl compound

What is this? C=O plus C=C?

π → π* becomes observable
4. Chromophores continued

• the combination of chromophores leads to shifts in band intensity: increased: hyperchromic effect
decreased: hypochromic effect

wavelength: increased: longer $\lambda_{\text{max}}$:  
- bathochromic effect
- red shifted $\pi \rightarrow \pi^*$ band  
- less energetic light
- through conjugation

\[
\begin{align*}
\text{C} & \quad \text{C} = \text{C} \quad \text{C} = \text{C} \\
\lambda_1,\text{max} & < \lambda_2,\text{max}
\end{align*}
\]

\[
\begin{align*}
175 & \quad 217
\end{align*}
\]

decreased: shorter $\lambda_{\text{max}}$:  
- hypsochromic effect  
- blue shifted $n \rightarrow \pi^*$ band  
- more energetic light  
- through heteroatoms

\[
\begin{align*}
\begin{array}{c}
\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\lambda_1,\text{max} & > \lambda_2,\text{max}
\end{array}
\end{align*}
\]

\[
\begin{align*}
204 & \quad 293
\end{align*}
\]
4. Chromophores continued

• reason for a red shifted $\pi \rightarrow \pi^*$ band through conjugation:
  HOMO - LUMO gap becomes smaller upon conjugation

• acyclic conjugated:

  $MO$ (interaction) diagram for the $\pi$-orbitals of ethene and butadiene

  LCAO principle: linear combinations of atomic orbitals (p only)
4. Chromophores continued

• the red shift through conjugation can be dramatic:

\[
\beta\text{-carotene}
\]

\[
C_{40}H_{56}: U = 40 + 1 - \frac{1}{2}(56 - 0) = 41 - 28 = 13, 11 \text{ conjugated } C=C \Rightarrow \lambda_{\text{max}} 465 \text{ nm}
\]

orange!
4. Chromophores continued

• reason for a red shifted $\pi \rightarrow \pi^*$ band through conjugation

• reason for a **blue shifted** $n \rightarrow \pi^*$ band through heteroatoms:
  
  inductive effect: energy of $n_O$ is lowered

• $\pi \rightarrow \pi^*$ still shows a bathochromic shift:
  
  $\pi$-system is still extended through the heteroatom

\[
\begin{align*}
\text{C} & \equiv \text{C} \\
\text{C} & \equiv \text{O}
\end{align*}
\]

$n \rightarrow \pi^*$ $\lambda_{1,\text{max}} > \lambda_{2,\text{max}}$

$\pi \rightarrow \pi^*$ $\lambda_{1,\text{max}} < \lambda_{2,\text{max}}$
5. Absorption

- follows the Lambert-Beer law
  \[ A = \log \left( \frac{I_0}{I} \right) = \varepsilon c l \]

- \( \varepsilon \) is determined by the size of the absorbing system
  probability of the transition

- \( \varepsilon < 1000 \Rightarrow \log \varepsilon \approx 2-3 \): low intensity absorption
- \( \varepsilon \gg 1000 \Rightarrow \log \varepsilon \approx 4-5 \): high intensity absorption

- plotted is \( A \) or \( \varepsilon \) or \( \log \varepsilon \)
6. Materials

- **Central question:** Where does the material absorb?
- **solvent:** - should be transparent in the region of interest
  - “ideal” UV-Vis spectrum:

    | λ [nm] | A       |
    |--------|---------|
    | 200    |         |
    | 800    |         |

    short-wavelength cutoff: 
    - H₂O, CH₃CN 190 nm
    - CHCl₃ 240 nm

- **cuvette:** quartz, transparent to ≈ 200 nm
- **polymer,** transparent to ≈ 220 nm (PMMA)
- **optical glass,** transparent to only ≈ 350 nm

see Table 7.1
7. Spectrometer

- Beam in a UV-Vis spectrometer

Diode-array spectrophotometer

no movable parts:

faster

http://www.gmi-inc.com/Categories/spectrophotometers.htm

http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/uvvisab3.htm
8. Spectrum

- UV-Vis spectra are often not published
- x-y data of the extrema are reported instead

Info from this spectrum reported:

\[ \lambda_{\text{max}} \ 230 \text{ nm} \quad \log \varepsilon \ 4.2 \]
\[
\begin{array}{ccc}
272 & 3.1 \\
282 & 2.9 \\
\end{array}
\]

Info from this spectrum gained:

- no long-wavelength absorption:
  - not highly conjugated
- longer-wavelength low intensity:
  - probably forbidden, possibly \( n \rightarrow \pi^* \)
- shorter-wavelength high intensity:
  - probably allowed, possibly \( \pi \rightarrow \pi^* \)
9. Prediction of $\lambda_{\text{max}}$ of $\pi \rightarrow \pi^*$ transitions

I. Dienes and higher conjugated C=C

Why do we write $\text{cisoid}$ and not $\text{transoid}$? Conformation matters!

- acyclic dienes
  - butadiene
    - $s$-trans
      $\pi_1 \pi_2 \pi_3^* \pi_4^*$ 230 nm
    - $s$-cis
      $\pi_1 \pi_2 \pi_3^* \pi_4^*$ 271 nm

Interesting, but $s$-cis is not usually important in acyclic systems!

- cyclic dienes
  - transoid
  - cisoid

• use Woodward-Fieser rules to predict $\lambda_{\text{max}}$
9. Prediction of $\lambda_{\text{max}}$ of $\pi \rightarrow \pi^*$ transitions continued

I. Dienes and higher conjugated C=C

Woodward-Fieser rules

- calculate $\lambda_{\text{max}}$ from a base value...

\[
\begin{align*}
\text{acyclic (s-trans)} & \quad \text{transoid} & \quad \text{cisoid} \\
\text{base value [nm]} & \quad 214 & \quad 214 & \quad 253
\end{align*}
\]

- ...plus increments for structural features...

\[
\begin{align*}
\text{another conjugated C=C} & \quad \text{alkyl group or ring residue} & \quad \text{exocyclic C=C} \\
\text{increment [nm]} & \quad 30 & \quad 5 & \quad 5
\end{align*}
\]

- ...plus increments for other substituents

see Table 7.5
9. Prediction of $\lambda_{\text{max}}$ of $\pi \rightarrow \pi^*$ transitions continued

I. Dienes and higher conjugated C=C

Examples

\[
\begin{align*}
214 + 5 &= 219 \text{ nm} \\
214 + 30 &= 244 \text{ nm} \\
214 + 2 \times 5 + 5 &= 229 \text{ nm} \\
214 + 3 \times 5 + 5 &= 234 \text{ nm} \\
234 + 6 &= 240 \text{ nm}
\end{align*}
\]

Colour code: base system increments not important for absorption
9. Prediction of $\lambda_{\text{max}}$ of $\pi \rightarrow \pi^*$ transitions continued

I. Dienes and higher conjugated $C=C$

Examples

- Colour code: base system
  increments
  not important
  for absorption

\[
\begin{align*}
253 + 2 \times 5 &= 263 \text{ nm} \\
253 + 4 \times 5 + 2 \times 5 &= 283 \text{ nm} \\
253 + 2 \times 30 + 5 \times 5 + 3 \times 5 &= 353 \text{ nm}
\end{align*}
\]
9. Prediction of $\lambda_{\text{max}}$ of $\pi \to \pi^*$ transitions continued

II. Enones and higher conjugated C=O (ketones only)

Woodward rules

- calculate $\lambda_{\text{max}}$ from a base value...

\[
\begin{align*}
\text{acyclic (s-trans)} & : 215 \\
\text{6-membered ring} & : 215 \\
\text{5-membered ring} & : 202
\end{align*}
\]

- ...plus increments for structural features...

\[
\begin{align*}
\text{another conjugated C=C} & : 30 \\
\text{alkyl group or ring residue} & : \begin{align*}
in \alpha & : 10 \\
in \beta & : 12 \\
in \gamma & : 18
\end{align*} \\
\text{exocyclic C=C} & : 5 \\
\text{homocyclic (cisoid) diene} & : 39
\end{align*}
\]

- ...plus increments for other substituents

see Table 7.7
9. Prediction of $\lambda_{\text{max}}$ of $\pi \rightarrow \pi^*$ transitions continued

II. Enones and higher conjugated C=O

Examples

$\text{ Colour code: base system increments not important for absorption}$

$\text{Example 1:}$

$215 + 10 + 12 = 237 \text{ nm}$

$\text{Example 2:}$

$215 + 30 + 10 = 255 \text{ nm}$

$\text{Example 3:}$

$215 + 12 = 227 \text{ nm}$

$\text{Example 4:}$

$215 + 30 + 39 + 18 = 302 \text{ nm}$

$\text{Example 5:}$

$202 + 12 = 214 \text{ nm}$

$\text{Example 6:}$

$202 + 30 + 12 + 18 + 5 = 267 \text{ nm}$
9. Prediction of $\lambda_{\text{max}}$ of $\pi \rightarrow \pi^*$ transitions continued

III. Aromatic compounds

- good chromophore: 3 conjugated $C=C$, cis, in one ring

- conjugation effects as discussed earlier

- no quantitative treatment: $\lambda_{\text{max}}$ not easy to predict for substitution
Example

An alkene $C_{12}H_{16}$ and an unsaturated ketone $C_{11}H_{14}O$, both almost identical in structure (□□□), show UV absorptions at 269 and 286 nm, respectively. Give their structures.