Chapter 14 – Applications of Molecular Absorption Spectrometry

Read: pp 367-380

Problems: 14-1,2,8

\[ A(\lambda) = \varepsilon(\lambda)bc \]

\( \varepsilon \) values in UV/Vis molecular absorption spectrometry range from 0 to \( 10^5 \)!

\( \varepsilon = 8.7 \times 10^{19} \text{ PA} \)

Capture cross-section area \( \sim 10^{-15} \text{ cm}^2 \)

Probability of energy-absorbing transition 0-1
Absorbance Measurements in Gas vs. Liquid Phase

Solvent matters!!!

Polar solvents tend to obliterate the fine structure.

As a rule, same solvent system should be used when comparing absorption spectra for identification purposes.

Absorption spectra for vapor shows much fine structure (e.g., numerous rotational and vibrational states associated with excited electronic state are visible.)

In condensed state, less rotational freedom so rotational states not observed.

When chromophore is surrounded by solvent molecules, energies of vibrational levels are modified in a nonuniform way. Energy of a given state appears as a broad peak.
Peak heights and peak separation are distorted at wider bandwidths.

Loss of resolution accompanies wider slit widths.

Spectra for qualitative applications should be measured with minimum slit width.

**FIGURE 14-7** Spectra for reduced cytochrome c at four spectral bandwidths. (1) 20 nm, (2) 10 nm, (3) 5 nm, and (4) 1 nm. (Courtesy of Varian, Inc., Palo Alto, CA.)
Absorbing Species

\[ M + h\nu \rightarrow M^* \quad \text{Excitation event (10}^{-9} \text{ s)} \]

\[ M^* \rightarrow M + \text{heat or light} \quad \text{Relaxation event} \]

UV/Vis – excitation of bonding electrons!

Can be used for quantitative purposes and for functional group (type of bonding) information.
Absorbing Organic Molecules Containing $\sigma$, $\pi$ and n Electrons

Absorbing functional groups = chromophores

Olefins and aromatics

$\sigma \rightarrow \sigma^* < 185 \text{ nm}$

$n \rightarrow \sigma^* 150-250 \text{ nm}$

$\pi \rightarrow \pi^* 200-700 \text{ nm}$

TABLE 14-2 Absorption Characteristics of Some Common Chromophores

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Example</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$(nm)</th>
<th>$\epsilon_{\text{max}}$</th>
<th>$\pi \rightarrow \pi^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkene</td>
<td>$\text{C}_2\text{H}_3\text{CH}\equiv\text{CH}_2$</td>
<td>n-Heptane</td>
<td>177</td>
<td>13,000</td>
<td>$\pi \rightarrow \pi^*$</td>
</tr>
<tr>
<td>Alkyne</td>
<td>$\text{C}_2\text{H}_3\text{C} \equiv \text{C} \equiv \text{CH}_3$</td>
<td>n-Heptane</td>
<td>178</td>
<td>10,000</td>
<td>$\pi \rightarrow \pi^*$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>196</td>
<td>2000</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>225</td>
<td>160</td>
<td>—</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>$\text{CH}_3\text{C}\equiv\text{C} \equiv \text{CH}_3$</td>
<td>n-Hexane</td>
<td>186</td>
<td>1,000</td>
<td>$n \rightarrow \sigma^*$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>280</td>
<td>16</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>293</td>
<td>12</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>$\text{CH}_3\text{COH}$</td>
<td>Ethanol</td>
<td>204</td>
<td>41</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
<tr>
<td>Amido</td>
<td>$\text{CH}_3\text{CNH}_2$</td>
<td>Water</td>
<td>214</td>
<td>60</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
<tr>
<td>Azo</td>
<td>$\text{CH}_3\text{N} \equiv \text{NCH}_3$</td>
<td>Ethanol</td>
<td>339</td>
<td>5</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
<tr>
<td>Nitro</td>
<td>$\text{CH}_3\text{NO}_2$</td>
<td>Isooctane</td>
<td>280</td>
<td>22</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
<tr>
<td>Nitroso</td>
<td>$\text{C}_2\text{H}_3\text{NO}$</td>
<td>Ethyl ether</td>
<td>300</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>Nitrate</td>
<td>$\text{C}_2\text{H}_5\text{ONO}_2$</td>
<td>Dioxane</td>
<td>270</td>
<td>12</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
</tbody>
</table>

Conjugation = delocalization lowers energy level of $\pi^*$ orbital
Typical Absorption Spectra for Organic Molecules

$n \rightarrow \pi^*$ are often shifted to shorter wavelengths (hypsochromic or blue shift) with increasing solvent polarity.

$\pi \rightarrow \pi^*$ are often shifted to longer wavelengths (bathochromic or red shift) with increasing solvent polarity.

Figure 14-4  Ultraviolet spectra for typical organic compounds.
Absorption Involving d and f Electrons

Crystal-Field Theory

First and second transition-metal series. Compounds are colored as absorption occurs at visible wavelengths (300-700 nm).