Spectroscopy

Two features:
1). This excitation takes place only when the right energy is supplied – “discrete” or “non-continuous”
2). Not all excitations between the two energy levels are allowed – “selection rules”

\[ \Delta E = h \nu \]

\[ h = \text{Planck’s constant} \ (6.624 \times 10^{-27} \text{ erg}\cdot\text{s}); \nu = \text{frequency of the light required for the} \]

\[ \text{excitation (Hz or cycles/s)} \]

Since \( \nu = c/\lambda \) where \( c = \text{the velocity of the light (constant; 2.998 x 10^{10} \text{ cm/s}} \)

\( \lambda = \text{the wavelength (cm) of the light used,} \ \Delta E = h \nu \) can also be expressed as \( \Delta E = h c/\lambda \) (note that both \( h \) and \( c \) are constant numbers).

The Electromagnetic Spectrum and Absorption Spectroscopy

<table>
<thead>
<tr>
<th>spectral region</th>
<th>frequency (Hz or cycles/s)</th>
<th>wavelength (cm)</th>
<th>energy (Kcal/mol)</th>
<th>molecular energy</th>
<th>information obtainable</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-rays</td>
<td>( 10^{17} \sim 10^{18} )</td>
<td>( 10^8 \sim 10^7 )</td>
<td>( 10^8 \sim 10^7 )</td>
<td>electronic (inner-shell electrons)</td>
<td>•total molecular structures</td>
</tr>
<tr>
<td>ultraviolet (UV)</td>
<td>( 10^5 )</td>
<td>( 10^5 )</td>
<td>100</td>
<td>electronic (valence-shell electrons)</td>
<td>•chromophores</td>
</tr>
<tr>
<td>visible light</td>
<td>( 5 \times 10^{14} )</td>
<td>( 5 \times 10^5 )</td>
<td>50</td>
<td>electronic (valence-shell electrons)</td>
<td>•visible (colored) chromophores</td>
</tr>
<tr>
<td>infra-red (IR)</td>
<td>( 10^{13} \sim 10^{14} )</td>
<td>( 10^4 \sim 10^3 )</td>
<td>1 \sim 10</td>
<td>vibrational</td>
<td>•functional groups</td>
</tr>
<tr>
<td>microwaves</td>
<td>( 10^{10} \sim 10^{12} )</td>
<td>( 10^{-2} \sim 1 )</td>
<td>( 10^{-3} \sim 10^{-1} )</td>
<td>rotational</td>
<td>•rotamers</td>
</tr>
<tr>
<td>radiofrequency waves (NMR, ESR)</td>
<td>( 10^5 \sim 10^8 )</td>
<td>( 10^2 \sim 10^5 )</td>
<td>( 10^{-8} \sim 10^{-5} )</td>
<td>nuclear and electron spin states</td>
<td>•structural environment •connectivity</td>
</tr>
</tbody>
</table>

note: NMR = nuclear magnetic resonance; ESR = electron spin resonance

Conversion Factors between Energy Levels

<table>
<thead>
<tr>
<th></th>
<th>Kcal/mol</th>
<th>Hz (or cycles/s)</th>
<th>cm(^{-1}) (wavenumbers; waves/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Kcal/mol</td>
<td>1</td>
<td>1.05 x 10(^{13})</td>
<td>3.50 x 10(^{2})</td>
</tr>
<tr>
<td>1 Hz</td>
<td>9.53 x 10(^{-14})</td>
<td>1</td>
<td>3.33 x 10(^{-11})</td>
</tr>
<tr>
<td>1 cm(^{-1})</td>
<td>2.86 x 10(^{-3})</td>
<td>3.00 x 10(^{10})</td>
<td>1</td>
</tr>
</tbody>
</table>
Ultra-violet (UV) Spectroscopy (see Ege’s book: Section 12.1, pp 443 - 452)

Molecular absorption in the ultraviolet (UV) and visible regions of the electromagnetic spectrum corresponds to transitions between electronic energy levels in molecules. In practice, UV spectrometry is normally limited to conjugated systems or non-bonded electrons (or lone-pair) carrying atom attached to unsaturated C=C, C≡C bonds.

Particularly useful for the identification of chromophore units that show absorptions in the 210 – 340 nm region.

**chromophore**: a covalently unsaturated group responsible for electronic absorption (e.g., C=C and C=O) and often conjugated with another such group.

Typical conjugated systems: C=C-C=C (conjugated diene), C=C-C=O (conjugated α,β-unsaturated ketone, etc.

\[ A = \log \left( \frac{I}{I_0} \right) = \varepsilon l c \]

- \( \varepsilon \) = molar extinction coefficient (a numerical reflection of how strongly each chromophore group absorbs the light at the specific wavelength)
- \( c \) = sample concentration (mole/L); \( l \) = path length of the sample (cm)

**UV spectrum of isoprene**

![UV Spectrum of Isoprene](image)

- \( \varepsilon \) at 222.5 nm is ~10,000
- \( H_2C=CH(CH_3)-CH=CH_2 \) in methanol

**ethylene**

\[ H_2C=CH_2 \]

- \( \pi^* \) (anti-bonding orbital)
- \( \Delta E \)
- ~190 nm (strong)

**methyl vinyl ketone**

\[ H_2C=CH-C=O: \]

- lone pair (n)
- \( \pi^* \)
- \( \varepsilon \) at ~222.5 nm
- allowed, strong
- \( (\varepsilon \sim 10,000) \)
- \( \pi \)
- \( \pi_2 \rightarrow \pi_1^* \)
- excitation at ~215 nm
- extremely weak
- ~320 nm (\( \varepsilon \sim 20 \))