

The complement of the absorbed light gets transmitted.

The color of an object we see is due to the wavelengths transmitted or reflected. Other wavelengths are absorbed.

The more absorbed, the darker the color (the more concentrated the solution).

In spectrochemical methods, we measure the absorbed radiation.

## Table 16.1

### Colors of Different Wavelength Regions

| Wavelength Absorbed (nm) | Absorbed Color | Transmitted Color (Complement) |
|--------------------------|----------------|--------------------------------|
| 380–450                  | Violet         | Yellow-green                   |
| 450–495                  | Blue           | Yellow                         |
| 495–570                  | Green          | Violet                         |
| 570–590                  | Yellow         | Blue                           |
| 590–620                  | Orange         | Green-blue                     |
| 620–750                  | Red            | Blue-green                     |

The distance of one cycle is the wavelength ( $\lambda$ ).

The frequency ( $\nu$ ) is the number of cycles passing a fixed point per unit time.

$\lambda = c/\nu$  ( $c =$  velocity of light,  $3 \times 10^{10}$  cm s<sup>-1</sup>).

The shorter the wavelength, the higher the energy:  $E = h\nu$

This is why UV radiation from the sun burns you.

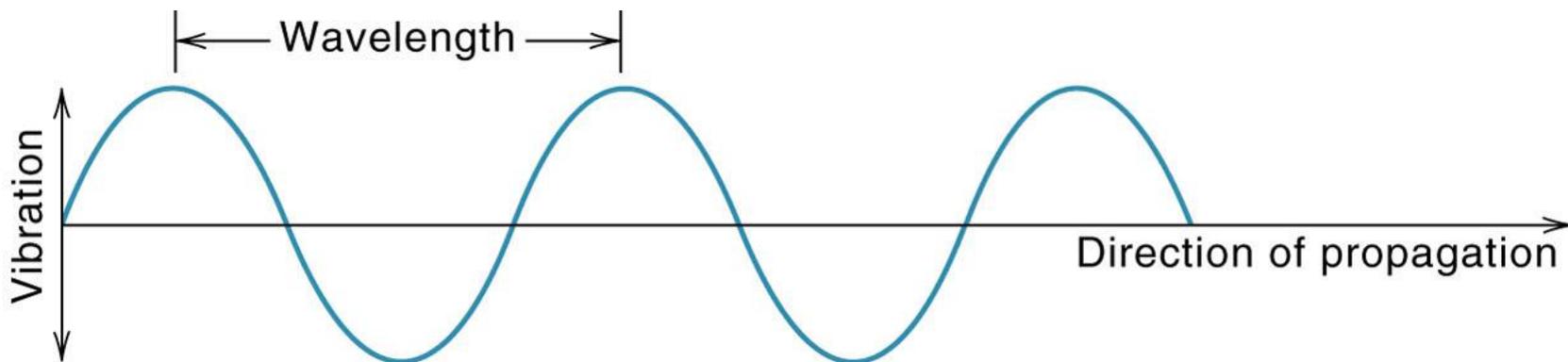


Fig. 16.1. Wave motion of electromagnetic radiation.

We see only a very small portion of the electromagnetic spectrum .

In spectrochemical methods, we measure the absorption of UV to far IR radiation.

UV = 200-380 nm

VIS = 280-780 nm

IR = 0.78  $\mu\text{m}$ -300  $\mu\text{m}$

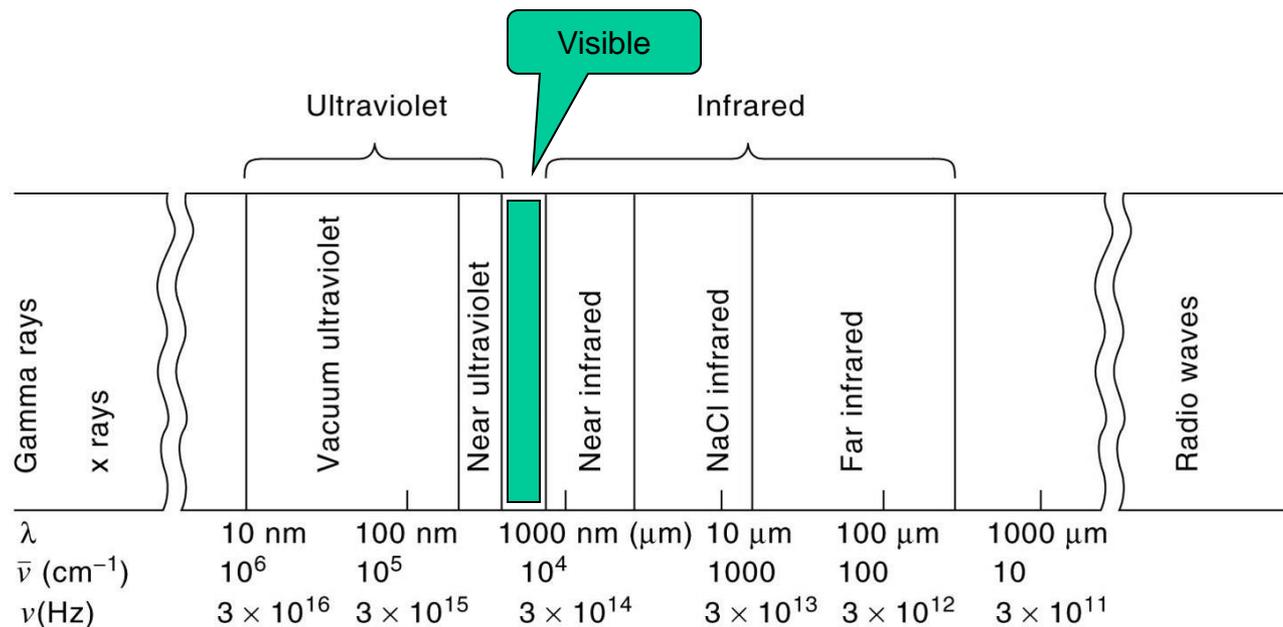


Fig. 16.2. Electromagnetic spectrum.

**A - pure rotational changes (far IR).**

**B - rotational-vibrational changes (near IR).**

**C - rotational-vibrational-electronic changes (visible and UV).**

**These transitions are all quantized.**

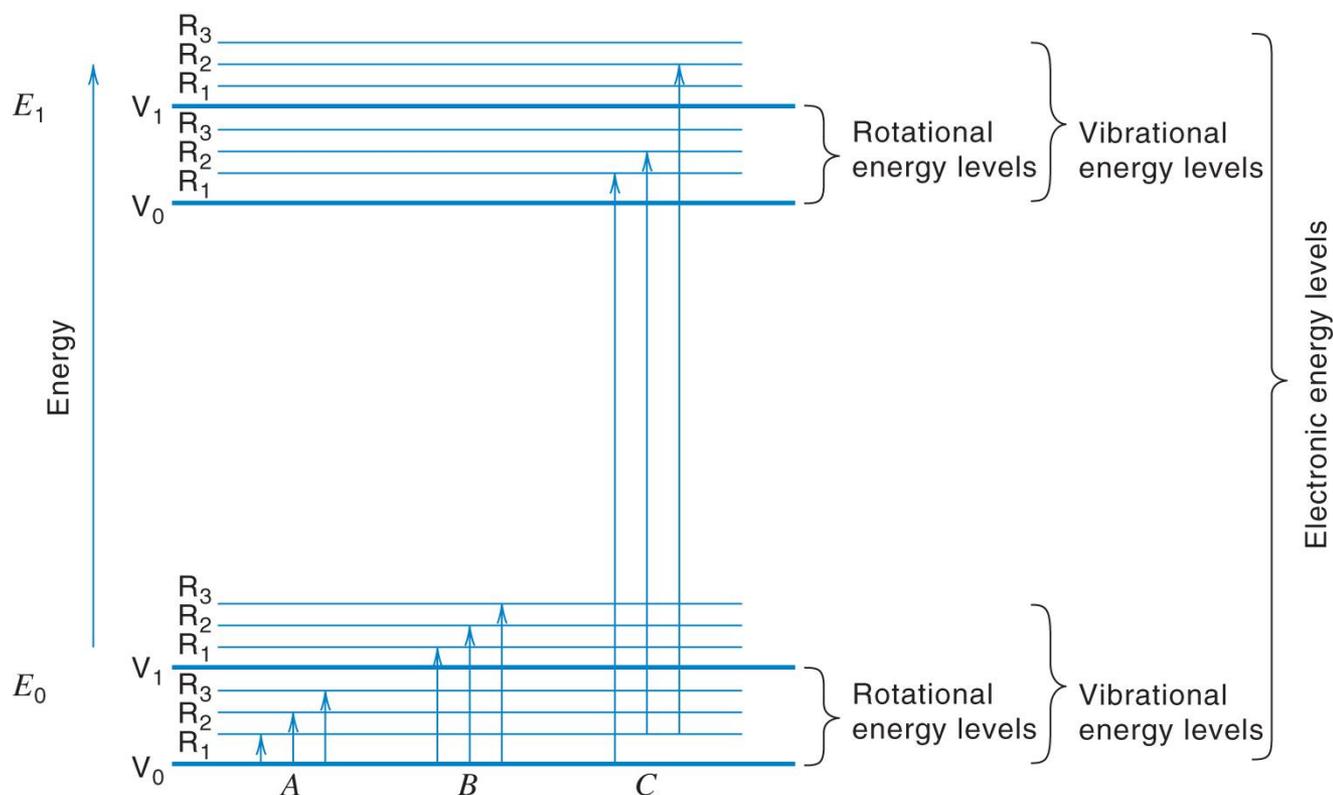
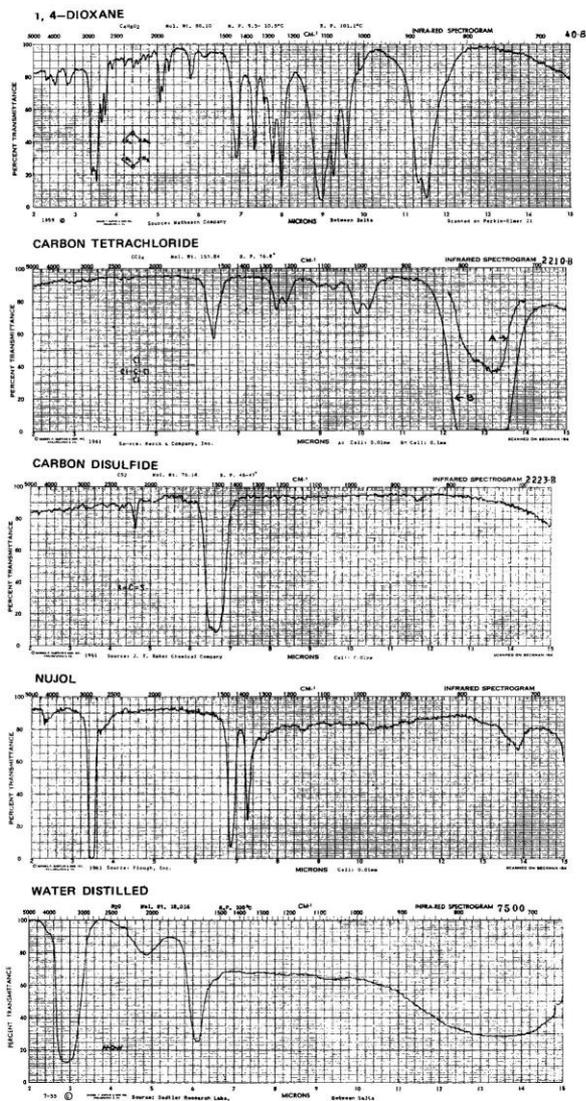


Fig. 16.3. Energy level diagram illustrating energy changes associated with absorption of electromagnetic radiation.  $E_0$  is electronic ground state and  $E_1$  is first electronic excited state.

The peaks are associated with vibrational modes within the molecule.  
(More in Fig. 16.8 on types of bonds that give peaks.)



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Fig. 16.4. Typical infrared spectra.

**Electronic transitions (at higher energy – shorter wavelengths) are superimposed on rotational and vibrational transitions.**

**These many discrete transitions result in a broad band of unresolved fine structure.**

**$\pi$  (double or triple bonds) and n (outer shell) electrons are responsible for most UV and Vis electronic transitions.**

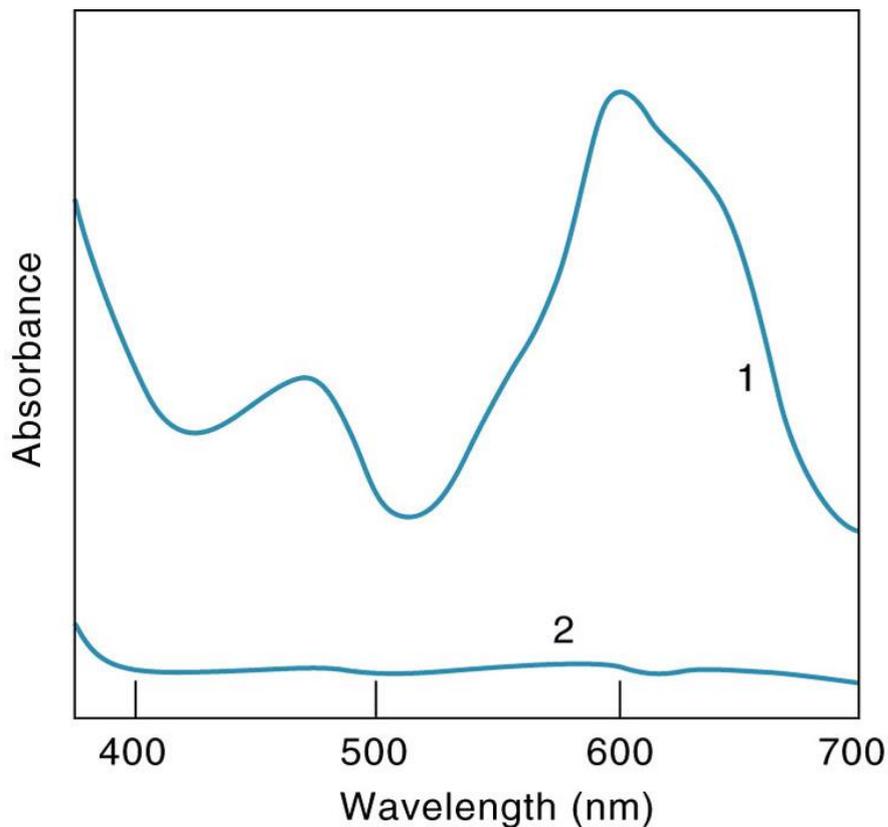


Fig. 16.5. Typical visible absorption spectrum. 1, Sample; 2, blank.

These are similar in structure to visible spectra.

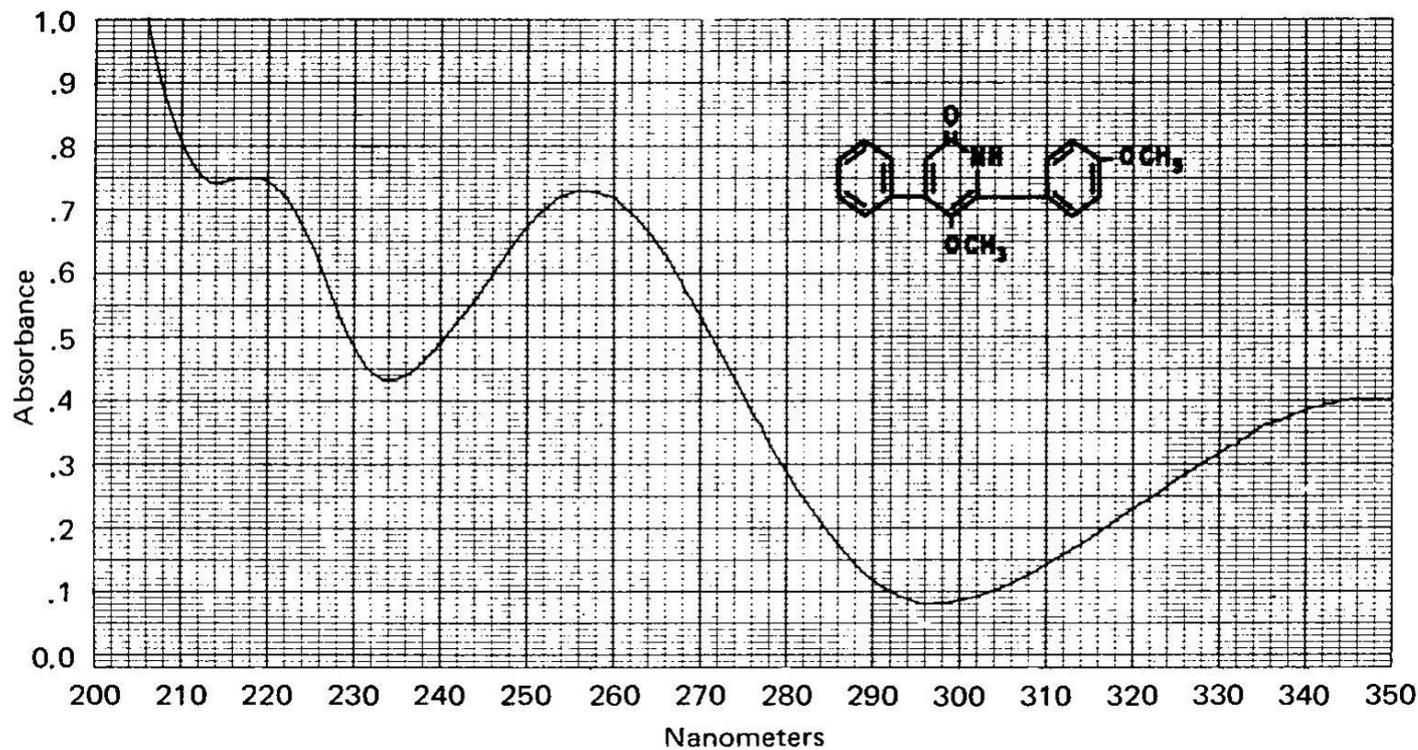


Fig. 16.6. Typical ultraviolet spectrum.

These groups absorb in the UV or visible regions.

Table 16.2

Electronic Absorption Bands for Representative Chromophores<sup>a</sup>

| Chromophore | System           | $\lambda_{\max}$ | $\epsilon_{\max}$ |
|-------------|------------------|------------------|-------------------|
| Amine       | —NH <sub>2</sub> | 195              | 2,800             |
| Ethylene    | —C=C—            | 190              | 8,000             |
| Ketone      | \                | 195              | 1,000             |
|             | C=O              | 270–285          | 18–30             |
| Aldehyde    | /                | 210              | Strong            |
|             | —CHO             | 280–300          | 11–18             |
| Nitro       | —NO <sub>2</sub> | 210              | Strong            |
| Nitrite     | —ONO             | 220–230          | 1,000–2,000       |
|             |                  | 300–400          | 10                |
| Azo         | —N=N—            | 285–400          | 3–25              |
| Benzene     |                  | 184              | 46,700            |
|             |                  | 202              | 6,900             |
|             |                  | 255              | 170               |
| Naphthalene |                  | 220              | 112,000           |
|             |                  | 275              | 5,600             |
|             |                  | 312              | 175               |
| Anthracene  |                  | 252              | 199,000           |
|             |                  | 375              | 7,900             |

<sup>a</sup>From M. M. Willard, L. L. Merritt, and J. A. Dean, *Instrumental Methods of Analysis*, 4th ed. Copyright © 1948, 1951, 1958, 1965, by Litton Educational Publishing, Inc., by permission of Van Nostrand Reinhold Company.

**Aromatic compounds are good absorbers of UV radiation.**

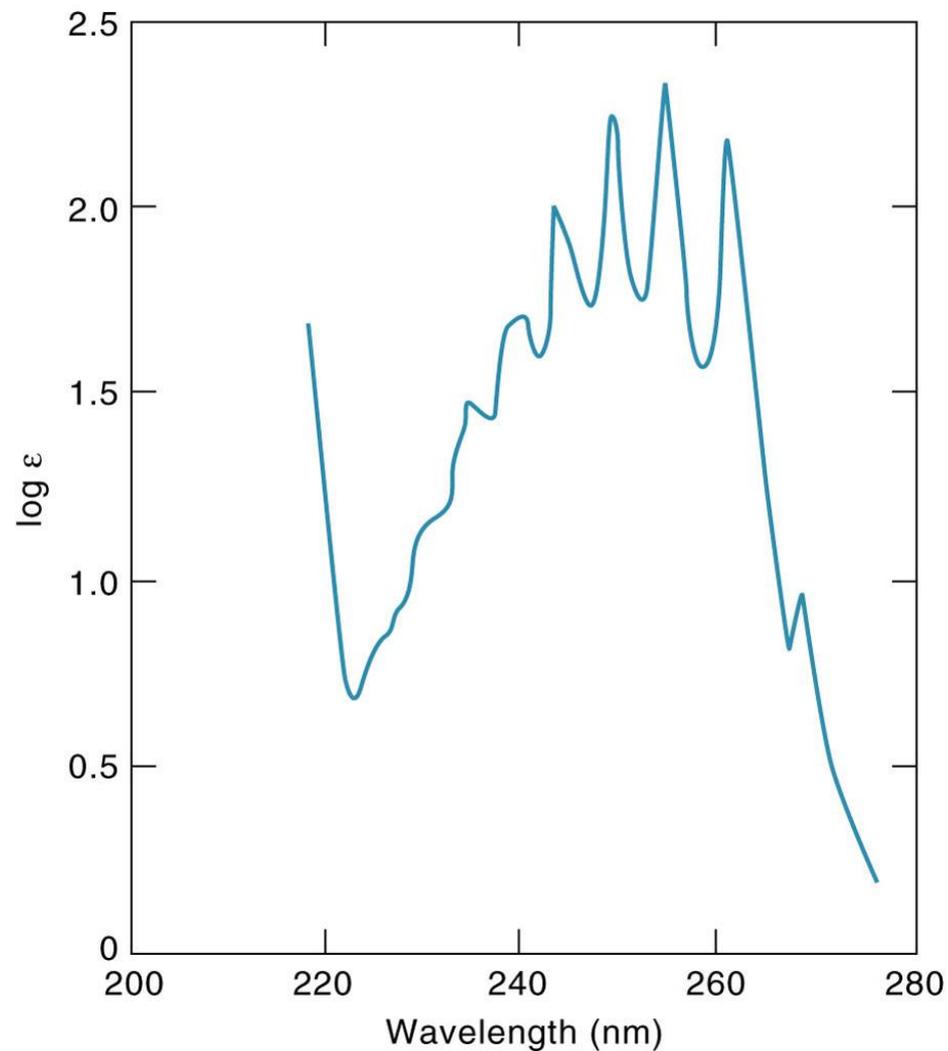


Fig. 16.7. Ultraviolet spectrum of benzene.

**Absorption in the 6- to 15- $\mu\text{m}$  region is very dependent on the molecular environment. This is called the fingerprint region.**

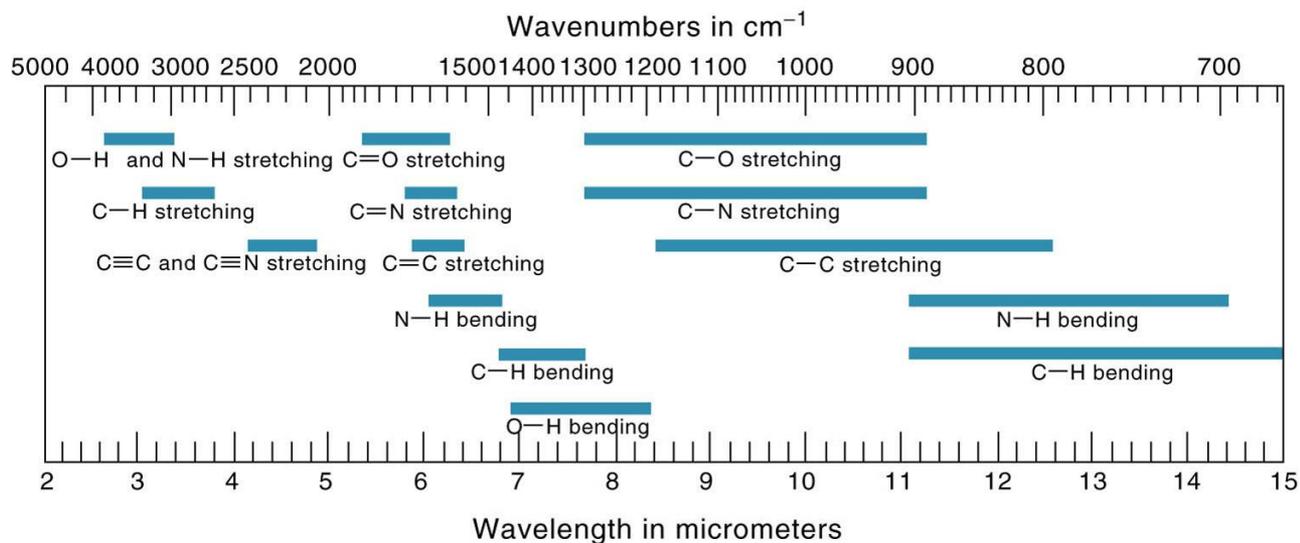


Fig. 16.8. Simple correlation of group vibrations to regions of infrared absorption.