Organic Identification

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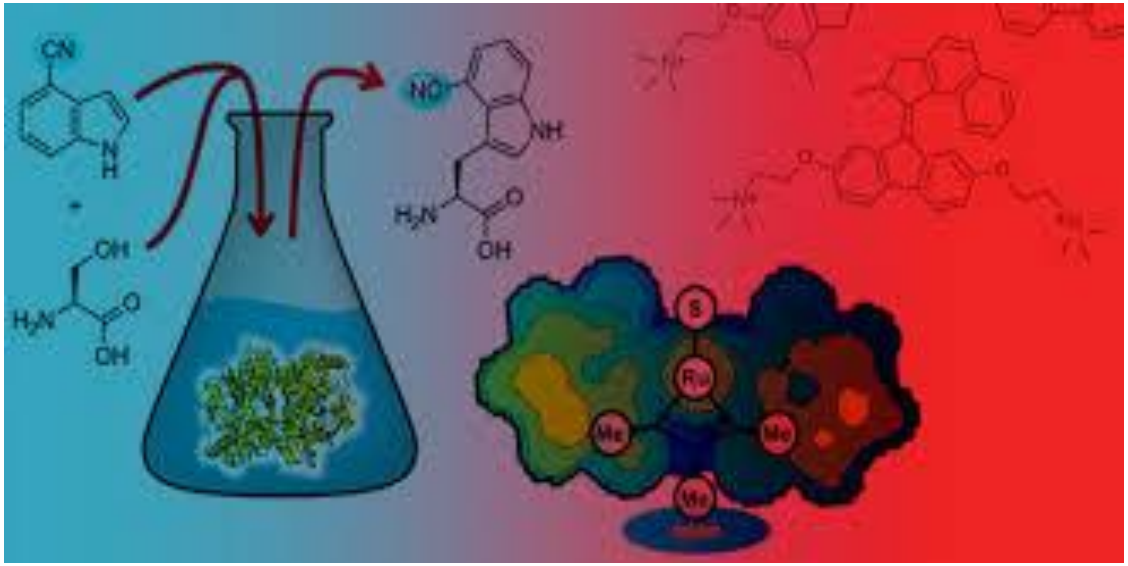

The Electromagnetic Spectrum

- The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments.

  This **electromagnetic spectrum** ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency (shown in the top equation below the chart).

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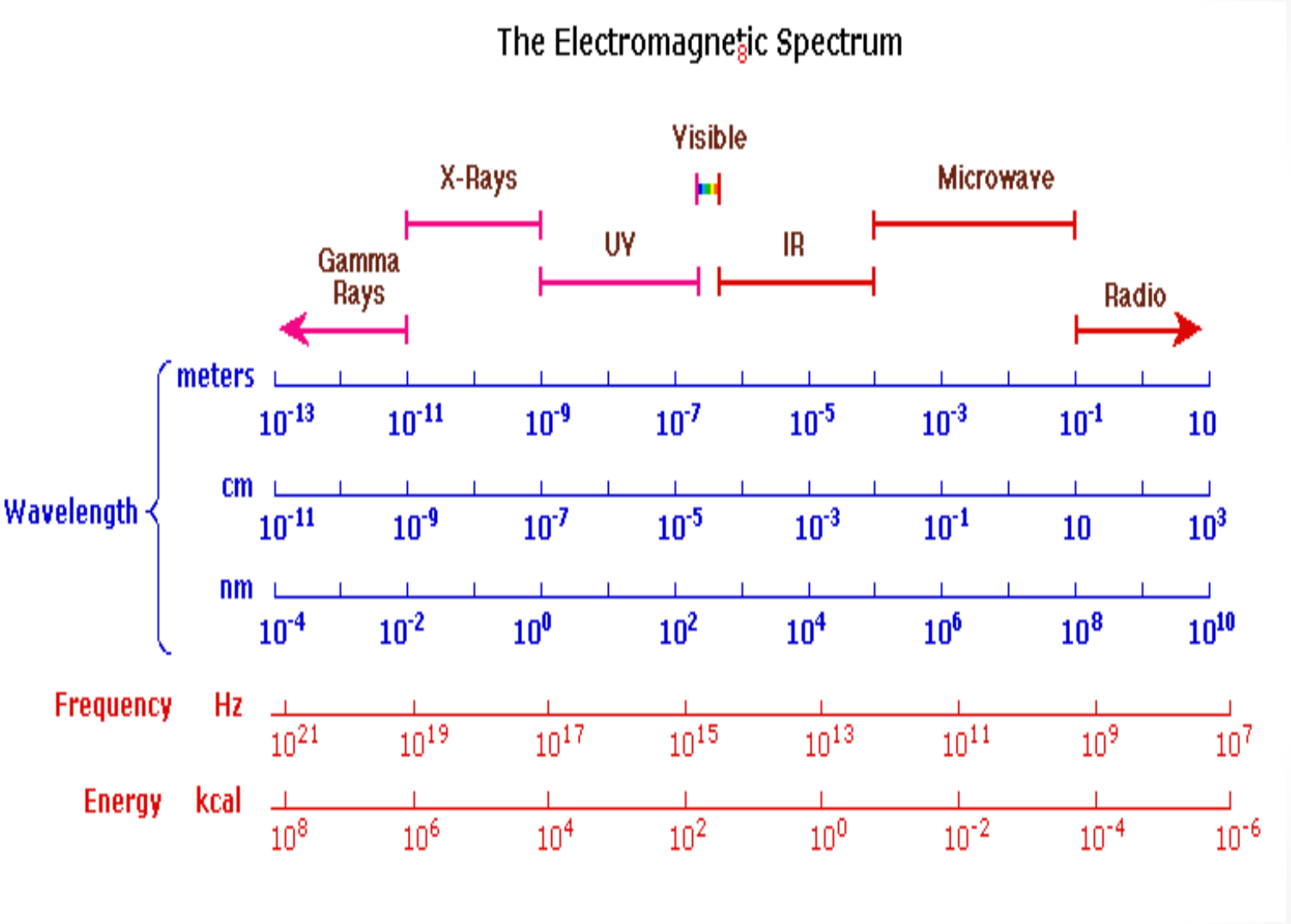
The Electromagnetic Spectrum
Visible
X-Rays
Microwave
UV
IR
Gamma Rays
Radio
Wavelength
meters
10^{-13} 10^{-11} 10^{-9} 10^{-7} 10^{-5} 10^{-3} 10^{-1} 10
cm
10^{-11} 10^{-9} 10^{-7} 10^{-5} 10^{-3} 10^{-1} 10 10^{3}
nm
10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8} 10^{10}
Frequency Hz
10^{21} 10^{19} 10^{17} 10^{15} 10^{13} 10^{11} 10^{9} 10^{7}
Energy kcal
10^{8} 10^{6} 10^{4} 10^{2} 10^{0} 10^{-2} 10^{-4} 10^{-6}

- The energy associated with a given segment of the spectrum is proportional to its frequency. The bottom equation describes this relationship, which provides the energy carried by a photon of a given wavelength of

$\nu = c/\lambda$ ν=frequency, λ=wavelength, c=velocity of light ($c = 3 * 10^{10}$ cm/sec)

$\Delta E = h\nu$ E=energy, ν=frequency, h=Planck's constant ($h = 6.6 * 10^{-27}$ erg sec)

To obtain specific frequency, wavelength and energy values us

UV-Visible Absorption Spectra

- To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum
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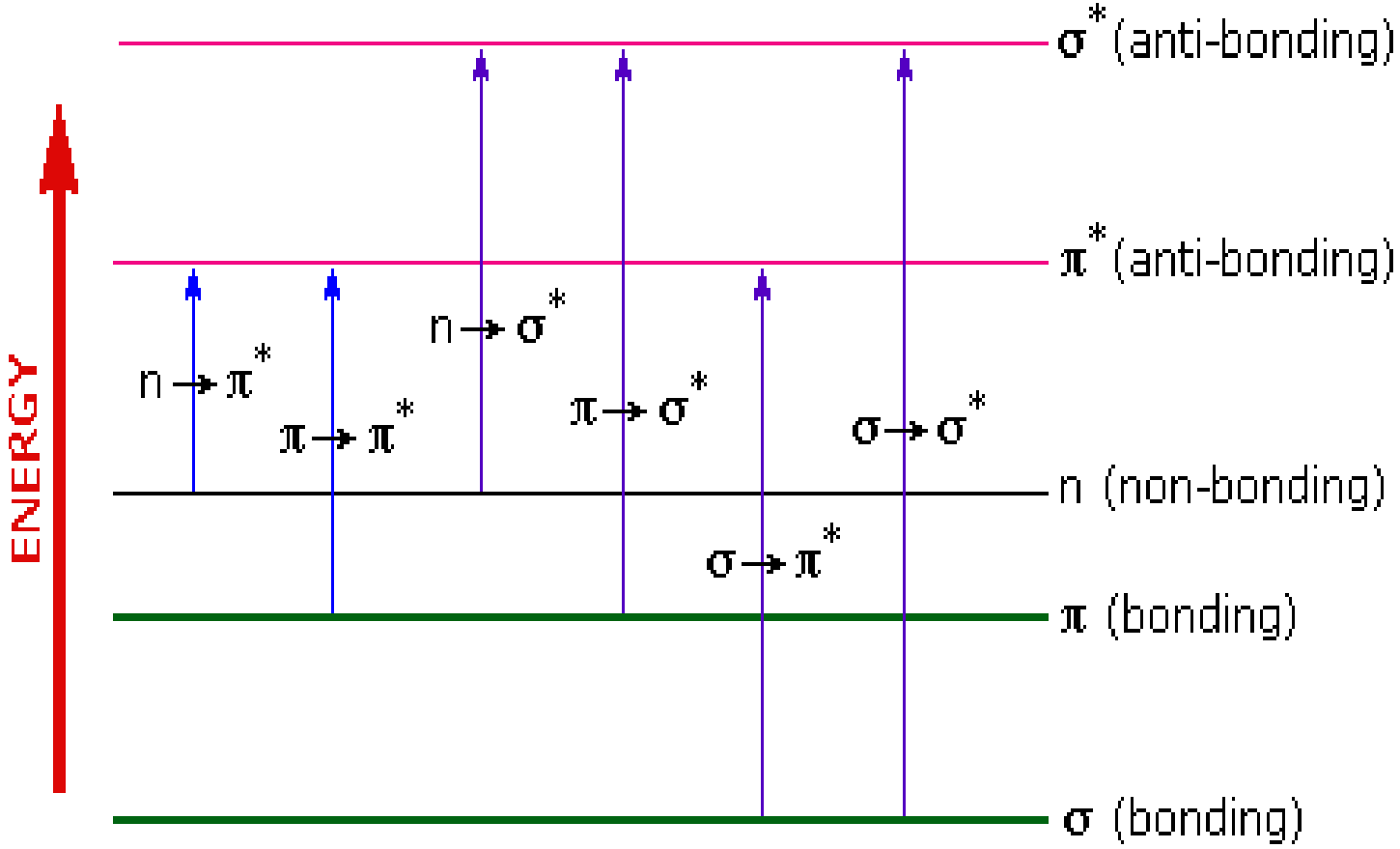
- The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis . The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy".

- . Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**, and the resulting species is called an **excited state**. For a review of molecular orbitals . When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength.

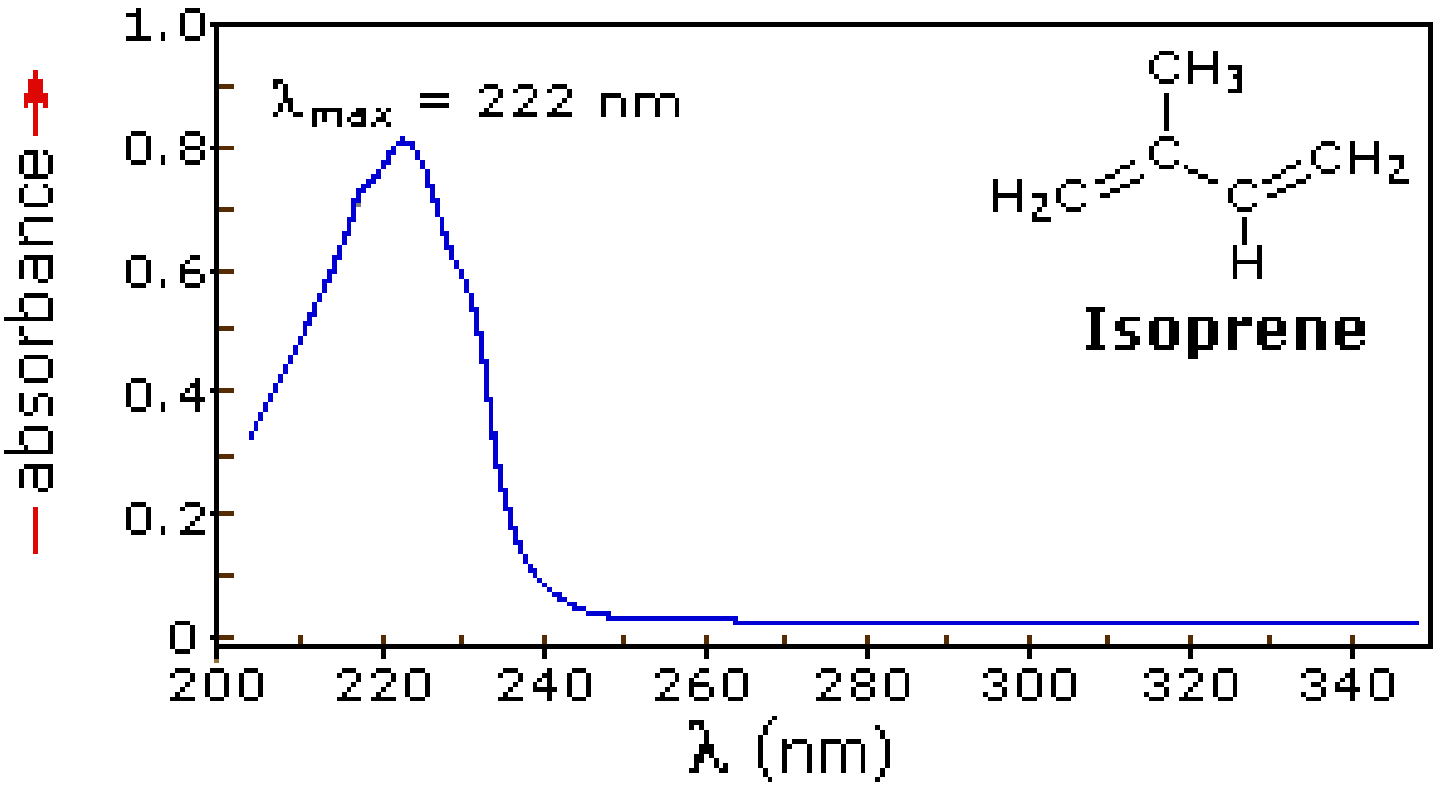
- . The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation

- Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). **Molar absorptivity** (ε) is defined as:


σ* (anti-bonding)
π* (anti-bonding)
n → σ*
n → π*
π → σ*
π → π*
σ → σ*
n (non-bonding)
σ → π*
π (bonding)
σ (bonding)
ENERGY

- If the isoprene spectrum on the right was obtained from a dilute hexane solution ($c = 4 * 10^{-5}$ moles per liter) in a 1 cm sample cuvette, a simple calculation using the above formula indicates a molar absorptivity of 20,000 at the maximum absorption wavelength. Indeed the entire vertical absorbance scale may be changed to a molar absorptivity scale once this information about the sample is in hand.

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane


absorbance
1.0
0.8
0.6
0.4
0.2
0
λ_{max} = 222 nm
200
220
240
260
280
300
320
340
λ (nm)
CH_3
H_2C
CH_2
H
Isoprene

- From the chart above it should be clear that the only molecular moieties likely to absorb light in the 200 to 800 nm region are pi-electron functions and hetero atoms having non-bonding valence-shell electron pairs. Such light absorbing groups are referred to as **chromophores**. A list of some simple chromophores and their light absorption characteristics is provided on the left above. The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm. Consequently, pure alcohol and ether solvents may be used for spectroscopic studies.

- The presence of chromophores in a molecule is best documented by UV-Visible spectroscopy, but the failure of most instruments to provide absorption data for wavelengths below 200 nm makes the detection of isolated chromophores problematic. Fortunately, conjugation generally moves the absorption maxima to longer wavelengths, as in the case of isoprene, so conjugation becomes the major structural feature identified by this technique.

- Molar absorptivities may be very large for strongly absorbing chromophores (>10,000) and very small if absorption is weak (10 to 100). The magnitude ofε reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.
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