Infrared (IR) Spectroscopy

Background: Carey, Ch 13.20

Electromagnetic Radiation

- Radiation is absorbed & emitted in *photons*. The defining characteristic of a photon is that its energy cannot be split into smaller pieces.
- Each *photon's* energy is defined by its frequency (ν) or wave length (λ) or wave number (wn)

$$E_{photon} = h\nu = hc/\lambda = hc(wn)$$

- Two constants appear in these formulas
  - h = Planck's constant, 6.63×10^{-34} J s
  - c = speed of light, 3.00×10^{8} m s^{-1} (or 3.00×10^{10} cm s^{-1})
- Wave number (wn) = $1/\lambda$

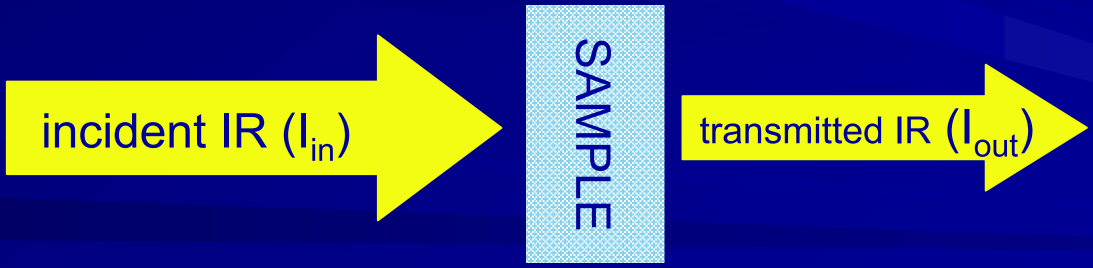
IR Radiation

- IR absorbed by organic molecules
  - 600-4000 cm^{-1}
  - Photon energy = hc(wn) = 1.2-8.0 x 10^{-20} J
  - *Molar* photon energy = 7.4-49 kJ/mol
    = 1.8-12 kcal/mol

- IR photon energy <<< covalent bond energy. Absorbing IR radiation should not trigger *substantial* chemical changes. But IR radiation contains more energy than random thermal motion at room temperature (~ 0.6 kcal/mol)

IR Spectrum

- Plot IR energy vs. %transmittance (%T)
  - Energy scale in wave numbers, wn (cm^{-1})
  - %T scale
    - Compares intensity of IR striking sample (I_{in}) with intensity of IR leaving sample (I_{out})
    - 100%T no light absorbed by sample
    - 0% all light absorbed by sample



incident IR (I_{in})

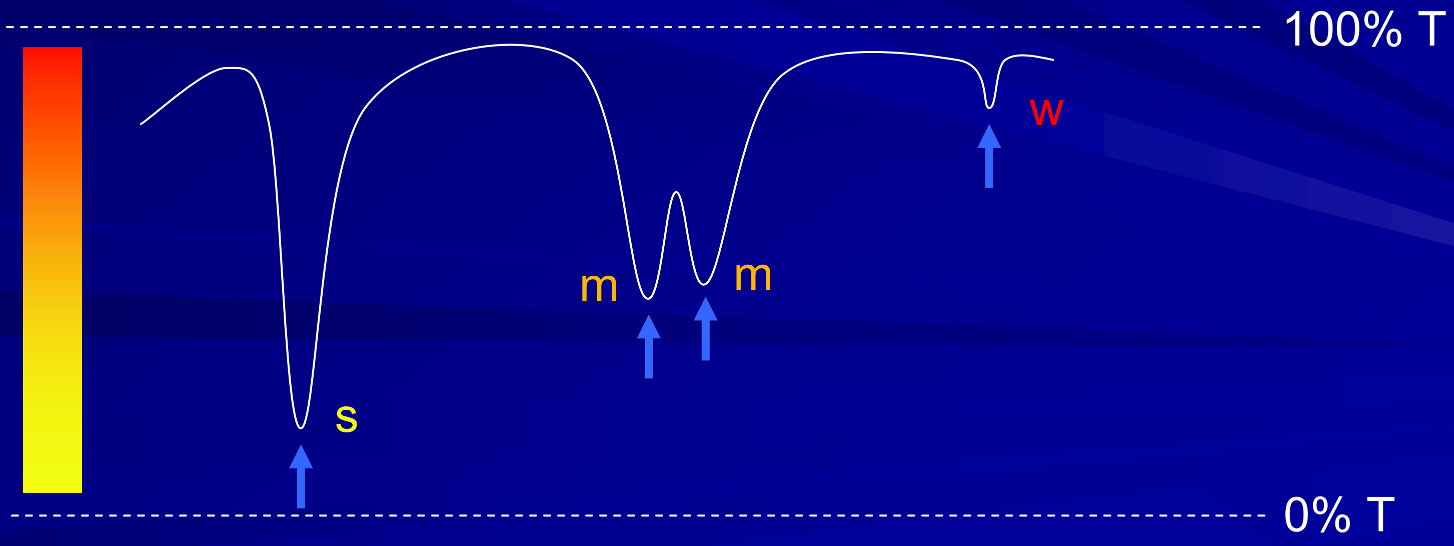
SAMPLE

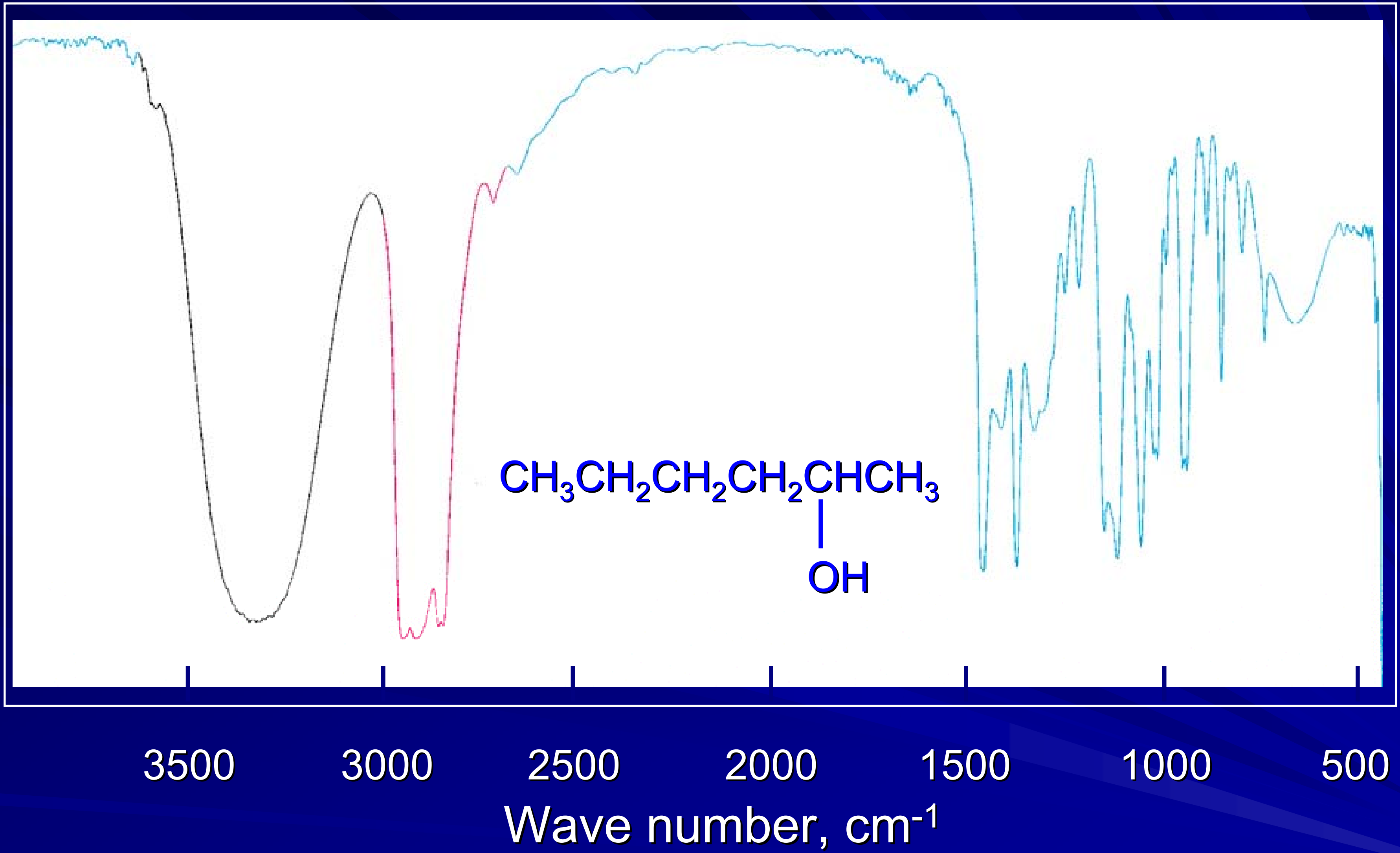
transmitted IR (I_{out})

$$\%T = 100 \times (I_{out} / I_{in})$$

IR Spectrum

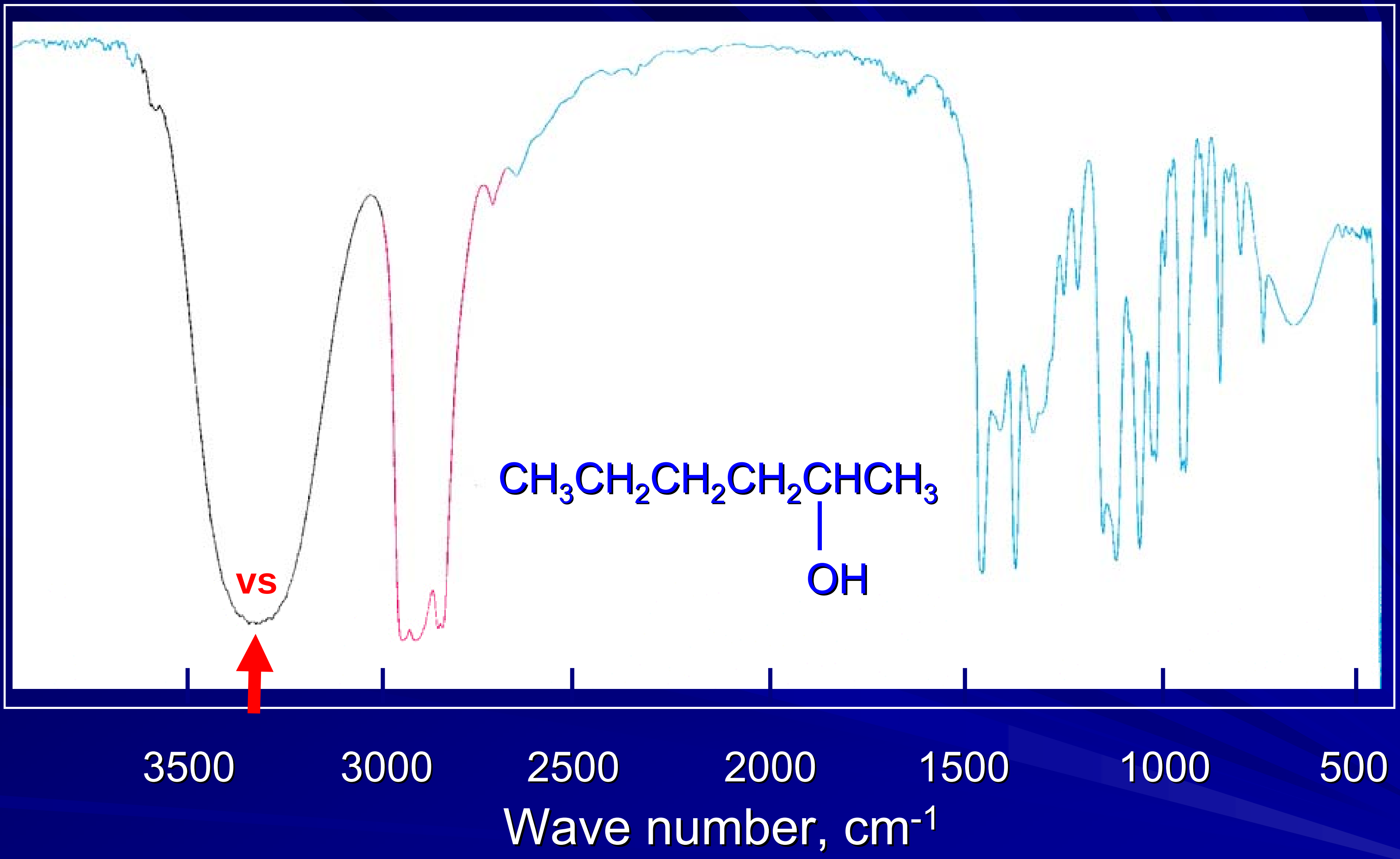
- Record
  - Wave number location of IR "band" (position of max %T)
  - Intensity of IR "band"
    - s = strong (low %T), m = medium, w = weak (high %T)
    - vs = very strong, vw = very weak





$$CH_3CH_2CH_2CH_2\underset{\displaystyle |\atop OH}{C}HCH_3$$

Where do you measure the position of the “black” band?
What is its intensity?



Where do you measure the position of the "black" band?
What is its intensity?

Energy Trends

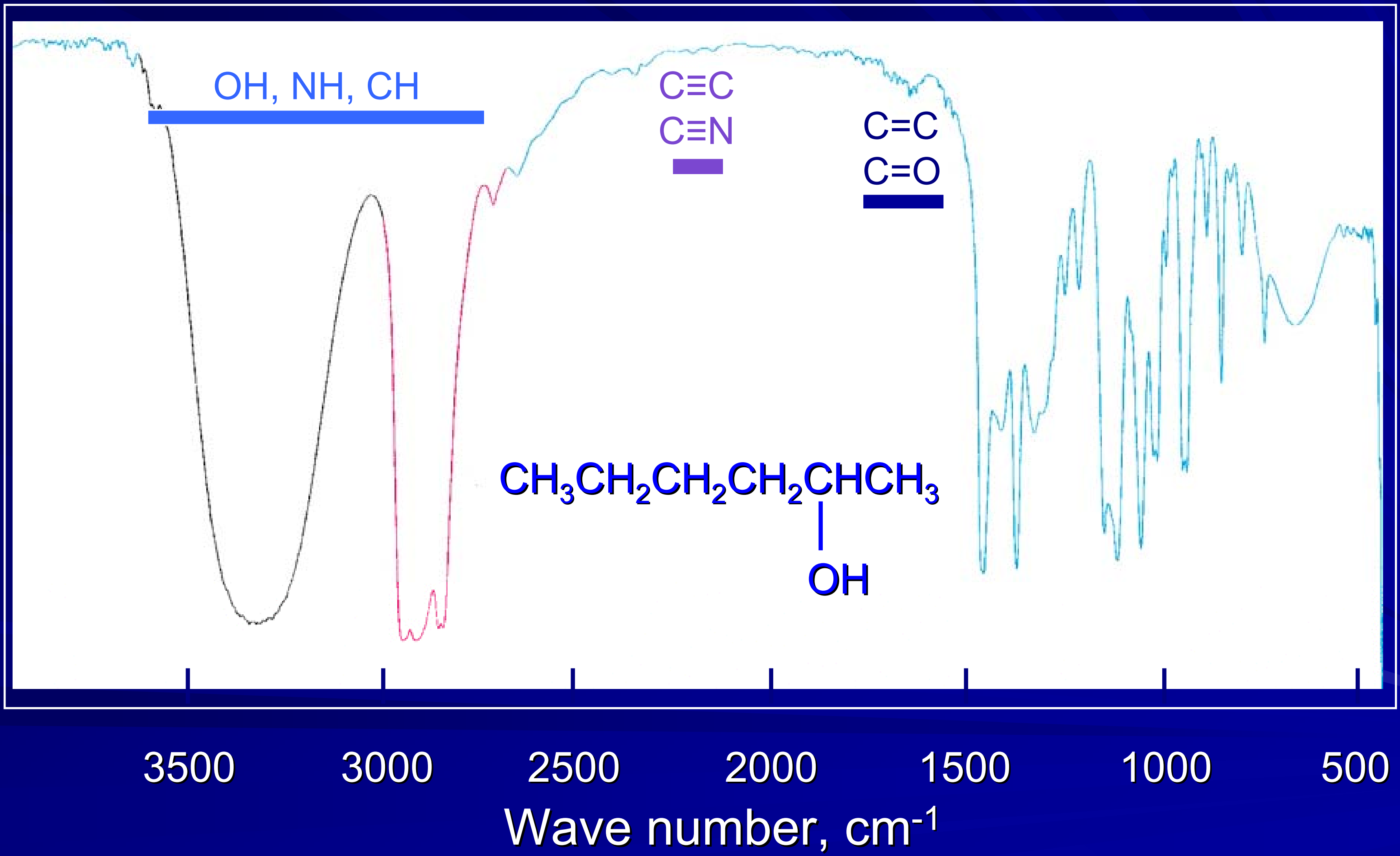
- Energy follows vibration frequency of atoms
  - Light atoms vibrate more rapidly
    - CH, NH, OH vibrations > 2800 cm^{-1}
  - Multiple bonds vibrate more rapidly
    - Triple bonds

      C≡C (2100-2200)   C≡N (2240-2280)
    - Double bonds

      C=O (1680-1750)   C=C (1620-1680)
    - Single bonds

      C–O (1025-1200)
- Stretching > Bending > Wagging/Twisting

Parsing a Spectrum



Francis A. Carey, *Organic Chemistry,* Fifth Edition. Copyright © 2003 The McGraw-Hill Companies, Inc. All rights reserved.

Fingerprint Region (<1500 cm^{-1})

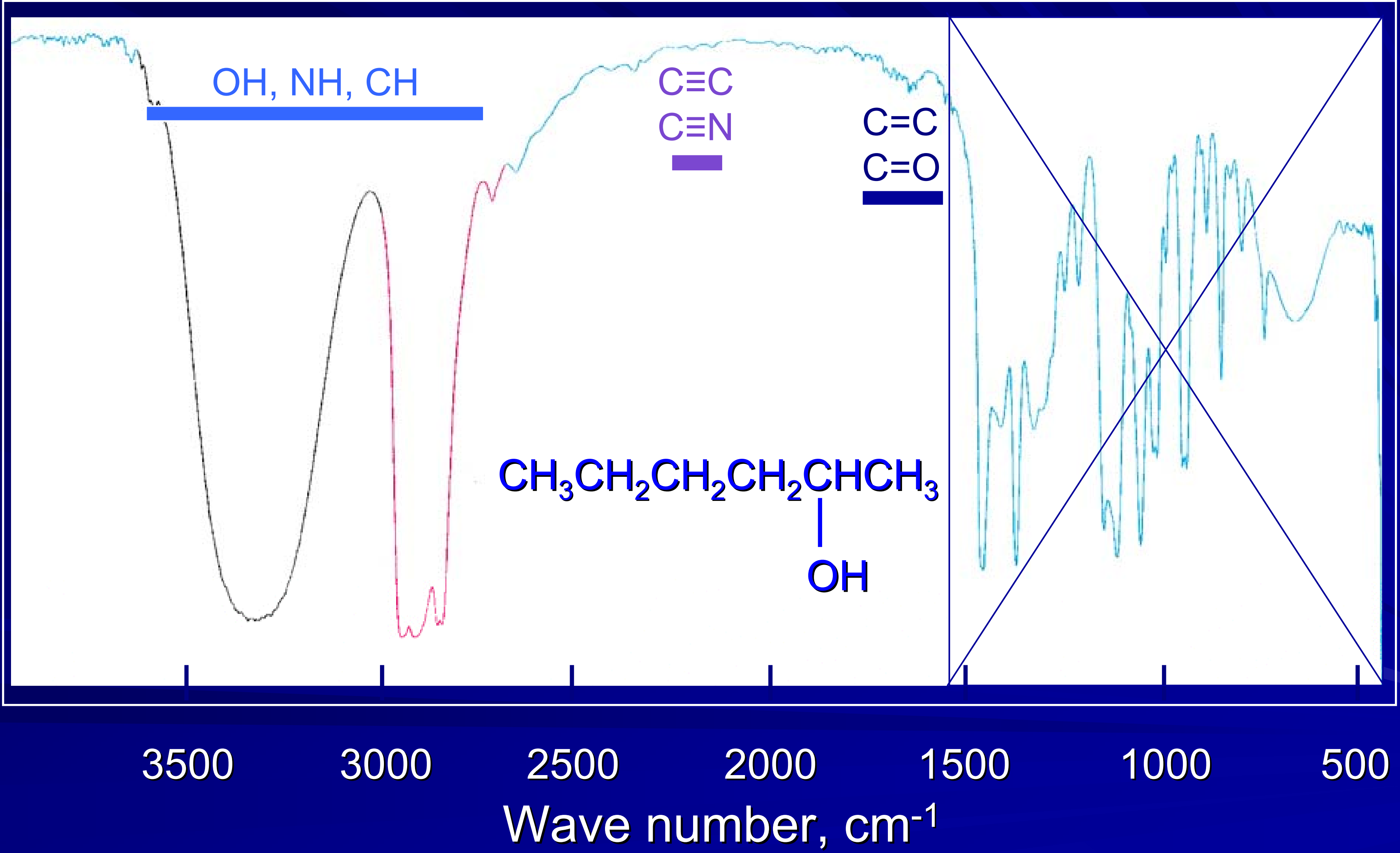
- Many bands & *many overlaps*
  - Heavy atom stretches
  - All bends, etc.

    Should have simple molecule (or *other* evidence for structure) before *interpreting* bands in this region

- Overall pattern reflects molecular structure

  Pattern from 1400-600 = “molecular fingerprint”

Fingerprint Region



Francis A. Carey, *Organic Chemistry,* Fifth Edition. Copyright © 2003 The McGraw-Hill Companies, Inc. All rights reserved.

Intensity Trends

- Follows change in dipole caused by vibrating atoms
  - Polar bonds (strong bond dipoles) absorb strongly
    - O–H
    - C=O, C≡N
    - C–O
  - Nonpolar bonds absorb weakly
    - C≡C, C=C
- Follows # overlapping bands
  - CH bands tend to overlap
  - Molecules contain many CH

→ CH absorptions tend to be strong

Complete Workshop Assignment

Download from Class Web Page

Use Table in Lab Manual

Turn in Completed Assignment