Lecture # 2

INFRARED SPECTROSCOPY

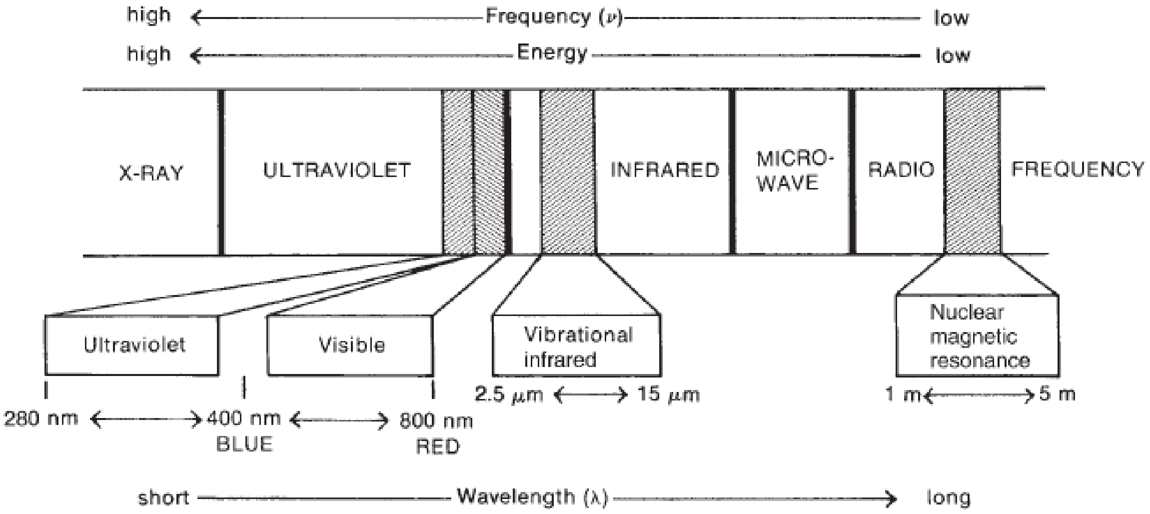


FIGURE 2.1 A portion of the electromagnetic spectrum showing the relationship of the vibrational infrared to other types of radiation.

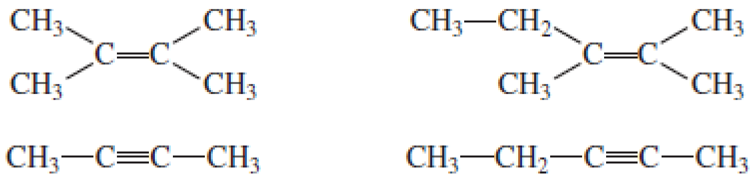
TABLE 2.1
TYPES OF ENERGY TRANSITIONS IN EACH REGION OF THE ELECTROMAGNETIC SPECTRUM

Region of Spectrum	Energy Transitions
X-rays	Bond breaking
Ultraviolet/visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radiofrequencies	Nuclear spin (nuclear magnetic resonance) Electronic spin (electron spin resonance)

$$\bar{\nu}\,(\mathrm{cm}^{-1}) = \frac{1}{\lambda\,(\mathrm{cm})} \qquad \nu\,(\mathrm{Hz}) = \bar{\nu}c = \frac{c\,(\mathrm{cm/sec})}{\lambda\,(\mathrm{cm})}$$

$$\boxed{\mathrm{cm}^{-1} = \frac{1}{(\mu\mathrm{m})} \times 10{,}000 \qquad \text{and} \qquad \mu\mathrm{m} = \frac{1}{(\mathrm{cm}^{-1})} \times 10{,}000}$$

Note, however, that not all bonds in a molecule are capable of absorbing infrared energy, even if the frequency of the radiation exactly matches that of the bond motion. Only those bonds that have a **dipole moment** that changes as a function of time are capable of absorbing infrared radiation.



Symmetric

Pseudosymmetric

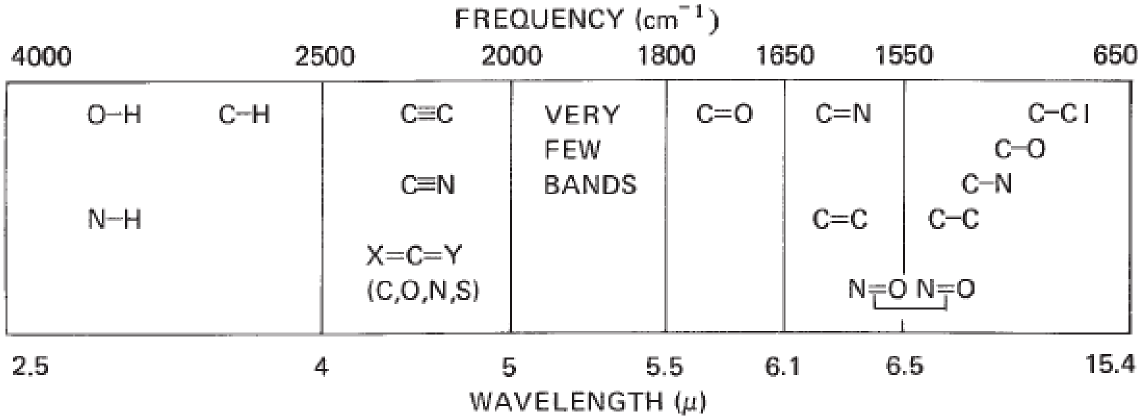
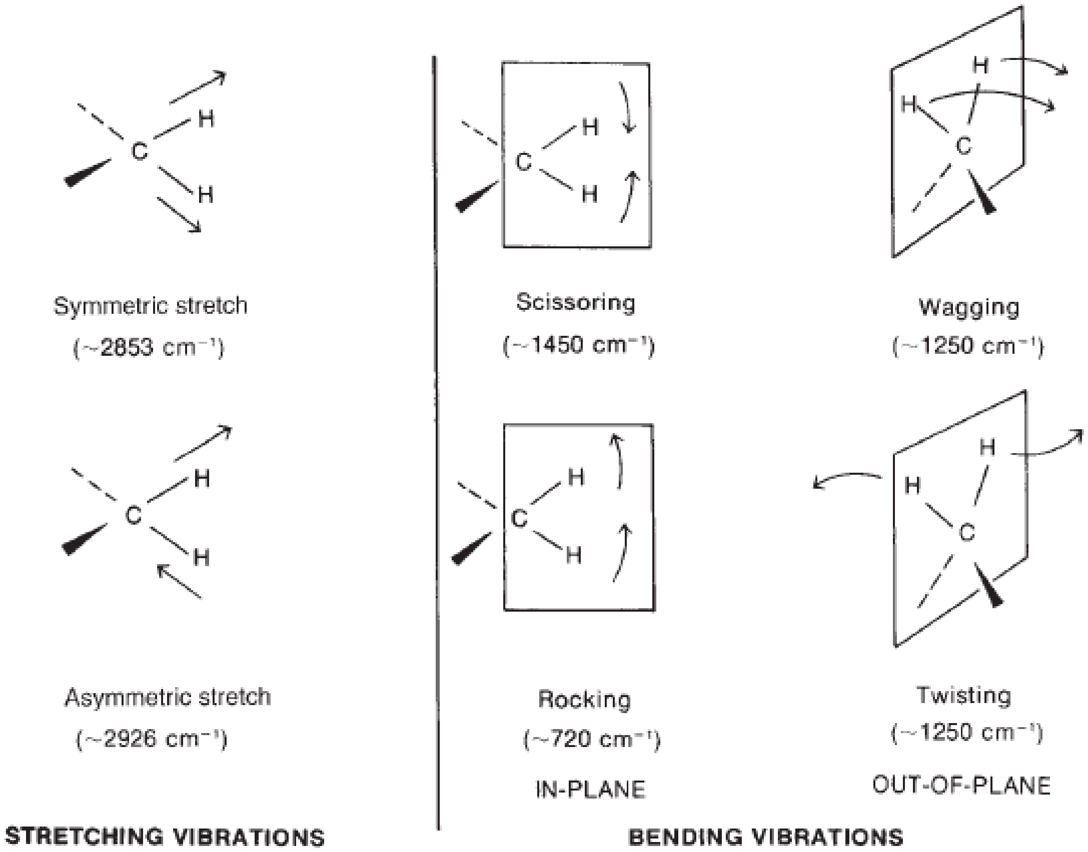
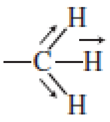
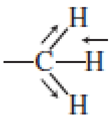
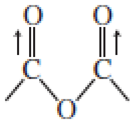
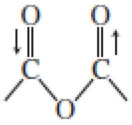
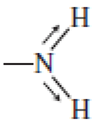
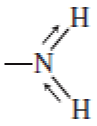
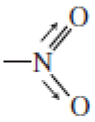
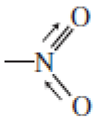


FIGURE 2.2 The approximate regions where various common types of bonds absorb (stretching vibrations only; bending, twisting, and other types of bond vibrations have been omitted for clarity).


Symmetric stretch
(~2853 cm⁻¹)
Asymmetric stretch
(~2926 cm⁻¹)
STRETCHING VIBRATIONS
Scissoring
(~1450 cm⁻¹)
Rocking
(~720 cm⁻¹)
IN-PLANE
Wagging
(~1250 cm⁻¹)
Twisting
(~1250 cm⁻¹)
OUT-OF-PLANE
BENDING VIBRATIONS
C
H

	Symmetric Stretch	Asymmetric Stretch
Methyl	 $\sim 2872\ \text{cm}^{-1}$	 $\sim 2962\ \text{cm}^{-1}$
Anhydride	 $\sim 1760\ \text{cm}^{-1}$	 $\sim 1800\ \text{cm}^{-1}$
Amino	 $\sim 3300\ \text{cm}^{-1}$	 $\sim 3400\ \text{cm}^{-1}$
Nitro	 $\sim 1350\ \text{cm}^{-1}$	 $\sim 1550\ \text{cm}^{-1}$

fundamental absorptions.

Overtones

When two vibrational frequencies ($\overline{\nu}_1$ and $\overline{\nu}_2$) in a molecule couple to give rise to a vibration of a new frequency within the molecule, and when such a vibration is infrared active, it is called a **combination band.** This band is the sum of the two interacting bands ($\overline{\nu}_{\text{comb}} = \overline{\nu}_1 + \overline{\nu}_2$). Not all possible combinations occur. The rules that govern which combinations are allowed are beyond the scope of our discussion here.

Difference bands are similar to combination bands. The observed frequency in this case results from the difference between the two interacting bands ($\nu_{\text{diff}} = \overline{\nu}_1 - \overline{\nu}_2$).

When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called **Fermi resonance.** Again, only certain combinations are allowed. Fermi resonance is often observed in carbonyl compounds.

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

In general, triple bonds are stronger than double or single bonds between the same two atoms and have higher frequencies of vibration (higher wavenumbers):

C≡C	C=C	C−C
$2150\ \text{cm}^{-1}$	$1650\ \text{cm}^{-1}$	$1200\ \text{cm}^{-1}$

$$\xleftarrow[\text{Increasing } K]{\qquad\qquad}$$

The C−H stretch occurs at about $3000\ \text{cm}^{-1}$. As the atom bonded to carbon increases in mass, the reduced mass (μ) increases, and the frequency of vibration decreases (wavenumbers get smaller):

C−H	C−C	C−O	C−Cl	C−Br	C−I
$3000\ \text{cm}^{-1}$	$1200\ \text{cm}^{-1}$	$1100\ \text{cm}^{-1}$	$750\ \text{cm}^{-1}$	$600\ \text{cm}^{-1}$	$500\ \text{cm}^{-1}$

$$\xrightarrow[\text{Increasing } \mu]{\qquad\qquad}$$

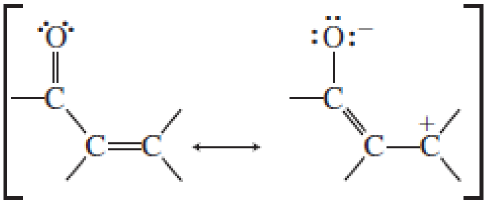
Bending motions occur at lower energy (lower frequency) than the typical stretching motions because of the lower value for the bending force constant *K*.

C−H stretching	C−H bending
$\sim 3000\ \text{cm}^{-1}$	$\sim 1340\ \text{cm}^{-1}$

Hybridization affects the force constant *K*, also. Bonds are stronger in the order $sp > sp^2 > sp^3$, and the observed frequencies of C—H vibration illustrate this nicely.

sp	sp^2	sp^3
≡C—H	=C—H	—C—H
3300 cm^{-1}	3100 cm^{-1}	2900 cm^{-1}

Resonance also affects the strength and length of a bond and hence its force constant *K*. Thus, while a normal ketone has its C=O stretching vibration at 1715 cm^{-1}, a ketone that is conjugated with a C=C double bond absorbs at a lower frequency, near 1675 to 1680 cm^{-1}. That is because resonance lengthens the C=O bond distance and gives it more single-bond character:



The Hooke's Law expression given earlier may be transformed into a very useful equation as follows:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$\bar{\nu}$ = frequency in cm^{-1}

c = velocity of light = 3×10^{10} cm/sec

K = force constant in dynes/cm

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \quad \text{masses of atoms in grams,}$$

$$\text{or} \quad \frac{M_1 M_2}{(M_1 + M_2)(6.02 \times 10^{23})}, \quad \text{masses of atoms in amu}$$

Removing Avogadro's number (6.02×10^{23}) from the denominator of the reduced mass expression (μ) by taking its square root, we obtain the expression

$$\bar{\nu} = \frac{7.76 \times 10^{11}}{2\pi c}\sqrt{\frac{K}{\mu}}$$

TABLE 2.2

CALCULATION OF STRETCHING FREQUENCIES FOR DIFFERENT TYPES OF BONDS

C=C bond:

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

$$K = 10 \times 10^5 \text{ dynes/cm}$$

$$\mu = \frac{M_C M_C}{M_C + M_C} = \frac{(12)(12)}{12 + 12} = 6$$

$$\bar{\nu} = 4.12\sqrt{\frac{10 \times 10^5}{6}} = 1682 \text{ cm}^{-1} \text{ (calculated)}$$

$$\bar{\nu} = 1650 \text{ cm}^{-1} \text{ (experimental)}$$

C—H bond:

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

$$K = 5 \times 10^5 \text{ dynes/cm}$$

$$\mu = \frac{M_C M_H}{M_C + M_H} = \frac{(12)(1)}{12 + 1} = 0.923$$

$$\bar{\nu} = 4.12\sqrt{\frac{5 \times 10^5}{0.923}} = 3032 \text{ cm}^{-1} \text{ (calculated)}$$

$$\bar{\nu} = 3000 \text{ cm}^{-1} \text{ (experimental)}$$

C—D bond:

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

$$K = 5 \times 10^5 \text{ dynes/cm}$$

$$\mu = \frac{M_C M_D}{M_C + M_D} = \frac{(12)(2)}{12 + 2} = 1.71$$

$$\bar{\nu} = 4.12\sqrt{\frac{5 \times 10^5}{1.71}} = 2228 \text{ cm}^{-1} \text{ (calculated)}$$

$$\bar{\nu} = 2206 \text{ cm}^{-1} \text{ (experimental)}$$