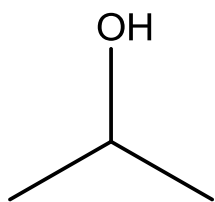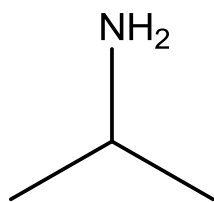# IR-Spectroscopy

# Infrared Spectroscopy

What does the **Infrared Spectroscopy do?**

**Infrared spectroscopy identifies the functional groups present in the molecule Required to investigate the structure of the molecule**
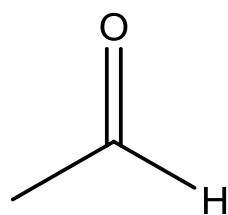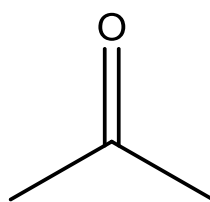
Examples of functional groups:

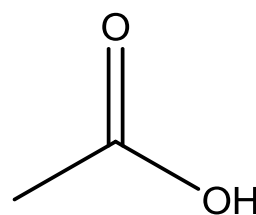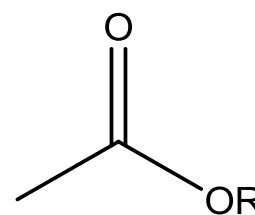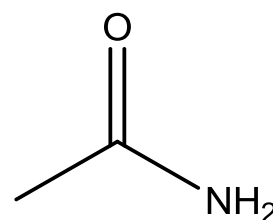| OH | NH$_2$ | O | O | O | O | O |
|----|--------|---|---|---|---|---|
| Alcohol | Amine | Aldehyde | Ketone | Acid | Ester | Amide |

**Functional groups are different due to the difference in atoms and their connectivity**

**Infrared spectroscopy distinguishes the bond based on the differences of atoms forming that bond**
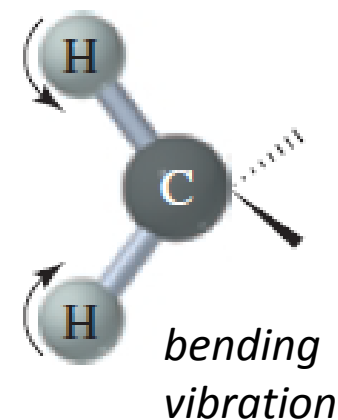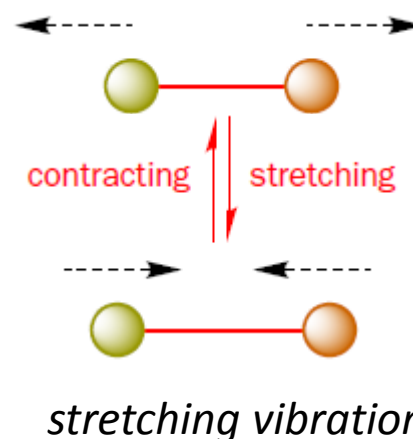
# Infrared Spectroscopy: Chemical Bonds

The covalent bonds in molecules are constantly vibrating

The bond behaves as if it were a vibrating spring connecting two atoms

A bond vibrates with both stretching and bending motions

A *stretch is a vibration occurring along the* line of the bond that changes the bond length

A *bend is a vibration that does not occur* along the line of the bond, but changes the bond angle.

contracting | stretching

*stretching vibration*
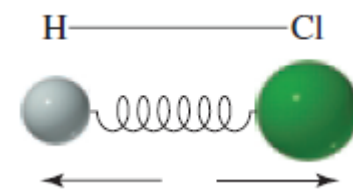
*bending vibration*

A diatomic molecule can undergo only a stretching vibration since it has **no bond angles**

The vibrations of a molecule containing three or more atoms are more complex

bending

symmetric stretch    asymmetric stretch    symmetric in-plane    asymmetric in-plane    symmetric out-of-plane    asymmetric out-of-plane
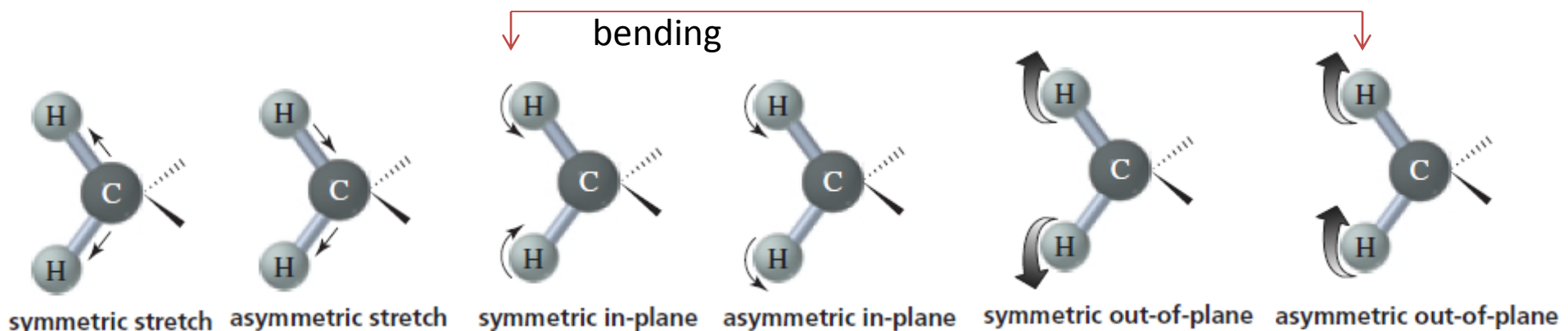
# Infrared Spectroscopy: How it works

Each stretching and bending vibration of a bond in a molecule corresponds to a characteristic energy

When a compound is exposed to a radiation of a energy that exactly matches with the energy corresponding to vibrations, the molecule will absorb energy

By experimentally determining the frequency of the energy absorbed by a particular compound, we can ascertain what kinds of bonds it has

In infrared spectroscopy, frequency of absorbed radiation is described in **wavenumber**, wavenumber is the number of waves in one centimeter, so it has units $cm^{-1}$

$$\tilde{\nu}(cm^{-1}) = \frac{10^4}{\lambda(\mu m)} \quad \text{(because 1 } \mu m = 10^{-4} \text{ cm)}$$

wavenumber is directly proportional to energy

*high energy* means *high frequencies* *large wavenumbers* *short wavelengths*

The stretching vibration of a C= O bond absorbs energy of wavenumber ~**1700 cm$^{-1}$**

$$\diagdown C{=}O \qquad O{-}H$$

~1700 cm$^{-1}$      ~3450 cm$^{-1}$

The stretching vibration of an O – H bond absorbs energy of wavenumber **~3450 cm$^{-1}$**

# Infrared Spectroscopy: How it works



$$\text{percent transmittance} = \frac{I_s}{I_r} \times 100$$
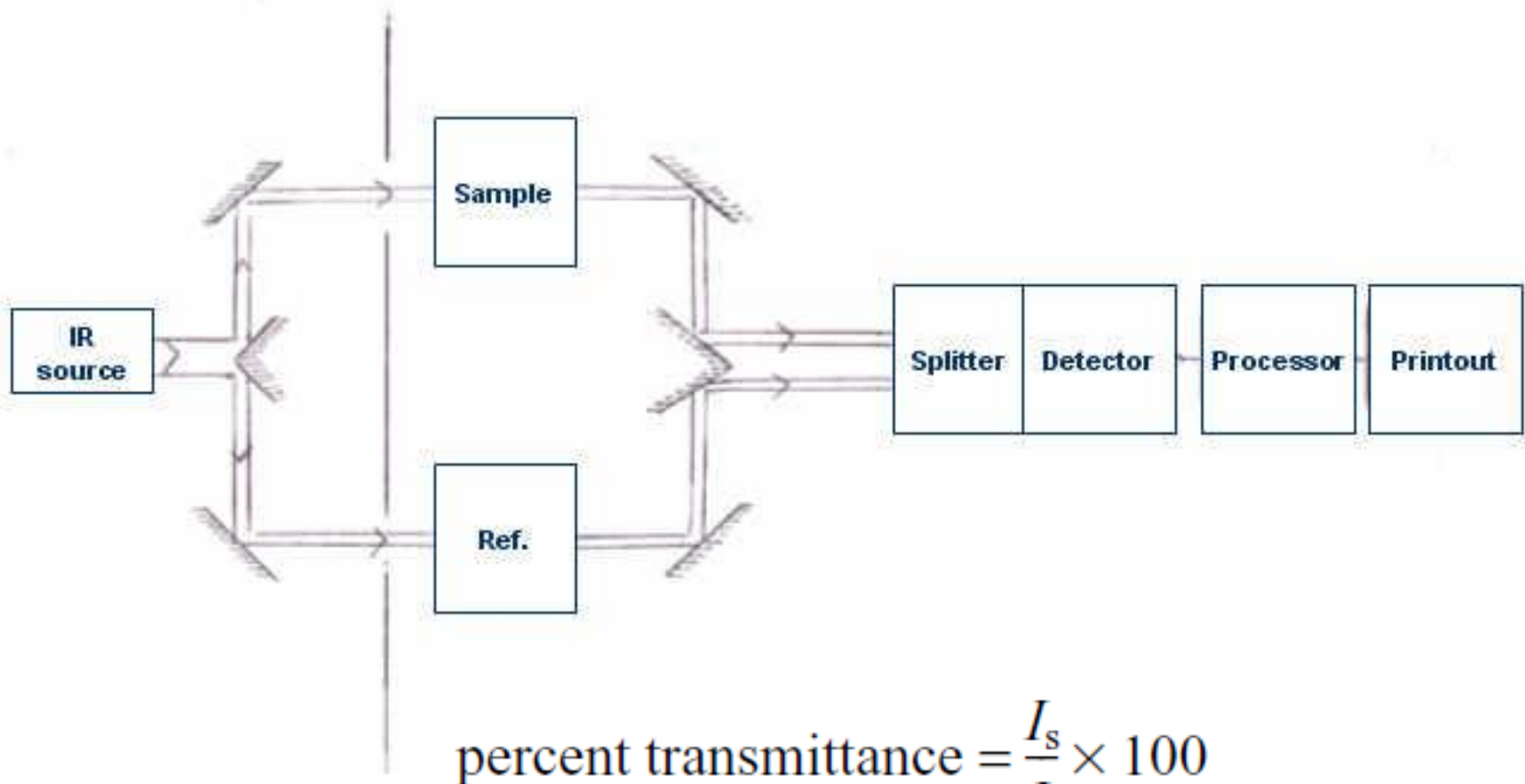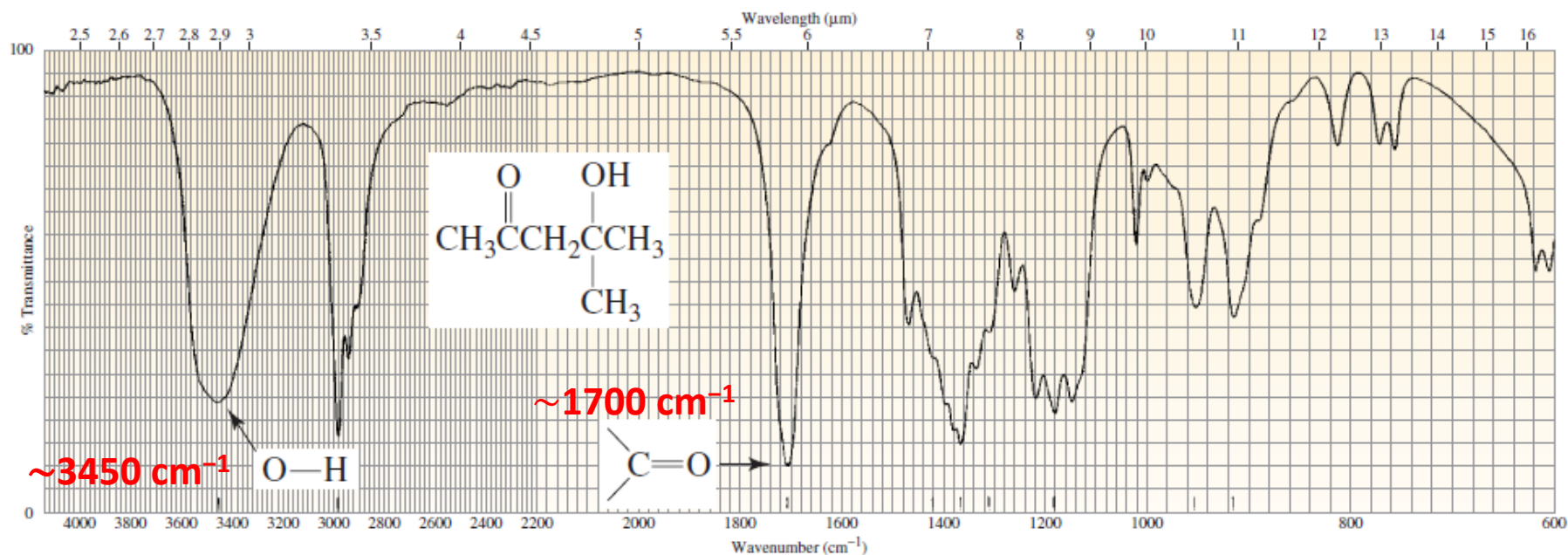
*$I_s$ is the intensity of the sample beam*

*$I_r$ is the intensity of the reference beam*

the transmittance is nearly 100%, meaning that the sample is nearly transparent to radiation of that frequency (does not absorb it)

# Infrared Spectroscopy



A plot of percent transmission of radiation versus the wavenumber (or wavelength) of the radiation transmitted

At 100% transmission, all the energy of the radiation passes through the molecule

Lower values of percent transmission mean that some of the energy is being absorbed by the compound

Each downward spike in the IR spectrum represents absorption of energy. The spikes are called **absorption bands**

# Infrared Spectroscopy: The Position of Absorption Bands

The amount of energy required to stretch a bond depends on the *strength of the bond* and the *masses of the bonded atoms*

*The stronger the bond, the greater the energy* required to stretch it, because a stronger bond corresponds to a tighter spring
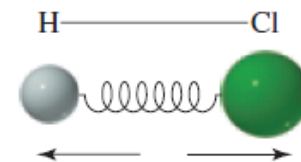
The frequency of the vibration is inversely related to the mass of the atoms attached to the spring, so heavier atoms vibrate at lower frequencies

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

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

*c = the speed of light and μ = reduced mass*

The wavenumber of an absorption can be calculated from the equation derived from **Hooke's law,** which describes the motion of a vibrating spring
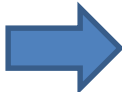
The equation relates the wavenumber ( $\tilde{\nu}$ ) of the stretching vibration to the force constant of the bond ( *K* ) *and the masses (m₁ & m₂) of the atoms (in grams) joined by the bond*

The force constant is a measure of the strength of the bond

*Stronger bonds and lighter atoms give rise to higher frequencies*

# Infrared Spectroscopy: The Position of Absorption Bands

$$\overline{v} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$$\Rightarrow \quad \overline{v} = \frac{7.76 \times 10^{11}}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$\overline{v}$ = frequency in cm$^{-1}$

$c$ = velocity of light = $3 \times 10^{10}$ cm/sec

$K$ = force constant in dynes/cm

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

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

$$\overline{v}(\text{cm}^{-1}) = 4.12\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{M_1 M_2}{M_1 + M_2}, \quad \text{where } M_1 \text{ and } M_2 \text{ are atomic weights}$$

$$K = \text{force constant in dynes/cm}$$

# Infrared Spectroscopy: The Position of Absorption Bands

C=C bond:

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

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

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

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

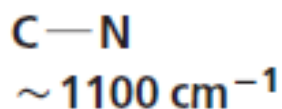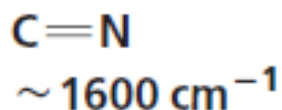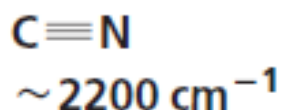$$\bar{v} = 1650 \text{ cm}^{-1} \text{ (experimental)}$$

Experimental and calculated values may vary considerably due to resonance, hybridization, and other effects that operate in organic molecules

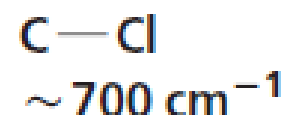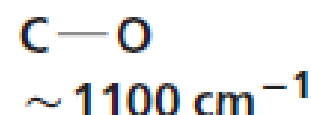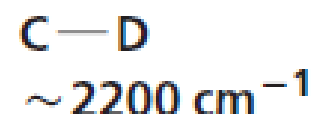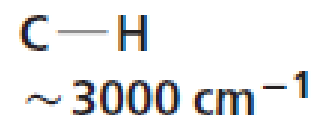# Infrared Spectroscopy: The Position of Absorption Bands

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

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

**Stronger bonds show absorption bands at larger wavenumbers**

C≡N
$\sim 2200$ cm$^{-1}$

C=N
$\sim 1600$ cm$^{-1}$

C—N
$\sim 1100$ cm$^{-1}$

**Lighter atoms show absorption bands at larger wavenumbers**

C—H
$\sim 3000$ cm$^{-1}$

C—D
$\sim 2200$ cm$^{-1}$

C—O
$\sim 1100$ cm$^{-1}$

C—Cl
$\sim 700$ cm$^{-1}$

Bond order affects bond strength
so bond order affects the position of absorption bands

**Higher** the bond order, higher will be the bond strength, **larger** will be the wavenumbers

Hybridization affects the force constant *K, also. Bonds are stronger in the order sp > sp² > sp³, 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$^{-1}$ |
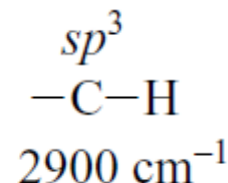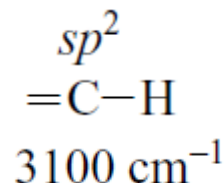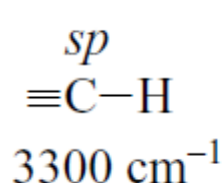
# Infrared Spectroscopy: Intensity of Peak

The intensity of an absorption band depends on the magnitude of the change in dipole moment associated with the vibration:

The greater the change in dipole moment, the more intense the absorption.

Dipole moment of a bond is equal to the magnitude of the charge on one of the bonded atoms, multiplied by the distance between the two charges

Increasing distance between the atoms increases the dipole moment.

O—H     >     N—H     >     C—H

increasing polarity

increasing intensity
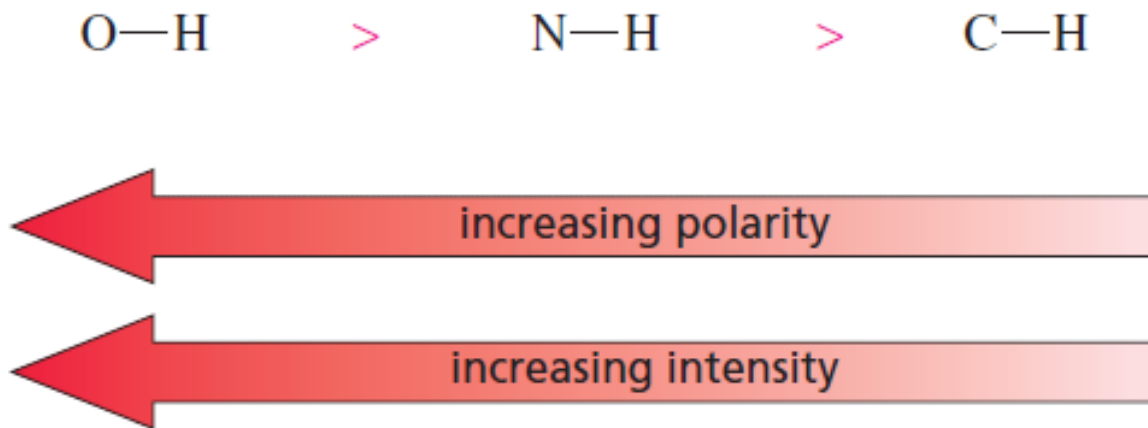
# Infrared Spectroscopy: Important IR Stretching Frequencies

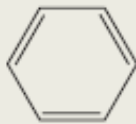| Type of bond | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| C≡N | 2260–2220 | medium |
| C≡C | 2260–2100 | medium to weak |
| C=C | 1680–1600 | medium |
| C=N | 1650–1550 | medium |
| (benzene ring) | ~1600 and ~1500–1430 | strong to weak |
| C=O | 1780–1650 | strong |
| C—O | 1250–1050 | strong |
| C—N | 1230–1020 | medium |
| O—H (alcohol) | 3650–3200 | strong, broad |
| O—H (carboxylic acid) | 3300–2500 | strong, very broad |
| N—H | 3500–3300 | medium, broad |
| C—H | 3300–2700 | medium |

# Infrared Spectroscopy: Resonance and Inductive Electronic Effects

Bond order affects bond strength, so bond order affects the position of absorption bands

Higher the bond order, higher will be the bond strength, larger will be the wavenumbers



2-pentanone

$C=O$ at 1720cm$^{-1}$

2-cyclohexenone

$C=O$ at 1680cm$^{-1}$
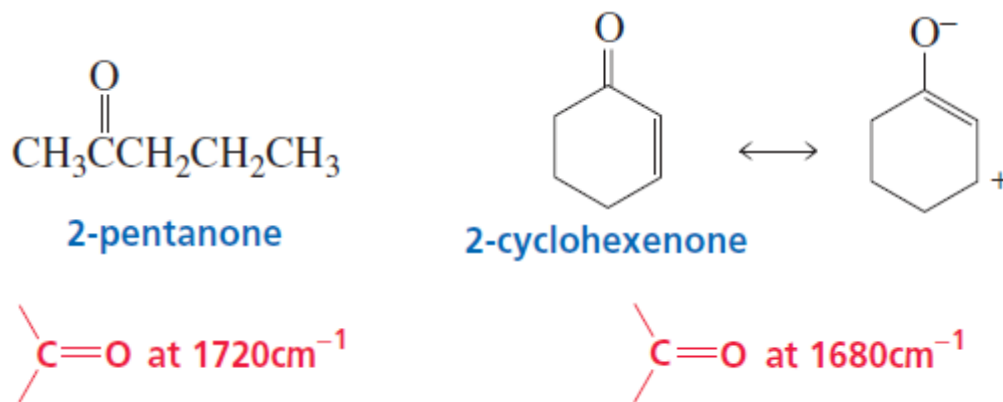
2-Cyclohexenone absorbs at a lower frequency because the carbonyl group has less double-bond character due to electron delocalization

Because a single bond is weaker than a double bond, a carbonyl group with significant single-bond character will stretch at a lower frequency than will one with little or no single-bond character

# Infrared Spectroscopy: Resonance and Inductive Electronic Effects

Putting an atom other than carbon next to the carbonyl group also causes the position of the carbonyl absorption band to shift

Direction of Shifts will depend on whether electron donating resonance effect or electron withdrawing inductive effect predominates

Negative inductive effect reduces the length of C=O bond thus increases the frequency of absorption

Resonance effect increases the length of C=O bond thus decreases the frequency of absorption

inductive electron withdrawal

resonance electron donation
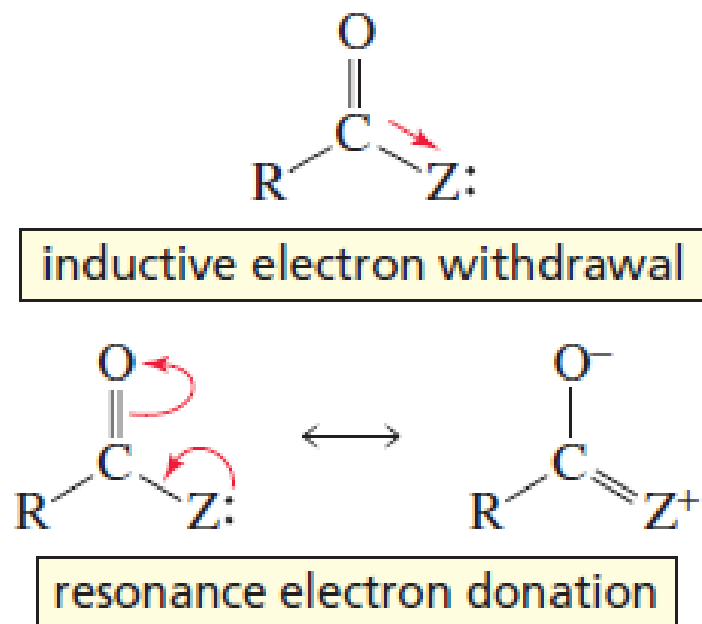
| Z | $\tilde{\nu}$ (C = O) |
|---|---|
| inductive effect predominates | |
| Cl | 1815–1785 |
| F | ~1869 |
| Br | 1812 |
| OH (monomer) | 1760 |
| OR | 1750–1735 |
| Resonance effect predominates | |
| NH$_2$ | 1695–1650 |
| SR | 1720–1690 |

# Looking forward

**IR -spectroscopy:**
**Examples of functional group identification**