


**Molecular Vibrations  
and  
IR Spectroscopy**



PGCC CHM 103 Sinex

## Vibrations

What is a vibration in a molecule?

Any change in shape of the molecule- stretching of bonds, bending of bonds, or internal rotation around single bonds

Can a vibration change the dipole moment of a molecule? ([Shockwave animation](#))

Asymmetrical stretching/bending and internal rotation change the dipole moment of a molecule. Asymmetrical stretching/bending are IR active.

Symmetrical stretching/bending typically does not. Not IR active

What wavelength of electromagnetic radiation is involved in causing vibrations in molecules?

Infrared (IR) electromagnetic radiation causes vibrations in molecules (wavelengths of 2500-25,000 nm or 2.5 - 25  $\mu\text{m}$ )

For a vibration at  $4111\text{ cm}^{-1}$  (the stretch in  $\text{H}_2$ ), how many vibrations occur in a second?


120 trillion vibration per second!!!!

$120 \times 10^{12}$  vibrations/second or one vibration every  $8 \times 10^{-15}$  seconds!

**WOW !!!!!**

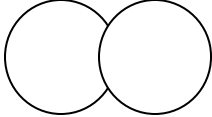
### How does the mass influence the vibration?

$\text{H}_2$



MM = 2 g/mole  
 $4111\text{ cm}^{-1}$

$\text{I}_2$



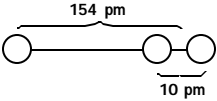
MM = 254 g/mole  
 $365\text{ cm}^{-1}$

The greater the mass - the lower the wavenumber

Estimate the wavenumber for the HI stretch.  $2919\text{ cm}^{-1}$

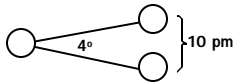
### How much movement occurs in the vibration of a C-C bond?

stretching vibration



For a C-C bond with a bond length of 154 pm, the variation is about 10 pm.

bending vibration



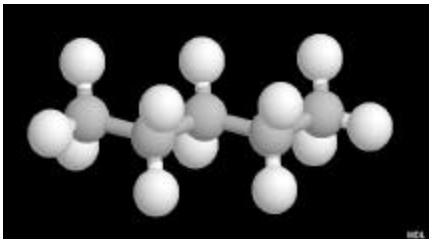
For C-C-C bond angle a change of  $4^\circ$  is typical. This moves a carbon atom about 10 pm.

### A little physics of electromagnetic radiation

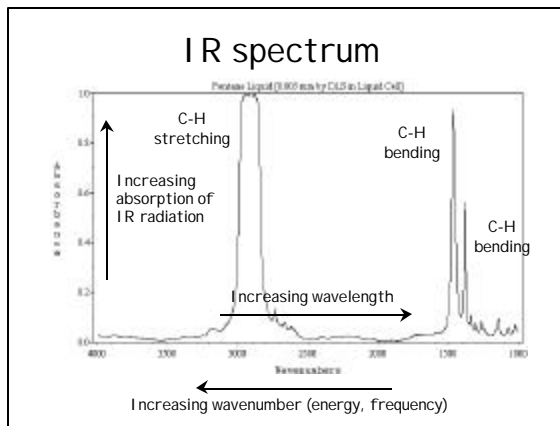
- Energy (E)  $E = hv = hc/\lambda = hc\nu'$ 
  - where h is Planck's constant, c is the speed of light,  $\nu'$  is frequency or the number of vibrations per second and  $\lambda$  is the wavelength
- Wavenumber ( $\nu'$ )  $\nu' = 1/\lambda$ 
  - given in  $\text{cm}^{-1}$
- Period (P)  $P = 1/\nu$ 
  - the time between a vibration

Energy, frequency, and wavenumber are directly proportional to each other.

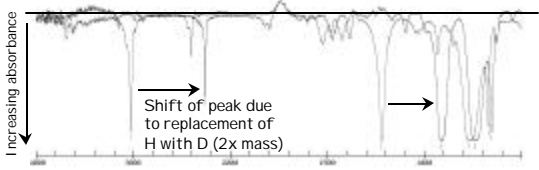
What type of vibrations would occur in pentane?



Let's examine the IR spectrum of pentane.



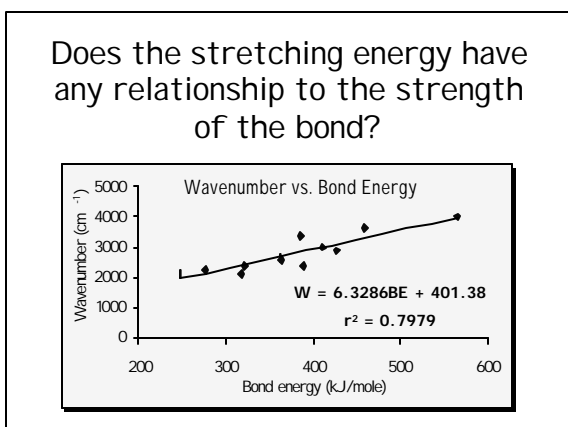
IR Spectra of chloroform and deuteriochloroform



Mode of vibration	CHCl <sub>3</sub> Calculated*	CHCl <sub>3</sub> Measured	CDCl <sub>3</sub> Measured
C-H stretching	3002	3020	2256
C-H bending	1120	1219	912
C-Cl stretching	701	773	737
C-Cl bending	418	671	652

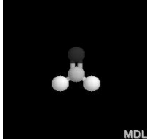
\* Spartan 02 AM1 minimization

- Some results
- Calculated values using computational software give lower wave numbers
  - Increasing mass of substituted atoms shifts wavenumbers to lower values  
(Excel spreadsheet)
  - Stretching energies > bending energies > internal rotation energies (occur at higher wavelengths)




Let's examine the carbonyl group on three compounds

formaldehyde



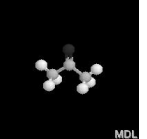
MDL

phosgene



MDL

acetone



MDL

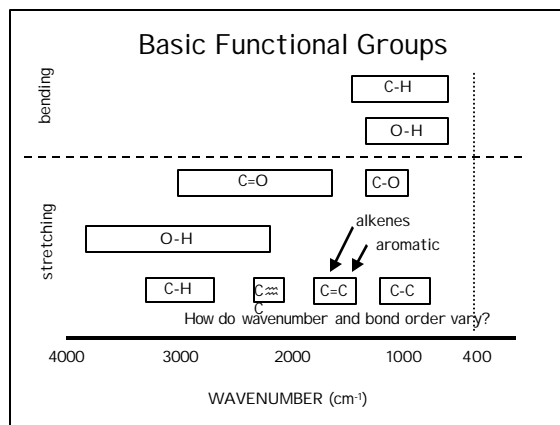
How does the C=O stretching energy compare for these three molecules?

2053 cm<sup>-1</sup>      1951 cm<sup>-1</sup>      1731 cm<sup>-1</sup>

The carbonyl group has a range of 1700-3000 cm<sup>-1</sup>.

### Functional group analysis in organic compounds

- Unlike atomic spectroscopy where sharp energy transitions occur due to well quantized electron transitions, molecular spectroscopy tends to show bands.
- Molecular vibrations are influenced by the surrounding groups!



### Use of IR spectra

- Identification of functional groups on a molecule - this is a very important tool in organic chemistry
- Spectral matching can be done by computer software and library spectra
- Since absorbance follows Beer's Law, can do quantitative analysis