

# Introduction to Computational Quantum Chemistry

## Lesson 06: Frequency Analysis (IR Spectra)

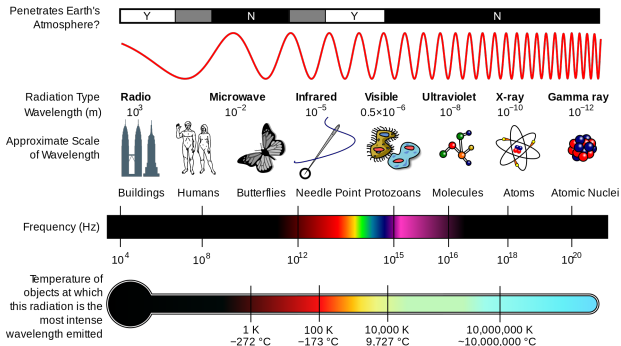


# Quick Review, Molecular Motions

- despite the typical graphical display of molecular structures, molecules are highly flexible and undergo multiple modes of motion over a range of time-frames
- motions involve rotations, translations, and changes in bond lengths, bond angles, dihedral angles, ring flips, methyl bond rotations.
- infrared (IR) spectroscopy: based on IR absorption by molecules as undergo vibrational and rotational transitions.

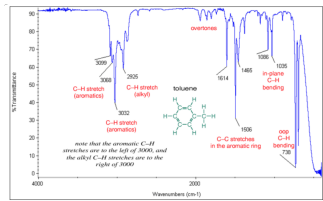
# Quick Review, Infrared (IR) spectroscopy

- wide range of types of electromagnetic radiation in nature.



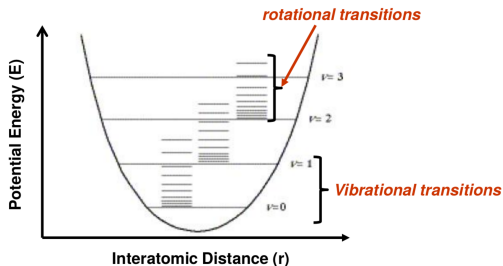
# Quick Review, Infrared (IR) spectroscopy

- IR radiation is in the range of  $12,800 - 10\text{cm}^{-1}$  or  $\lambda = 0.78 - 1000\mu\text{m}$ 
  - rotational transitions have small energy differences  
 $\leq 100\text{cm}^{-1}$ ,  $\lambda > 100\mu\text{m}$
  - vibrational transitions occur at higher energies
  - rotational and vibrational transitions often occur together
- typical IR spectrum for Organic Molecule



# Quick Review, Infrared (IR) spectroscopy

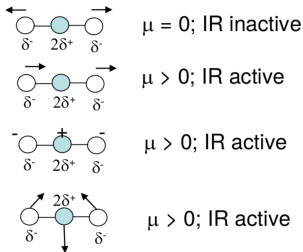
- potential energy resembles classic Harmonic Oscillator



# IR Active Vibrations

- in order for molecule to absorb IR radiation:  
vibration at same frequency as the source and also, must have a change in its net dipole moment as a result of the vibration

$\text{CO}_2$ :  $3(3)-5 = 4$  modes

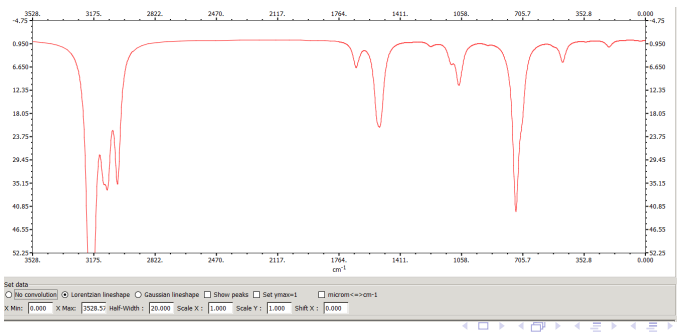


# Activity I: Calculation of Vibration Frequencies

- using Gaussian, performed calculations on these three molecules:
  - Toluene, 2-Propanone and 2-Propanol
- Geometry Optimization and Frequency Calculations using:
  - HF/6-31G(d) for Opt and Freq
  - B3LYP/6-31G(d) for Opt and Freq
  - MP2/6-31G(d) for Opt and Freq

# Activity II: Visualization of In Silico IR Spectra

- open **Gabedit**
- under **Tools** Menu open IR Spectrum and read from **Gaussian output file**
- you will be redirected to XY GabeditPlot, chose **Lorentzian lineshape** and set the wavenumber to  $cm^{-1}$ .
- the partial set up should something look like this:

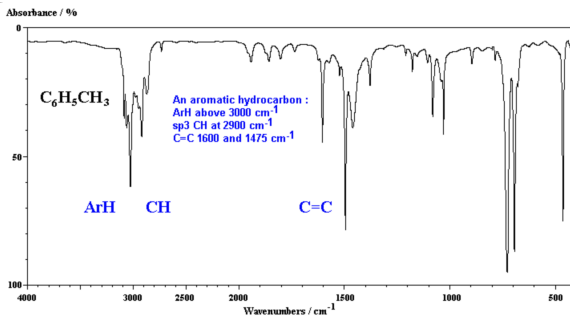




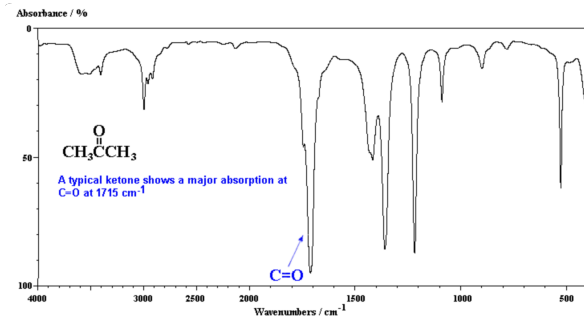
## Activity II: Visualization of In Silico IR Spectra

- open the **Display Vibration** menu
  - right click and go to **Animation > Vibration > Read a Gaussian output file**
  - you can see the individual **Frequencies** and **IR Intensities** as well as **Play** the actual vibrations on the screen.
- compare the *In Silico* quantitative values and the IR spectra to the experimental spectra presented in the following slides
- how are the three methods [**HF, DFT(B3LYP), and MP2**] differ when it comes to producing the molecular vibrational values? relative to the experiment which method is accurate?

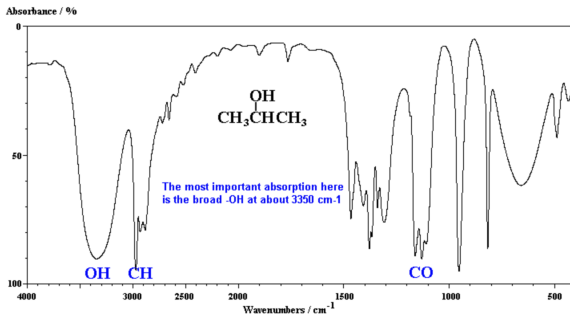
# Toluene IR Spectra



# 2-Propanone IR Spectra



# 2-Propanol IR Spectra



# Assignment - Further Exploration/Meditation ;)

- using the each respected optimize geometries of the previous job performed calculations on these three molecules:
  - **HF/6-311G(d,p)** for Opt and Freq
  - **B-LYP/6-311G(df,p)** for Opt and Freq
  - **MP2/6-311G(d,p)** for Opt and Freq
- compare the results with the experimental IR Spectra
- is there an improvement?
- are the results method dependent or basis set dependent?

# Conclusions

- it's been an established fact that the computed quantum chemical harmonic vibrational frequencies are typically larger than the values observed experimentally.
  - a major source of this disagreement is the neglect of anharmonicity effects in the theoretical treatment.
  - errors also arise because of incomplete incorporation of electron correlation and the use of finite basis sets.
- thus one be careful when it comes to choosing a method of calculation and basis sets while balancing with the size of the molecule being considered.
- several studies suggested that a **scaling factors** for the vibrational frequencies of a particular theoretical procedures must be applied and it gave improve results.

**END**