

## **Today**

Sections 13.10 - 13.18  
Infrared Spectroscopy

## **Second Class from Today**

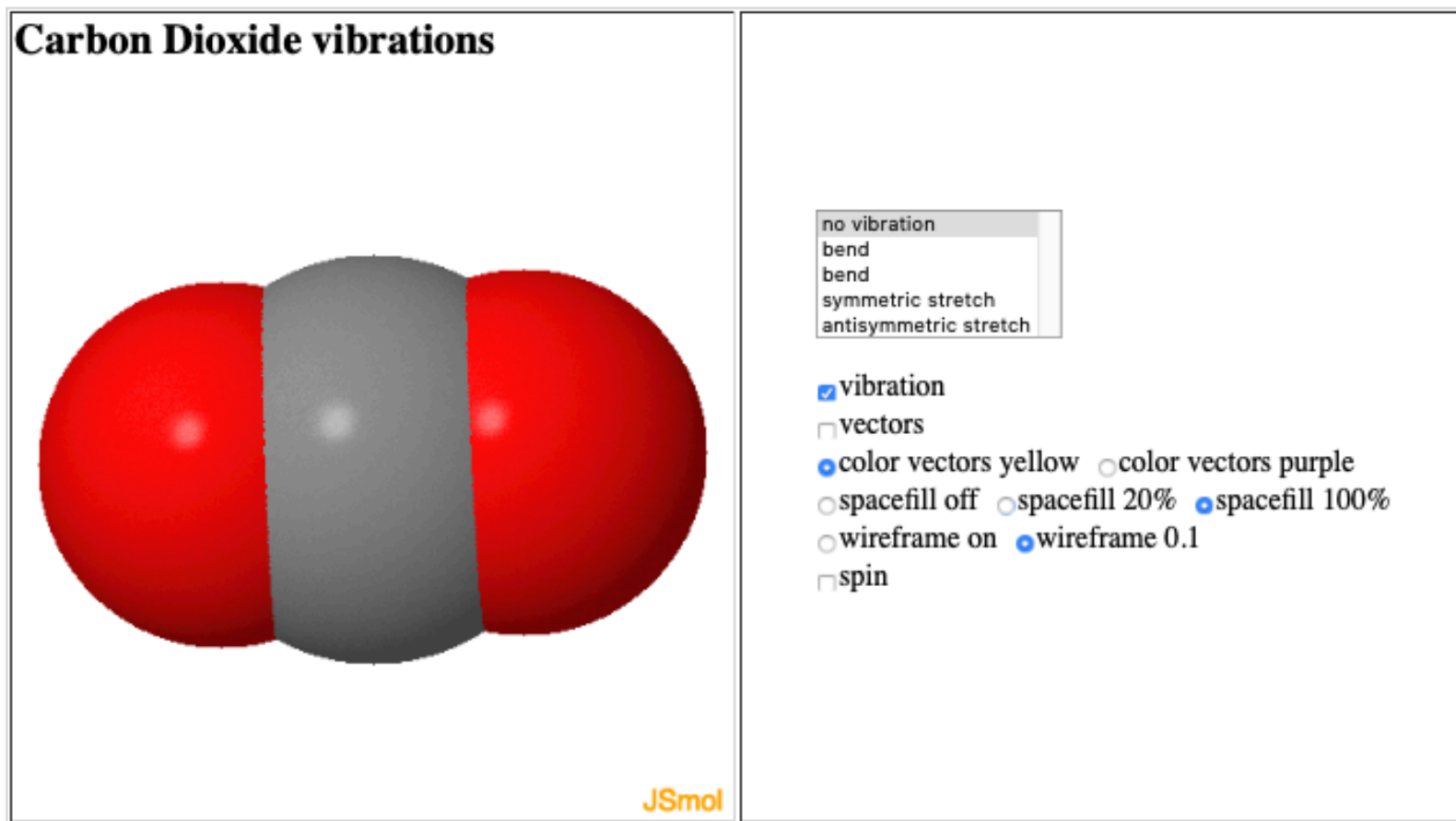
Section 14.1 - 14.9  
Introduction to Nuclear Magnetic Resonance,  
Shielding, Chemical Shift, and Integration

## **Next Class**

Sections 13.10 - 13.18  
Infrared Spectroscopy

## **Third Class from Today**

Section 14.10 - 17  
Splitting and Multiplicity





A **vibration that changes the dipole of a molecule** creates an oscillating electric field that **can interact with Infra-red light**. Consider the vibrations of the greenhouse gas CO<sub>2</sub>.

vibration needs to create an oscillating electric field

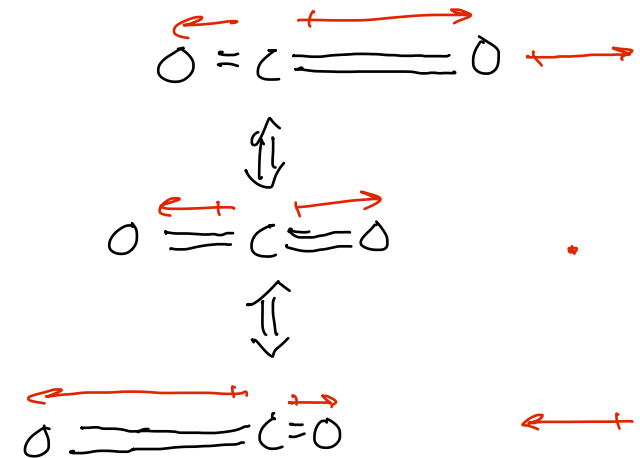
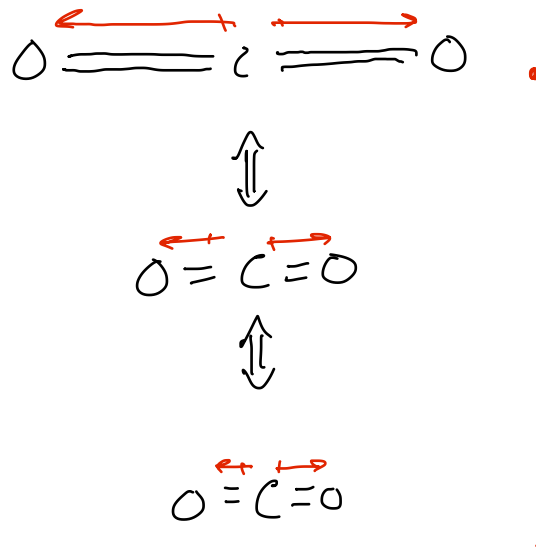
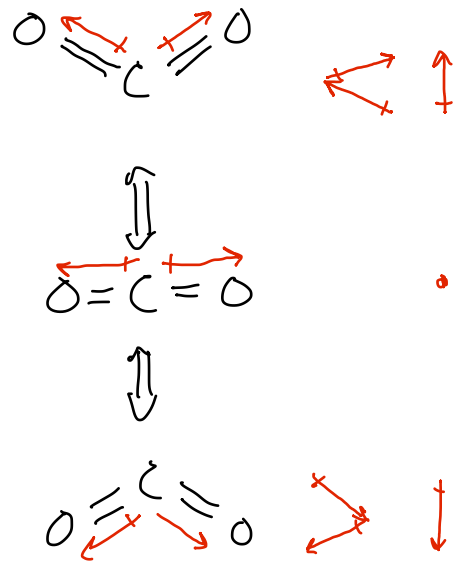
This is an IR active vibration

$O=C=O$  not a polar molecule

IR inactive

IR active

dipole changes



# An Example Spectrum

## Section 13.10

Transmitted light is observed light that is absorbed is "missing" and causes a peak

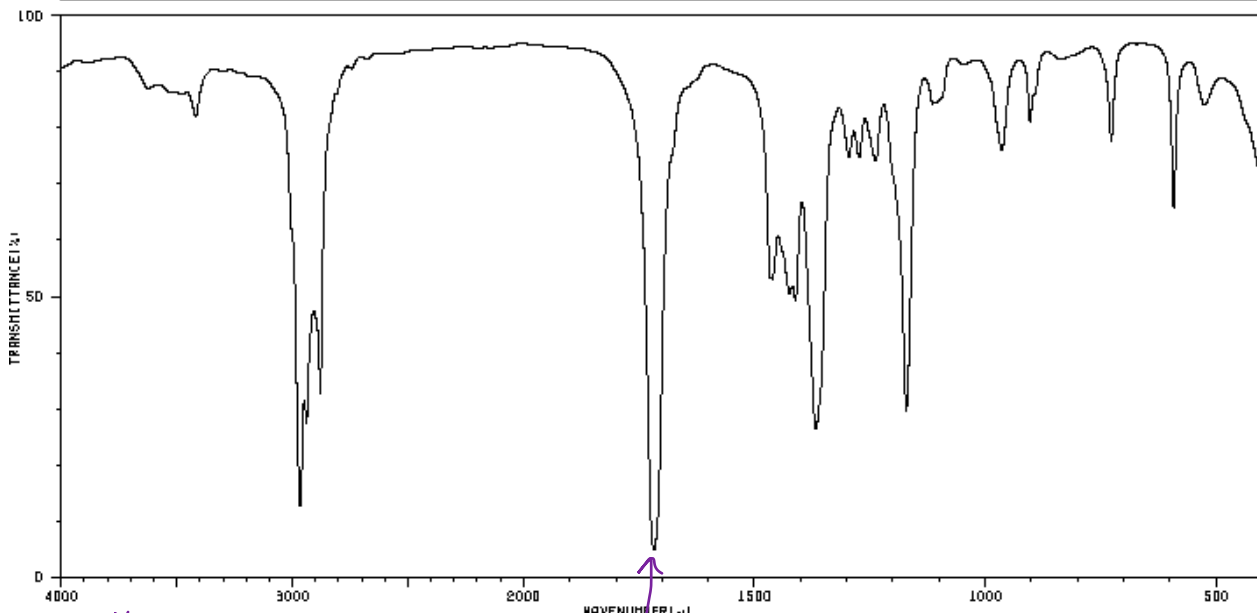
Important to identify technique + identify

solvents if used

100

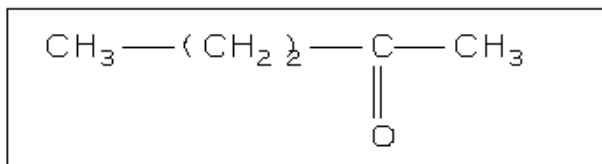
0

HIT-NO=1985 SCORE= ( ) SDBS-NO=2673 IR-NIDA-00433 : LIQUID FILM  
 2-PENTANONE  
 C<sub>5</sub>H<sub>10</sub>O



cm⁻¹ %T

3419	79	1426	49	1114	81	692	64
2966	12	1412	47	1105	81	526	81
2939	26	1367	25	1100	81		
2879	31	1296	72	964	72		
1717	4	1274	72	903	79		
1467	50	1237	72	894	81		
1461	60	1172	28	727	74		



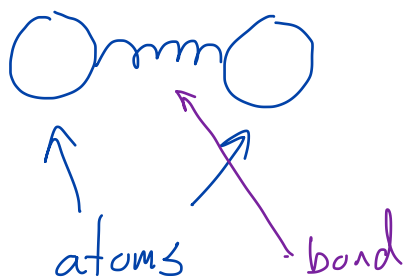
intense peaks have low transmittance

# Positions of IR Bands

Section 13.11, 13.12, 13.13

## Hooke's Law

Force to displace  
 $F = kx$  spring



## Harmonic Oscillator

frequency of oscillation  
 $f = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$   
 force constant  
 for object with mass  $m$

## Frequency of IR Absorbed

$$\bar{\nu} = \frac{1}{2\pi c} \left[ \frac{f(m_1 + m_2)}{m_1 m_2} \right]$$

Force constant for the bond  
 strong bond large  $f$   
 vibrate at higher freq

weak bonds small  $f$   
 vibrate at lower freq

H	C, N, O	Cl
1	12 14 16	35

$$\frac{12+1}{12}$$

$$\frac{12+12}{144}$$

$$\frac{12+35}{420}$$

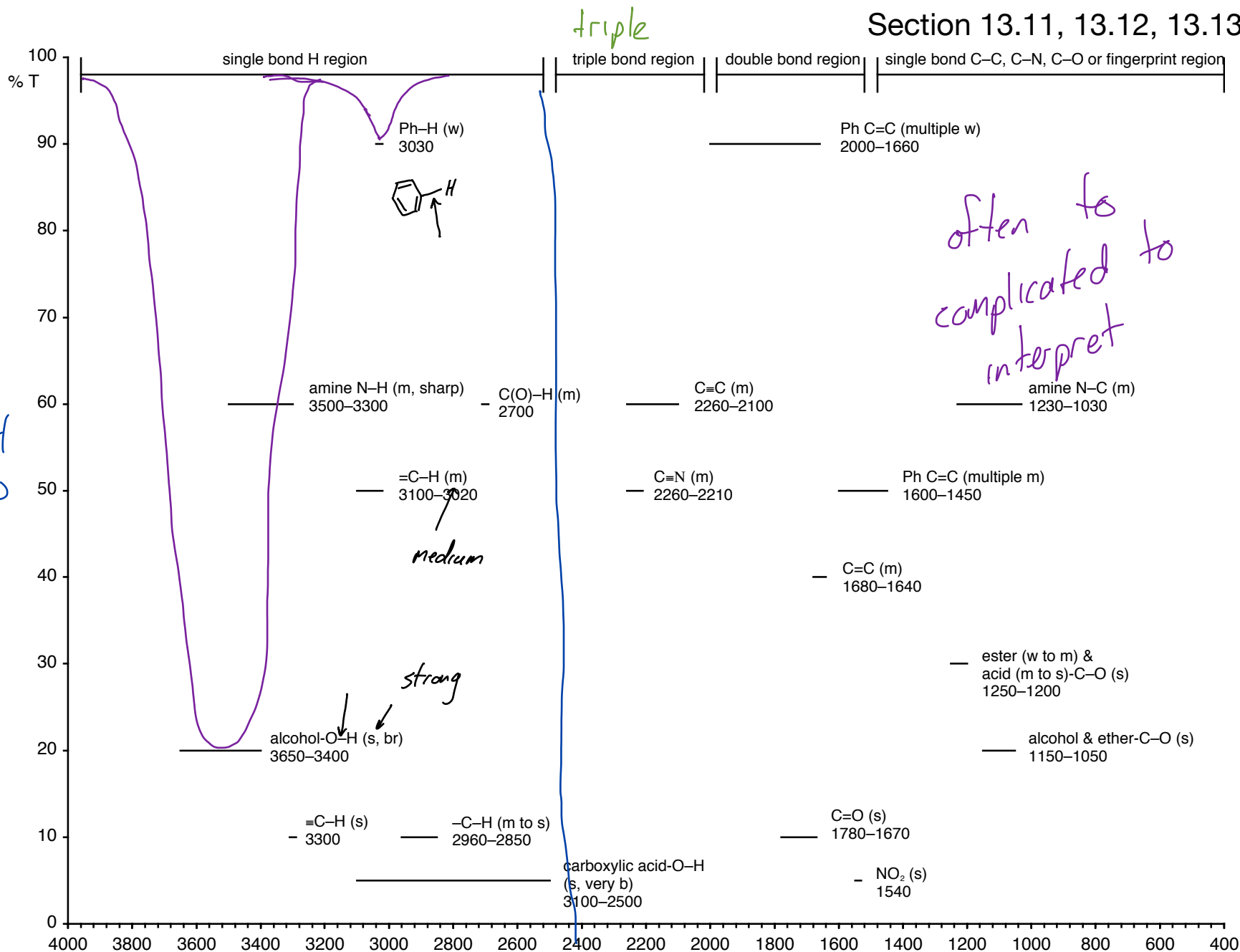
high freq

lower freq

# Guides

C-H  
 O-H  
 N-H  
 high freq  
 because of  
 the small H  
 2400 - 4000  
 C=C C-N  
 C=O  
 < 2400

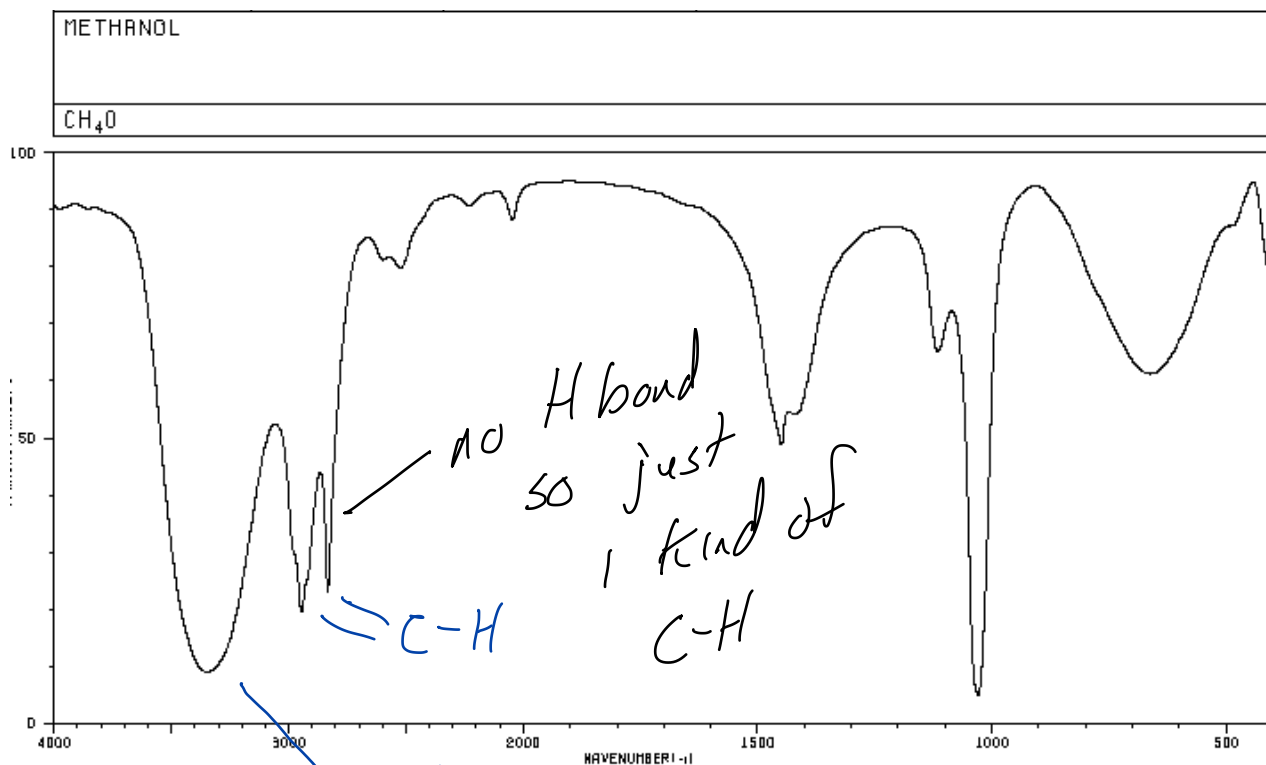
# Section 13.11, 13.12, 13.13



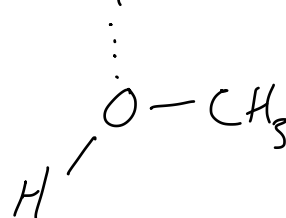
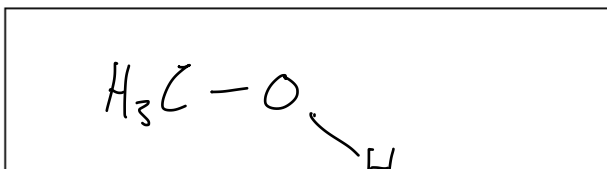
reciprocal centimeters is used because it is proportional to energy, — cm<sup>-1</sup>  
 the numbers are a convenient size, and tradition

# Intensity and Shape, OH vs CH

Large dipole changes result in intense peaks

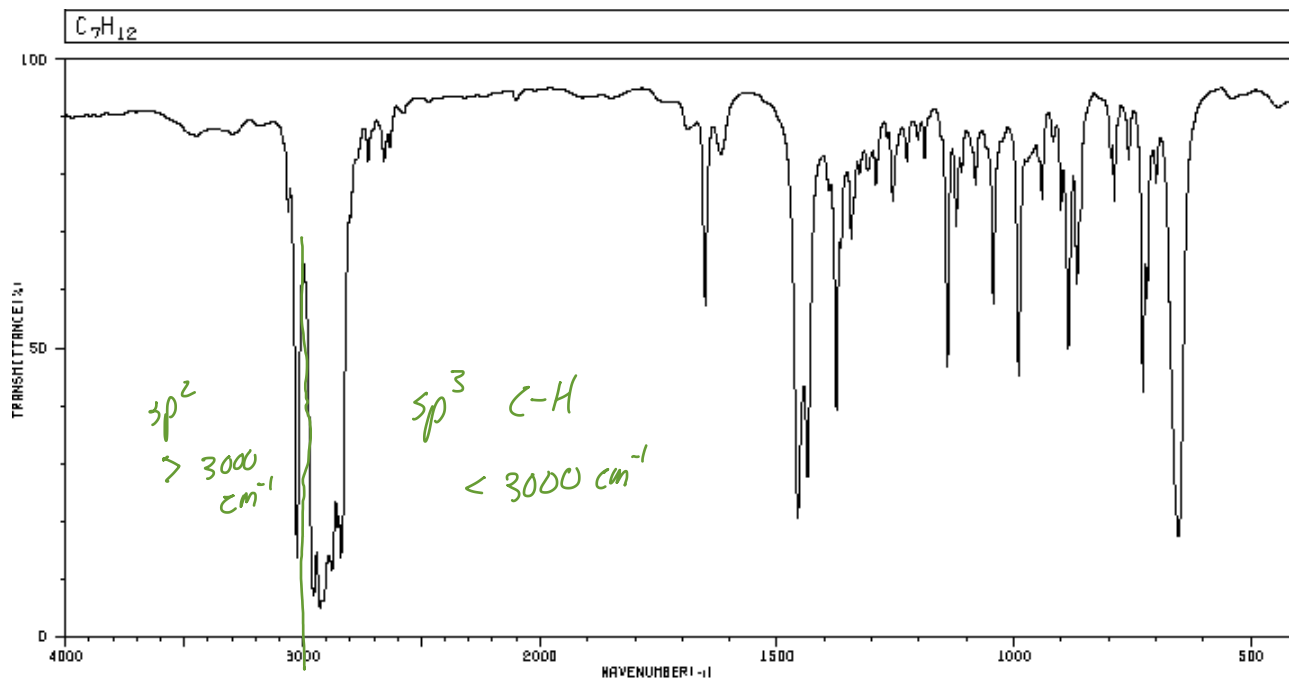


3347	6	1116	62
3336	8	1030	4
2945	16	662	56
2833	22		
2522	77		
2046	84		
1450	47		

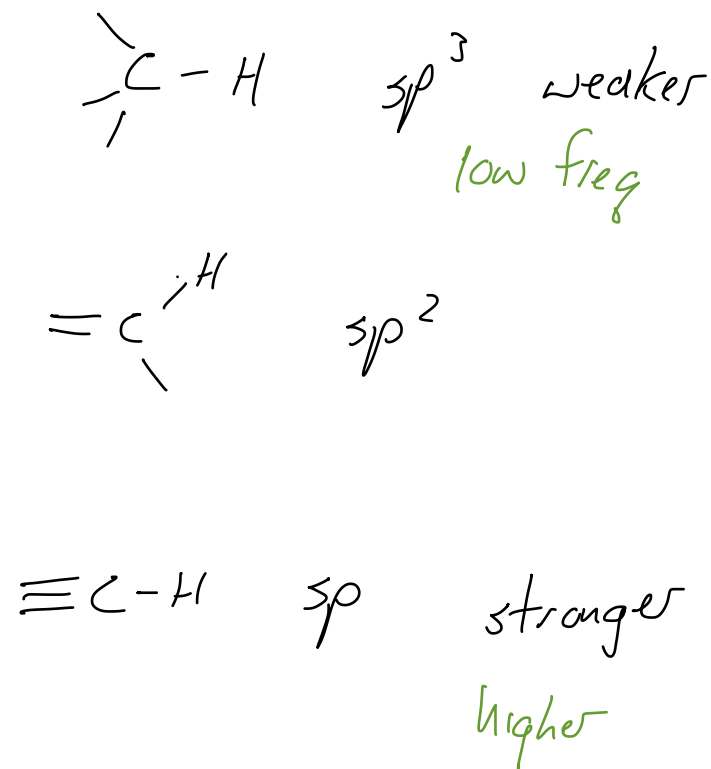
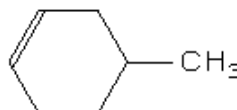


O-H peaks are to the left of C-H peaks  
 O-H peaks are broad  
 C-H peaks are sharp  
 H bonding changes the strength of the O-H bond so in solution there are many O-H bonds with different strengths as H-bond interactions form and break

# Fine Tuning Position, CH's



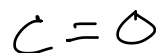
3063	70	2839	19	1344	66	1122	68	866	47
3025	13	1651	55	1326	77	1111	77	867	58
2954	6	1458	20	1309	77	1081	74	769	72
2928	4	1436	26	1292	74	1044	66	728	41
2915	6	1390	74	1256	72	990	43	719	57
2878	10	1375	37	1227	79	941	72	701	74
2852	18	1366	64	1141	44	901	70	663	16



position of C-H can tell us whether C=C db are present

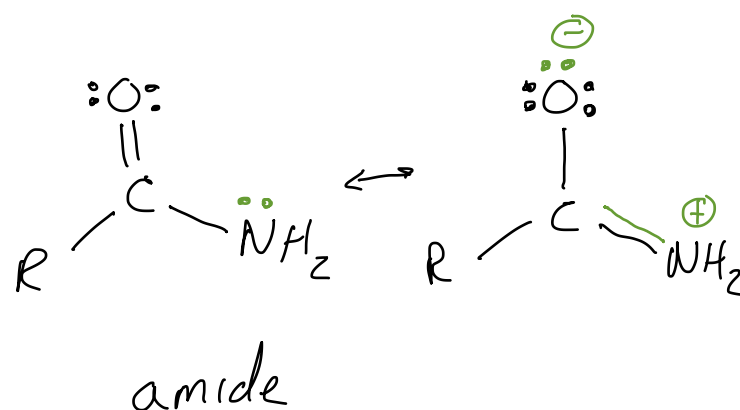
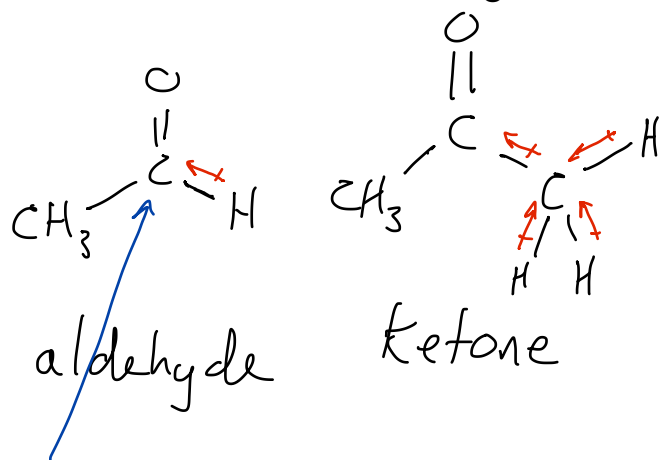
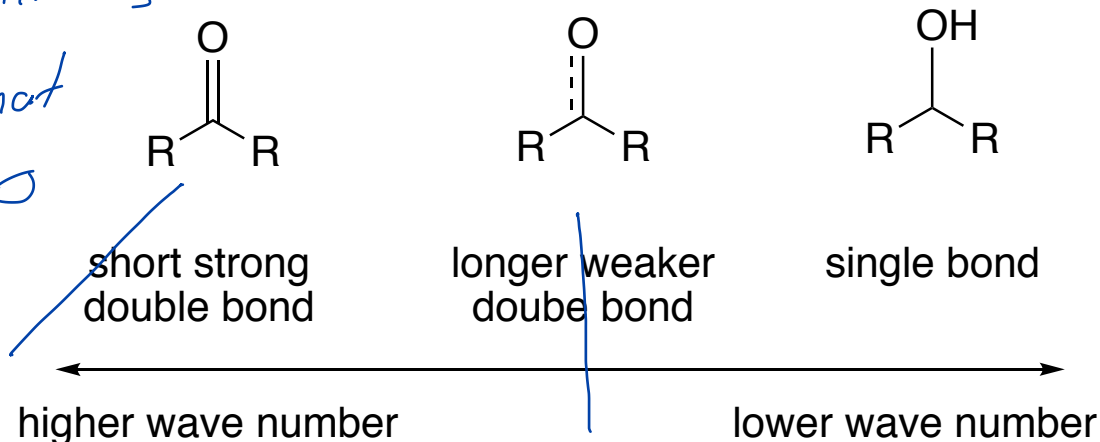


# Fine Tuning Identification of Carbonyl Peaks



$C=O$  vibrate at different frequencies based on what is bonded to  $C=O$

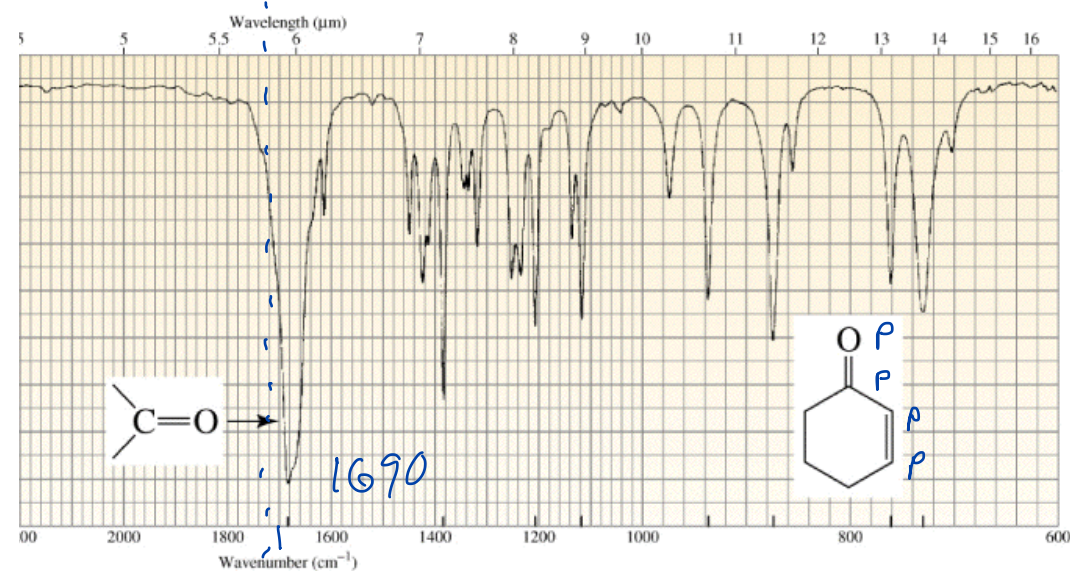
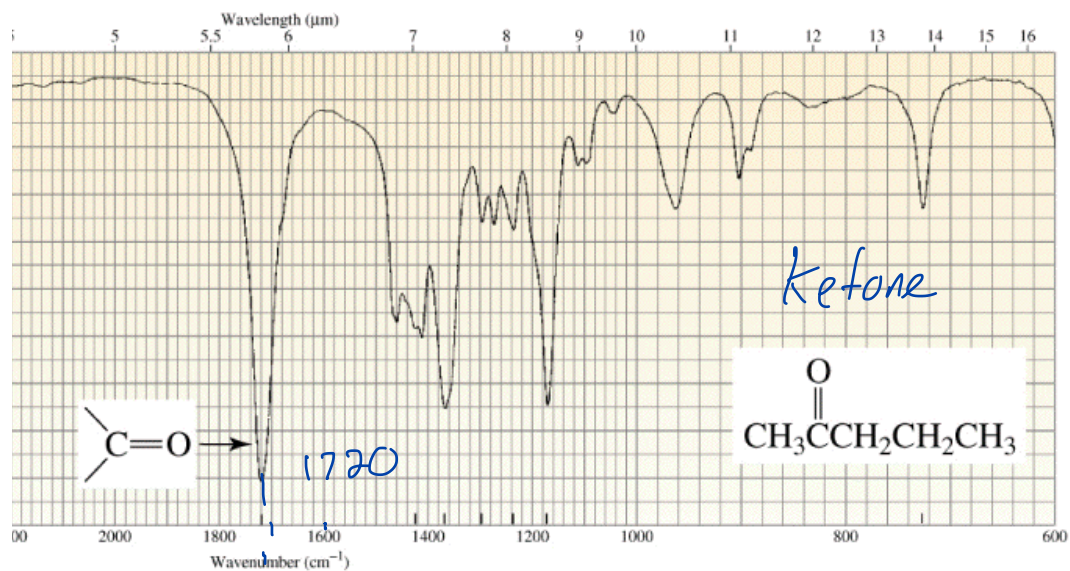
$$\bar{\nu} = \frac{1}{2\pi c} \left[ \frac{f(m_1 + m_2)}{m_1 m_2} \right]$$



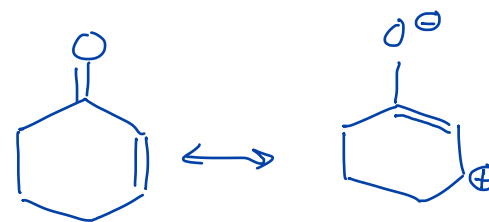
$C$  gets less  $e^-$  density from  $H$  as compared to  $e^-$  density from  $CH_3$  group so  $C$  is more  $\oplus$  and  $C=O$  bond is stronger

$e^-$  delocalization causes  $C=O$  to be weaker

# Fine Tuning Position, C=O's

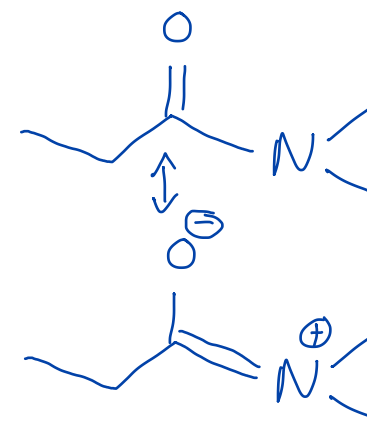
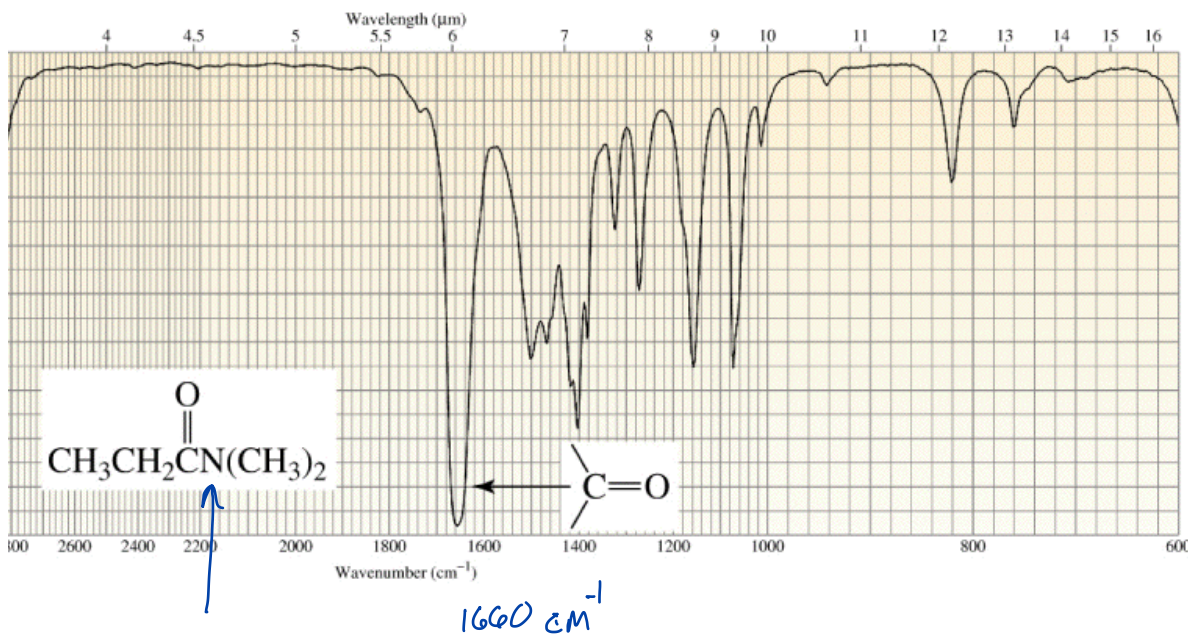
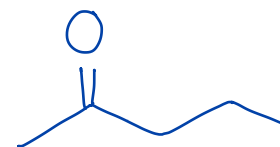
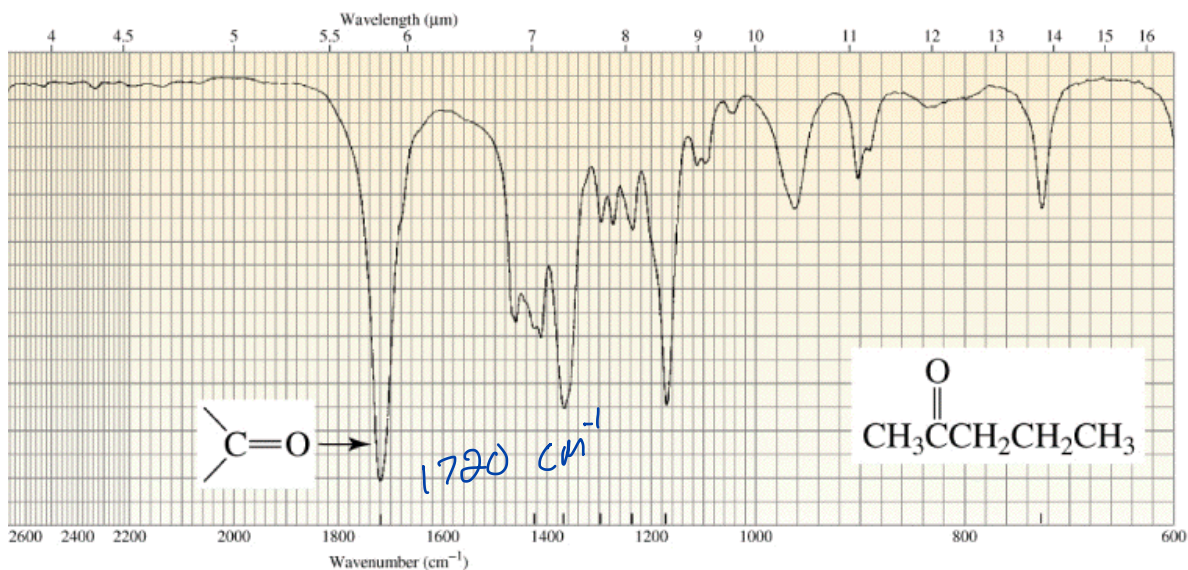


$e^-$  delocalization lowers vib Freq of  $\text{C}=\text{O}$



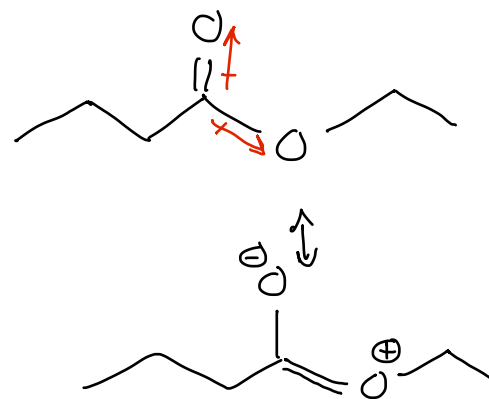
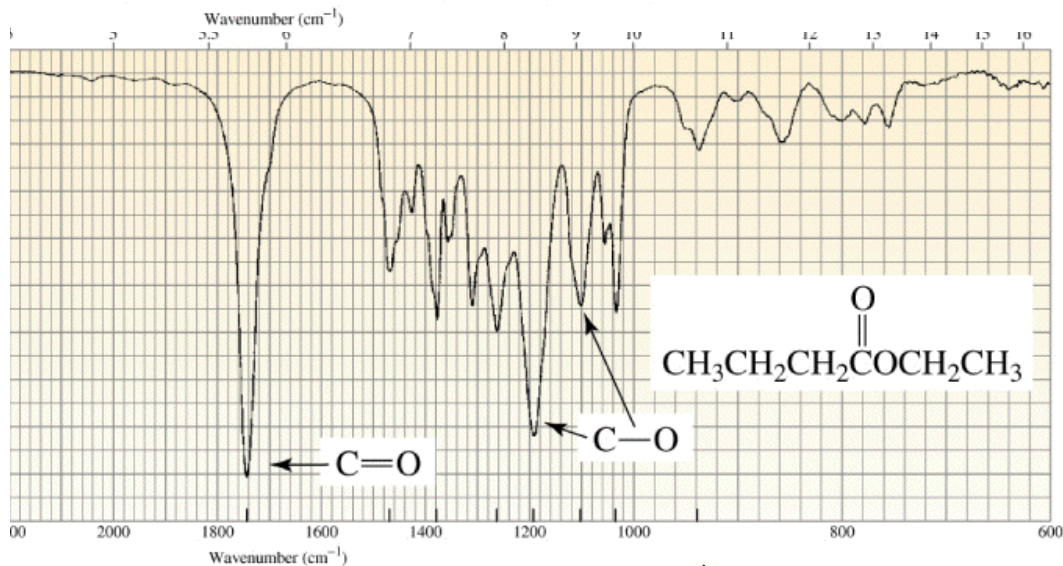
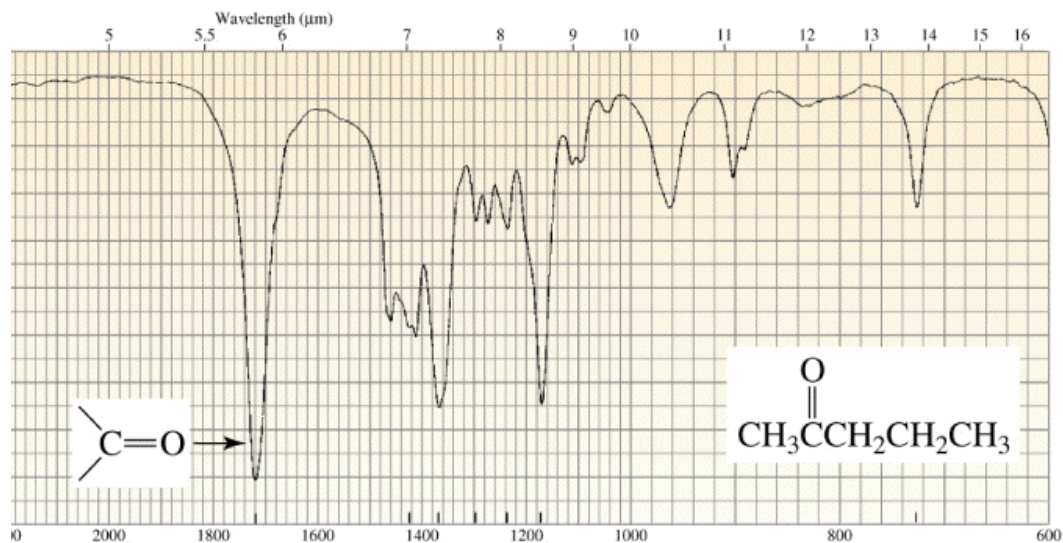
because the  $\text{C}=\text{O}$  bond has less  $\pi$  bonding character

# Fine Tuning Position, C=O's



delocalized e<sup>-</sup>'s  
make C=O weaker

# Fine Tuning Position, C=O's



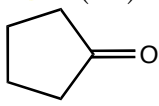
despite the  $e^-$  delocalization the presence of two enegy. O atoms causes the C to bond more strongly to the O as compared to the ketone

## IR Interpretation Guide

Additional information for analyzing C=O stretches:

**aldehyde:** RC(=O)H **1730**, R=CHC(=O)H 1705

**unstrained ketone:** RC(=O)R **1715**, R=CHC(=O)R 1690

strained ketone:  1750

**ester:** RC(=O)OR **1735**, R=CHC(=O)OR 1715.

**amide:** R(C=O)NH<sub>2</sub> < **1700**

**acid:** **1710** usually broad for a C=O

Additional information for analyzing C-H stretches:

If sp<sup>3</sup> C-H stretch at < 3000 cm<sup>-1</sup> then look around 1400, sp<sup>3</sup> C-H bend is at 1430 and if peak at 1380 also present then sp<sup>3</sup> C-H is CH<sub>3</sub>.

If sp<sup>2</sup> C-H stretch at > 3000 cm<sup>-1</sup>, and not benzene gives rise to bending vibrations from 1000-600.

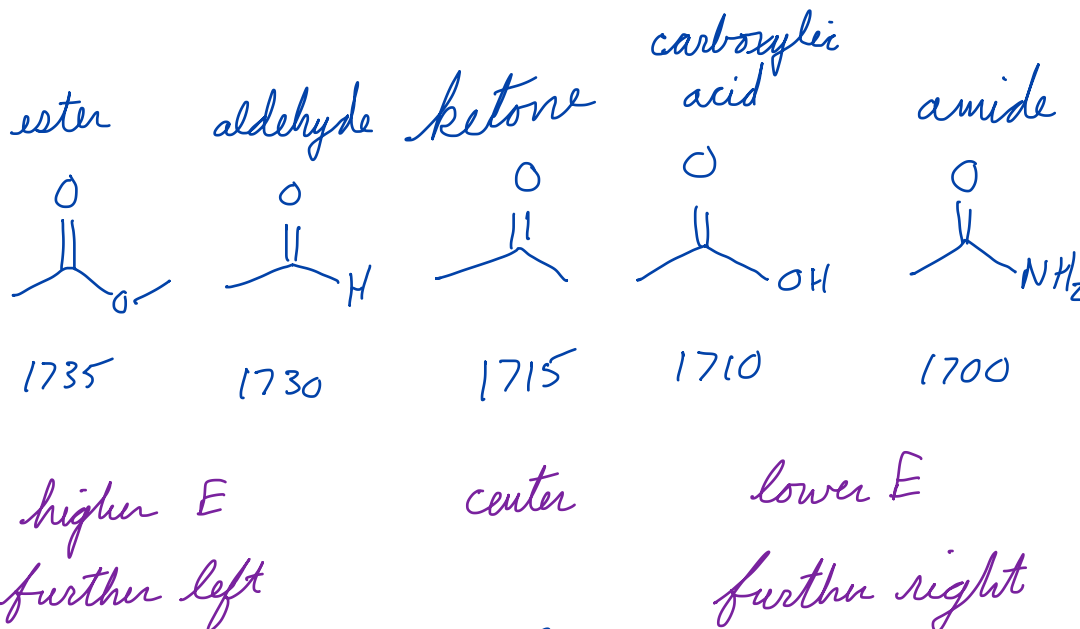
Some abbreviations for vibrational modes

- ν stretching
- δ in-plane bending or deformation
- ρ<sub>w</sub> wagging
- ρ<sub>r</sub> rocking
- ρ<sub>t</sub> twisting
- π out-of-plane bending

Abbreviations used to further characterize vibration modes

- a antisymmetric
- s symmetric
- d degenerate

For example, references to ν<sub>s</sub>(C-Cl) are references to the symmetrical stretching mode of a C to Cl bond.



note the trend, not the exact positions of the peaks