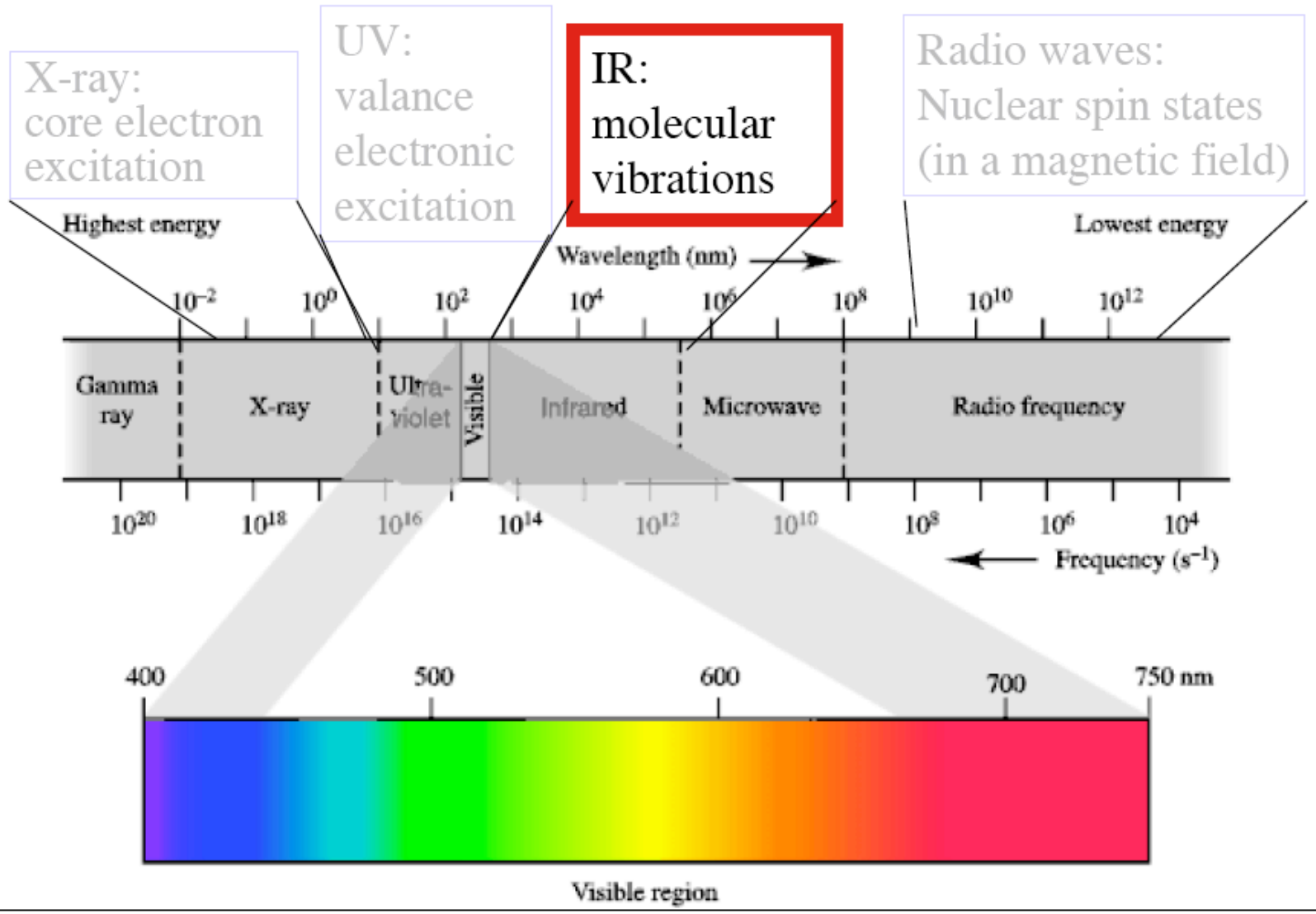
GOOD VIBRATIONS WITH IR SPECTROSCOPY:



http://ep.llnl.gov/msds/orgchem/spectroscopy.html#IR:

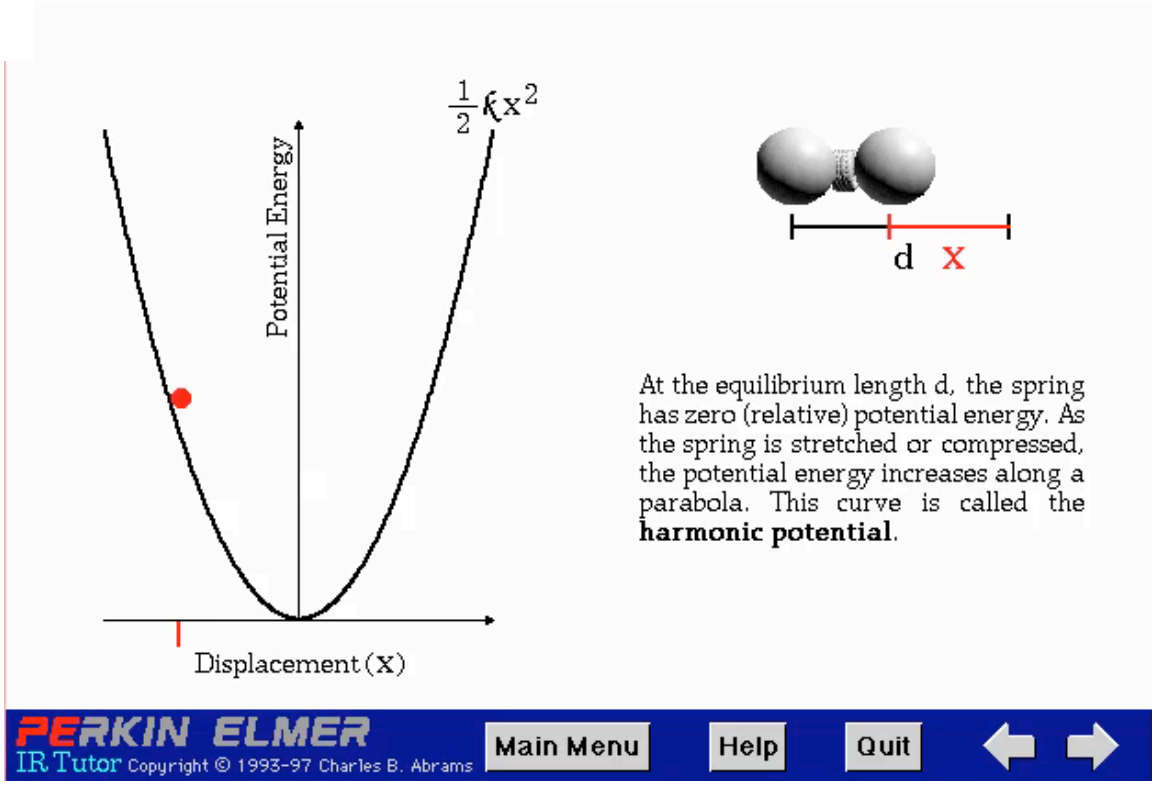
http://orgchem.colorado.edu/hndbksupport/irtutor/IRtheory.pdf

IR tutor http://members.aol.com/charlieabr/downloads.html

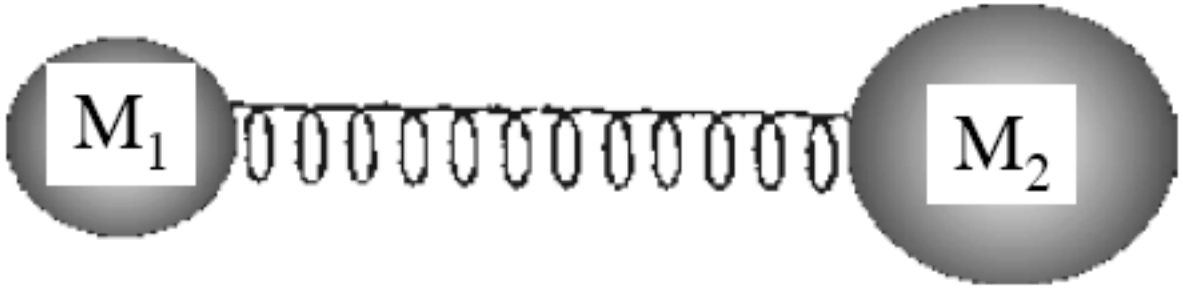
http://www.cem.msu.edu/~parrill/AIRS/

Model of a Simple Molecule

A diatomic molecule can be modelled by a spring with force constant k attached to two balls of mass m. This is called the **classical harmonic oscillator** model.



http://www.columbia.edu/itc/chemistry/chem-c1403/ir_tutor/IRTUTOR.htm



$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k\,(m + M)}{m \cdot M}}$$

$\bar{\nu} = \nu/c = 1/\lambda$

wavenumbers

frequency

wavelength

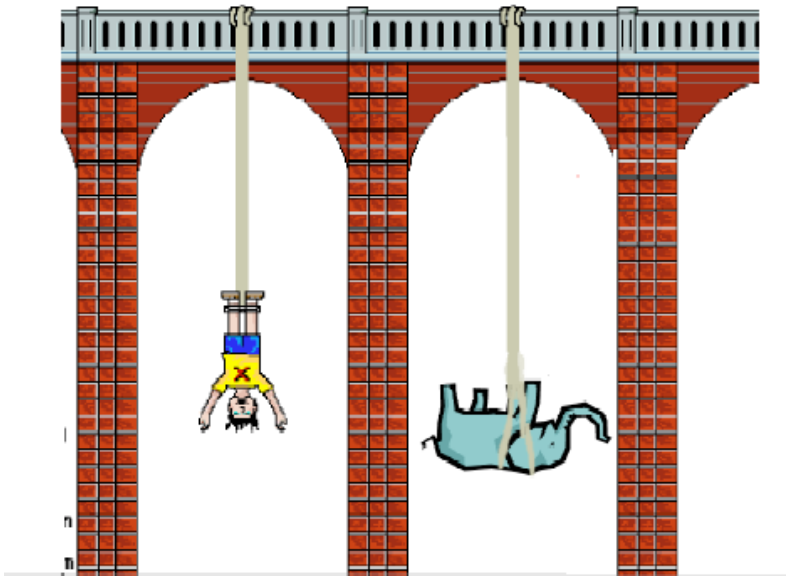
$\bar{\nu}$ units: cm^{-1}

• for excitation to occur, there must be an exact match between the frequency of the applied radiation and the frequency of the vibration

• in different compounds, the same type of functional group absorb in the same region of the IR

Factors that determine $\bar{\nu}$

1. Mass: larger mass = lower frequency (longer wavelength)



Factors that determine $\bar{\nu}$

2. Bond strength (k)

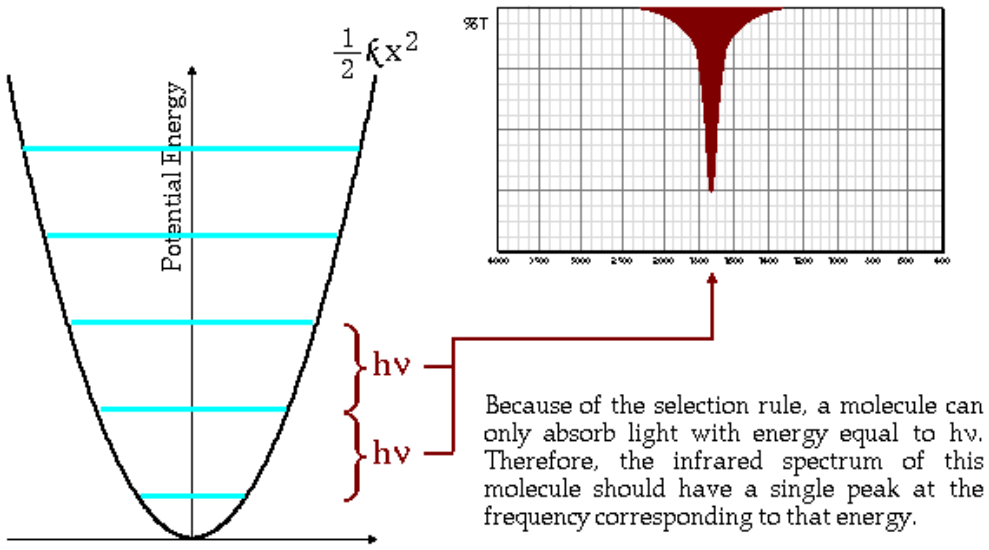
Stronger bonds (tighter springs) vibrate with higher frequency

3. Type of vibration

Stretching (along the line of the chemical bond)
Vs
Bending (out of line with the chemical bond)

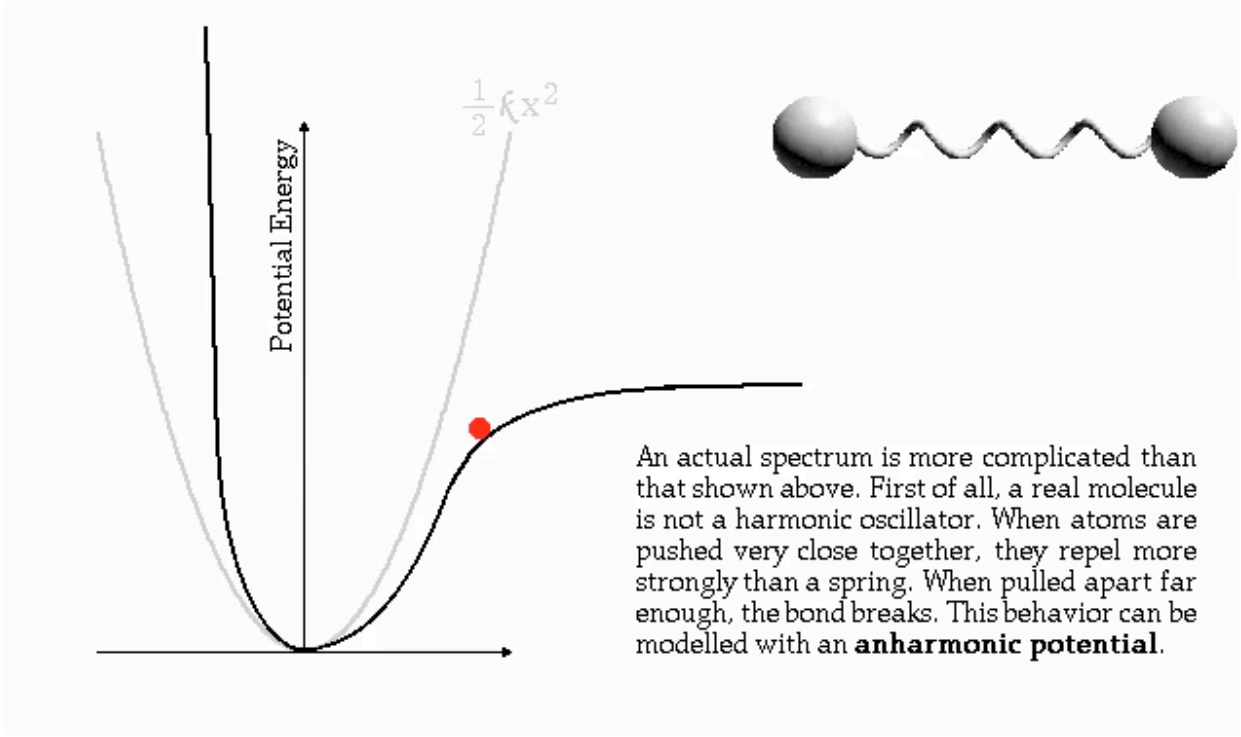
For the same bond, stretch is higher energy (i.e. higher frequency)

Energy levels are quantized

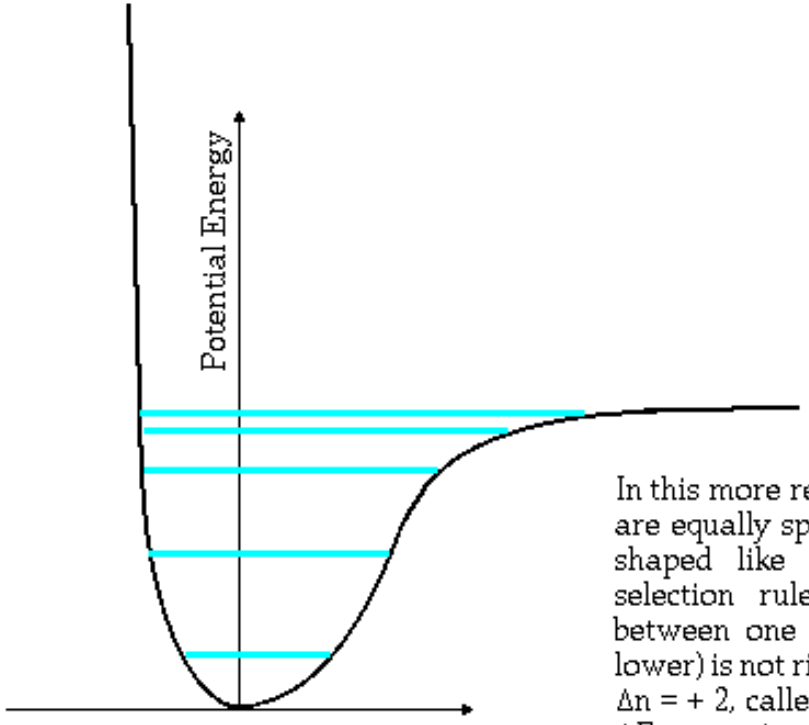


Because of the selection rule, a molecule can only absorb light with energy equal to hν. Therefore, the infrared spectrum of this molecule should have a single peak at the frequency corresponding to that energy.

Energy potential of diatomic molecules

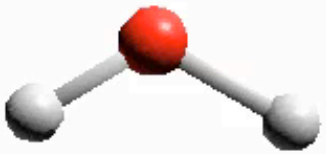


Energy levels are quantized



In this more realistic model, the energy levels are equally spaced only in the region that is shaped like the harmonic potential. The selection rule, which allowed transitions between one level and the next higher (or lower) is not rigorously true. A transition with $\Delta n = +2$, called an **overtone**, corresponds to ΔE approximately $2h\nu$.

Beyond diatomic molecules



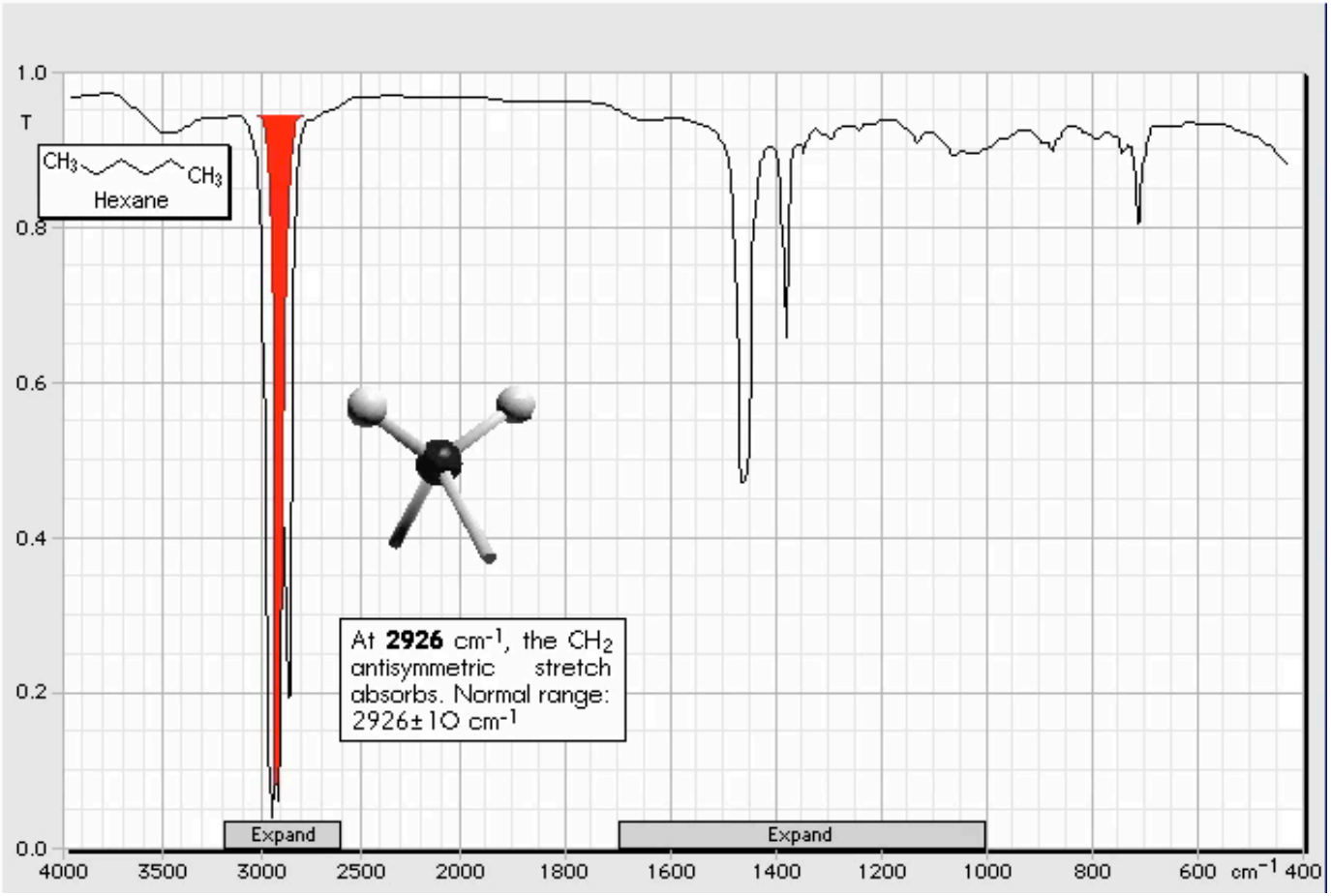
More Complicated Molecules

Even H_2O has more complicated vibrations than the simple diatomic molecules studied in the previous section. How can this motion be understood using the quantum harmonic oscillator theory? (Press the right arrow to find out!)

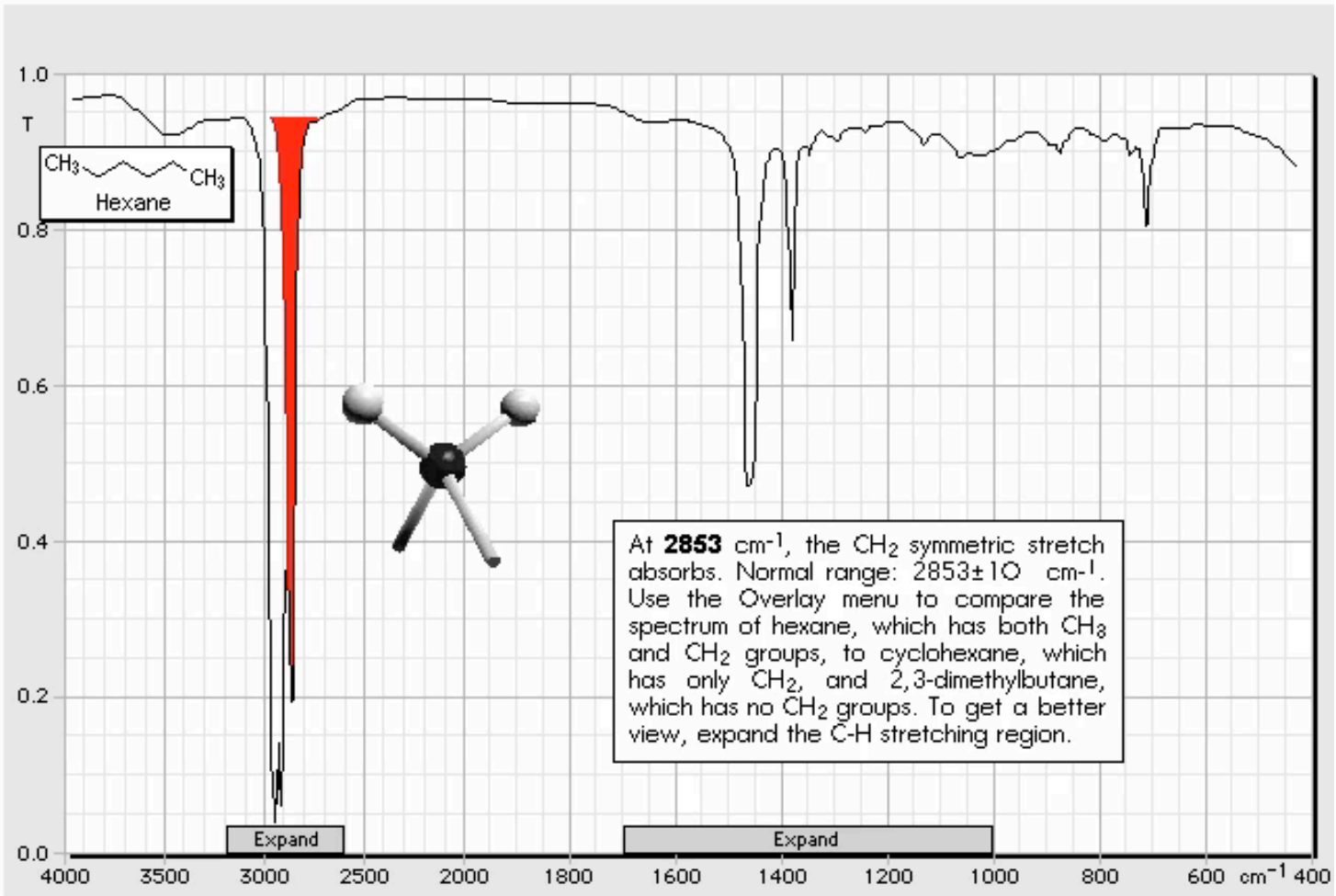
Coupled interactions occur when

1) vibrations of bonds related by symmetry
2) common atoms between groups
3) independent groups absorb at same frequency

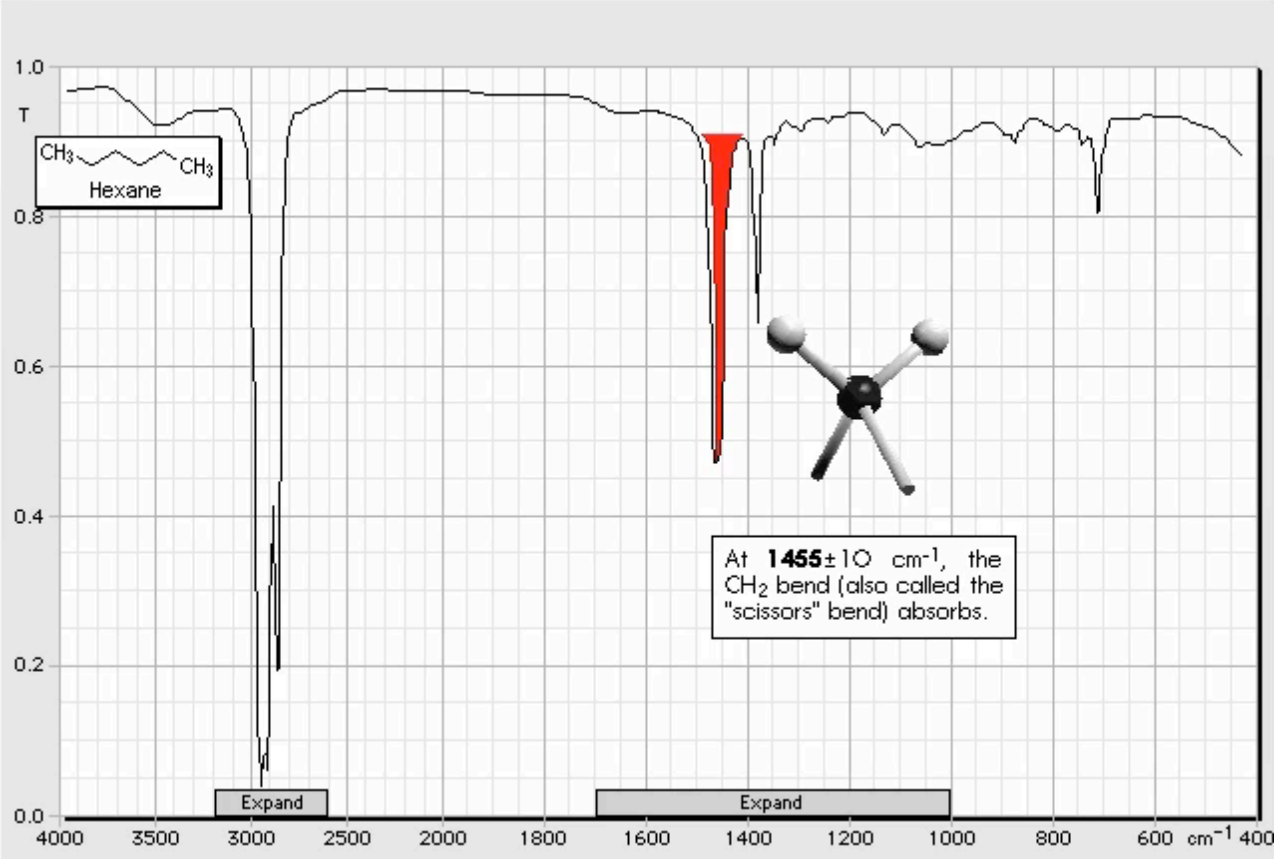
Coupled interactions: Antisymmetric Stretch



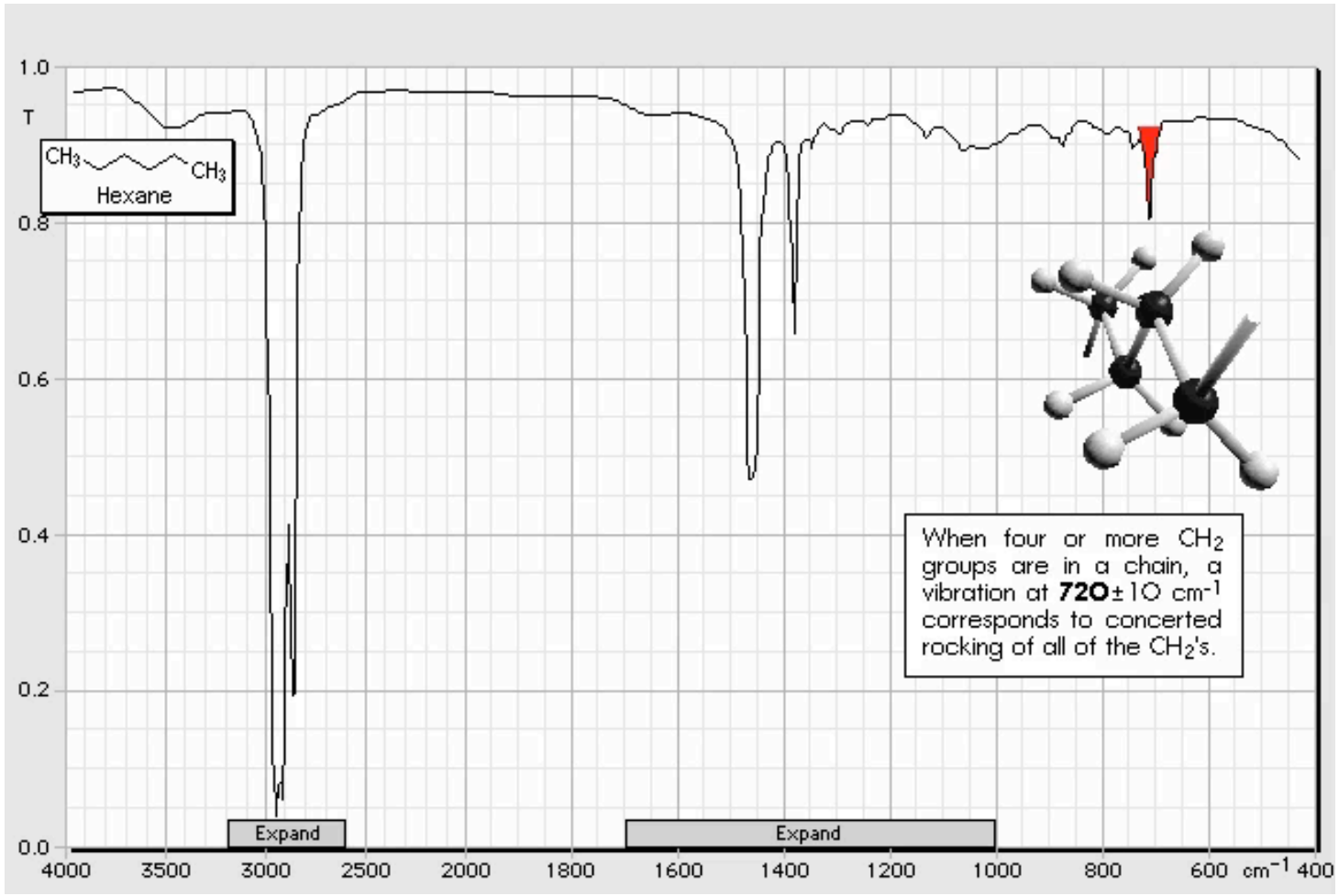
Coupled interactions: Symmetric Stretch



Coupled interactions: Antisymmetric bend (scissors)



Coupled interactions: Symmetric bend (rocking)

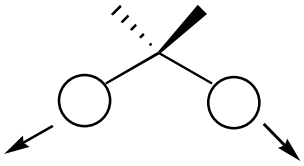


Coupled interactions occur when

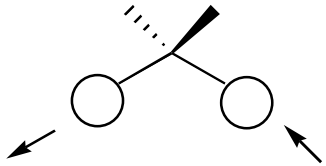
1) vibrations of bonds related by symmetry
2) common atoms between groups
3) independent groups absorb at same frequency

Commonly observed for CH_2 groups

Stretches



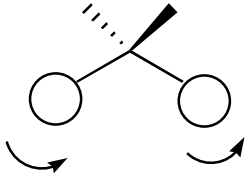
symmetrical



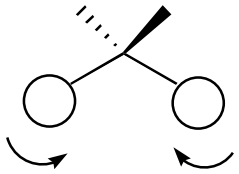
unsymmetrical

Bends

in plane

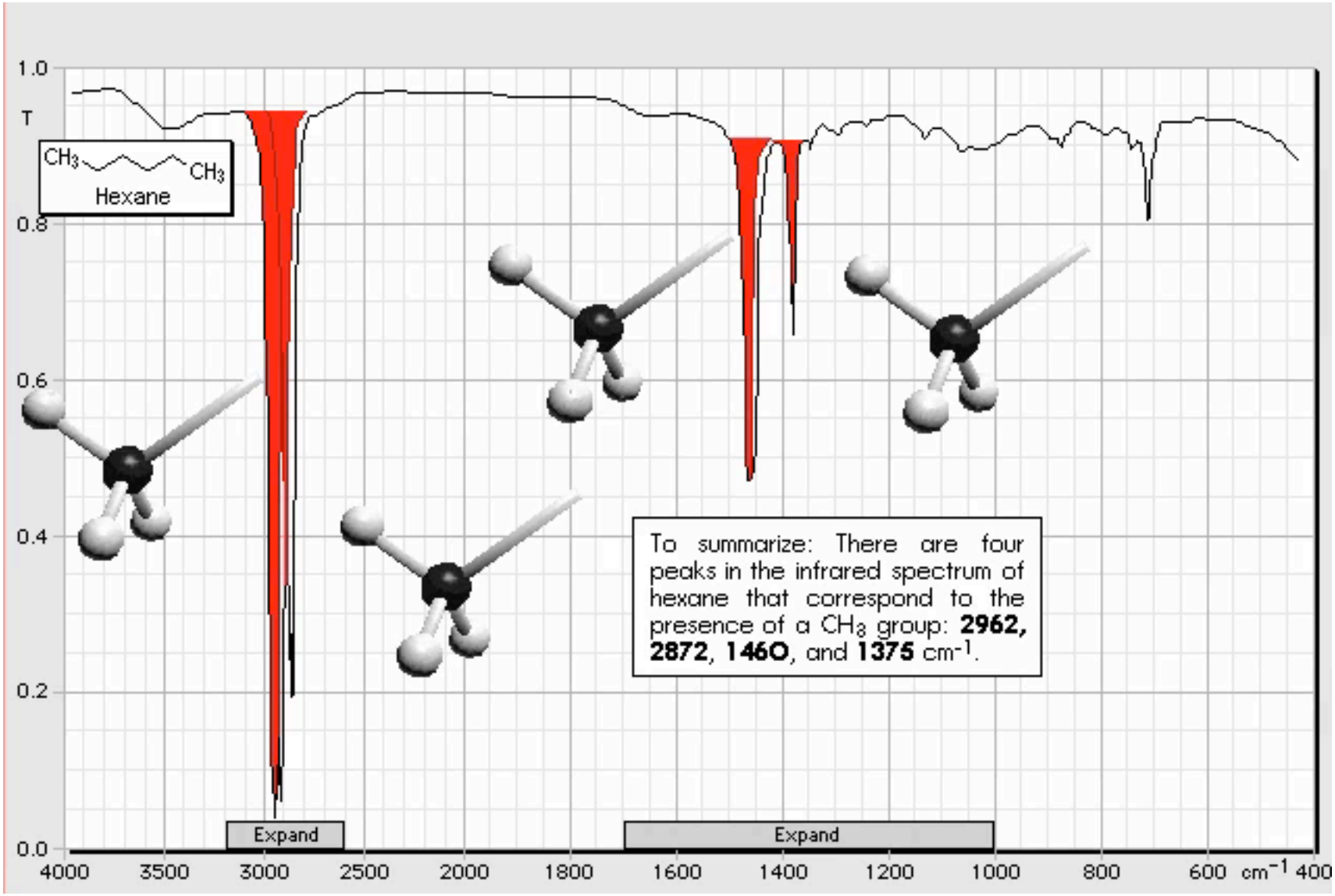


rock
(symmetrical)

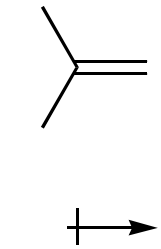


scissor
(unsymmetrical)

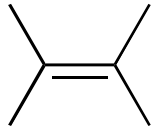
All together



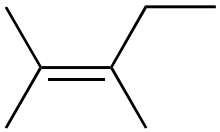
To see molecules in IR, transition must result in a dipole change



IR active



IR stretch
essentially absent



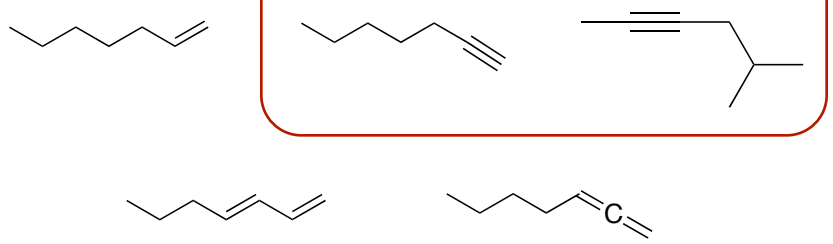
IR stretch
essentially absent

Table 11.2 Structural Units and Absorption Frequencies

BOND		TYPE OF COMPOUND	FREQUENCY (CM^{-1})
	(stretch)	Alkane	2800–3000
	(stretch)	Alkenes, aromatics	3000–3100
≡C—H	(stretch)	Alkynes	3300
—O—H	(stretch)	Alcohols, phenols	3600–3650 (free) 3200–3500 (H-bonded) (broad)
—OH	(stretch)	Carboxylic acids	2500–3300
—N—H	(stretch)	Amines	3300–3500 (doublet for NH_2)
	(stretch)	Aldehyde	2720 and 2820
	(stretch)	Alkenes	1600–1680
	(stretch)	Aromatic	1500 and 1600
—C≡C—	(stretch)	Alkynes	2100–2270
	(stretch)	Aldehydes, ketones	1680–1740
—C≡N	(stretch)	Nitriles	2220–2260
C—N	(stretch)	Amines	1180–1360
—C—H	(bending)	Alkane	1375 (methyl)
—C—H	(bending)	Alkane	1460 (methyl and methylene)
—C—H	(bending)	Alkane	1370 and 1385 (isopropyl split)
—C—H	(bending)	$R—CH=CH_2$	1000–960 and 940–900
—C—H	(bending)	$R_2C=CH_2$	915–870
—C—H	(bending)	*cis* RCH=CHR	790–650
—C—H	(bending)	*trans* RCH=CHR	990–940
—C—H	(out-of-plane bending)	*mono* subst. benzene	770–730 and 710–690
—C—H	(out-of-plane bending)	*o*-subst. benzene	770–735
—C—H	(out-of-plane bending)	*m*-subst. benzene	810–750 and 710–690
—C—H	(out-of-plane bending)	*p*-subst. benzene	860–800
—C—O	(stretch)	Primary alcohol	1050–1085
—C—O	(stretch)	Secondary alcohol	1085–1125
—C—O	(stretch)	Tertiary alcohol	1125–1200
—C—O	(stretch)	Phenol	1180–1260

CASE STUDIES

case study 1



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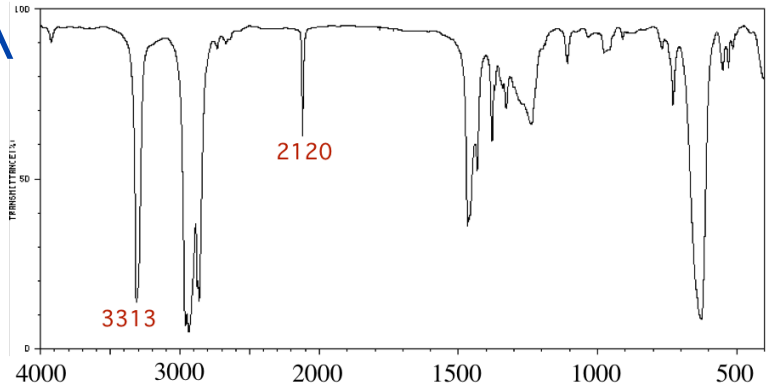

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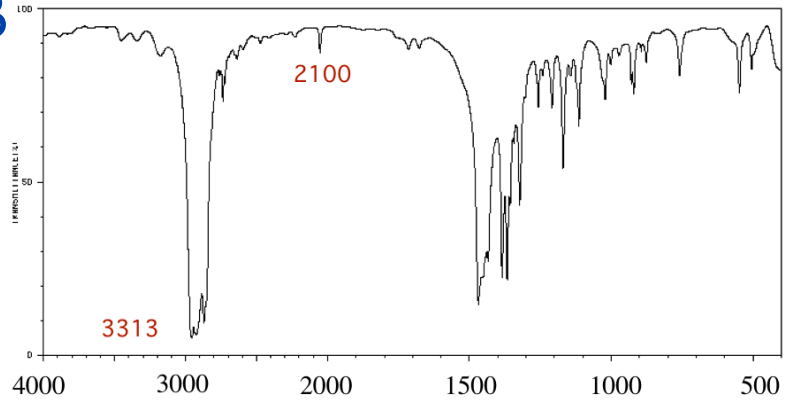

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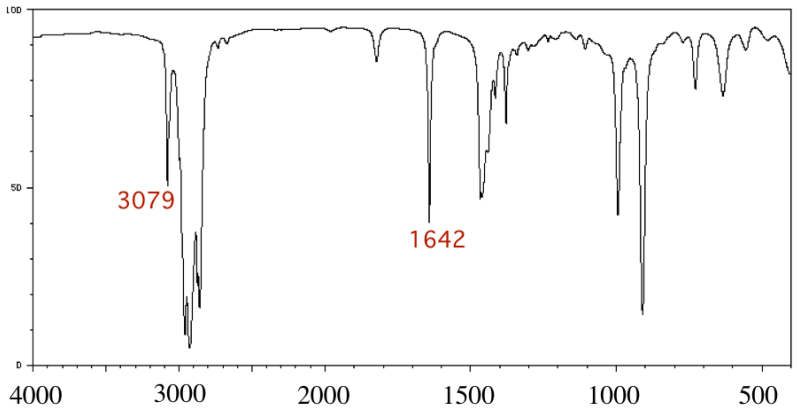

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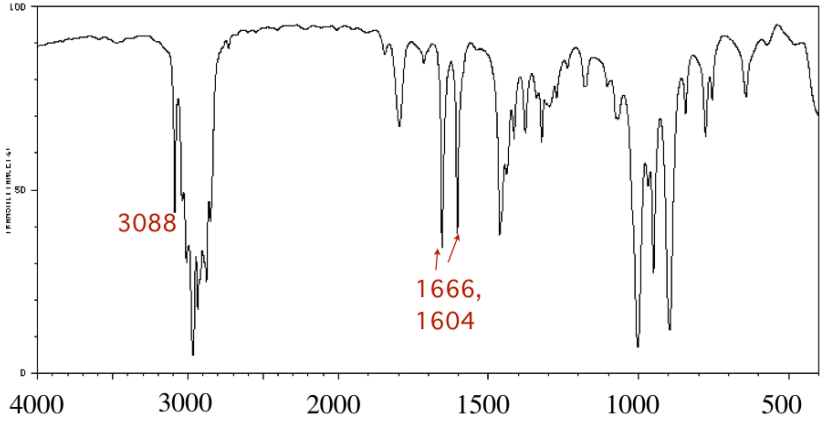

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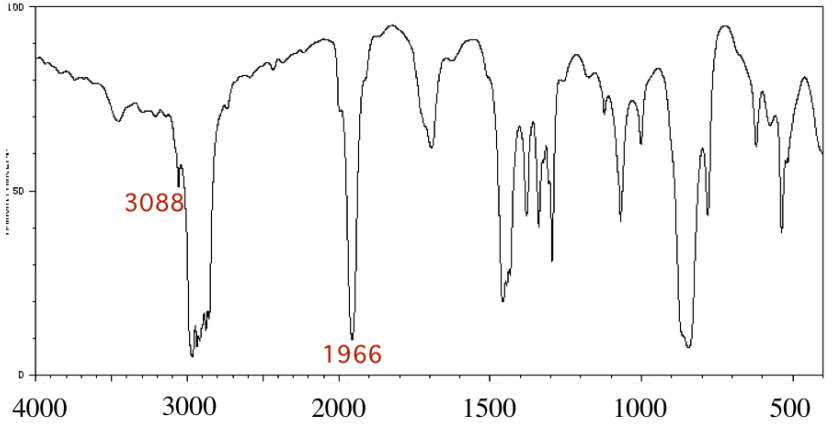


Alkynes

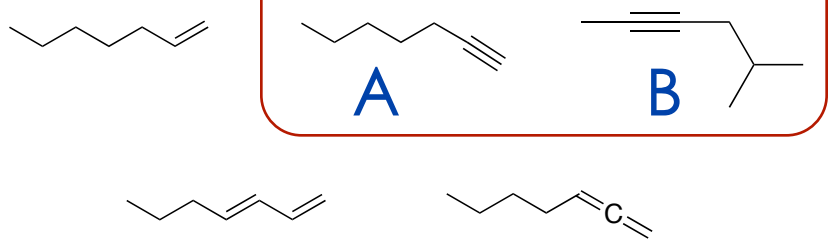
- —C≡C— stretch: weak absorption at 2260-2100 cm^{-1}

  - not observed for symmetrical alkynes
  - *very weak* for 'pseudo' symmetric alkynes
  - terminal alkynes (R-C≡C-H) absorptions are stronger than internal (R-C≡C-R) absorptions

- C≡C–H stretch:
  - 3333–3267 cm^{-1}
  - strong, narrow (as compared to OH or NH)

- C≡C–H bend:
  - 700-610 cm^{-1}: broad, strong absorption
  - 1400-1220 cm^{-1}, overtone of above

case study 1



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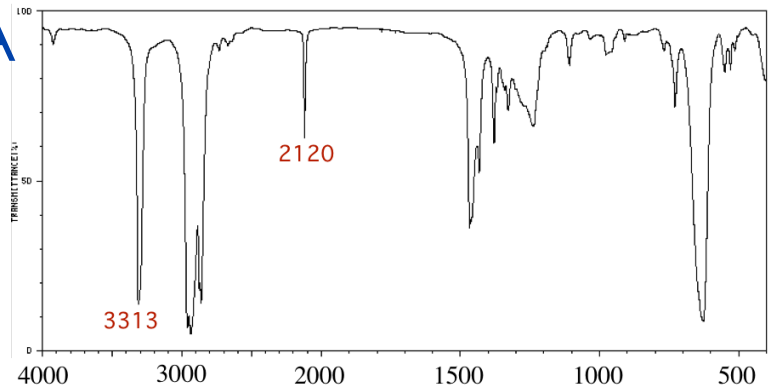

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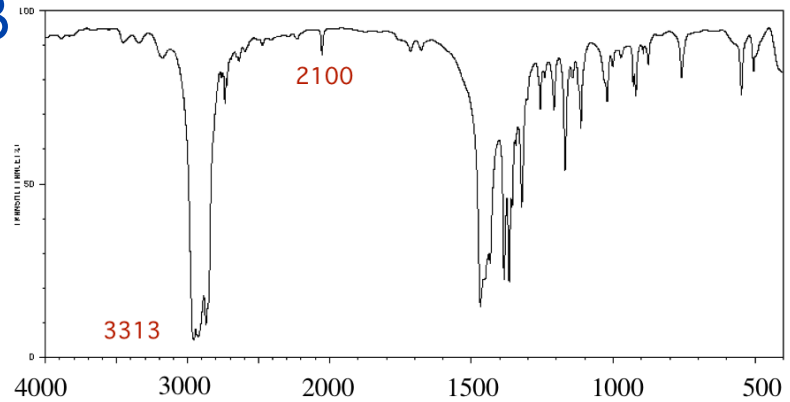

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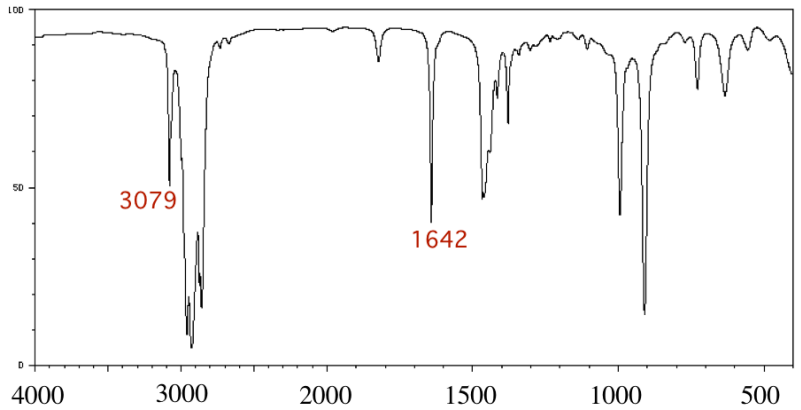

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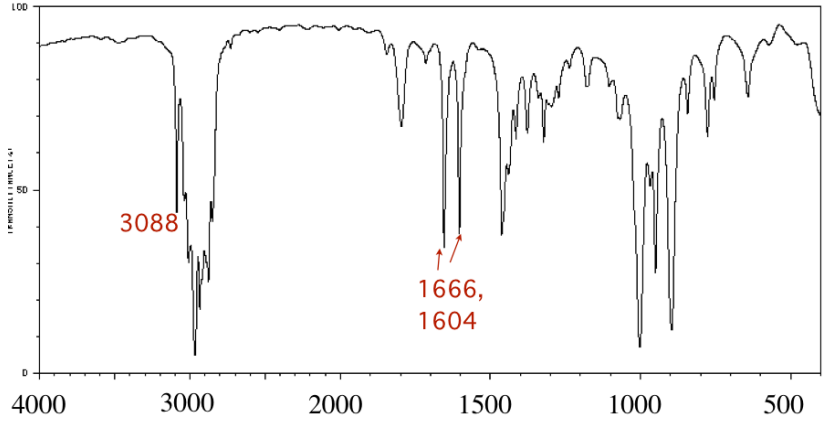

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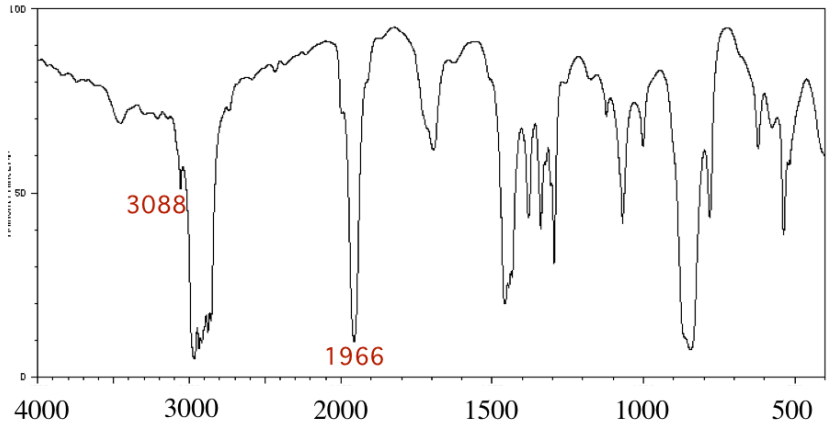
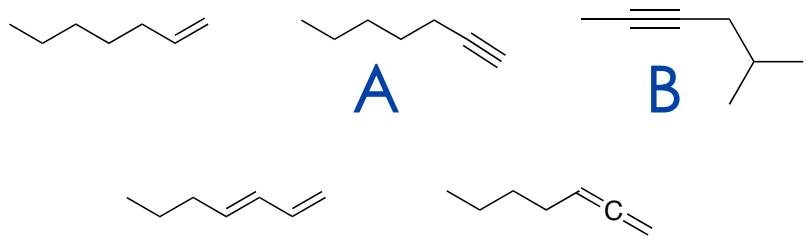


case study 1



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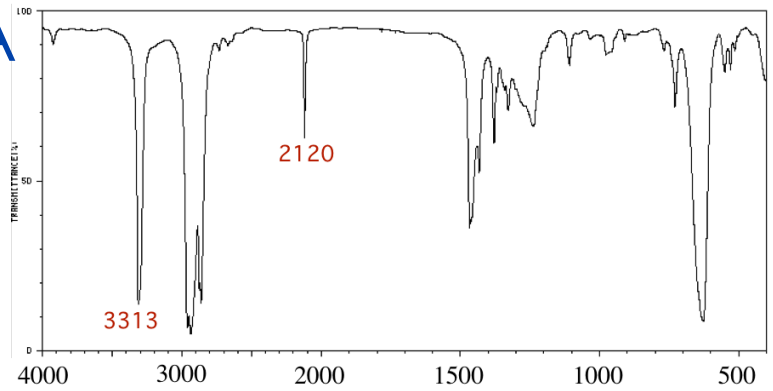

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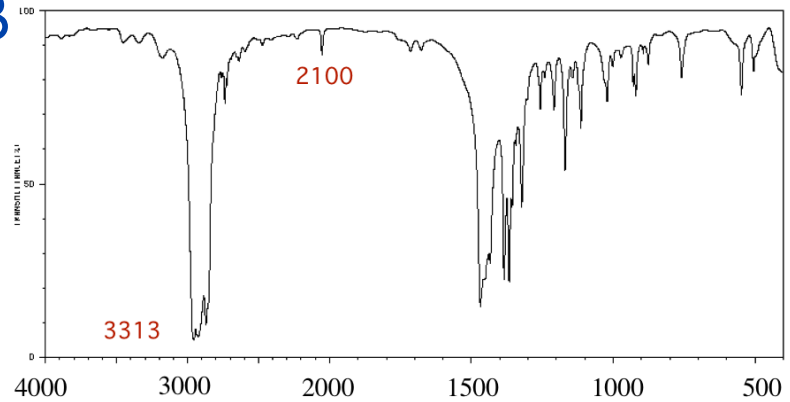

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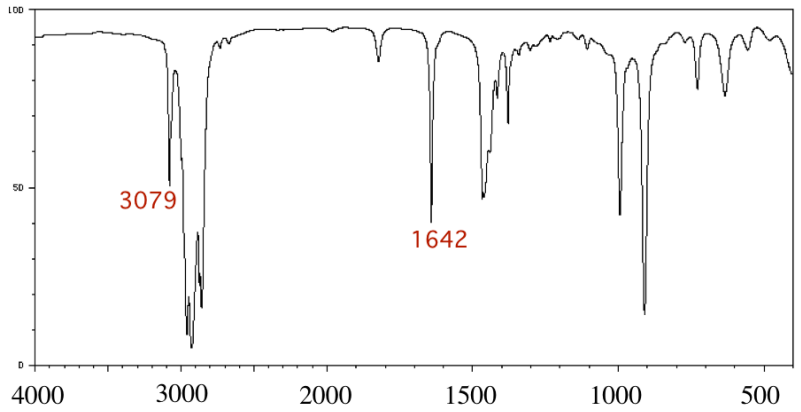

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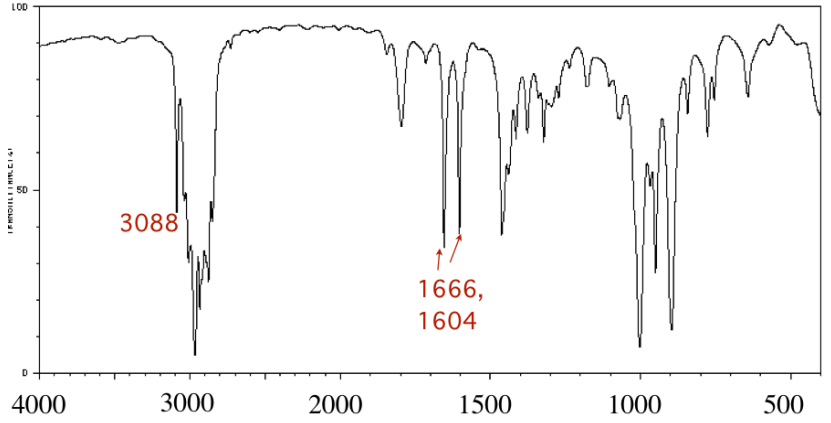

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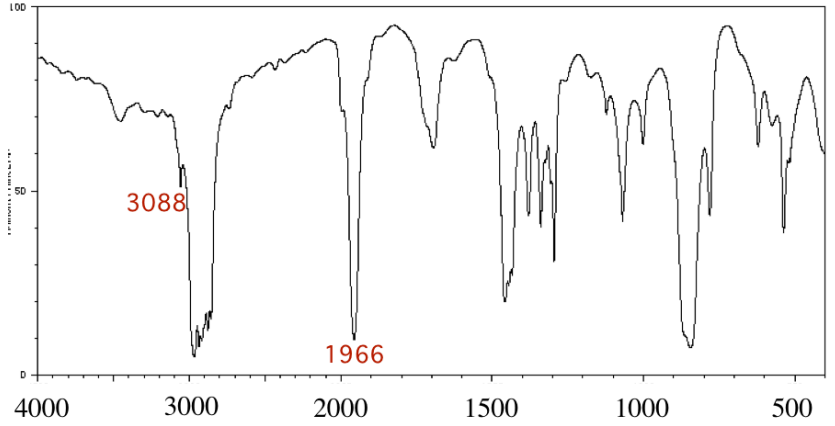
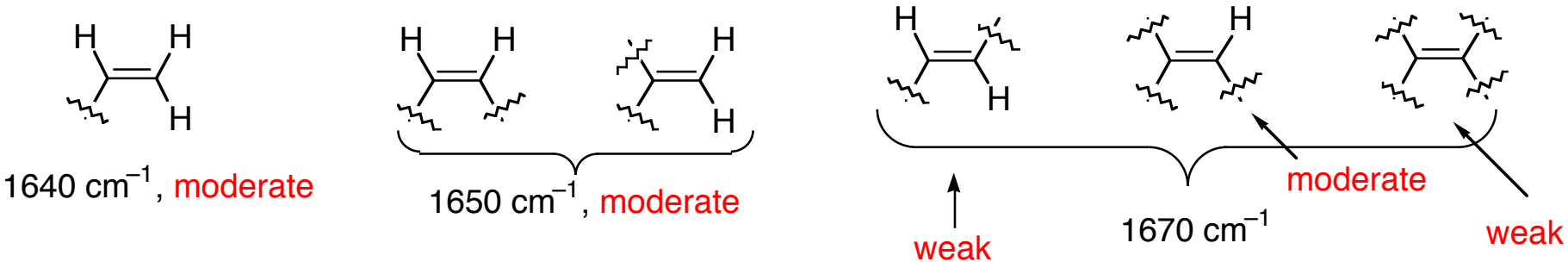


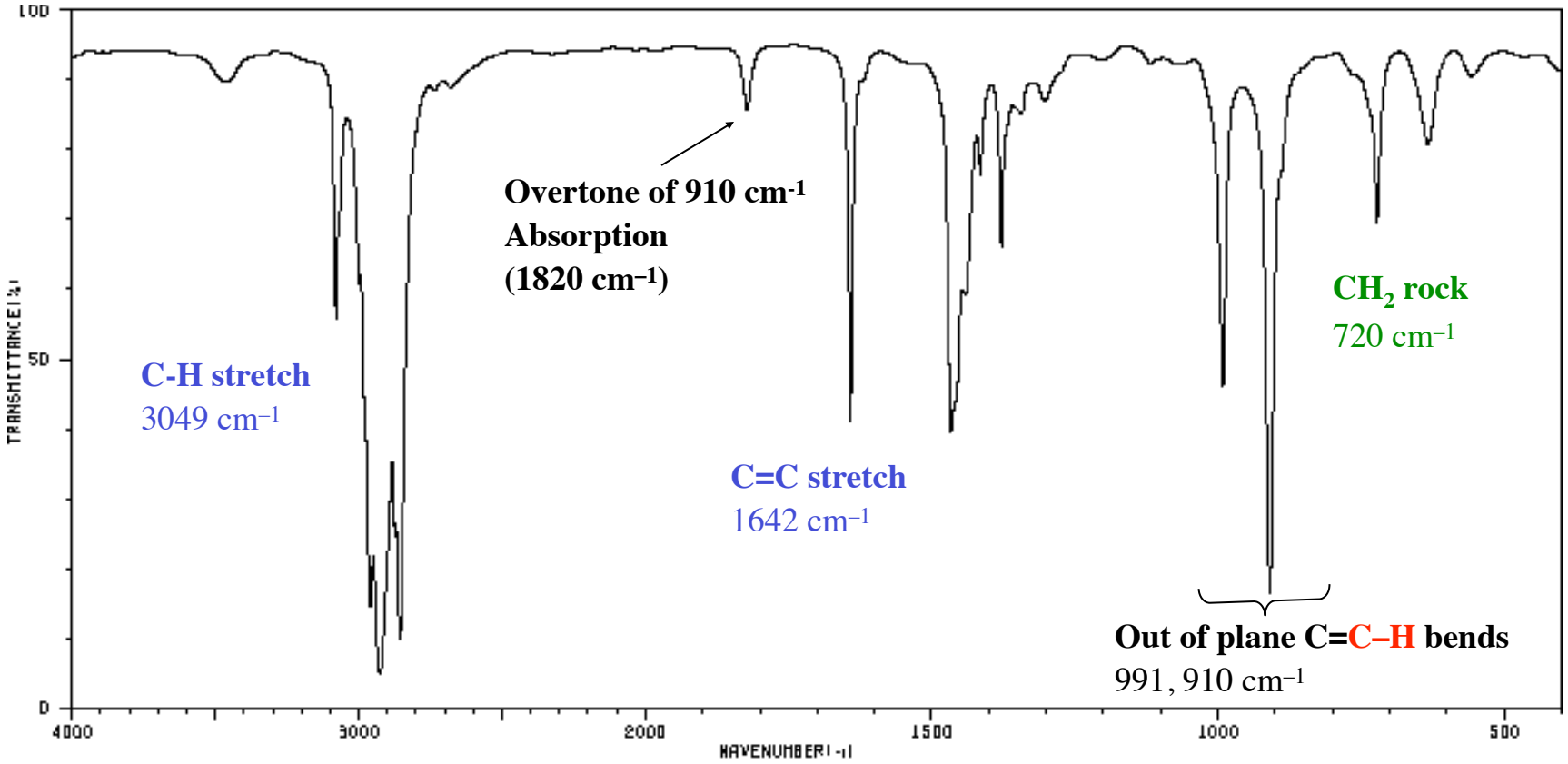
Unconjugated Alkenes

- linear alkenes:
  - C=C stretch: moderate to weak absorption at 1667-1640 cm^{-1}

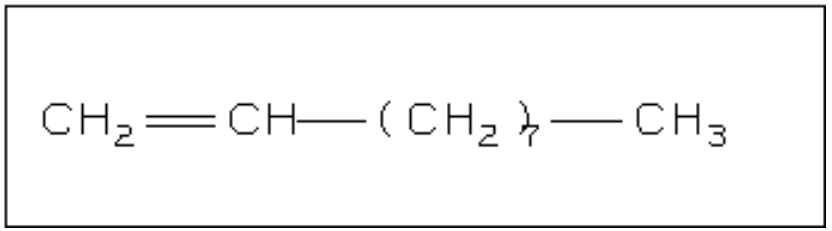


- C=**C–H**:
  - stretch: ≥ 3000 cm^{-1}

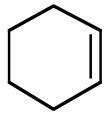
Unconjugated Alkenes



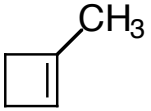
1-decene



• cyclic alkenes:
- C=C stretch: sensitive to ring strain

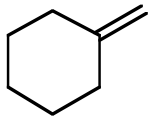

1650 cm^{-1}


1566 cm^{-1}



1641 cm^{-1}

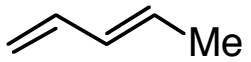

1640 cm^{-1}


1650 cm^{-1}

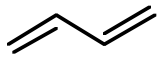

1781 cm^{-1}

• cumulated alkenes:
- C=C=C stretch (asymmetric): 2000–1900 cm^{-1}

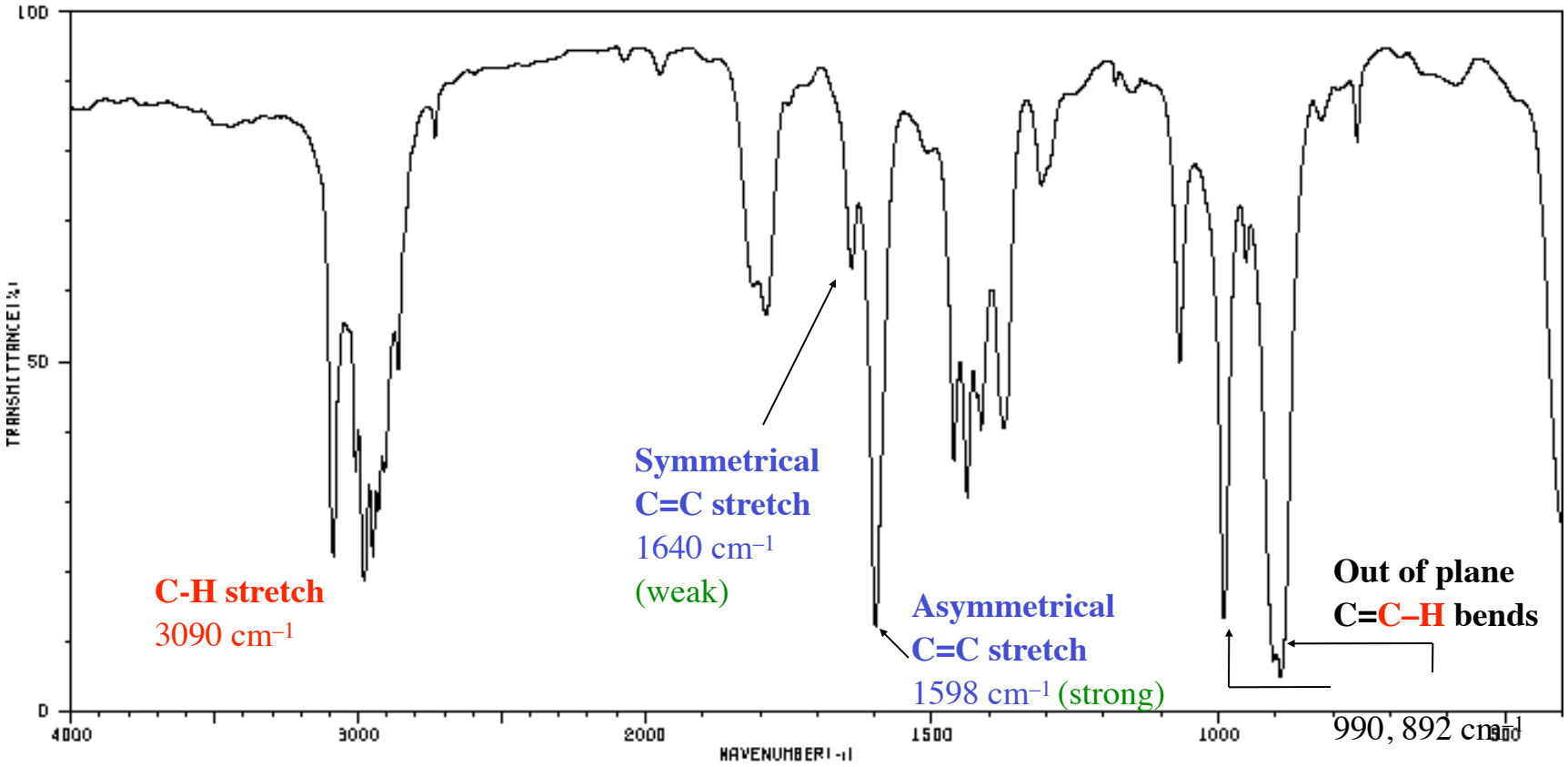
• conjugated alkenes:
-the alkene bond stretching vibrations in alkenes w/o a center of symmetry give rise to two C=C stretches
-for symmetrical molecules, e.g. butadiene, only the asymmetric stretch is observed

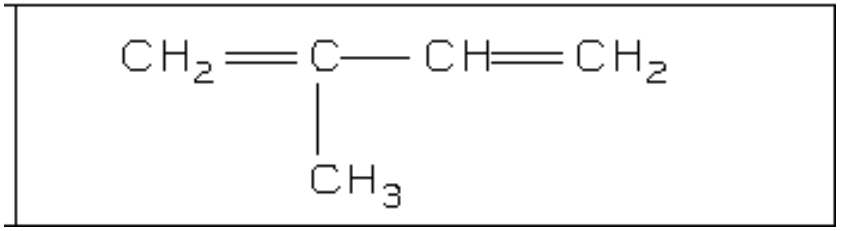


1650 cm^{-1} (as)
1600 cm^{-1} (s)

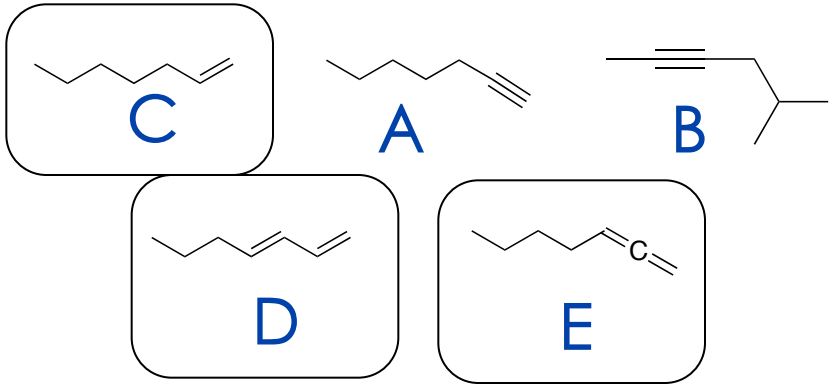

1600 cm^{-1} (as)

Conjugated Double Bonds

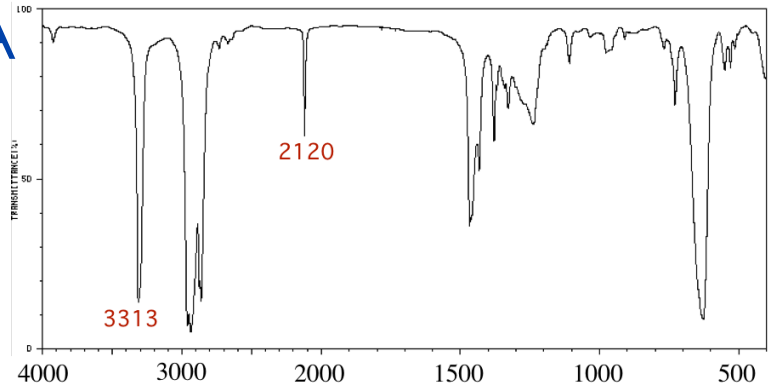




case study 1



A



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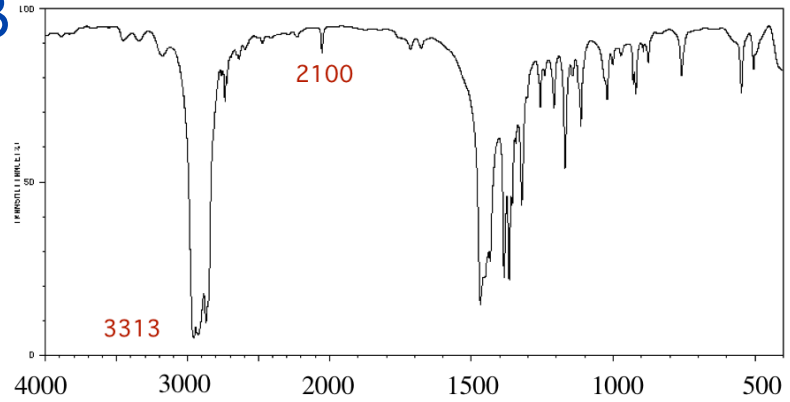

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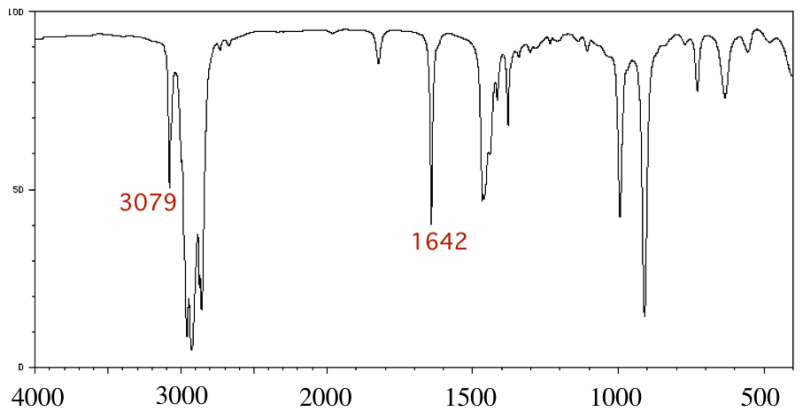

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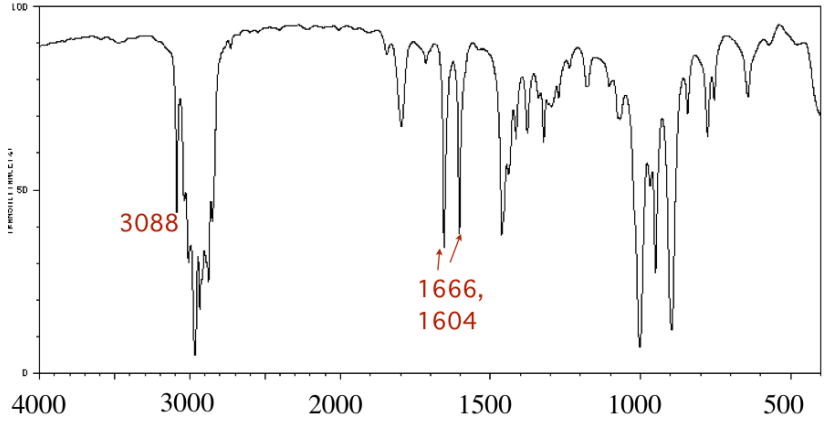
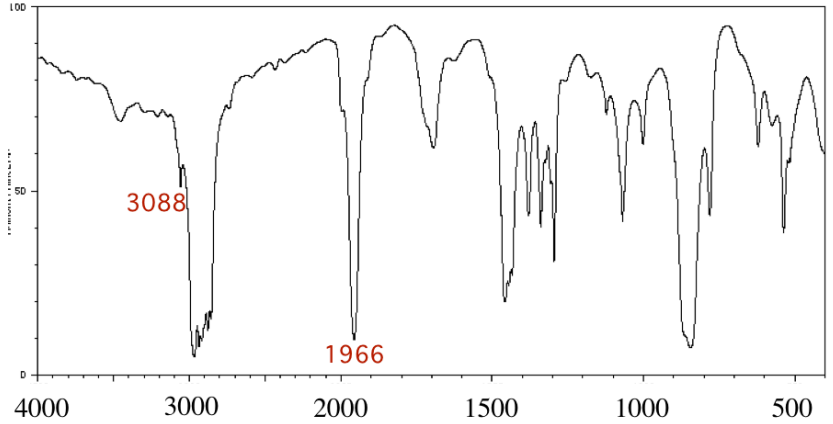
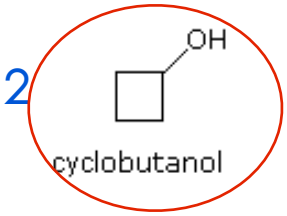


E

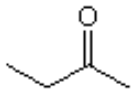


case study 2

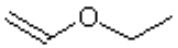
case study 2



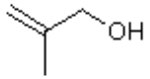
cyclobutanol



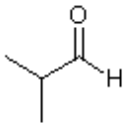
2-butanone



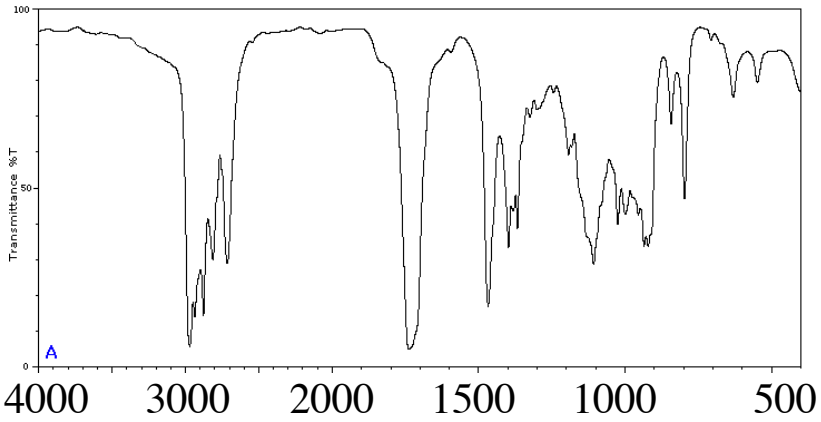
ethyl vinyl ether

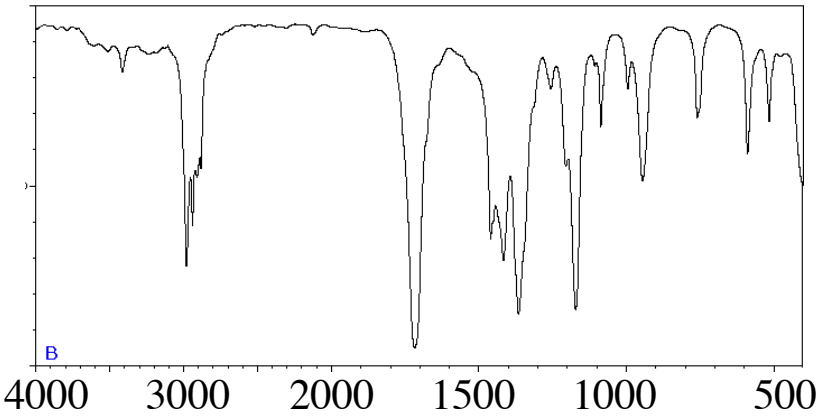


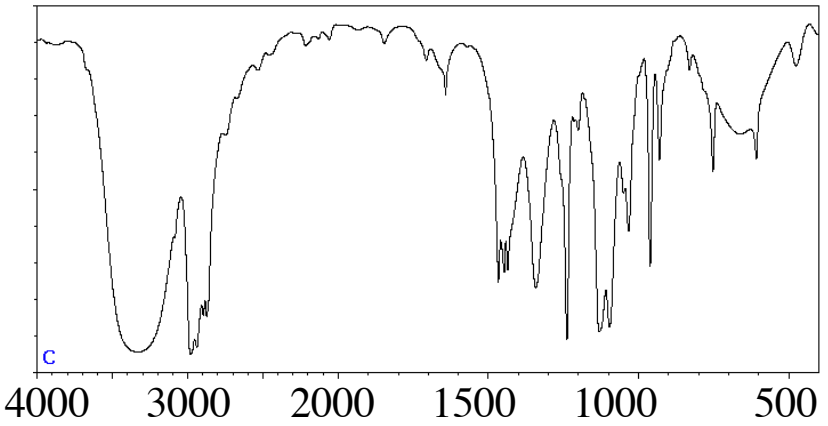
2-methyl-2-propen-1-ol

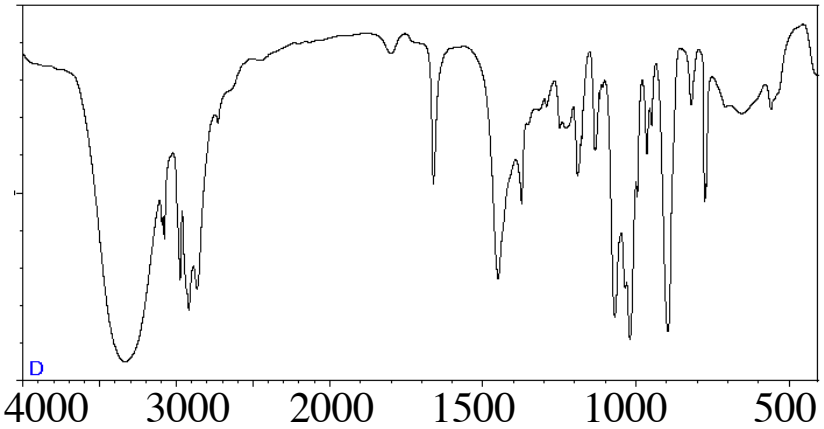


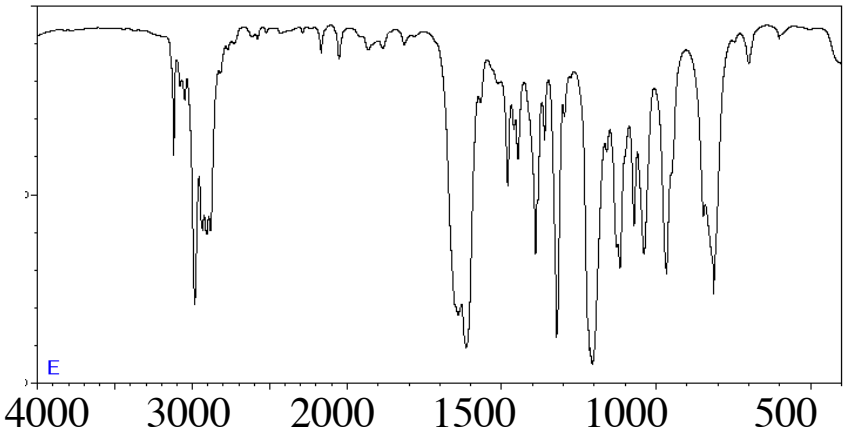
2-methylpropanal





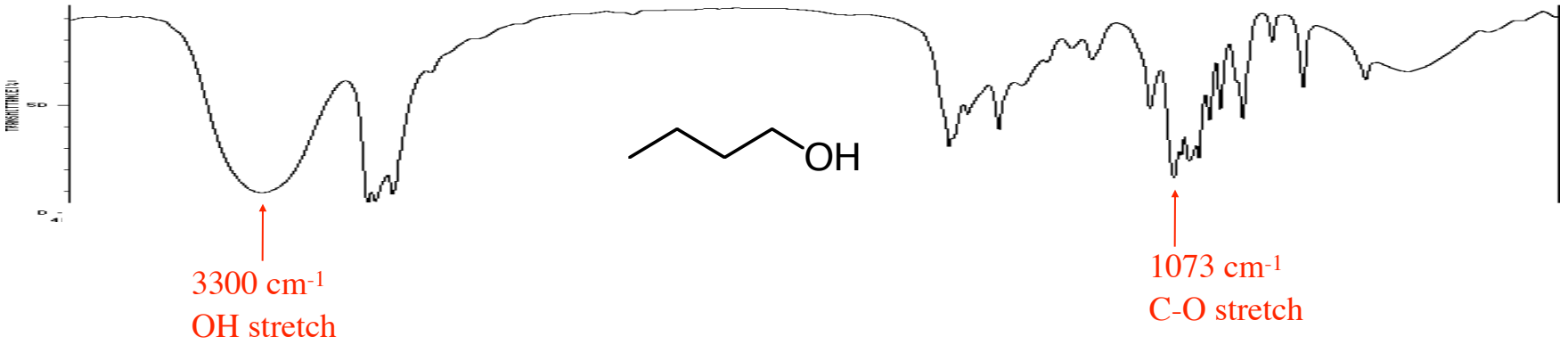






Alcohols and Phenols

- O-H stretch is typically very broad and located at 3550-3200 cm^{-1}
  - broadening is due to hydrogen bonding

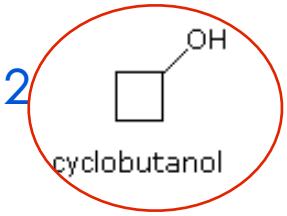


C–O stretching Vibrations

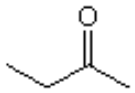
- Alcohols (1260-1000 cm^{-1})
- Phenols (1800-1260 cm^{-1})

primary alcohol: 1050-1085 cm^{-1}
secondary alcohol: 1085-1125 cm^{-1}
tertiary alcohol: 1125-1200 cm^{-1}

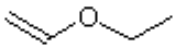
case study 2



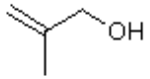
cyclobutanol



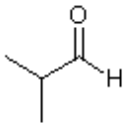
2-butanone



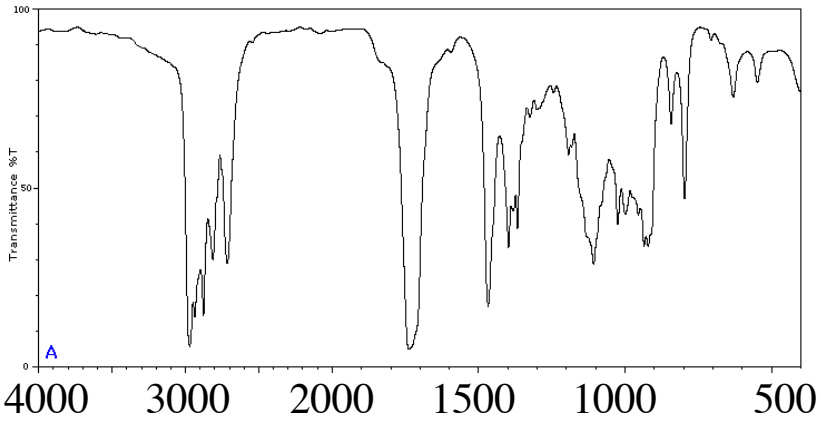
ethyl vinyl ether

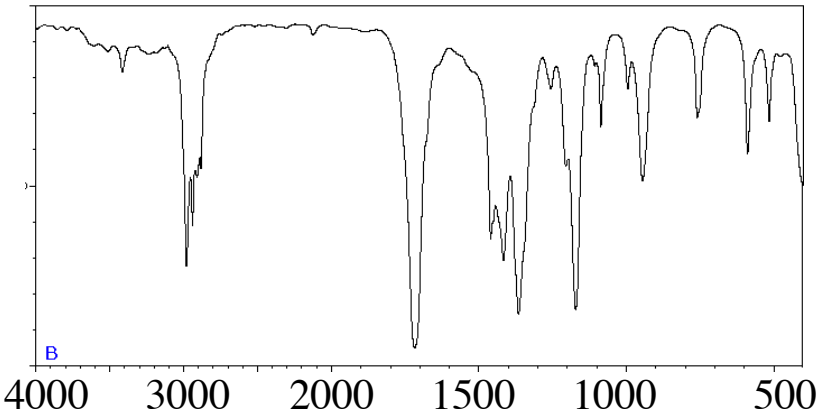


2-methyl-2-propen-1-ol

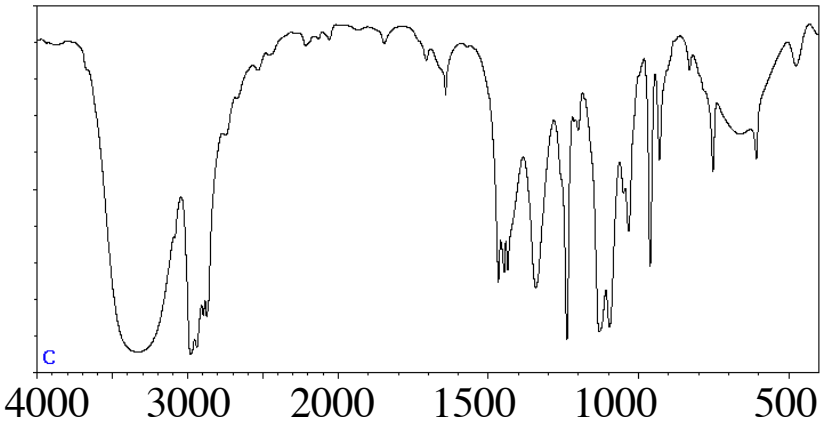


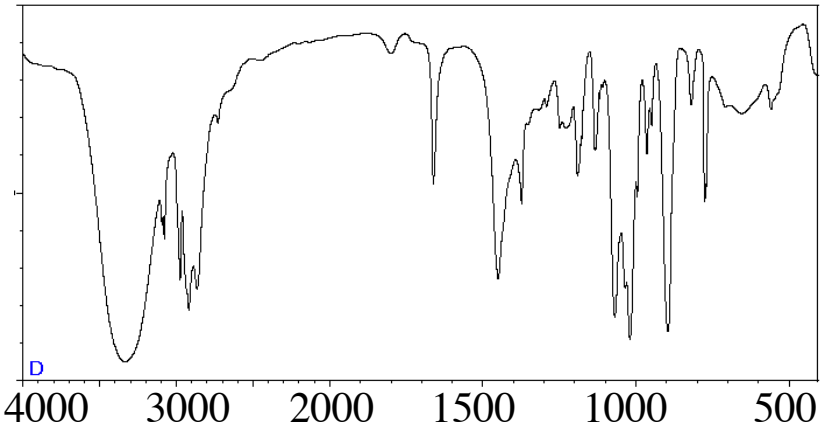
2-methylpropanal

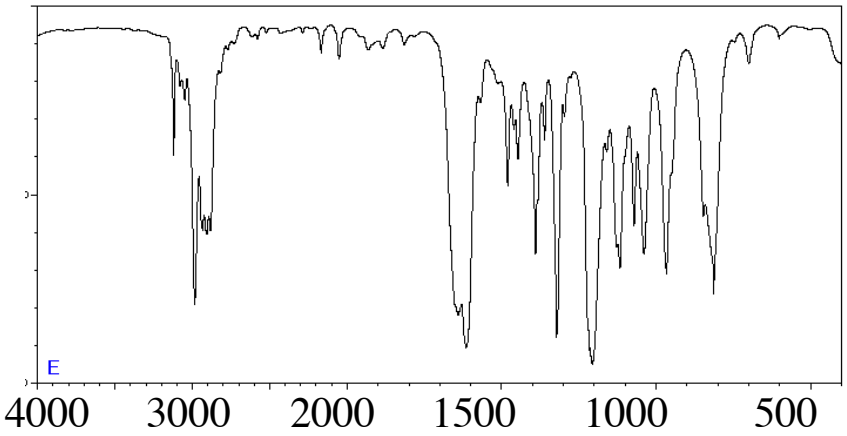




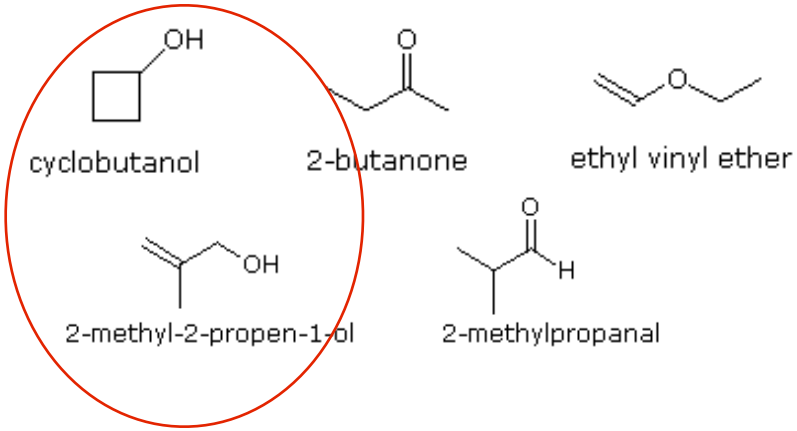
CLICKERS

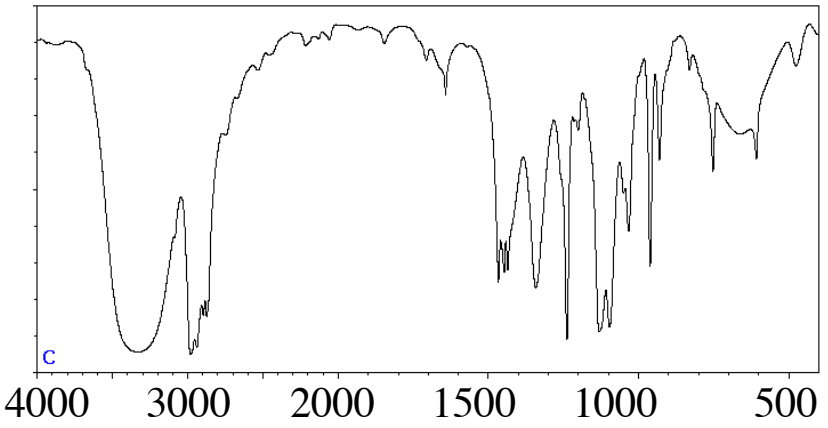


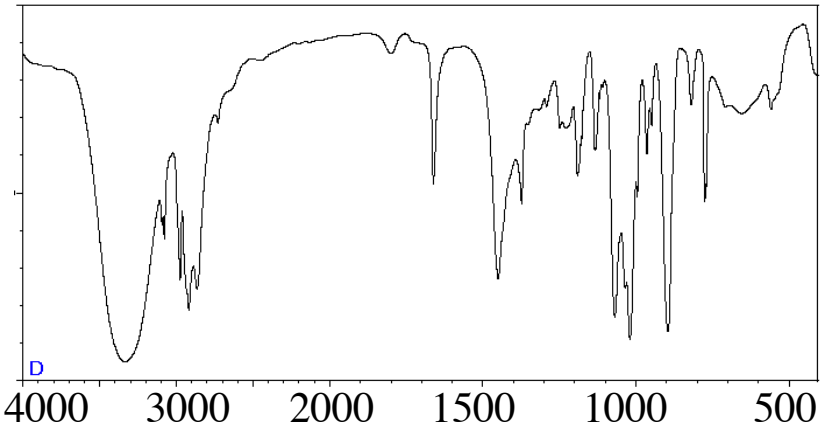




case study 2



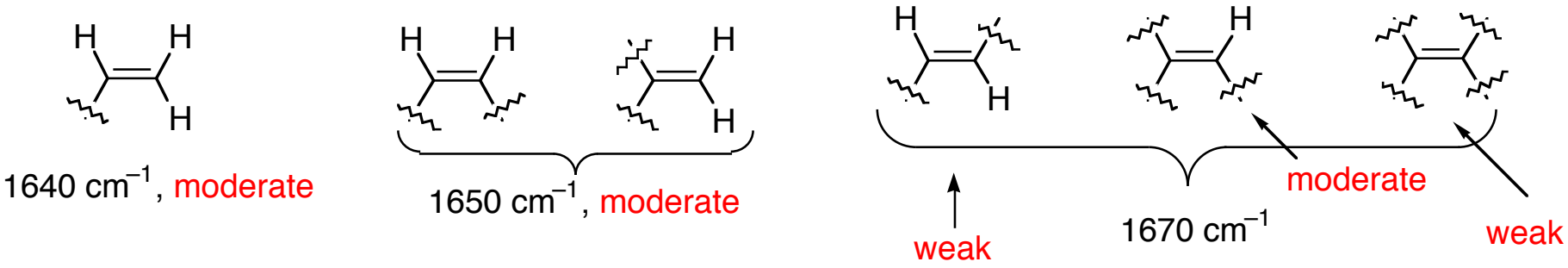




HOW DO WE DISTINGUISH THESE?

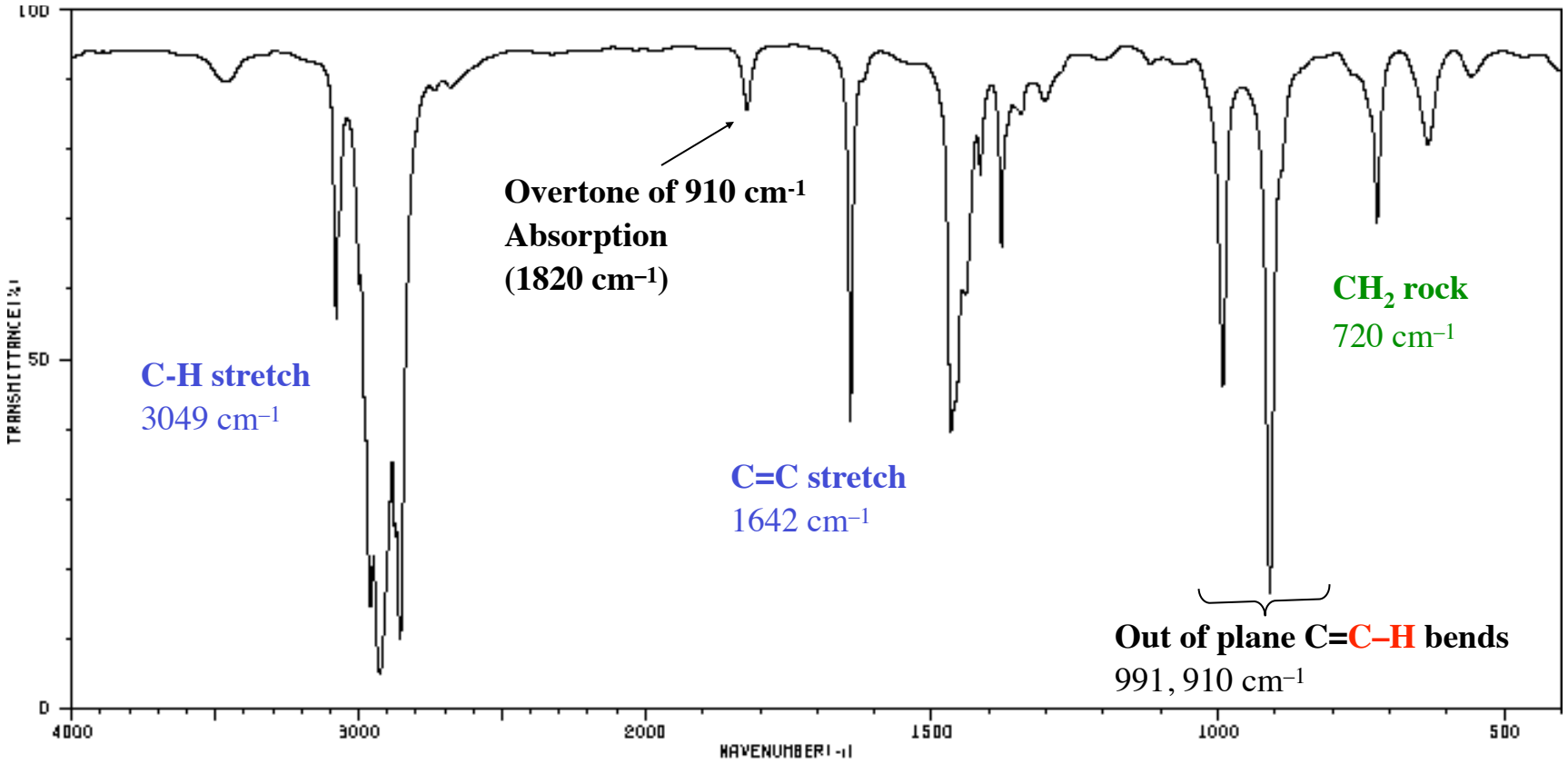
Unconjugated Alkenes

- linear alkenes:
  - C=C stretch: moderate to weak absorption at 1667-1640 cm^{-1}

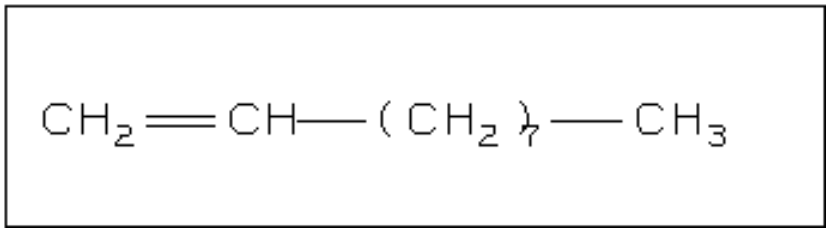


- C=**C–H**:
  - stretch: ≥ 3000 cm^{-1}

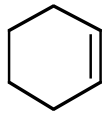
Unconjugated Alkenes



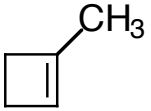
1-decene



• cyclic alkenes:
- C=C stretch: sensitive to ring strain

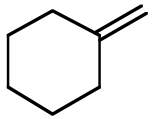

1650 cm^{-1}


1566 cm^{-1}



1641 cm^{-1}

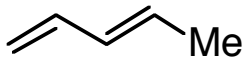

1640 cm^{-1}


1650 cm^{-1}

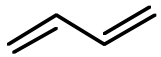

1781 cm^{-1}

• cumulated alkenes:
- C=C=C stretch (asymmetric): 2000–1900 cm^{-1}

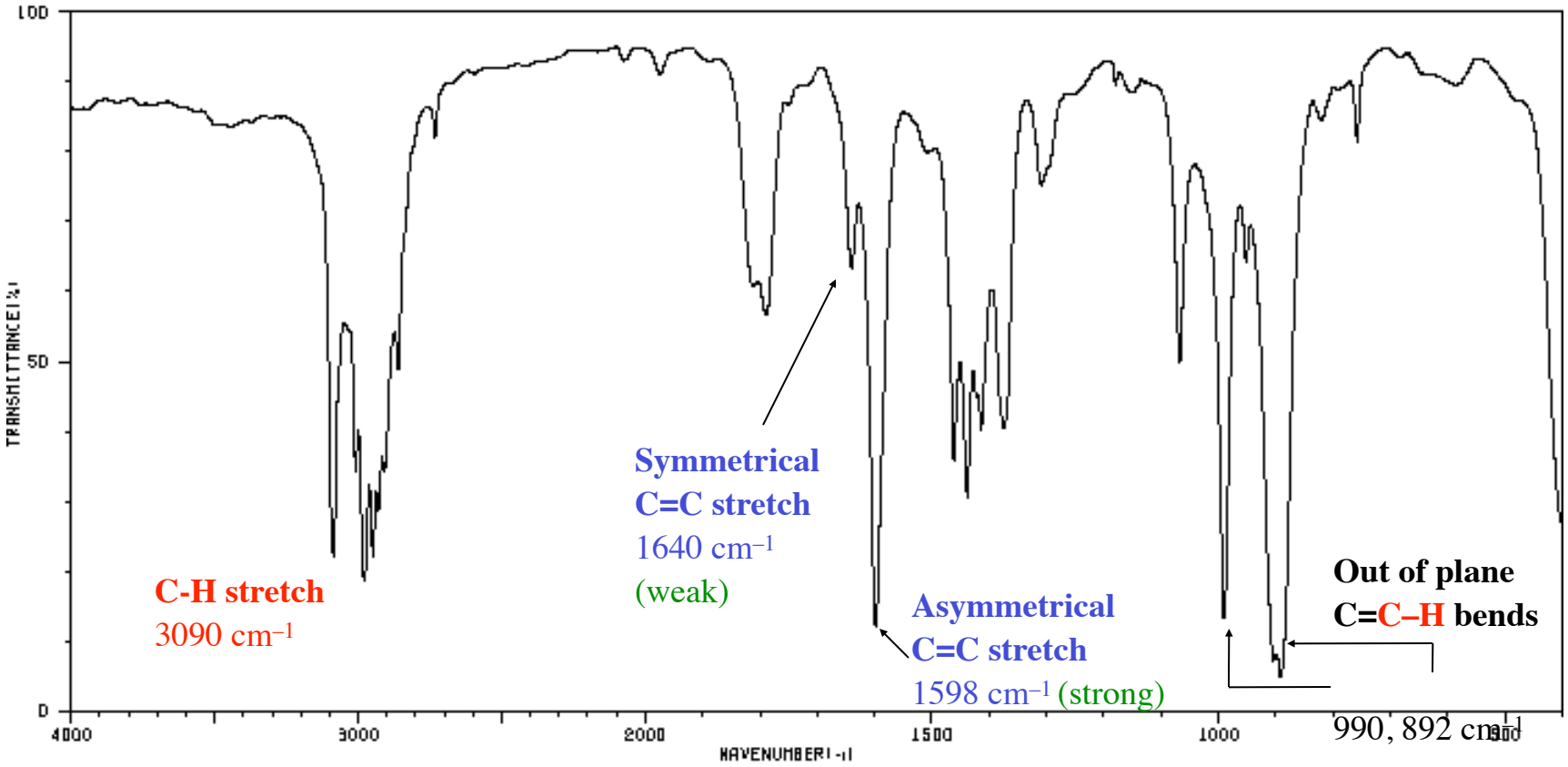
• conjugated alkenes:
-the alkene bond stretching vibrations in alkenes w/o a center of symmetry give rise to two C=C stretches
-for symmetrical molecules, e.g. butadiene, only the asymmetric stretch is observed

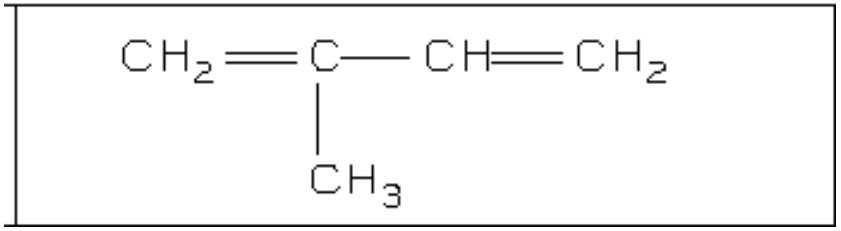


1650 cm^{-1} (as)
1600 cm^{-1} (s)


1600 cm^{-1} (as)

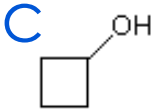
Conjugated Double Bonds



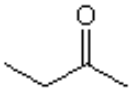


case study 2

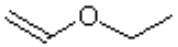
C



cyclobutanol

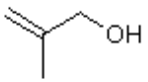


2-butanone

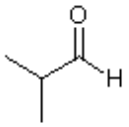


ethyl vinyl ether

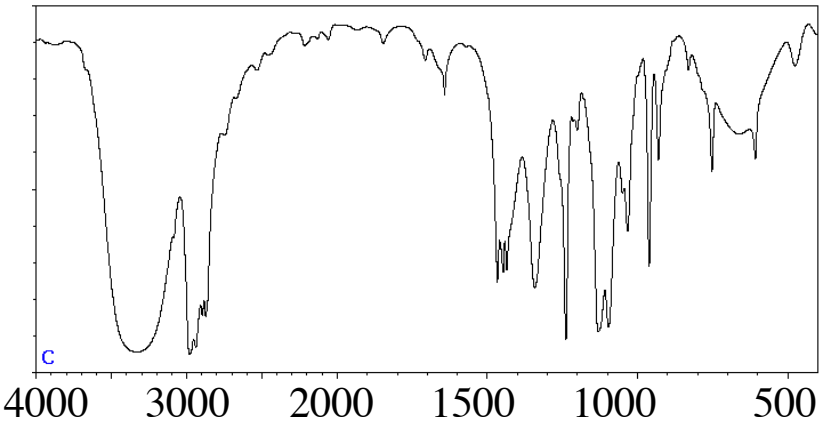
D

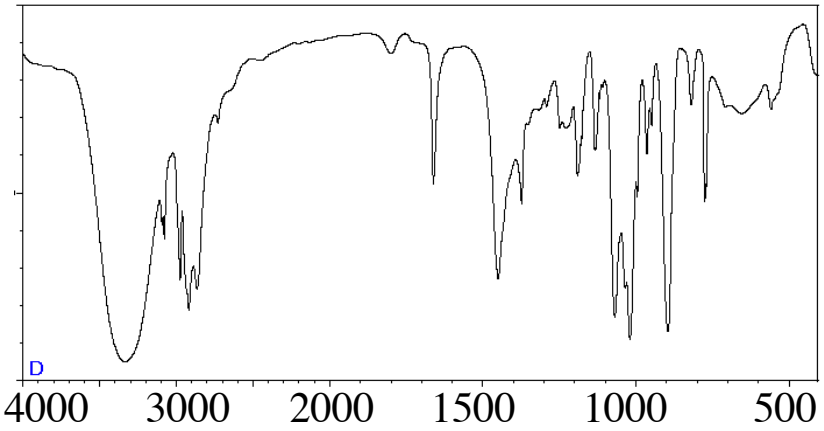


2-methyl-2-propen-1-ol

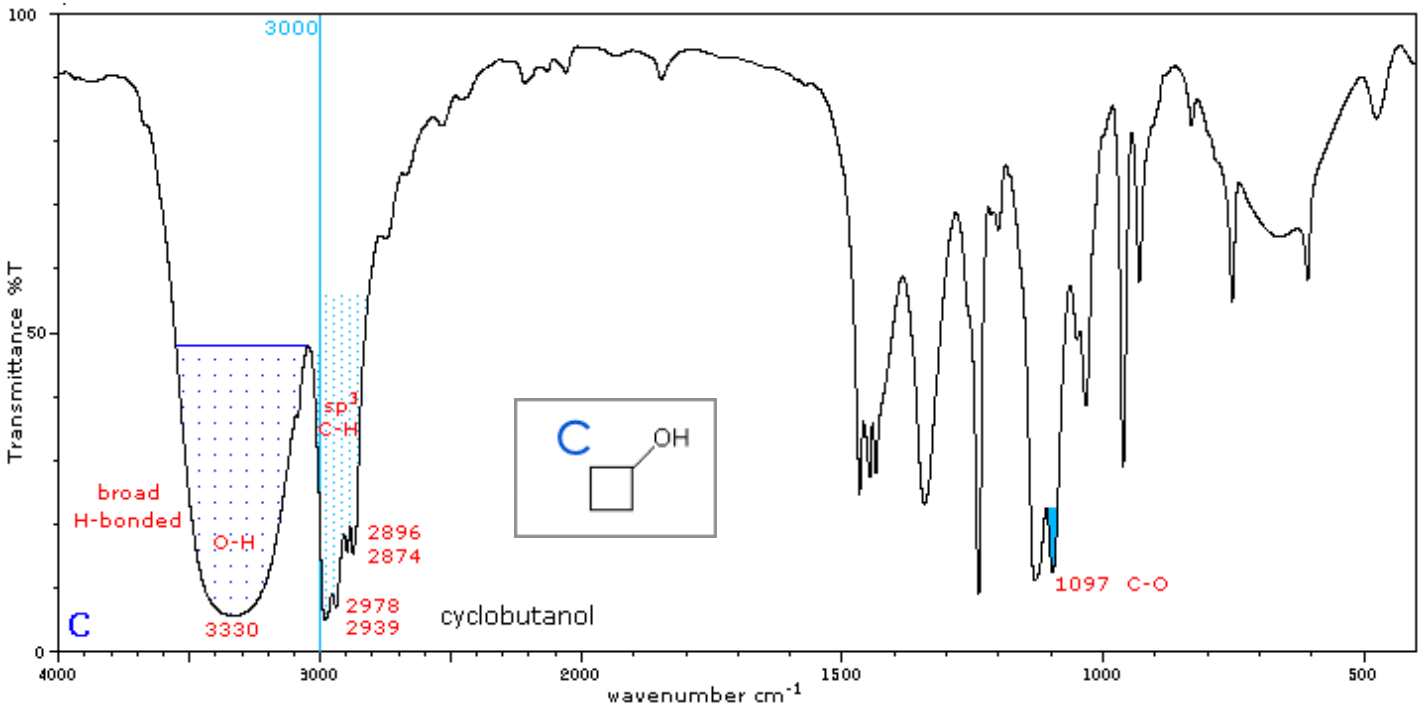


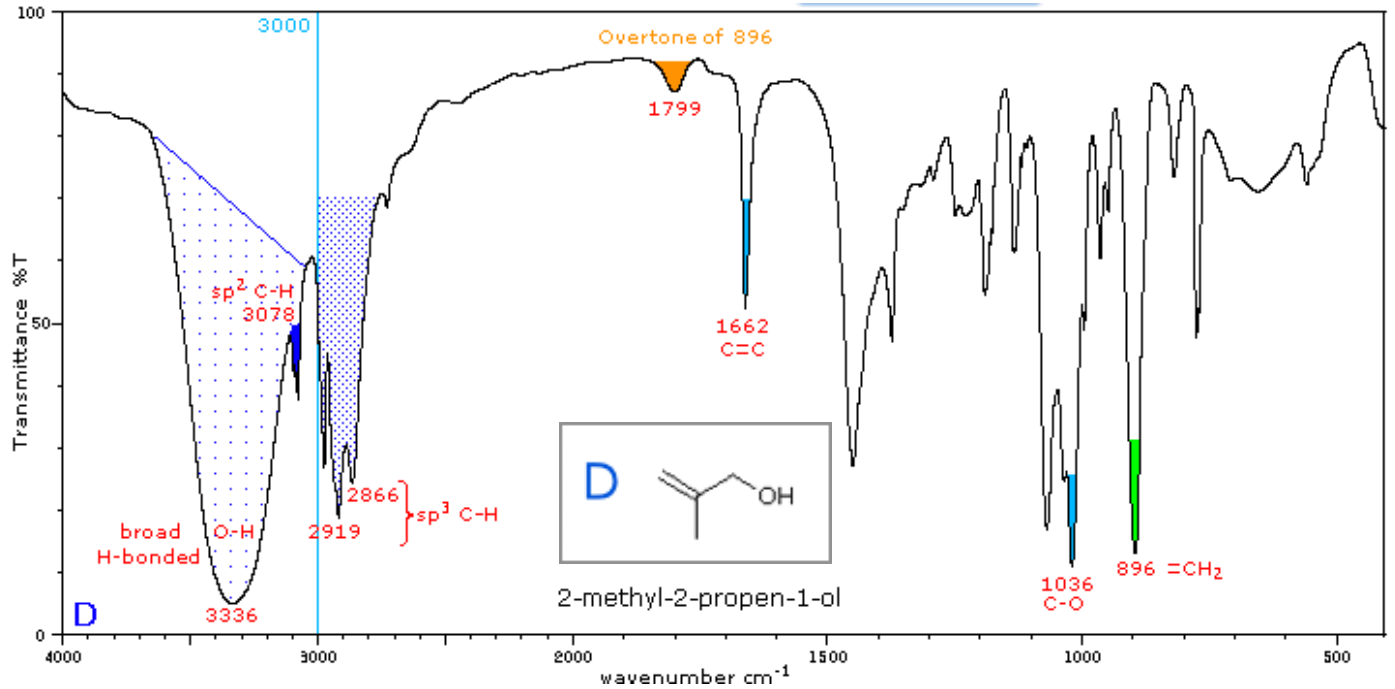
2-methylpropanal





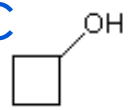
clickers


100
50
0
Transmittance %T
3000
broad
H-bonded
O-H
3330
sp3
C-H
2896
2874
2978
2939
C
OH
1097 C-O
C
cyclobutanol
4000
3000
2000
1500
1000
500
wavenumber cm-1

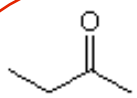

100
50
0
Transmittance %T
3000
Overtone of 896
1799
sp2 C-H
3078
broad
H-bonded
O-H
3336
2919
2866
sp3 C-H
1662
C=C
D
OH
2-methyl-2-propen-1-ol
1036
C-O
896 =CH2
D
4000
3000
2000
1500
1000
500
wavenumber cm-1

case study 2

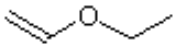
C



cyclobutanol

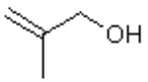


2-butanone

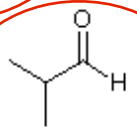


ethyl vinyl ether

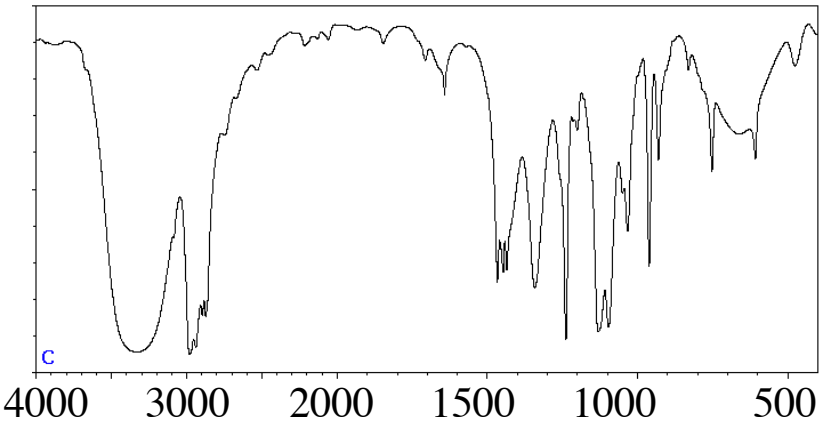
D

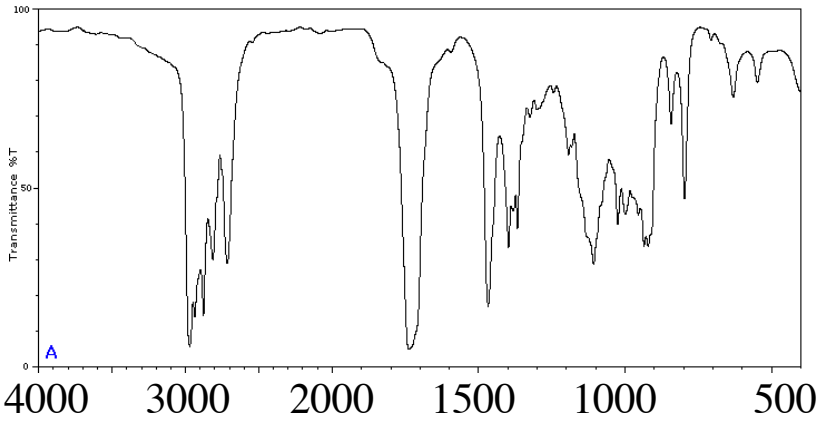


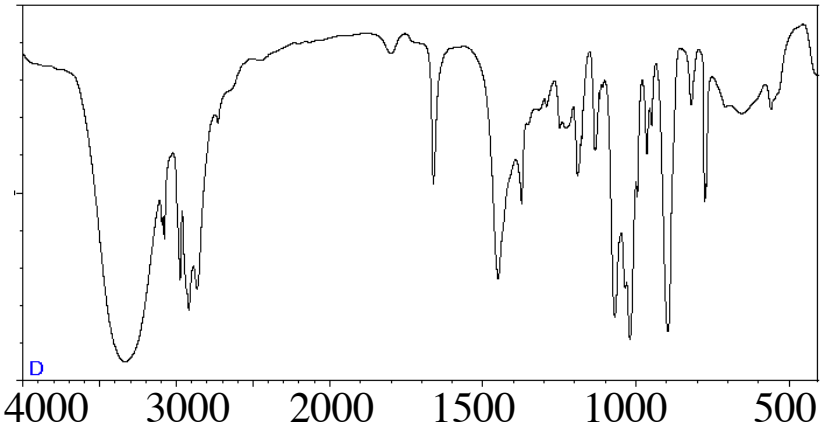
2-methyl-2-propen-1-ol

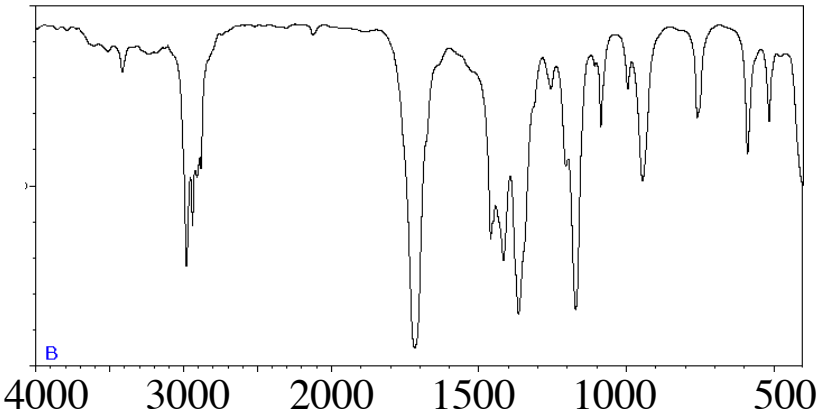


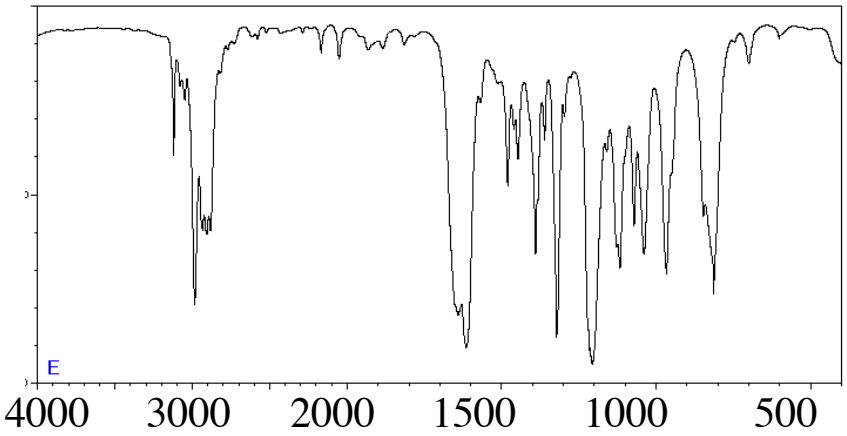
2-methylpropanal











Carbonyls

C=O stretch– easily recognized, intense band

• Ketones, aldehydes, acids, esters, lactones, acid halides, anhydrides, amides and lactams all show C=O stretching in the region 1870-1540 cm^{-1}.

• Position is determined by (1) physical state (2) electronic and mass of neighboring groups (3) conjugation (4) hydrogen bonding (5) ring strain

Ketones

- aliphatic: 'normal' position of a neat aliphatic ketone is ~1715 cm^{-1}

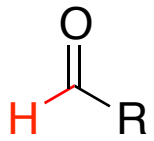
Aldehydes

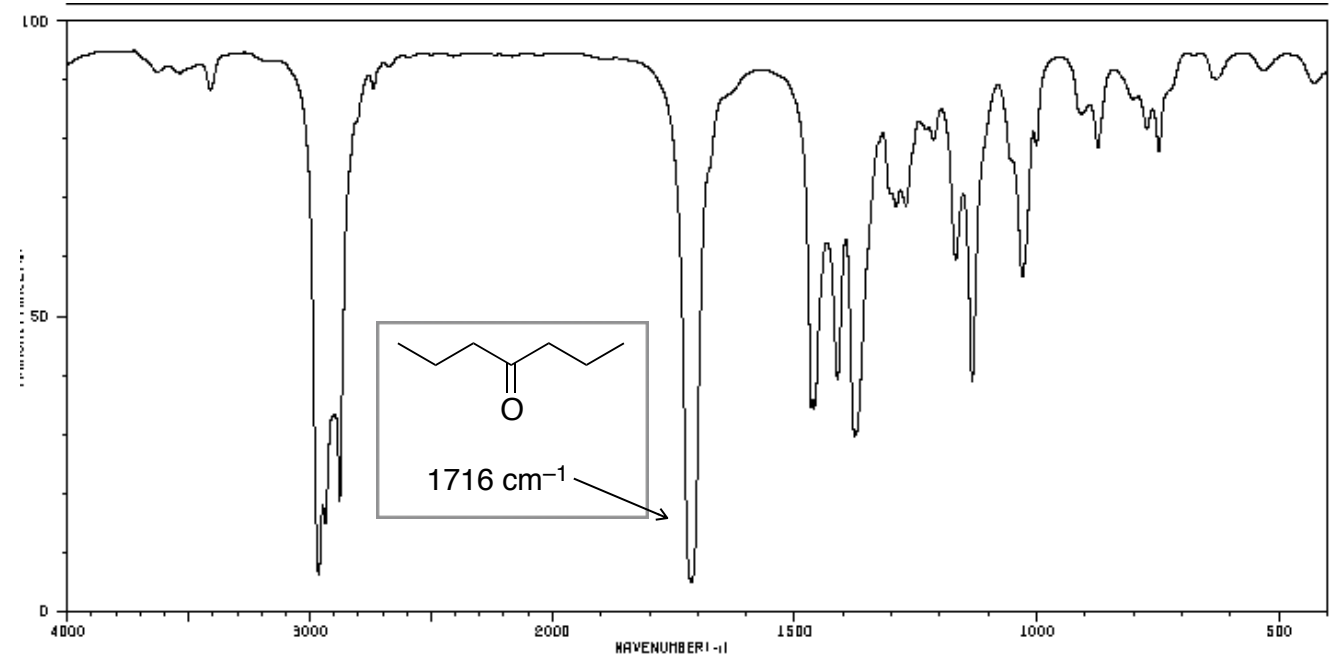
C=O stretch

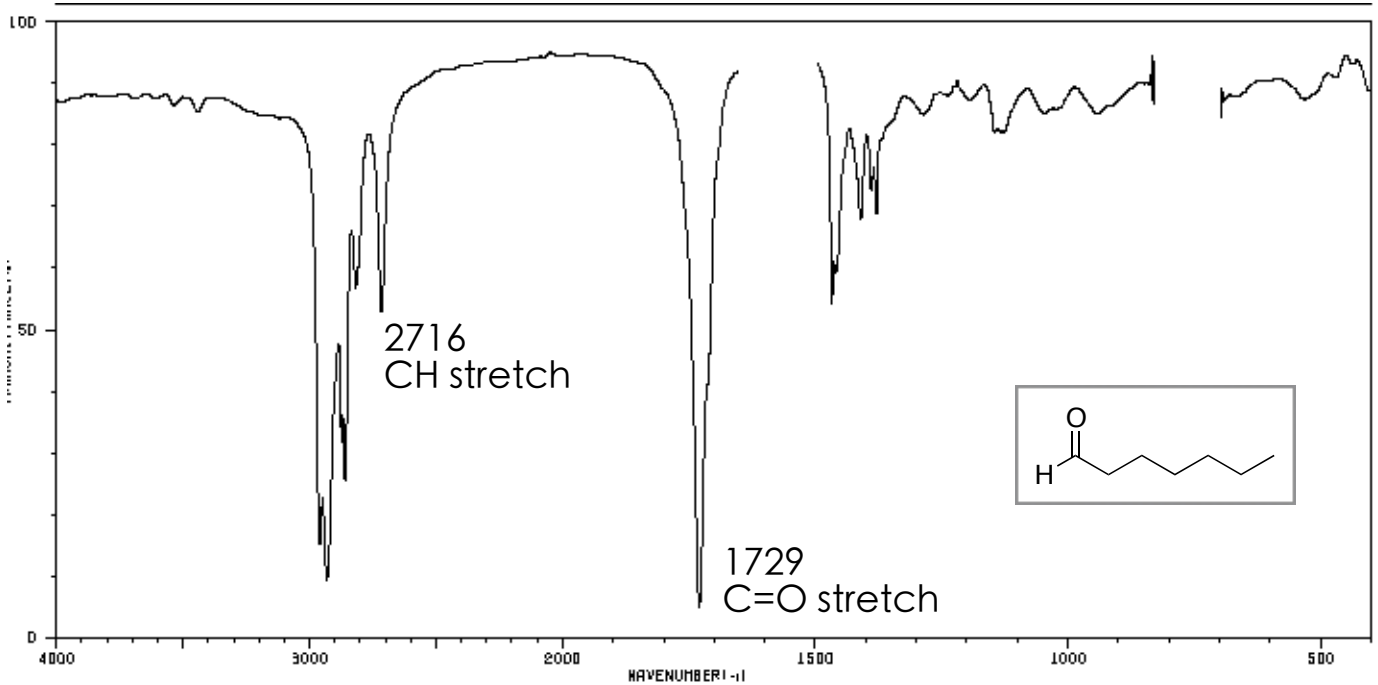
- Aliphatic aldehydes: C=O stretch at 1740-1720 cm^{-1}

C–H stretch

2830–2695 cm^{-1} Often, two bands are observed (the other is a result of an overtone of the C–H bend of the aldehyde)

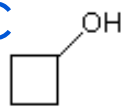



100
50
0
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
O
1716 cm−1


100
50
0
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
2716
CH stretch
1729
C=O stretch
O
H

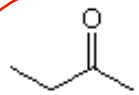
case study 2

C

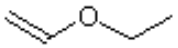


cyclobutanol

B

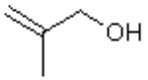


2-butanone

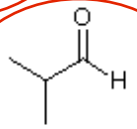


ethyl vinyl ether

D

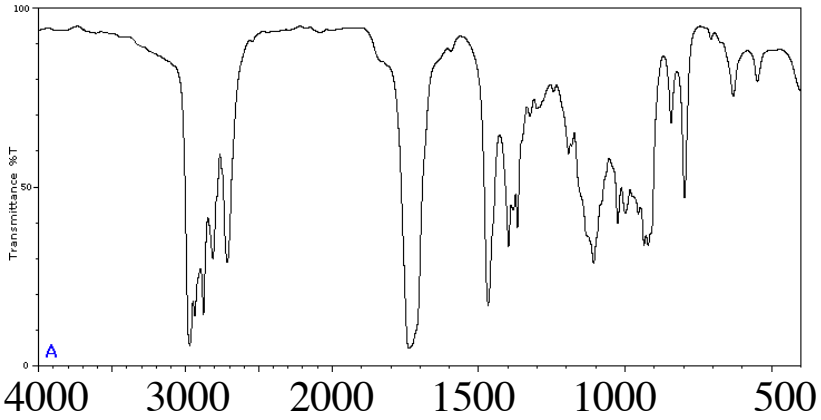


2-methyl-2-propen-1-ol

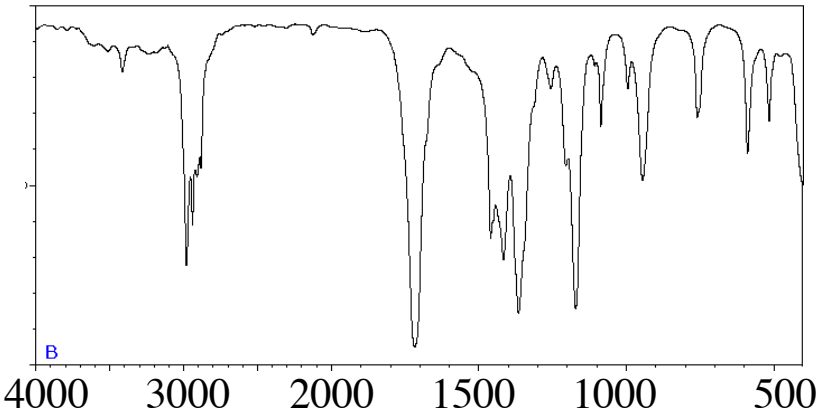


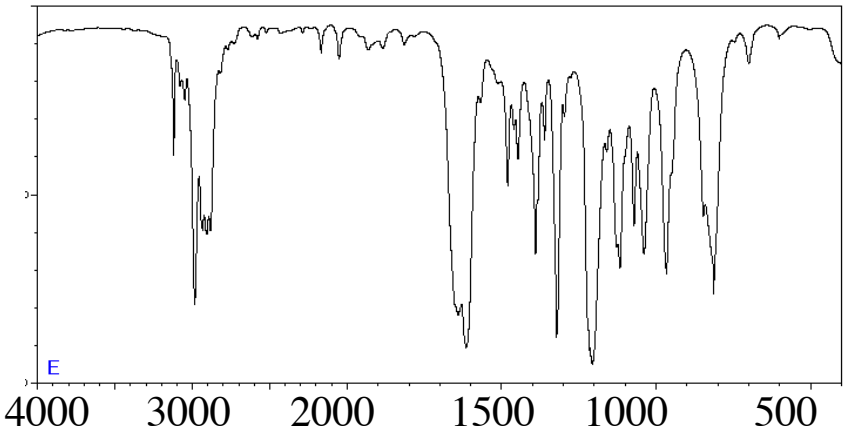
A

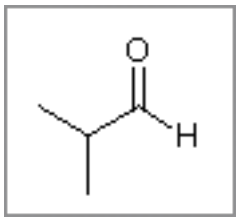
2-methylpropanal

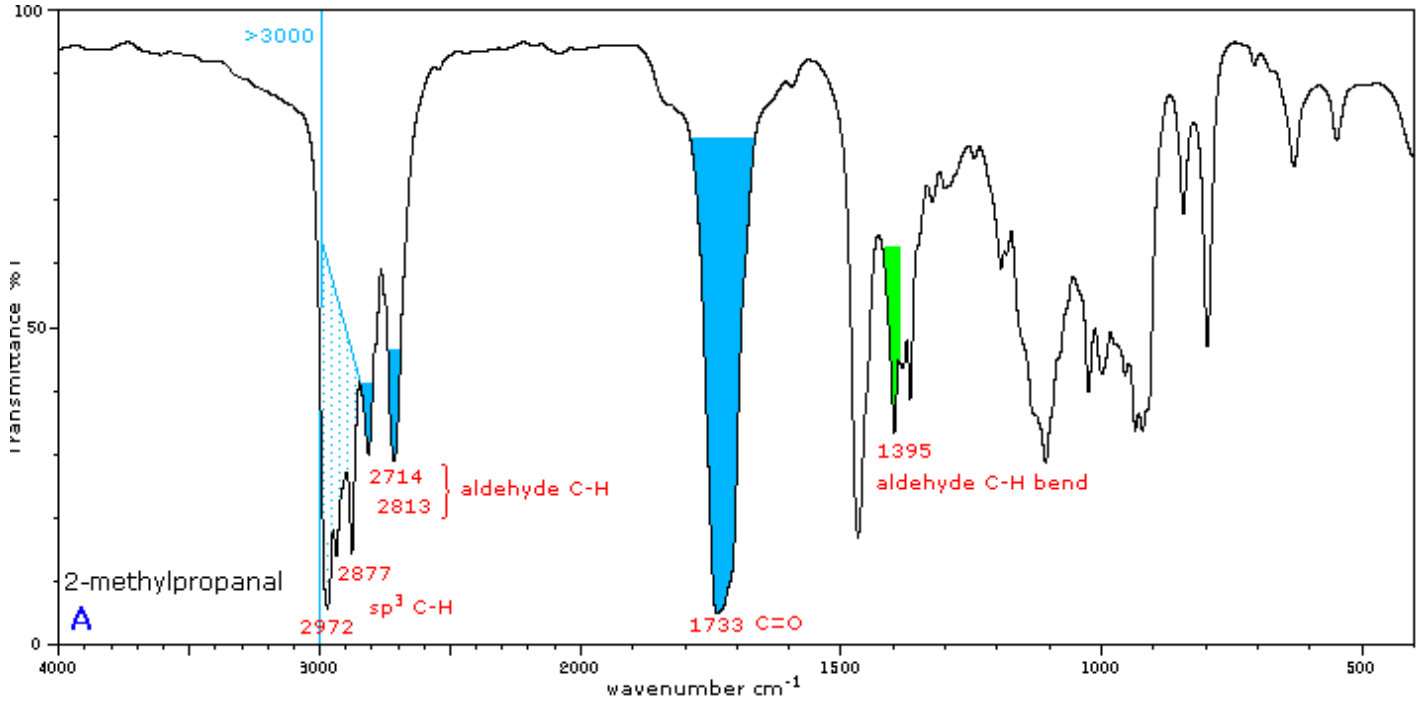


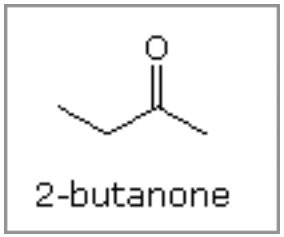
clickers

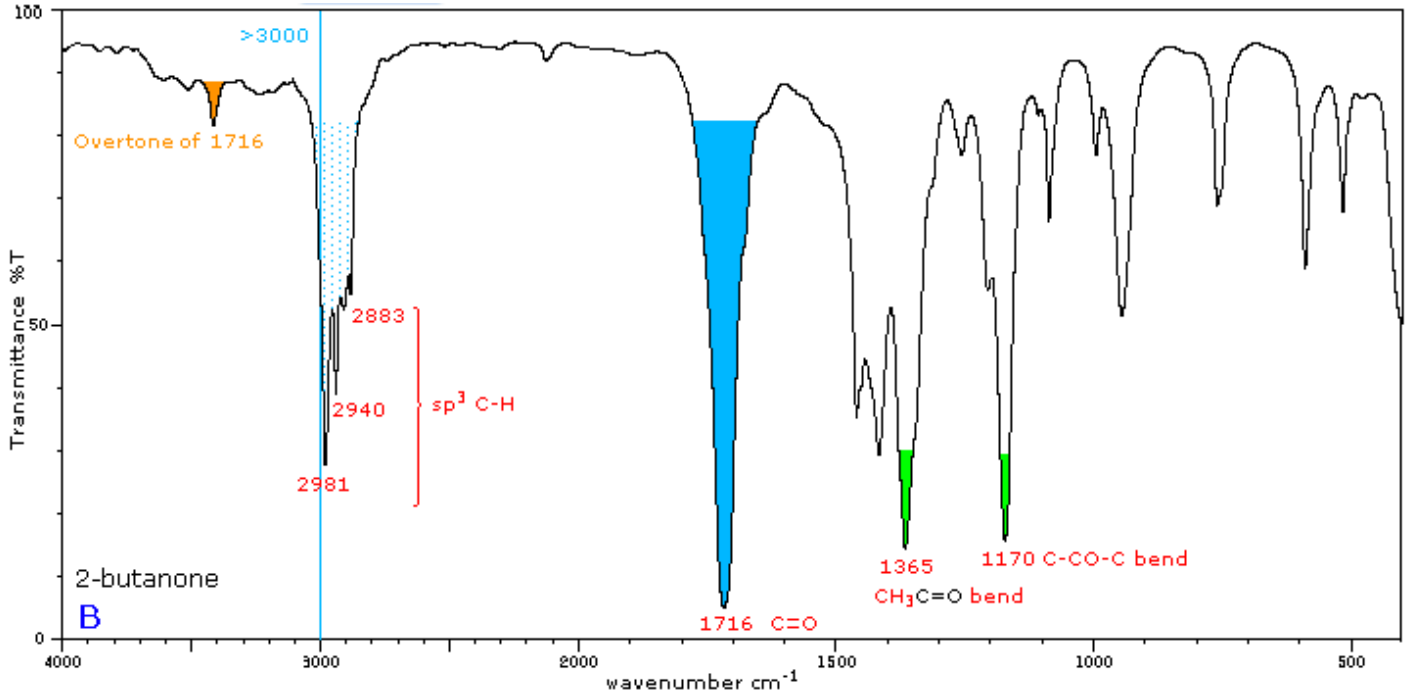


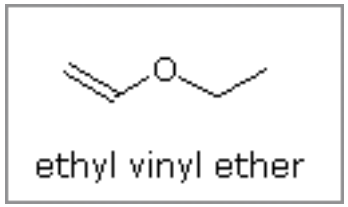





100
50
0
Transmittance %T
>3000
2714
2813
aldehyde C-H
2877
2972
sp3 C-H
1733 C=O
1395
aldehyde C-H bend
2-methylpropanal
A
4000
3000
2000
1500
1000
500
wavenumber cm-1


2-butanone


100
50
0
Transmittance %T
>3000
Overtone of 1716
2883
2940
2981
sp3 C-H
1716 C=O
1365
CH3C=O bend
1170 C-CO-C bend
2-butanone
B
4000
3000
2000
1500
1000
500
wavenumber cm-1



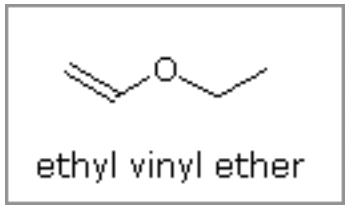
Ethers

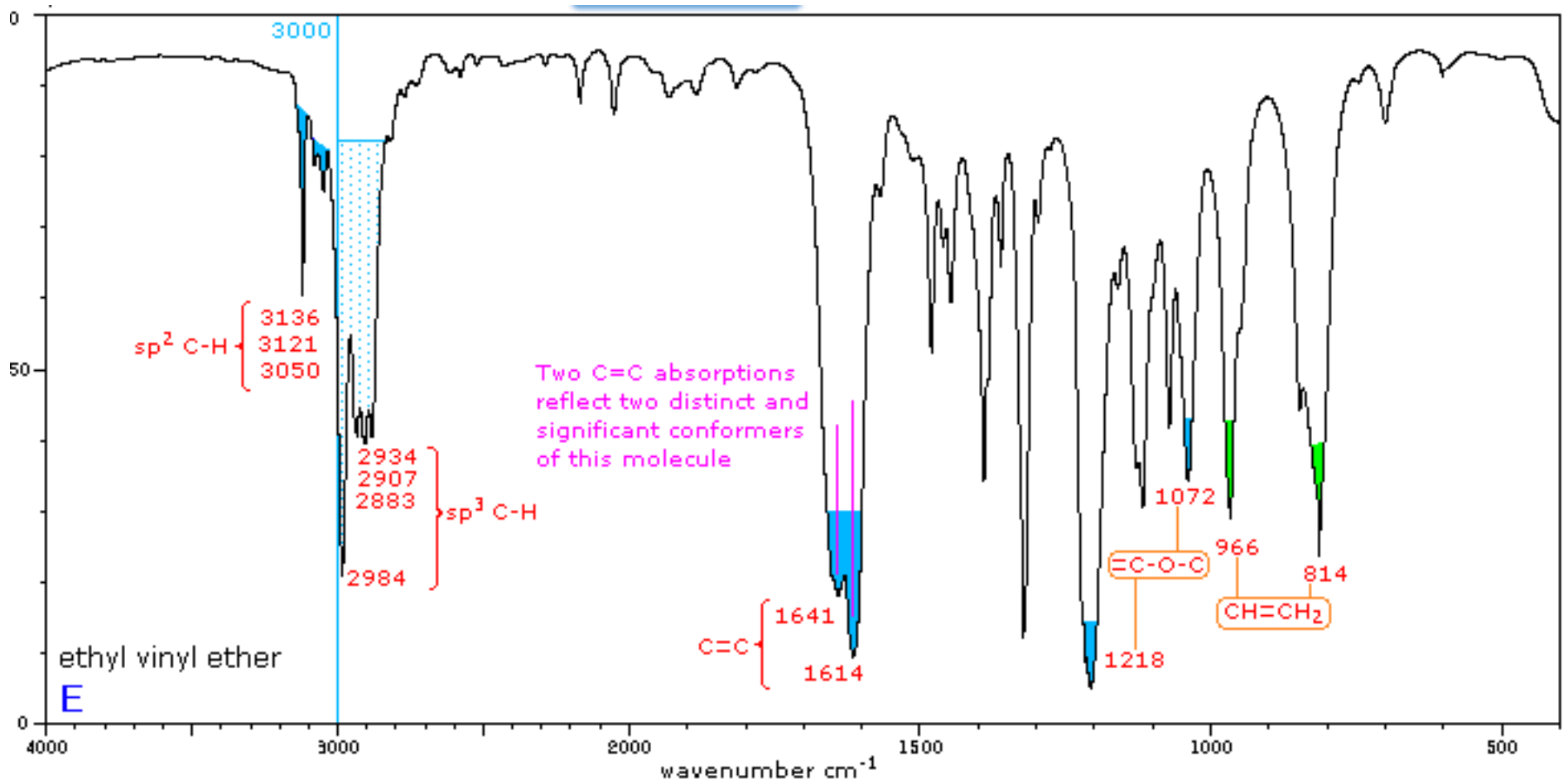
- C–O–C stretching bands are most characteristic bands
  - strong because of strong dipole moment

aliphatic ethers: strong band due to asymmetrical stretching, 1150-1085 cm^{-1} (usually 1125 cm^{-1})
weak band due to symmetrical stretching (lower freq)

Alkyl aryl ethers: asymmetrical stretch at 1275-1200 cm^{-1}
symmetrical stretch at 1075-1020 cm^{-1}

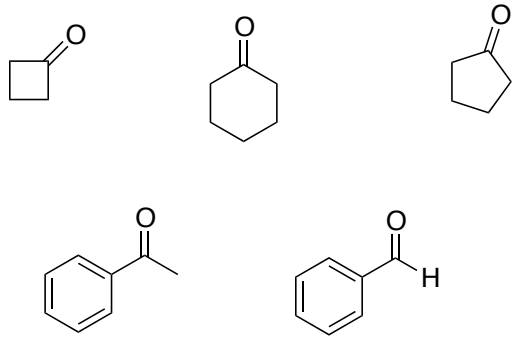
Vinyl alkyl ethers: asymmetrical stretch at 1225-1200 cm^{-1}
symmetrical stretch at 1075-1020 cm^{-1}


O
ethyl vinyl ether

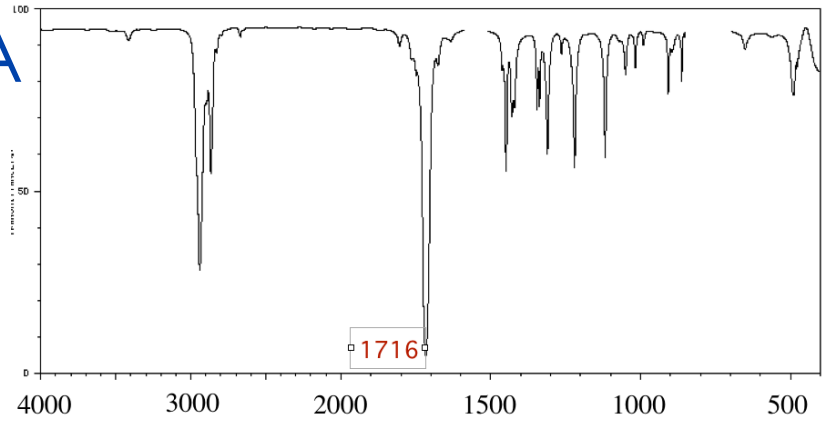

0
50
0
3000
sp2 C-H
3136
3121
3050
2934
2907
2883
sp3 C-H
2984
Two C=C absorptions
reflect two distinct and
significant conformers
of this molecule
C=C
1641
1614
1072
=C-O-C
1218
966
CH=CH2
814
ethyl vinyl ether
E
4000
3000
2000
1500
1000
500
wavenumber cm-1

case study 3

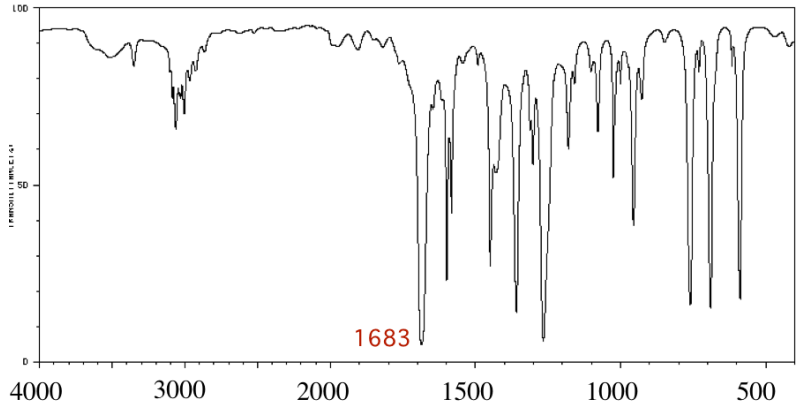
case study 3



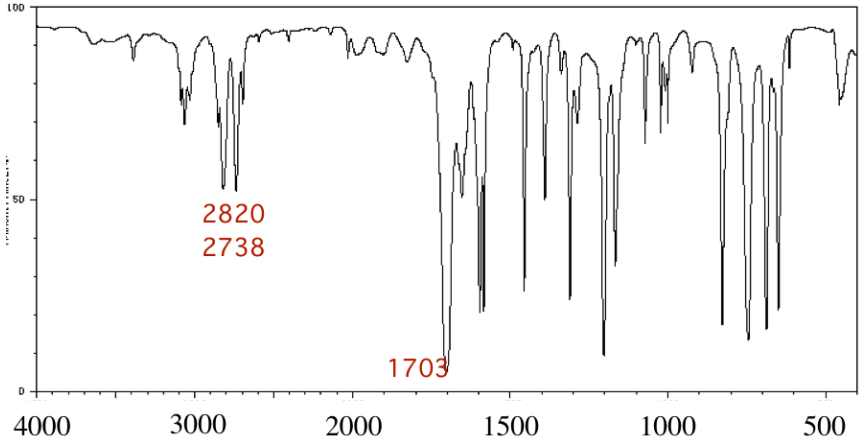
A



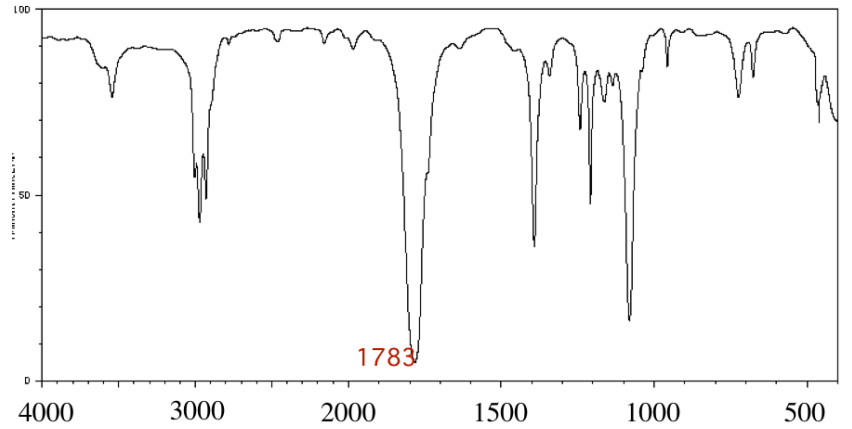
B



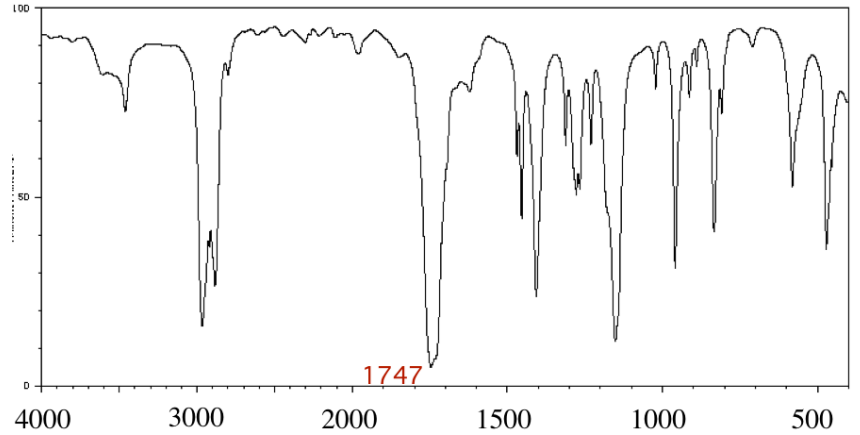
C



D



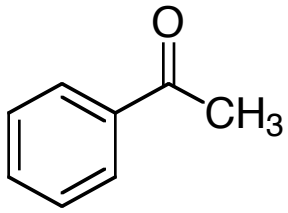
E



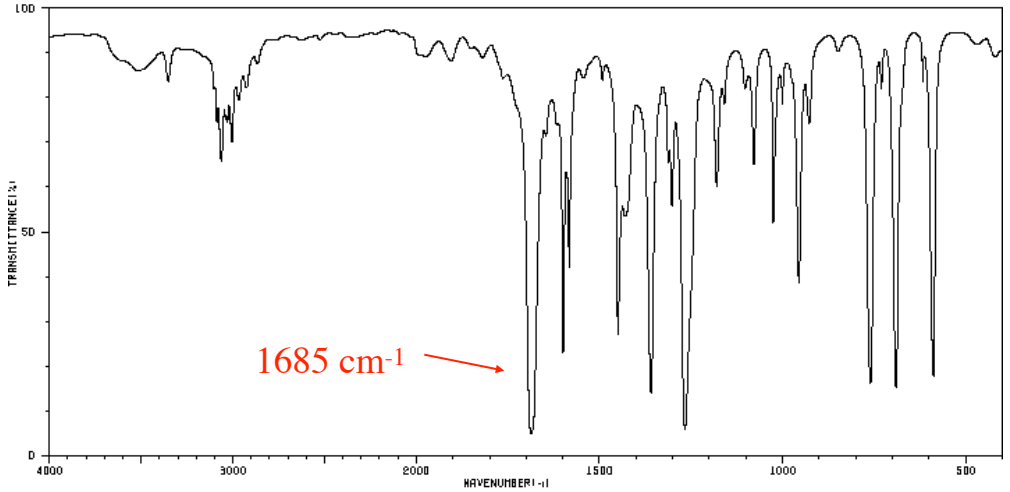
Ketones

- aliphatic: 'normal' position of a neat aliphatic ketone is ~1715 cm^{-1}

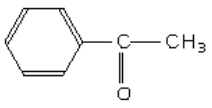
- conjugation: shifts position to lower frequency
  alkene or phenyl group causes absorption in the 1685-1666 cm^{-1} region. For α,β-unsaturated carbonyls, 2 absorptions may be observed



1685 cm^{-1}



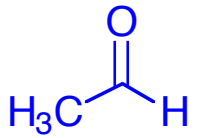
3604	84	2967	77	1545	81	1267	6	966	37
3352	81	2925	79	1492	81	1181	58	928	72
3087	72	2867	84	1450	26	1160	74	761	15
3063	64	1686	4	1430	62	1103	79	731	79
3040	72	1646	68	1360	13	1079	62	691	14
3029	72	1599	21	1313	82	1025	50	616	61
3006	68	1583	41	1303	63	1001	74	588	17



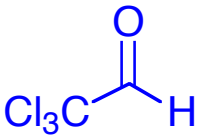
Aldehydes

C=O stretch

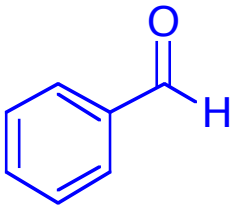
- Aliphatic aldehydes: C=O stretch at 1740-1720 cm^{-1}
- Electron withdrawing groups shift to higher frequency
- Conjugative groups shift to lower frequency (1710-1685 cm^{-1})



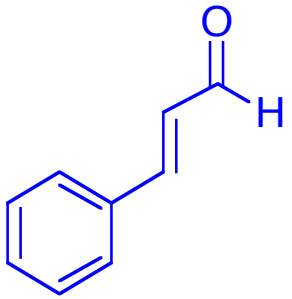
1730 cm^{-1}



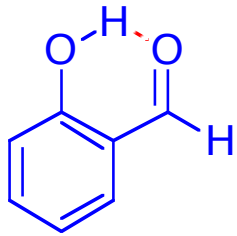
1768 cm^{-1}



1703 cm^{-1}



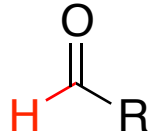
1678 cm^{-1}



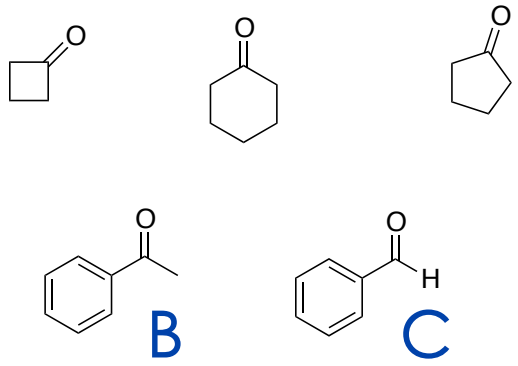
1666 cm^{-1}

C–H stretch

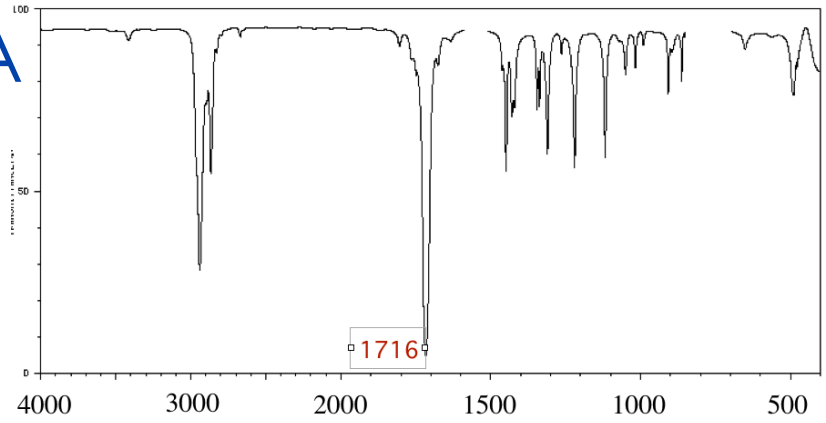
2830–2695 cm^{-1} Often, two bands are observed (the other is a result of an overtone of the C–H bend of the aldehyde)



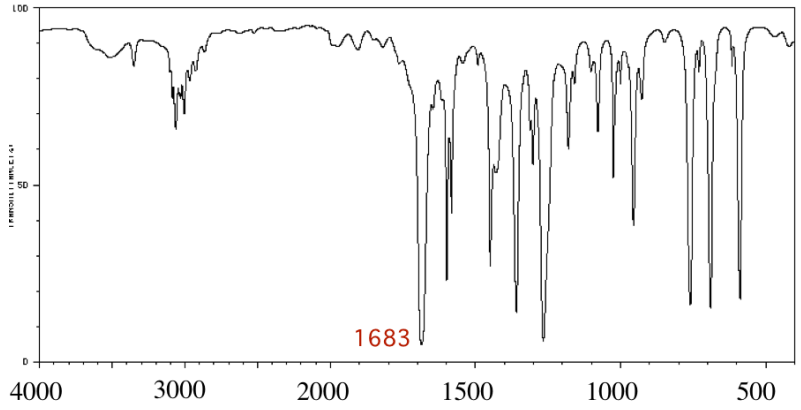
case study 3



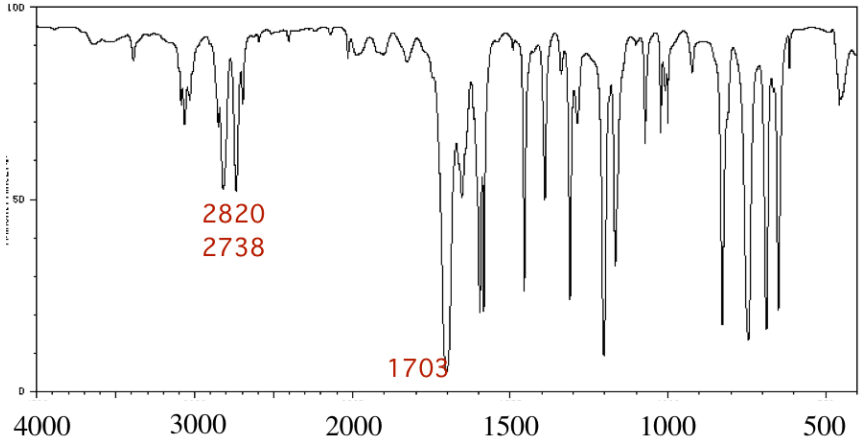
A



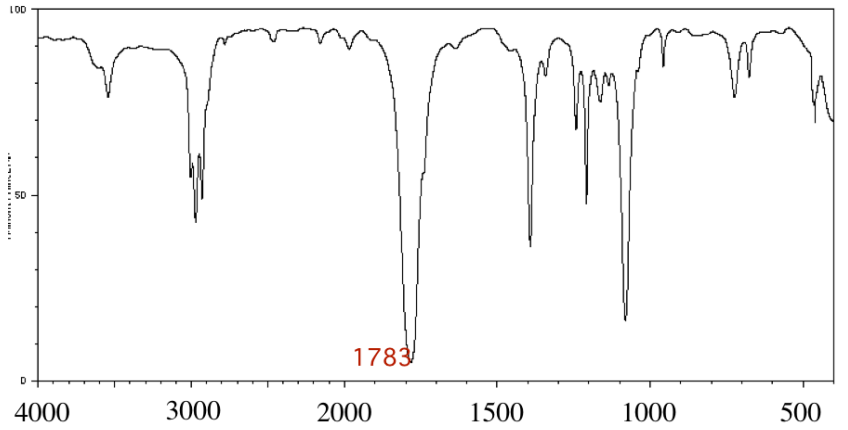
B



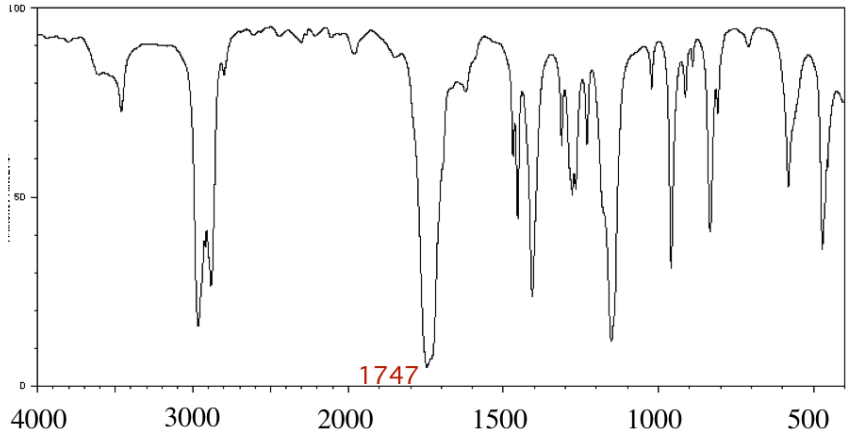
C



D

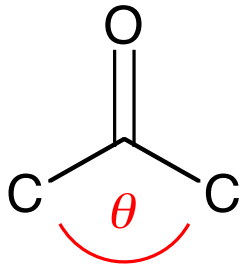


E

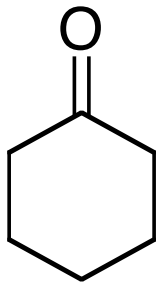


Cyclic Ketones

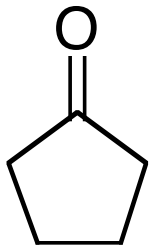
The bond angle influences the absorption frequency of the C=O



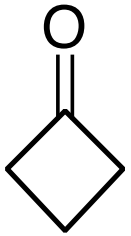
In strained rings, interaction with the adjacent
C-C bonds increases the frequency of C=O stretching



1715 cm^{-1}

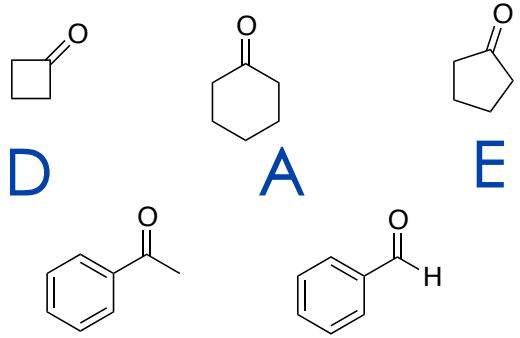


1751 cm^{-1}

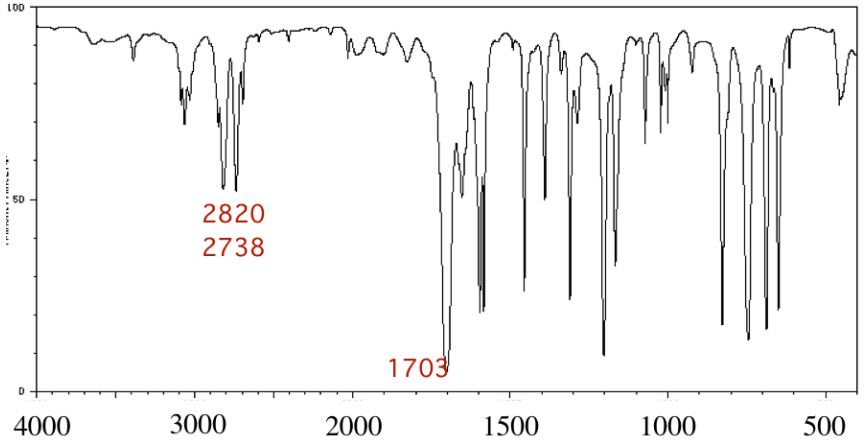


1775 cm^{-1}

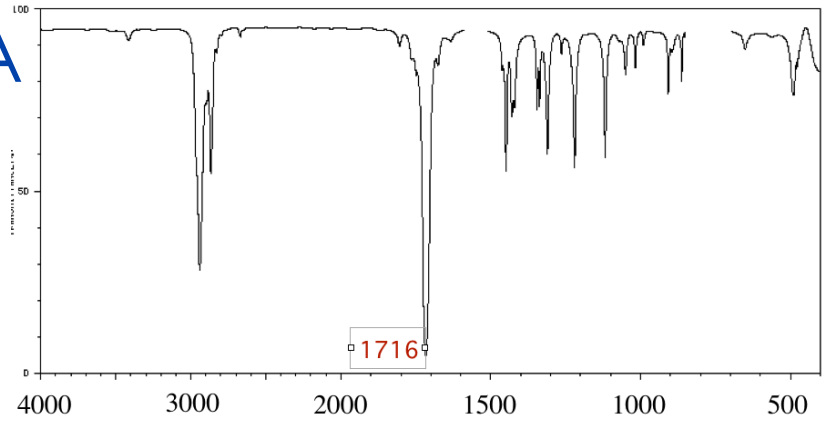
case study 3



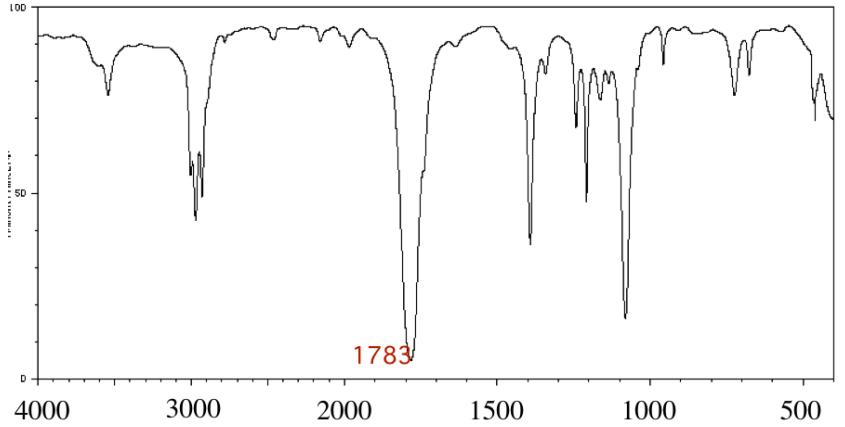
C



A



D



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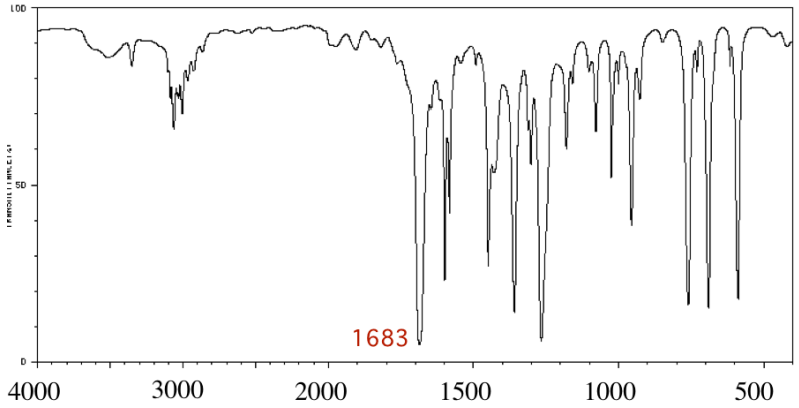
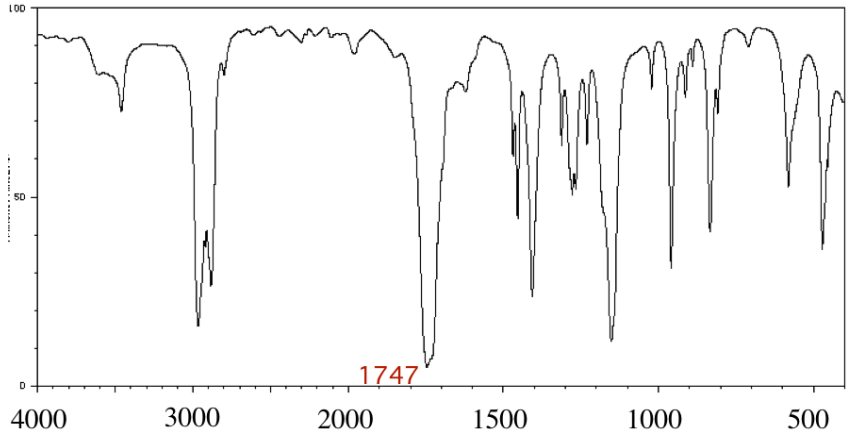
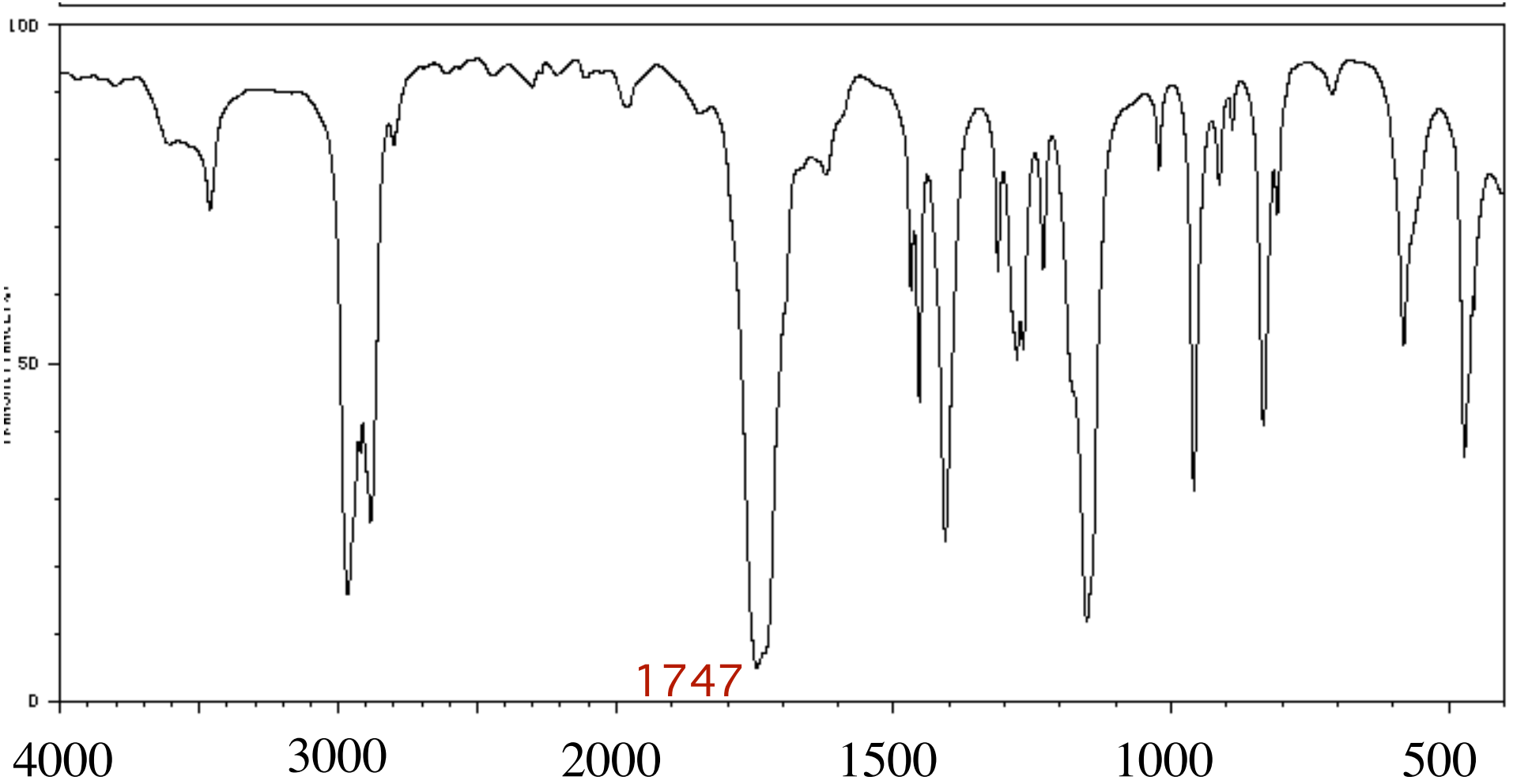


E





3462	70	1622	74	1231	62	810	70
2966	15	1470	58	1153	11	710	86
2921	35	1455	42	1023	74	582	50
2884	25	1408	22	969	30	473	36
2800	79	1313	60	913	74	463	47
1980	84	1278	49	891	81	457	55
1747	4	1267	60	834	39