

# INFRARED SPECTROSCOPY (IR)

*Theory and Interpretation of IR  
spectra*

# ORGANIC STRUCTURE DETERMINATION

*How do we know:*

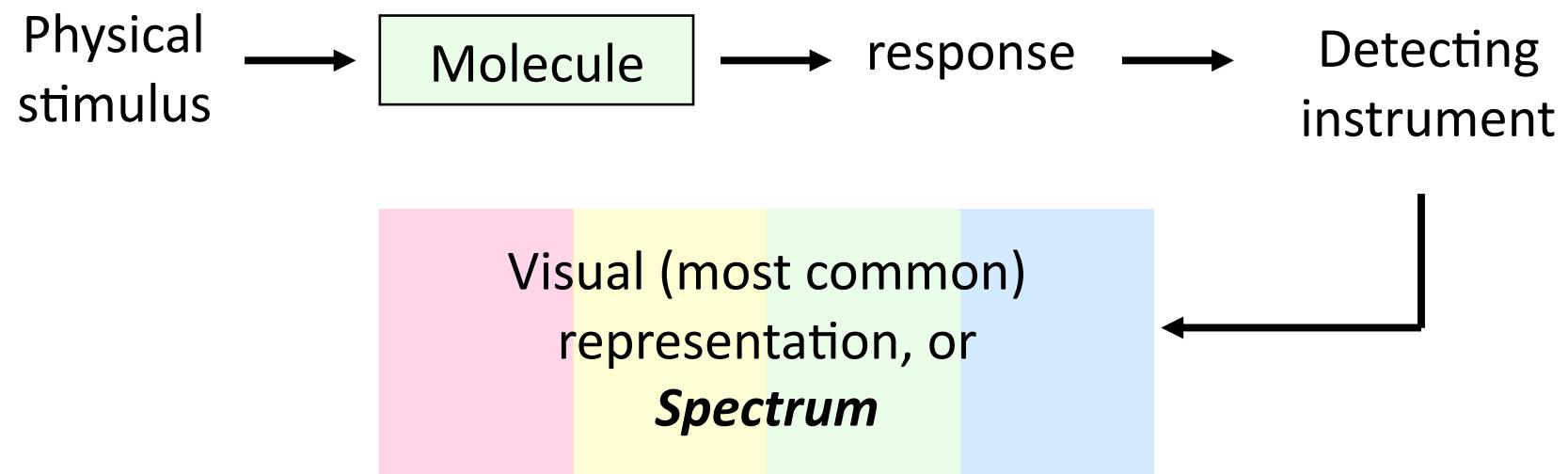
- How atoms are connected together?
- Which bonds are single, double, or triple?
- What functional groups exist in the molecule?
- If we have a specific stereoisomer?

The field of organic structure determination attempts to answer these questions.

# INSTRUMENTAL METHODS OF STRUCTURE DETERMINATION

- ***Infrared Spectroscopy (IR)*** – Triggering molecular vibrations through irradiation with infrared light. Provides mostly information about the presence or absence of certain functional groups.
- ***Nuclear Magnetic Resonance (NMR)*** – Excitation of the nucleus of atoms through radiofrequency irradiation. Provides extensive information about molecular structure and atom connectivity.
- ***Mass spectrometry (MS)*** – Bombardment of the sample with electrons and detection of resulting molecular fragments. Provides information about molecular mass and atom connectivity.
- ***Ultraviolet spectroscopy (UV)*** – Promotion of electrons to higher energy levels through irradiation of the molecule with ultraviolet light. Provides mostly information about the presence of conjugated  $\pi$  systems and the presence of double and triple bonds.

# SPECTROSCOPY - Study of spectral information



Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum.

# SPECTRUM INTERPRETATION PROCESS

1. Recognize a *pattern*.
2. Associate patterns with *physical parameters*.
3. Identify possible meanings, i.e. *propose explanations*.

Once a spectrum is obtained, the main challenge is to extract the information it contains in abstract, or hidden form.

This requires the recognition of certain patterns, the association of these patterns with physical parameters, and the interpretation of these patterns in terms of meaningful and logical explanations.

# ELECTROMAGNETIC SPECTRUM

Most organic spectroscopy uses **electromagnetic energy, or radiation**, as the physical stimulus.

Electromagnetic energy (such as visible light) has no detectable mass component. In other words, it can be referred to as “pure energy.”

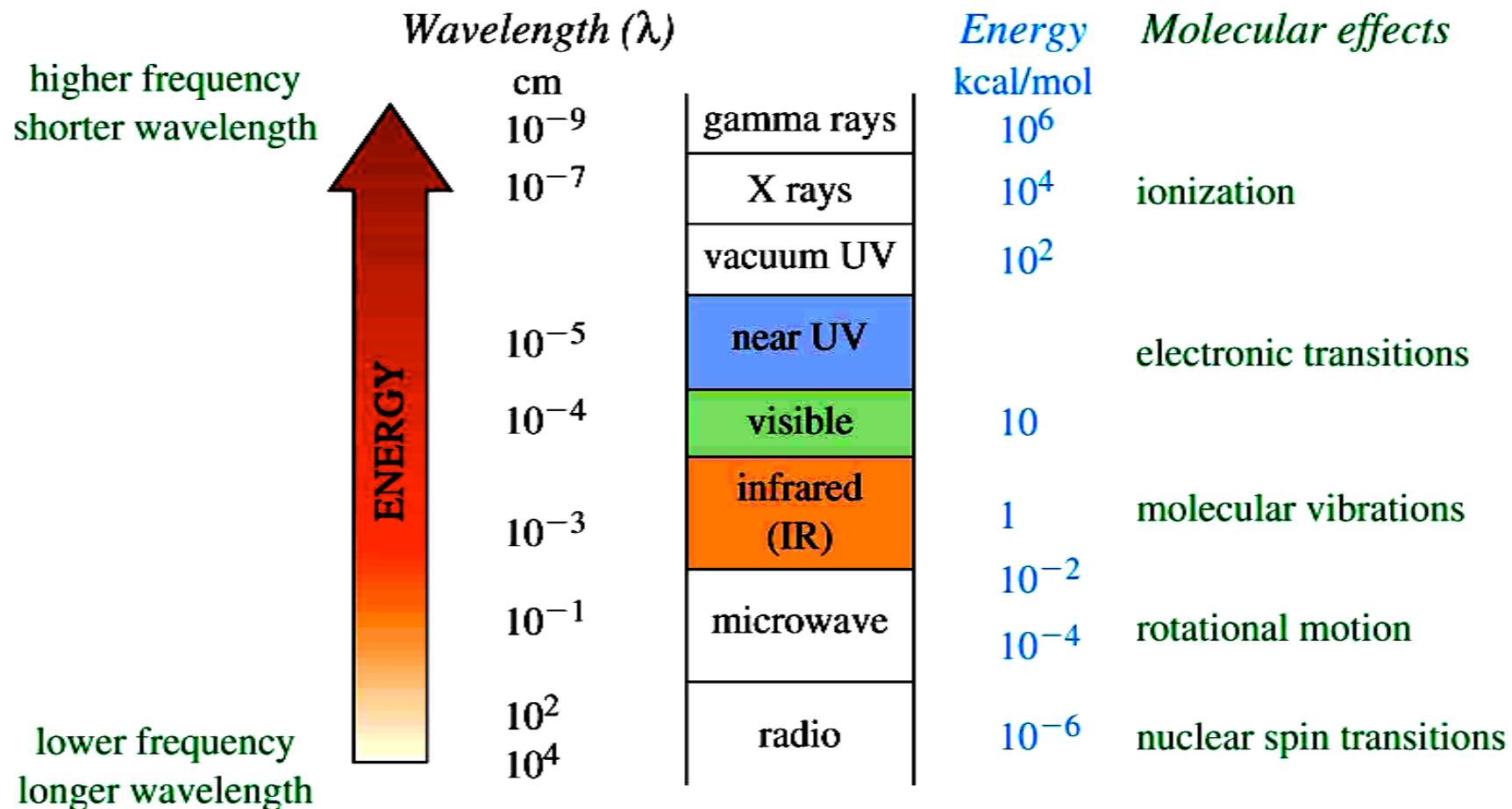
Other types of radiation such as alpha rays, which consist of helium nuclei, have a detectable mass component and therefore cannot be categorized as electromagnetic energy.

The important parameters associated with electromagnetic radiation are:

- **Energy (E)**: Energy is directly proportional to frequency, and inversely proportional to wavelength, as indicated by the equation below.
- **Frequency ( $\mu$ )**
- **Wavelength ( $\lambda$ )**

$$E = h\mu$$

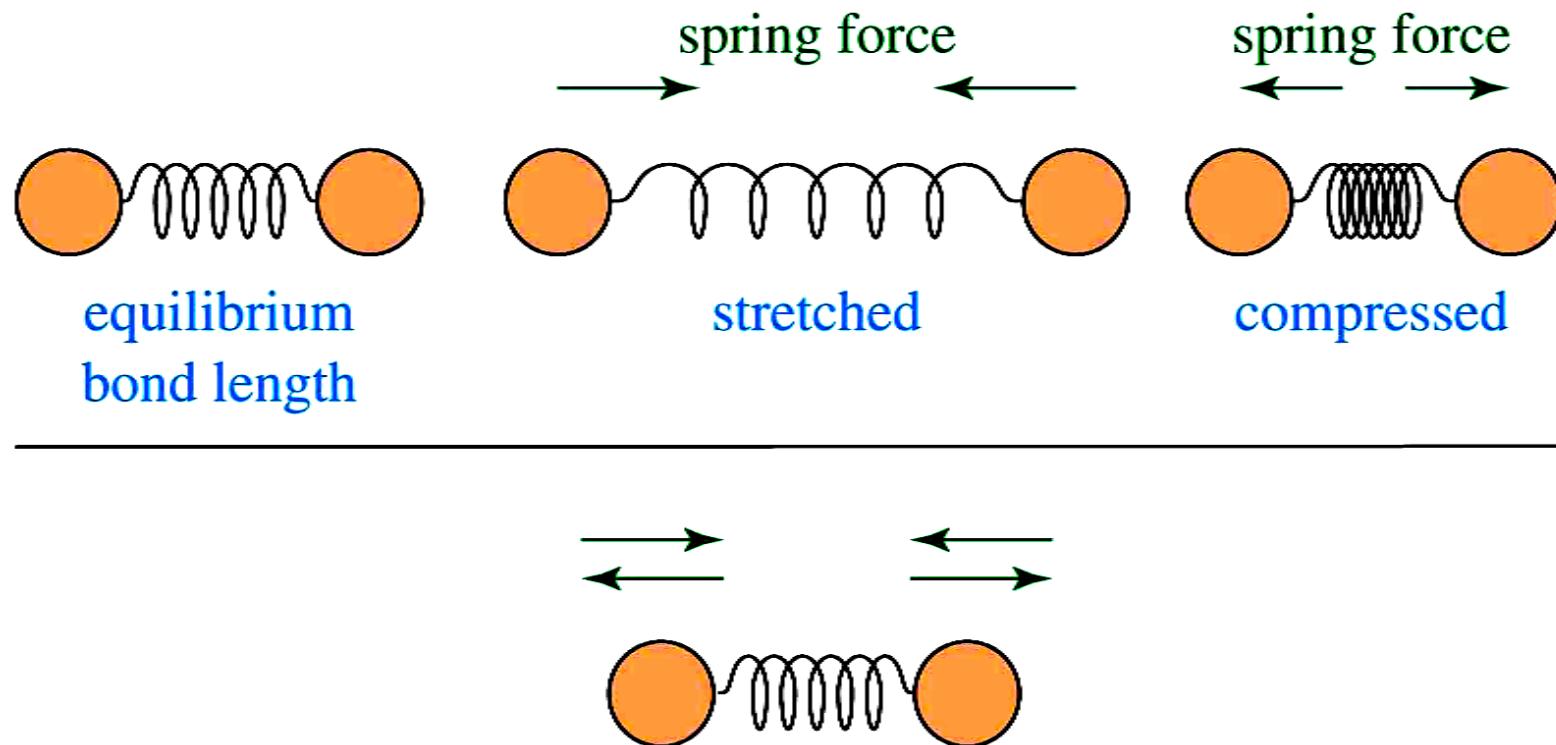
# EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

# Molecular Vibrations

**Specific** bonds respond to (absorb) **specific** frequencies



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

# Molecular Vibrations

Infrared radiation is largely thermal energy.

It induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two masses, or atoms.

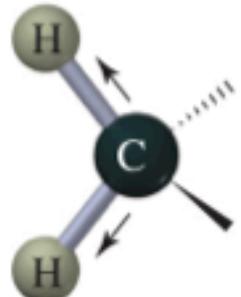
**Specific** bonds respond to (absorb) **specific** frequencies.

If the bond is stretched, a restoring force pulls the two atoms together toward their equilibrium bond length.

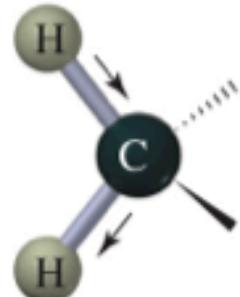
- If the bond is compressed, the restoring force pushes the two atoms apart.
- If the bond is stretched or compressed and then released, the atoms vibrate.

# Stretching and Bending Vibrations

Stretching vibrations

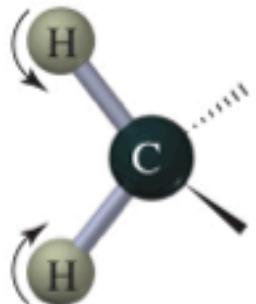


symmetric stretch

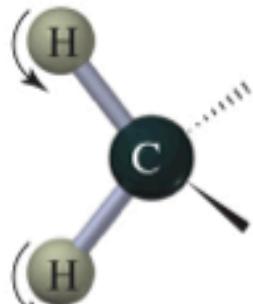


asymmetric stretch

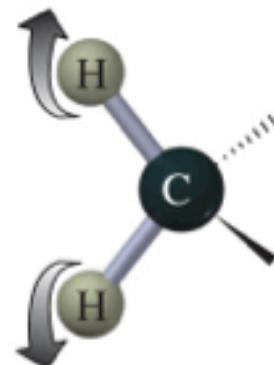
Bending vibrations



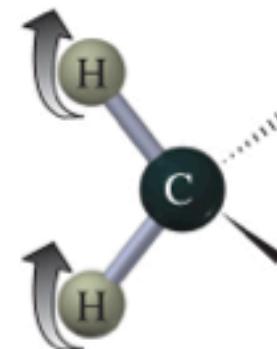
symmetric in-plane  
bend (scissor)



asymmetric in-plane  
bend (rock)



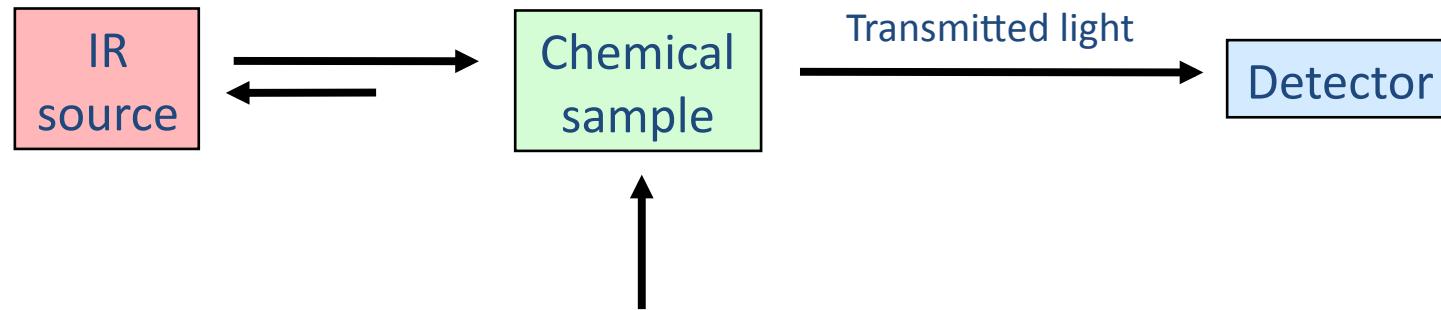
symmetric out-of-plane  
bend (twist)



asymmetric out-of-plane  
bend (wag)

# TRANSMISSION vs. ABSORPTION

When a chemical sample is exposed to the action of **IR LIGHT**, it can **absorb** some frequencies and **transmit** the rest. Some of the light can also be reflected back to the source.

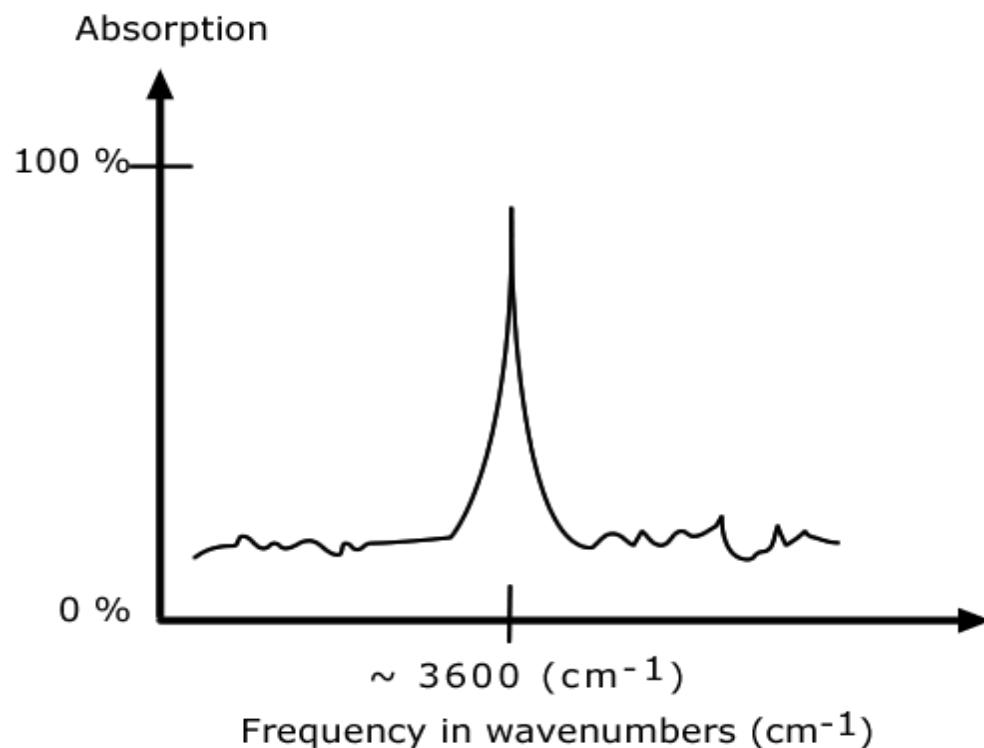


From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies.

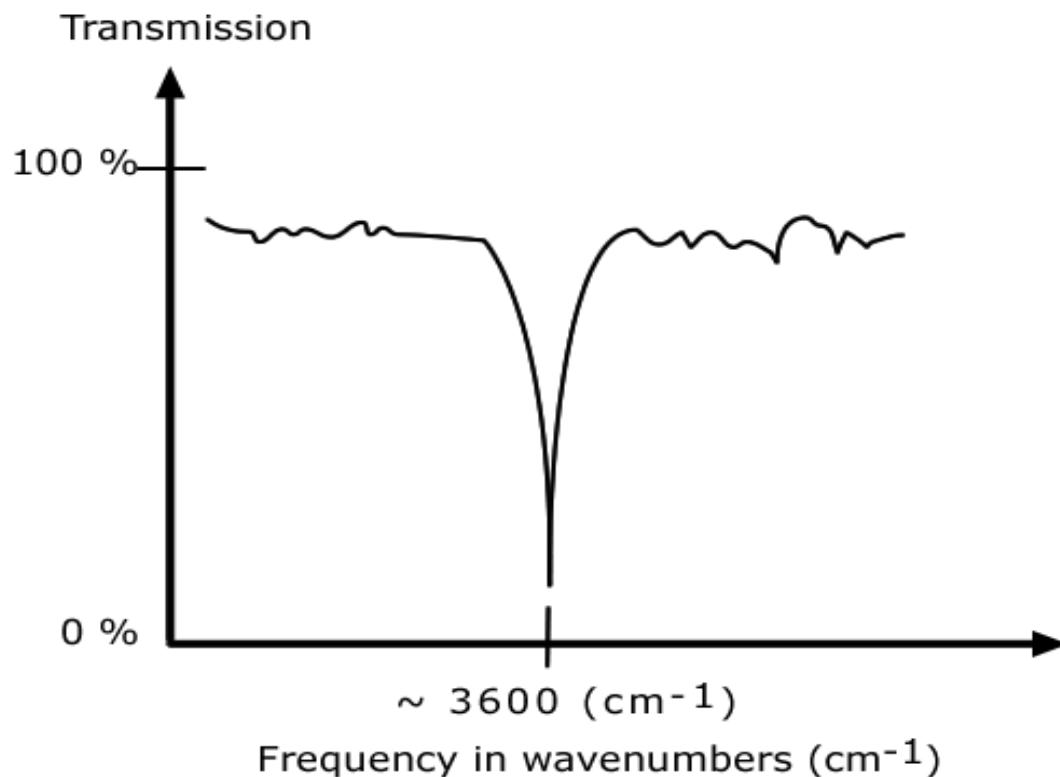
# AN IR SPECTRUM IN ABSORPTION MODE

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the x-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the y-axis in percentage units.



The graph above shows a spectrum in **absorption** mode.

# AN IR SPECTRUM IN TRANSMISSION MODE



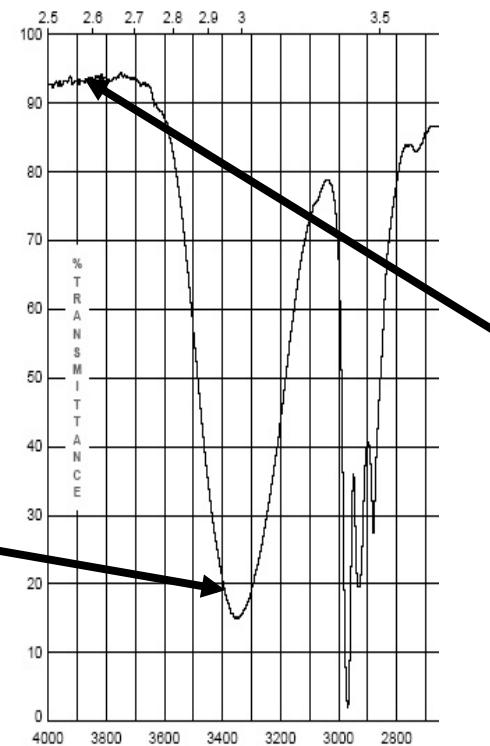
The graph above shows a spectrum in **transmission** mode.  
This is the most commonly used representation and the one found in most chemistry and spectroscopy books. Therefore we will use this representation.

# IR SPECTRUM

Each stretching and bending vibration occurs with a characteristic frequency as the atoms and charges involved are different for different bonds

The y-axis on an IR spectrum is in units of % transmittance

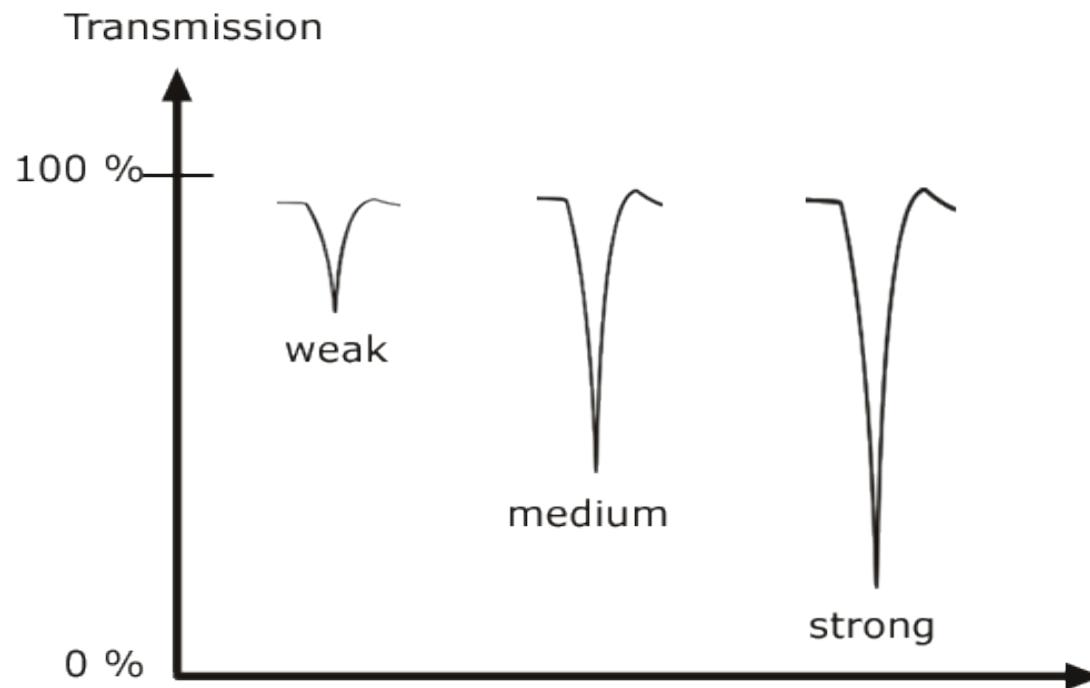
In regions where the EM field of an osc. bond interacts with IR light of the same  $\nu$  – transmittance is low (light is absorbed)



In regions where no osc. bond is interacting with IR light, transmittance nears 100%

# CLASSIFICATION OF IR BANDS

IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.



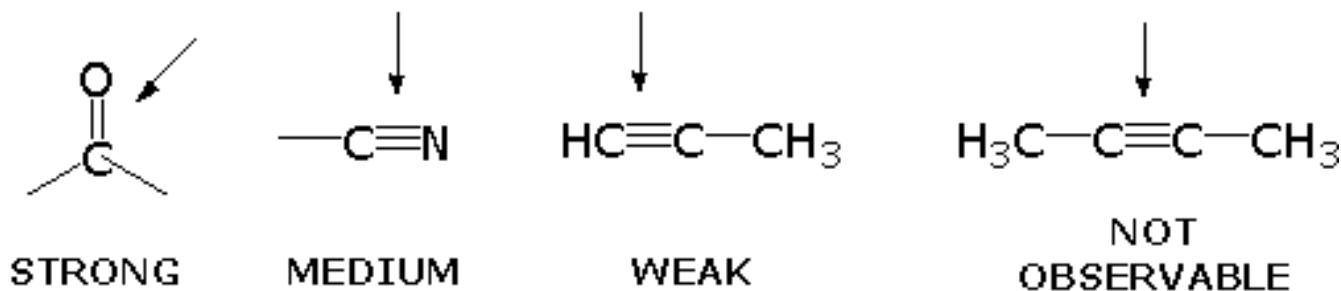
# INFRARED ACTIVE BONDS

Not all covalent bonds display bands in the IR spectrum.

**Only polar bonds do so. These are referred to as IR active.**

The intensity of the bands depends on the magnitude of the **dipole moment** associated with the bond in question:

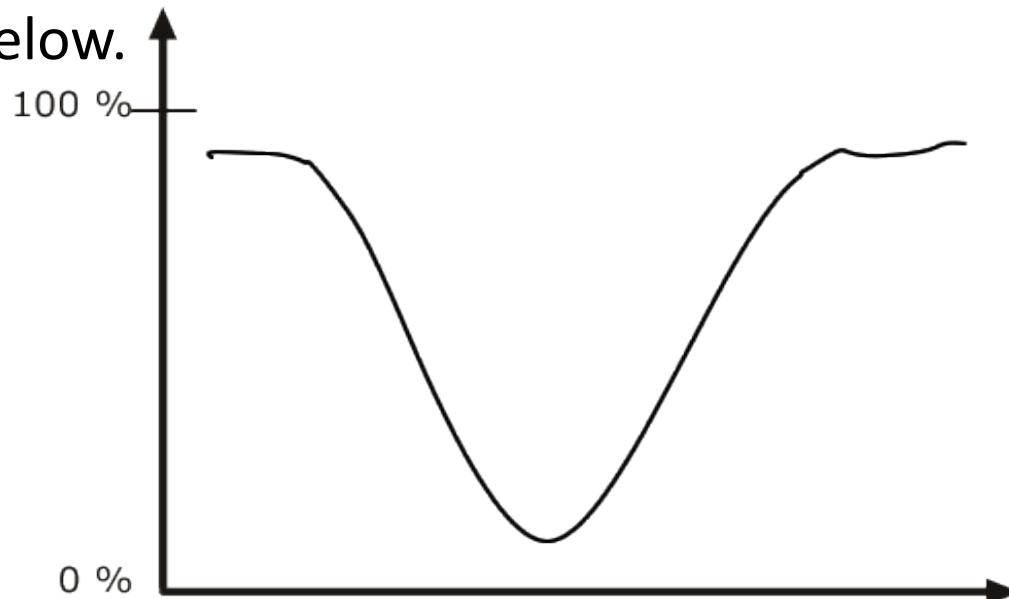
- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.



# INFRARED BAND SHAPES

Infrared band shapes come in various forms. Two of the most common are **narrow** and **broad**. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.



# IR SPECTROSCOPY

- Where a particular bond absorbs in the IR depends on bond strength and atom mass.
- Stronger bonds vibrate at a higher frequency, so they absorb at higher wavenumbers.
- Bonds with lighter atoms vibrate at higher frequency, so they absorb at higher wavenumbers.
- Bonds can be thought of as springs with weights on each end.
- The strength of the spring is analogous to the bond strength, and the mass of the weights is analogous to atomic mass.
- For two springs with the same weight on each end, the stronger spring vibrates at a higher frequency.
- For two springs of the same strength, springs with lighter weights vibrate at a higher frequency than those with heavier weights.

# IR SPECTROSCOPY

- Hooke's Law describes the relationship of frequency to mass and bond length.

The frequency of bond vibration can be derived from Hooke's law, which describes the motion of a vibrating spring:

Hooke's law

$$\tilde{v} = k \sqrt{\frac{f}{m}}$$

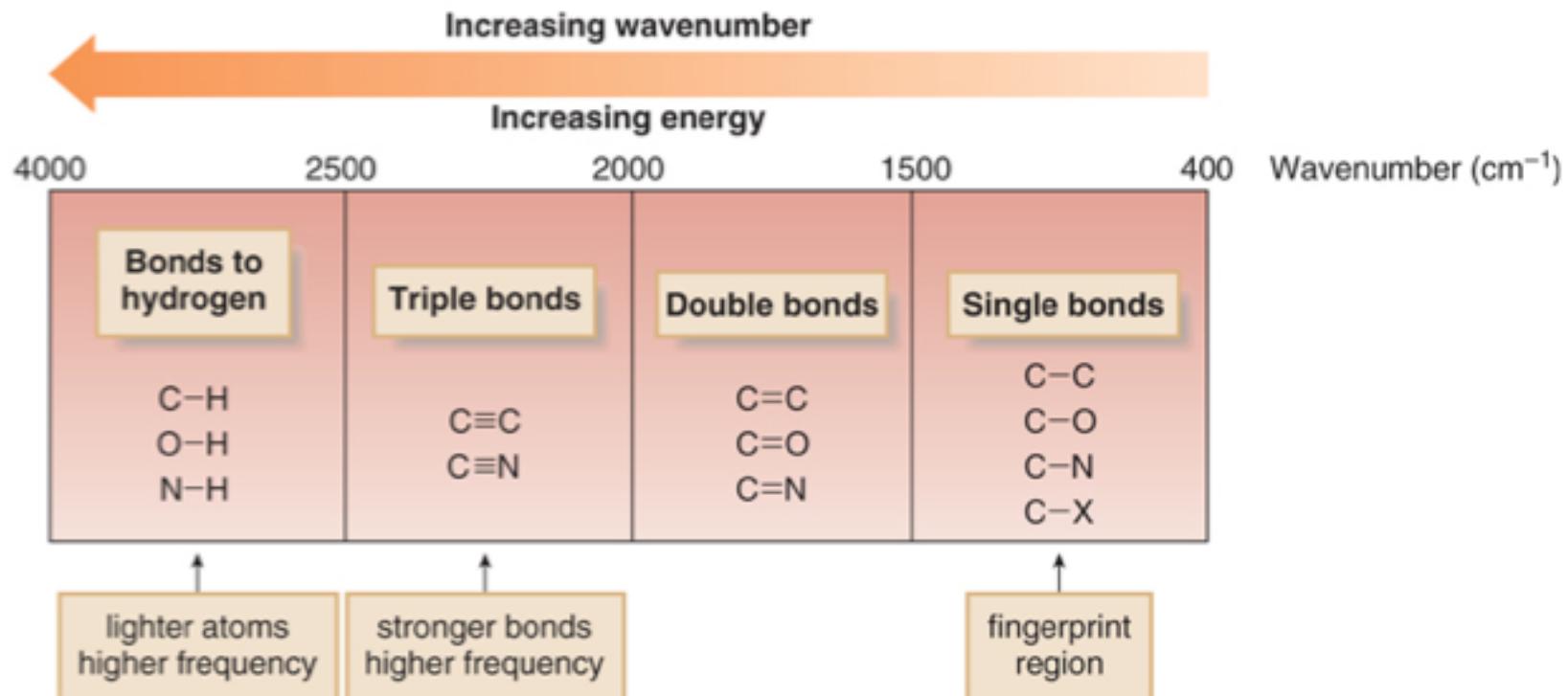
stronger bond  $\rightarrow$  higher frequency  
smaller mass  $\rightarrow$  higher frequency

$f$  = force constant  
 $m$  = mass  
 $k$  = constant

- The force constant ( $f$ ) is the strength of the bond (or spring). The larger the value of  $f$ , the stronger the bond, and the higher the  $\tilde{v}$  of vibration.
- The mass ( $m$ ) is the mass of atoms (or weights). The smaller the value of  $m$ , the higher the  $\tilde{v}$  of vibration.

# IR ABSORPTION RANGE

The four primary regions of the IR spectrum



# INFORMATION OBTAINED FROM IR SPECTRA

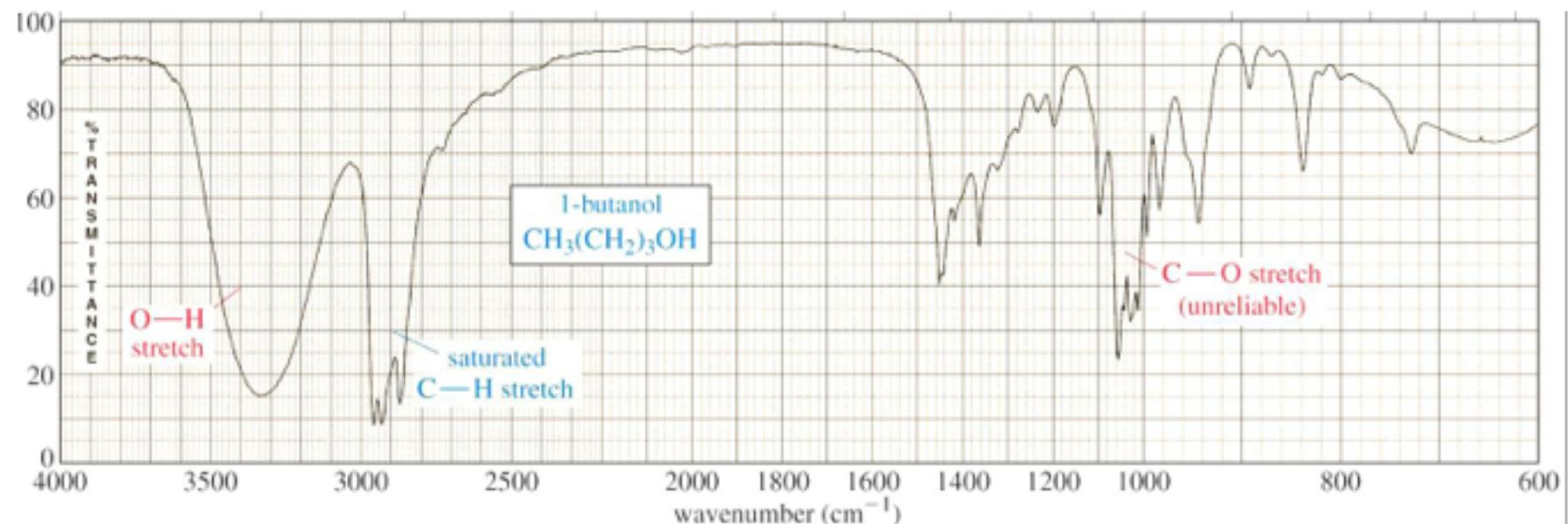
- IR is most useful in providing information about the presence or absence of specific **functional groups**.
- IR can provide a **molecular fingerprint** that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
- IR provides information on molecular fragments, specifically functional groups.
- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

# IR ABSORPTION RANGE

- The typical IR absorption range for covalent bonds is **600 - 4000 cm<sup>-1</sup>**. The graph shows the regions of the spectrum where the following types of bonds normally absorb.
- Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm<sup>-1</sup>** range is called the **fingerprint region**.
- This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm<sup>-1</sup>.

# THE FINGERPRINT REGION

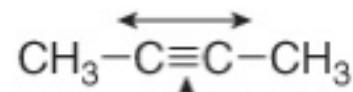
Functional Group Region      Fingerprint Region



# IR SPECTROSCOPY

- For a bond to absorb in the IR, there must be a change in dipole moment during the vibration.
- Symmetrical nonpolar bonds do not absorb in the IR. This type of vibration is said to be IR inactive.

Stretching along the bond axis  
does not change the dipole moment.

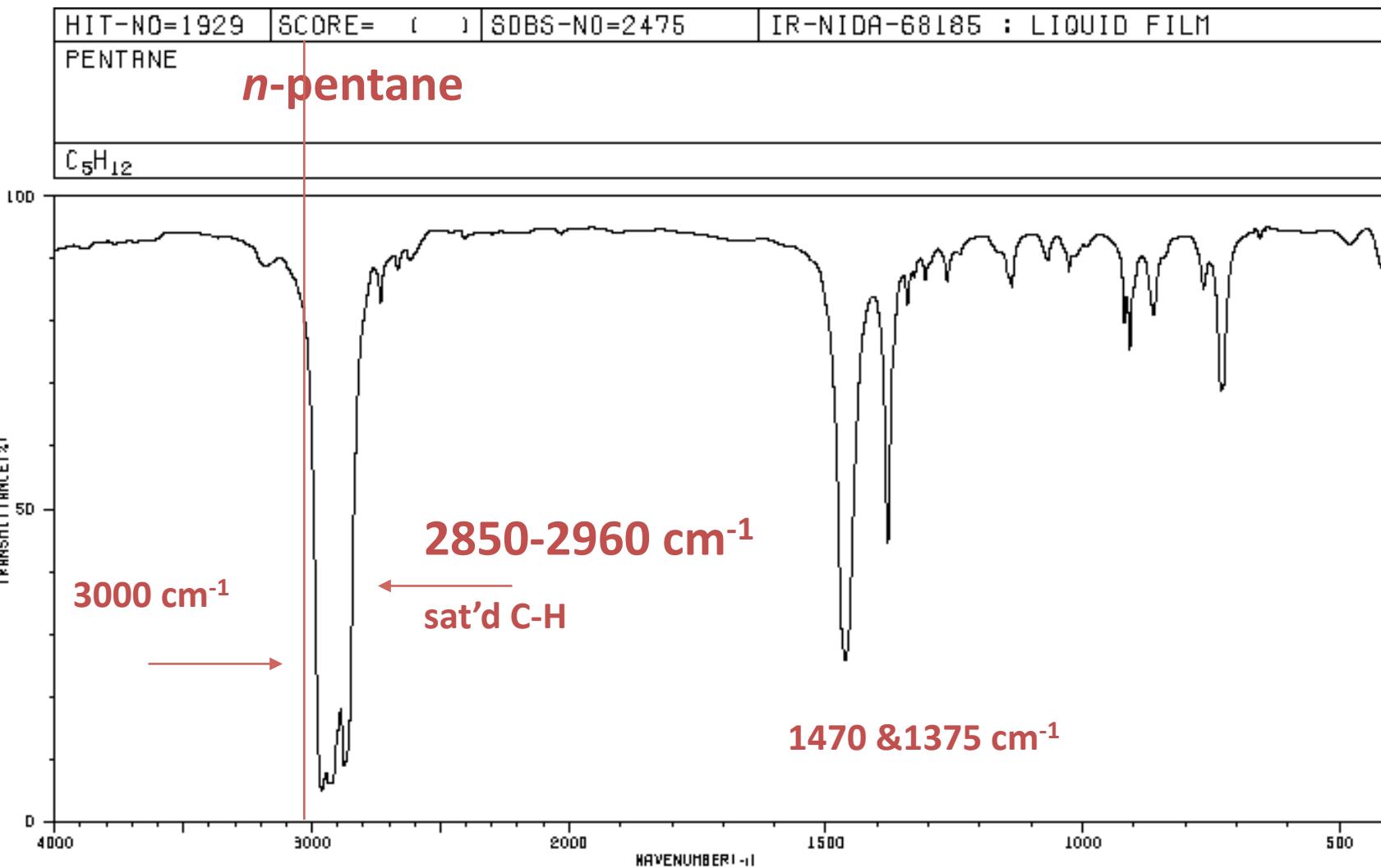


nonpolar bond  
IR inactive

# IR SPECTROSCOPY of Alkanes

**Alkanes** – combination of C-C and C-H bonds

C-H	2850-2960 cm <sup>-1</sup> (stretches), ~3000 cm <sup>-1</sup>
C-C	1350-1470 cm <sup>-1</sup>
CH <sub>2</sub> -CH <sub>2</sub>	1450-1470 cm <sup>-1</sup>
CH <sub>2</sub> -CH <sub>3</sub>	1360-1390 cm <sup>-1</sup>
CH <sub>3</sub>	1450 cm <sup>-1</sup> (asymmetric) and 1375 cm <sup>-1</sup> (symmetric)
(CH <sub>3</sub> ) <sub>2</sub> CH	1380 and 1370 cm <sup>-1</sup>
(CH <sub>3</sub> ) <sub>3</sub> C	1395 (medium) and 1370 (strong) cm <sup>-1</sup>

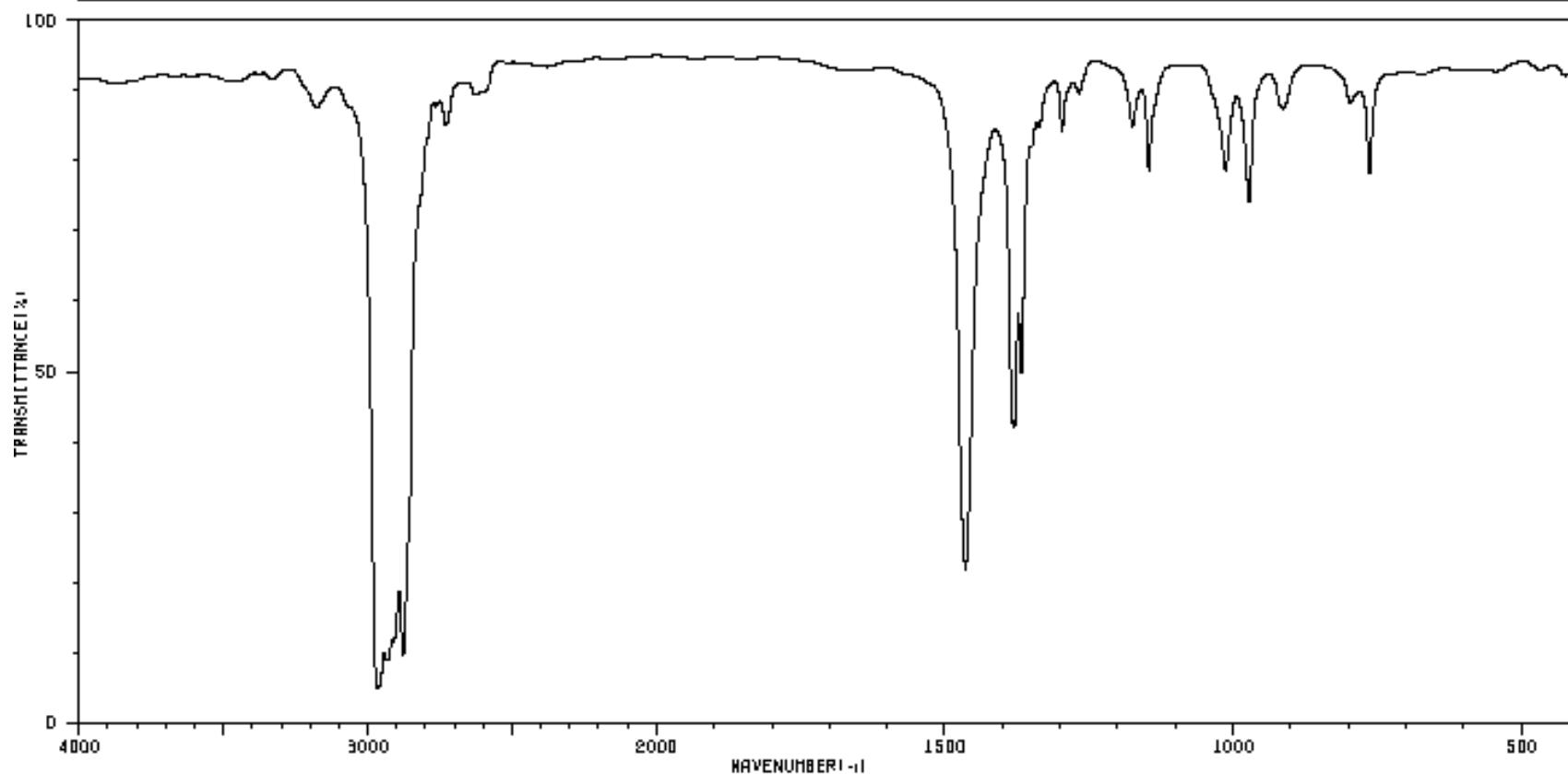


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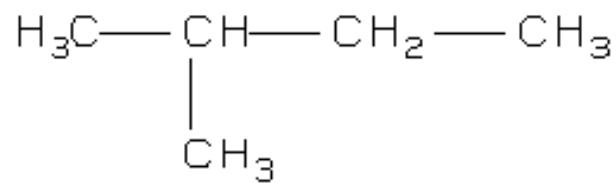
ISOPENTANE

## 2-methylbutane (isopentane)

C<sub>5</sub>H<sub>12</sub>



3176	84	1464	21	1013	77
2964	4	1380	41	972	70
2953	8	1368	47	913	84
2878	9	1297	81	797	84
2733	81	1268	86	764	74
2627	86	1175	81		
2604	86	1147	77		

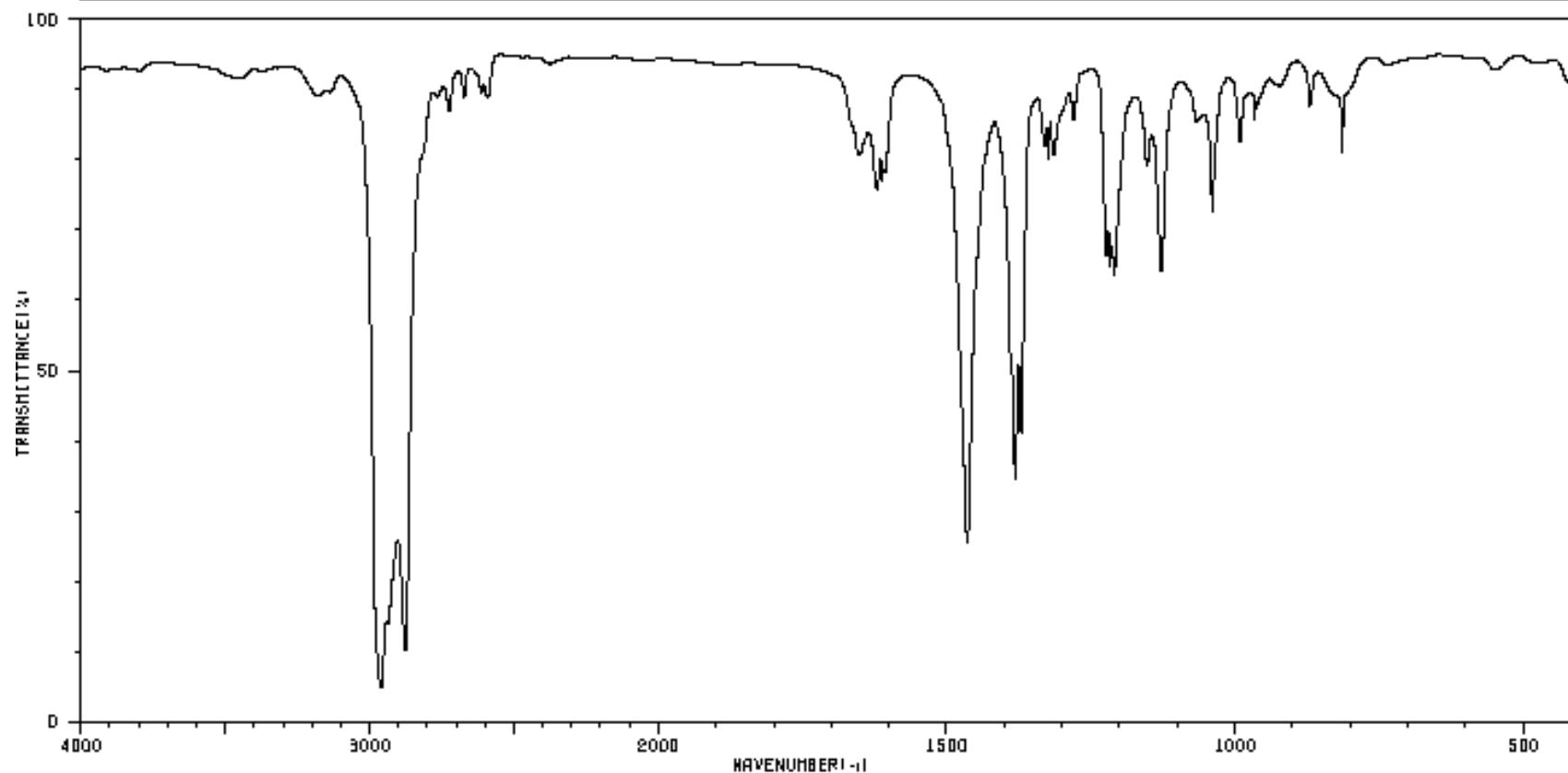


HIT-NO=1104 SCORE= ( ) SDBS-NO=654 IR-NIDA-02888 : LIQUID FILM

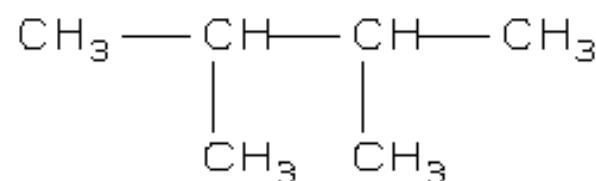
2,3-DIMETHYLBUTANE

## 2,3-dimethylbutane

C<sub>6</sub>H<sub>14</sub>



3176	86	2691	86	1381	33	1218	62	960	84
2959	4	1651	77	1371	39	1209	60	870	84
2938	13	1621	72	1330	79	1153	77	823	66
2876	9	1613	74	1323	77	1128	62	814	79
2722	84	1607	74	1315	77	1039	70		
2673	86	1454	24	1280	81	991	79		
2614	86	1389	48	1223	64	966	81		

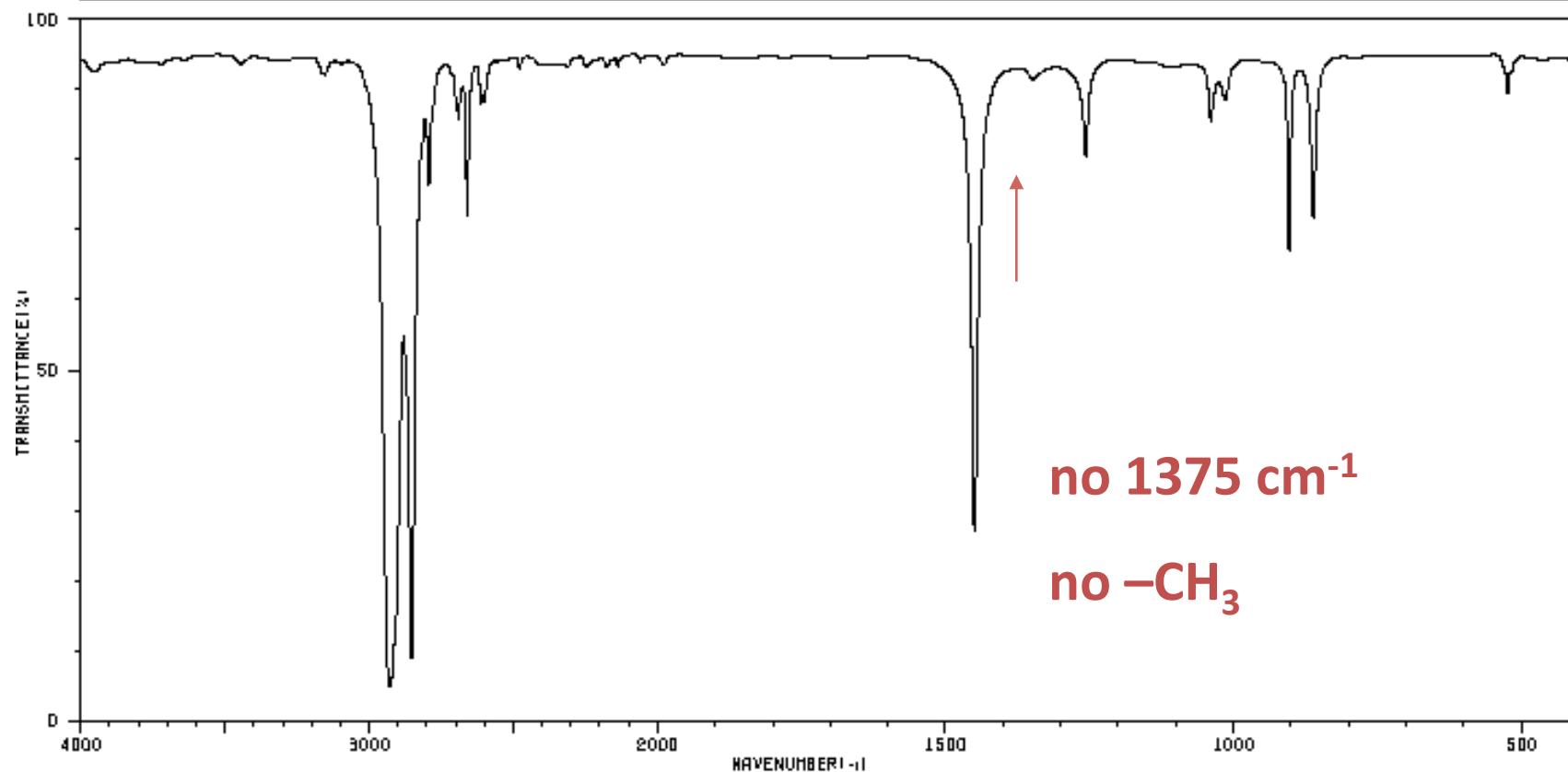


HIT-NO=1236 SCORE= ( ) SDBS-NO=897 IR-NIDA-05221 : LIQUID FILM

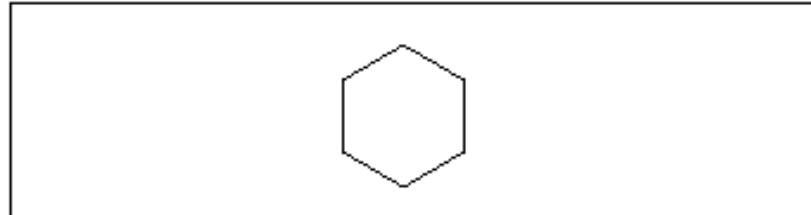
CYCLOHEXANE

## cyclohexane

C<sub>6</sub>H<sub>12</sub>



2928	4	1460	26
2853	8	1257	77
2794	72	1039	81
2690	81	1016	84
2661	70	904	64
2613	84	862	68
2699	84	624	86



# IR SPECTROSCOPY of Alkenes

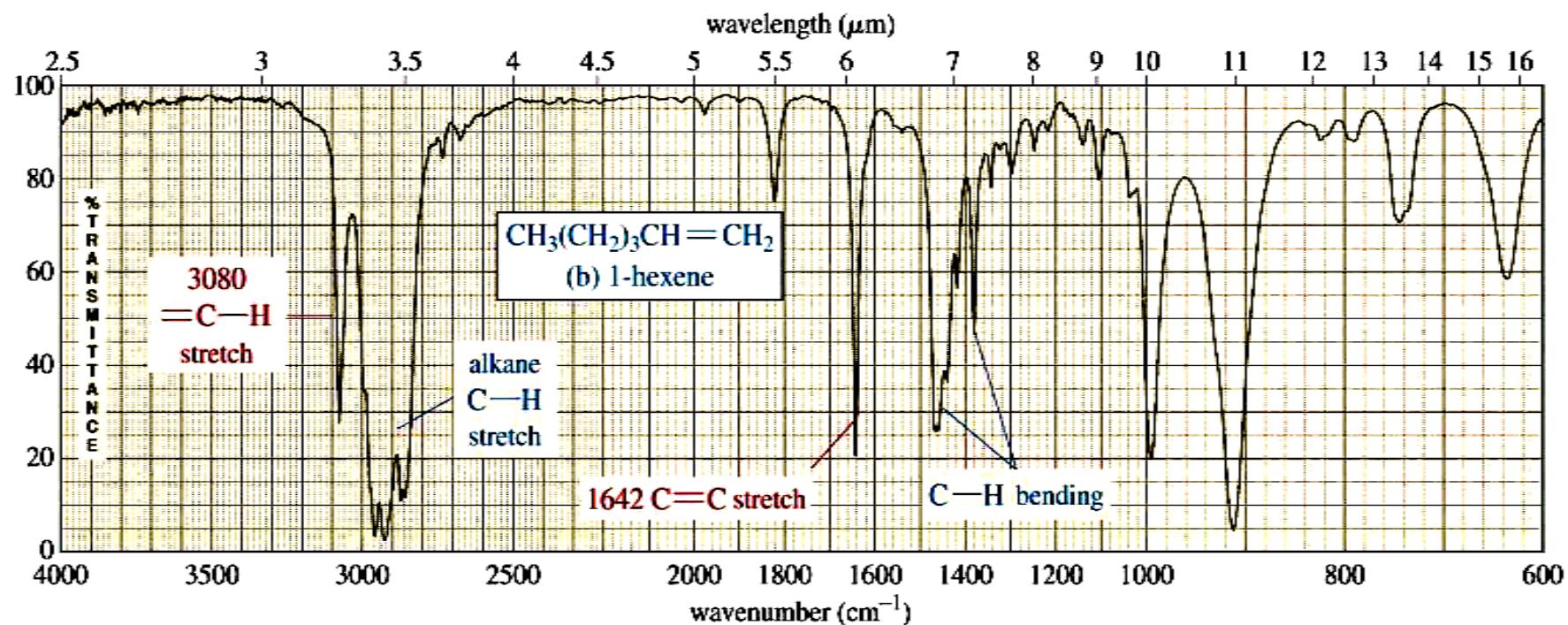
C=C                            1680 – 1640 cm<sup>-1</sup>  
=C-H (stretch)                3080 – 3020 cm<sup>-1</sup> (~3100 cm<sup>-1</sup>)

=C-H (oop bending)

Monosubstituted	920 -910 (s) and 1000 – 990 (s) cm <sup>-1</sup>
1,1-Disubstituted	880 – 900 (s) cm <sup>-1</sup>
cis-Disubstituted	730 – 675 (s) cm <sup>-1</sup>
trans-Disubstituted	975 – 965 (s) cm <sup>-1</sup>
Trisubstituted	810 – 780 (m) cm <sup>-1</sup>
Tetrasubstituted	

# IR SPECTRUM OF ALKENES

Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm<sup>-1</sup>**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm<sup>-1</sup>** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm<sup>-1</sup> (see next slide)



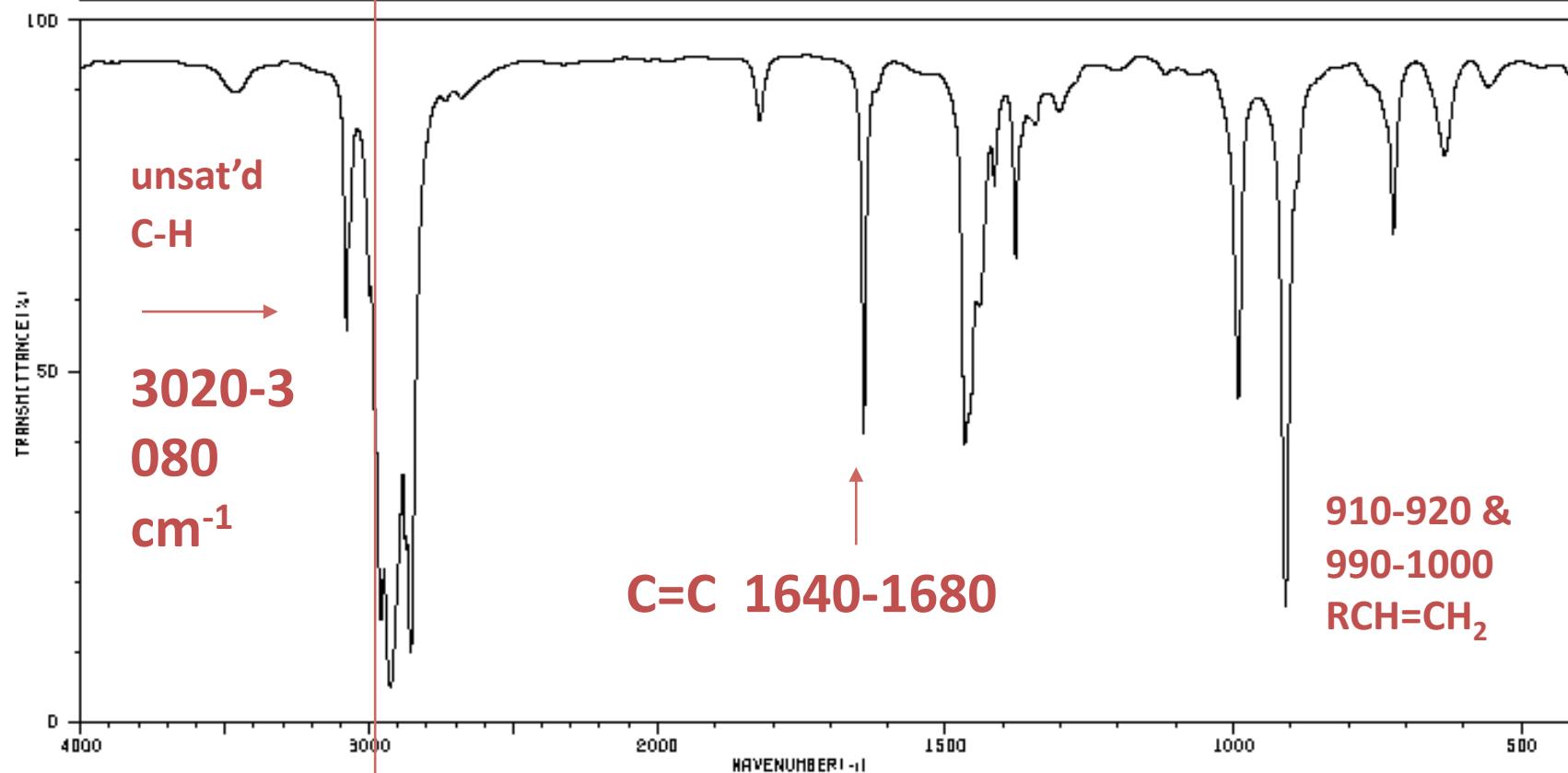
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

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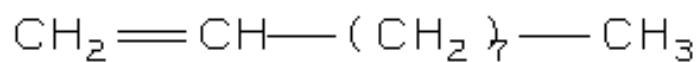
1-DECENE

## 1-decene

C<sub>10</sub>H<sub>20</sub>



3467	86	2874	29	1379	64
3457	86	2856	9	1343	81
3079	53	2678	86	1303	84
3068	68	1822	81	991	44
2998	58	1642	39	910	15
2958	13	1457	38	723	86
2926	4	1416	72	633	77

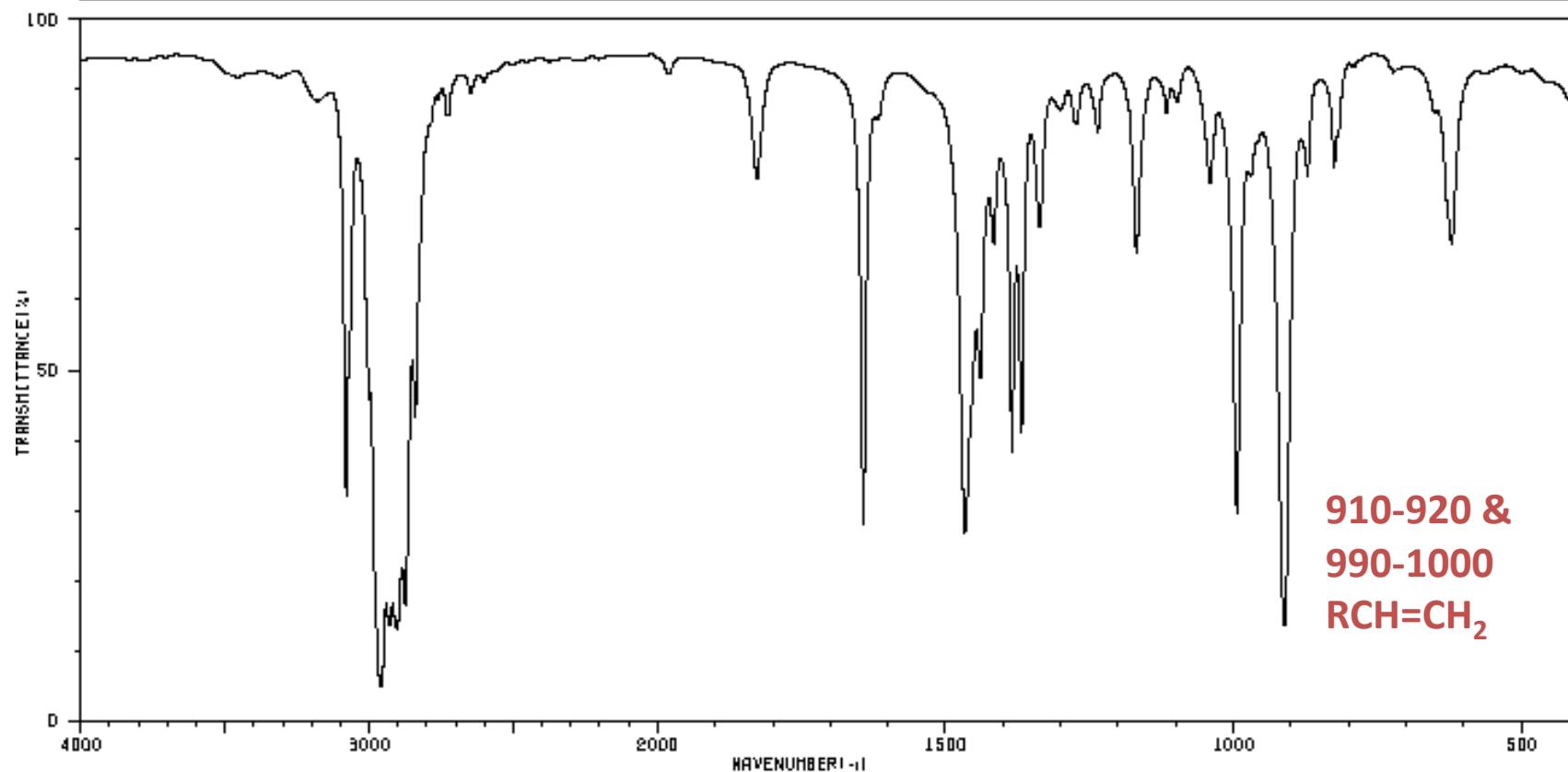


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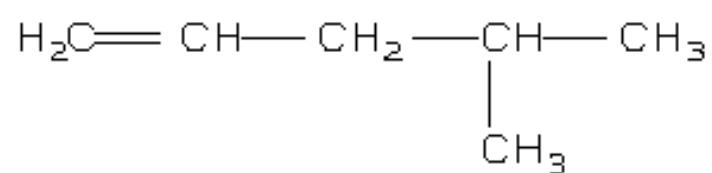
4-METHYL-1-PENTENE

**4-methyl-1-pentene**

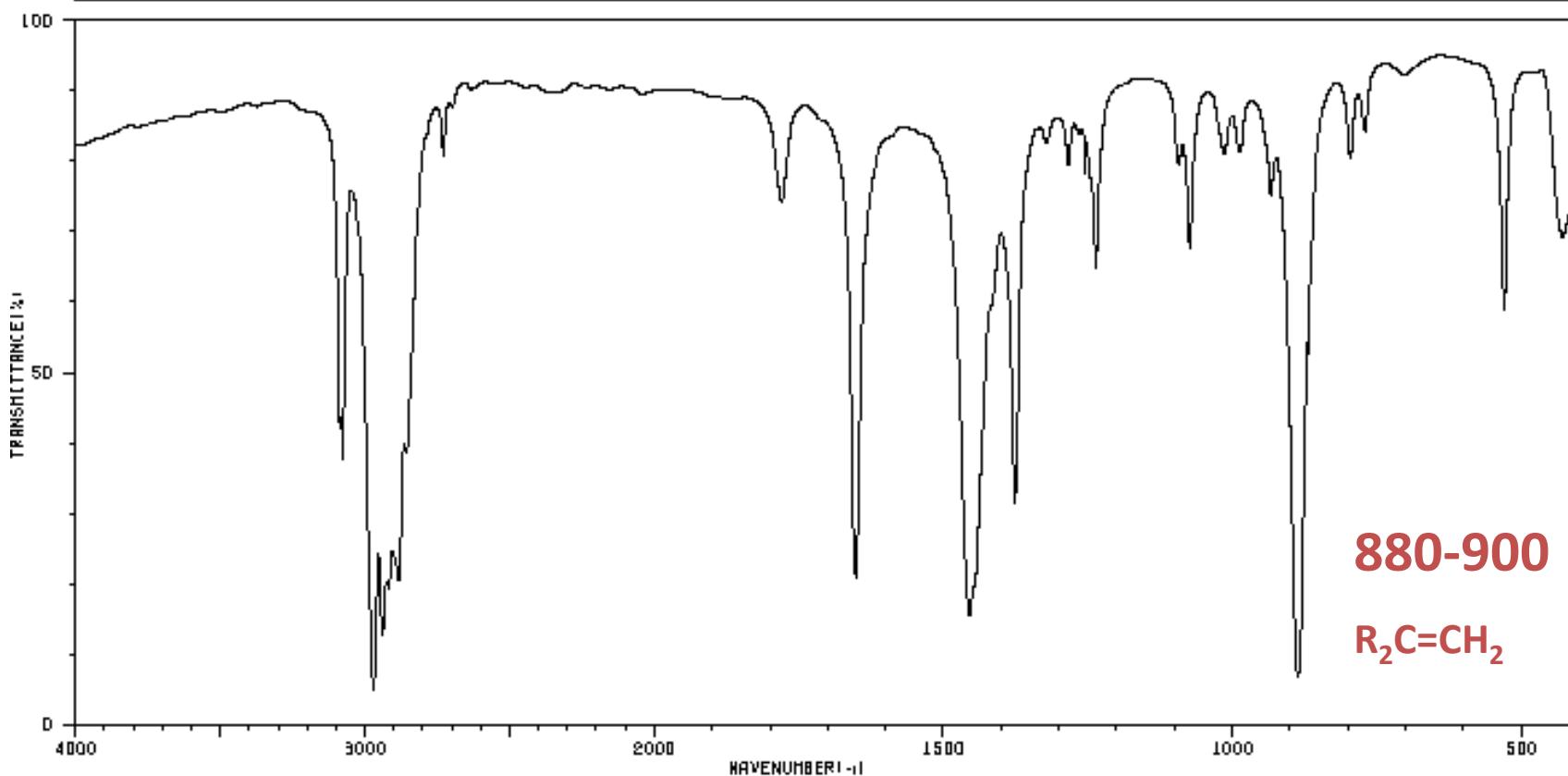
C<sub>6</sub>H<sub>12</sub>



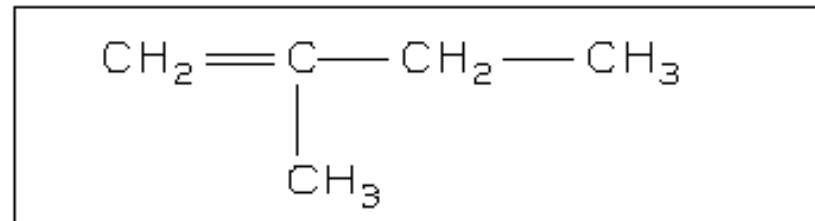
3178	84	2727	84	1386	37	1116	84	622	66
3079	31	2648	86	1368	39	1098	84		
2960	4	1828	74	1337	86	1041	74		
2929	13	1643	26	1300	84	994	28		
2904	12	1467	26	1274	81	911	13		
2874	15	1440	47	1236	81	871	74		
2839	42	1417	66	1169	64	826	77		



HIT-NO=1774	SCORE= ( )	SDBS-NO=2176	IR-NIDA-03075 : LIQUID FILM
2-METHYL-1-BUTENE			
<b>2-methyl-1-butene</b>			
$C_5H_{10}$			

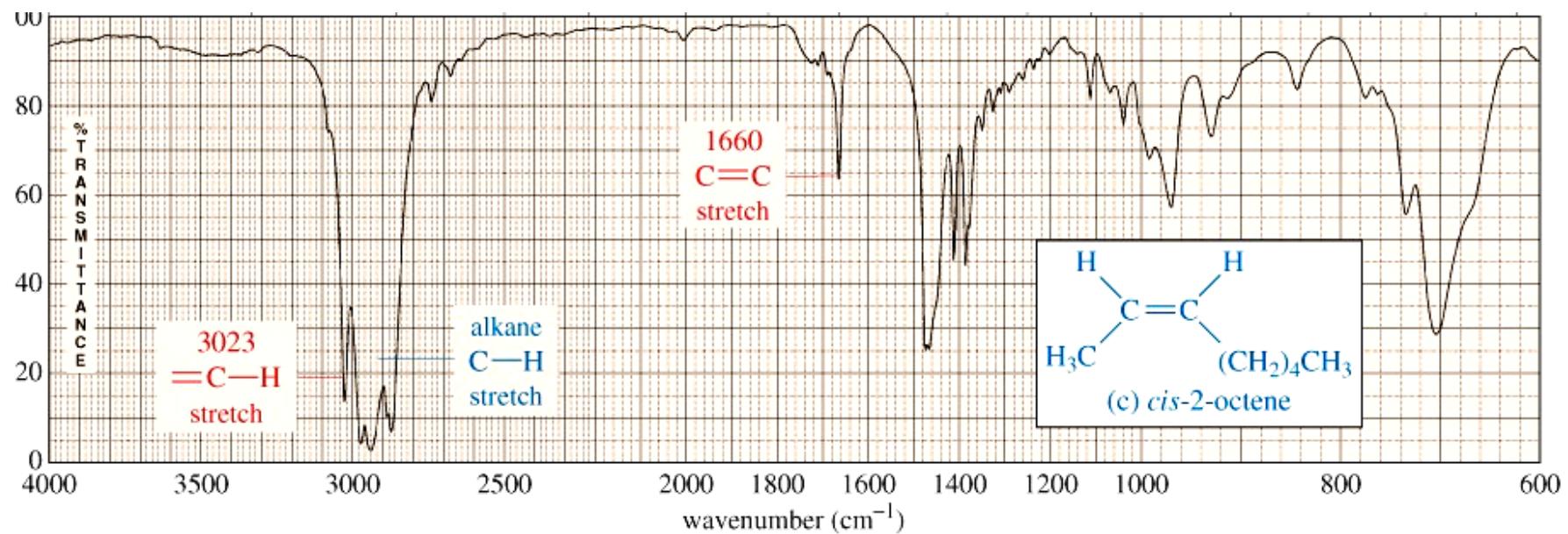


3087	41	2728	77	1266	74	887	6
3077	36	1780	72	1237	62	869	50
2970	4	1651	20	1093	77	796	77
2939	12	1466	14	1074	64	770	81
2919	18	1377	30	1014	79	530	57
2863	20	1322	79	987	79	429	66
2856	37	1284	77	933	72		



# IR SPECTRUM OF ALKENES

This spectrum shows that the band appearing around  $3080\text{ cm}^{-1}$  can be obscured by the broader bands appearing around  $3000\text{ cm}^{-1}$ .

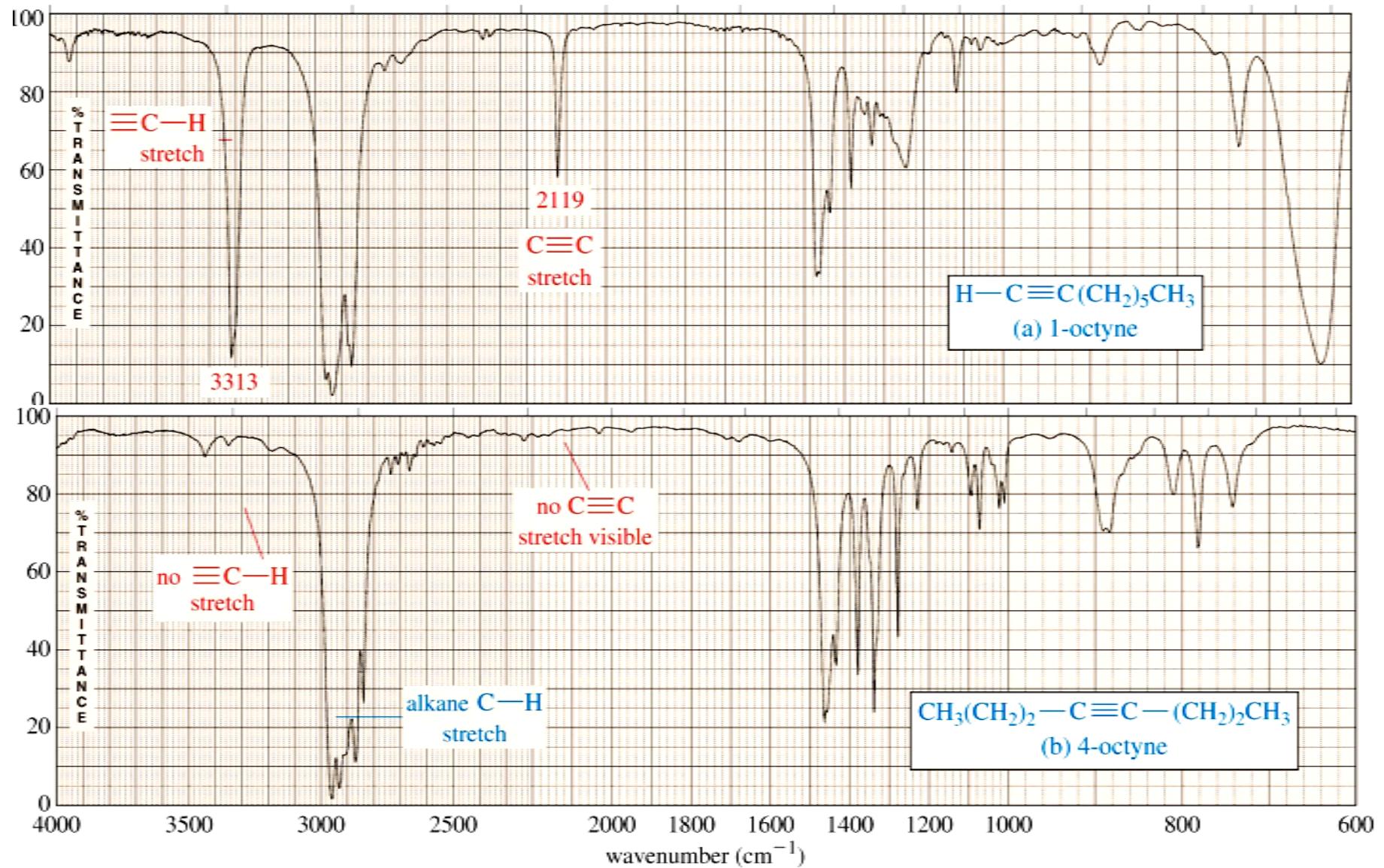


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

# IR SPECTROSCOPY of Alkynes

- Terminal C-H (sp)  $3300 \text{ cm}^{-1}$
- Terminal C-C triple bd  $2250 - 2150 \text{ cm}^{-1}$
- Internal symmetrical C-C triple bond is absent
- Internal asymmetric C-C triple bd  $2250 - 2150 \text{ cm}^{-1}$  is very weak

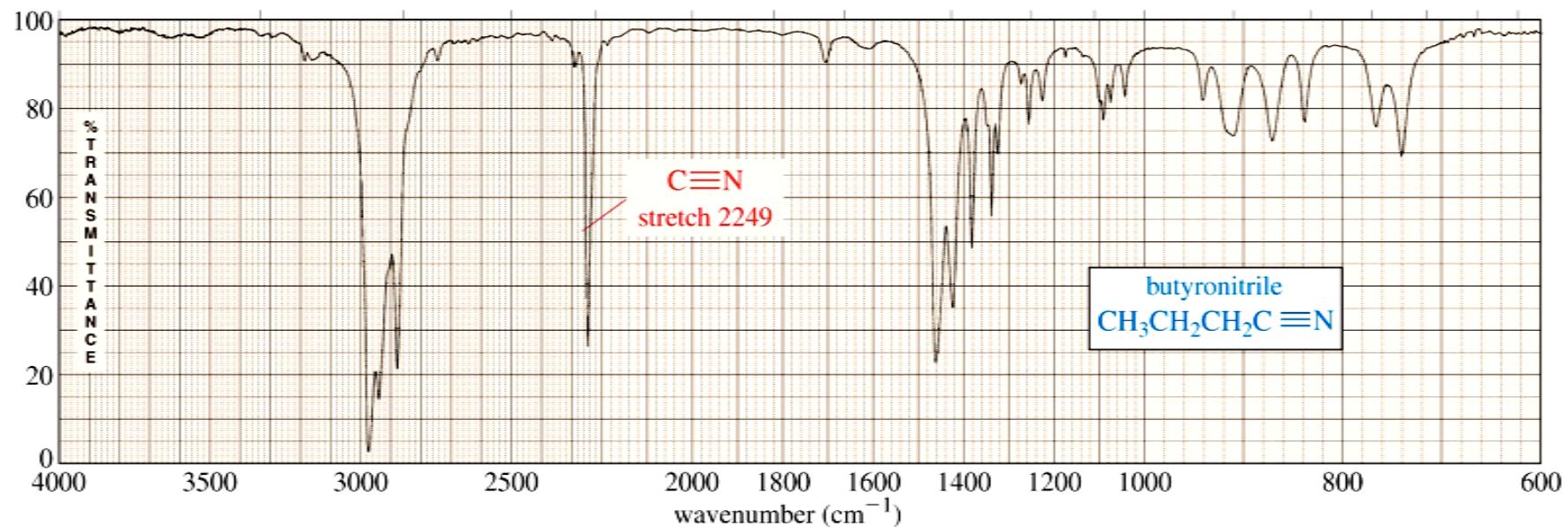
# IR SPECTRUM OF ALKYNES



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

# IR SPECTRUM OF A NITRILE

In a manner very similar to alkynes, nitriles show a prominent band around **2250 cm<sup>-1</sup>** caused by the **CN triple bond**. This band has a sharp, pointed shape just like the alkyne C-C triple bond, but because the CN triple bond is more polar, this band is stronger than in alkynes.



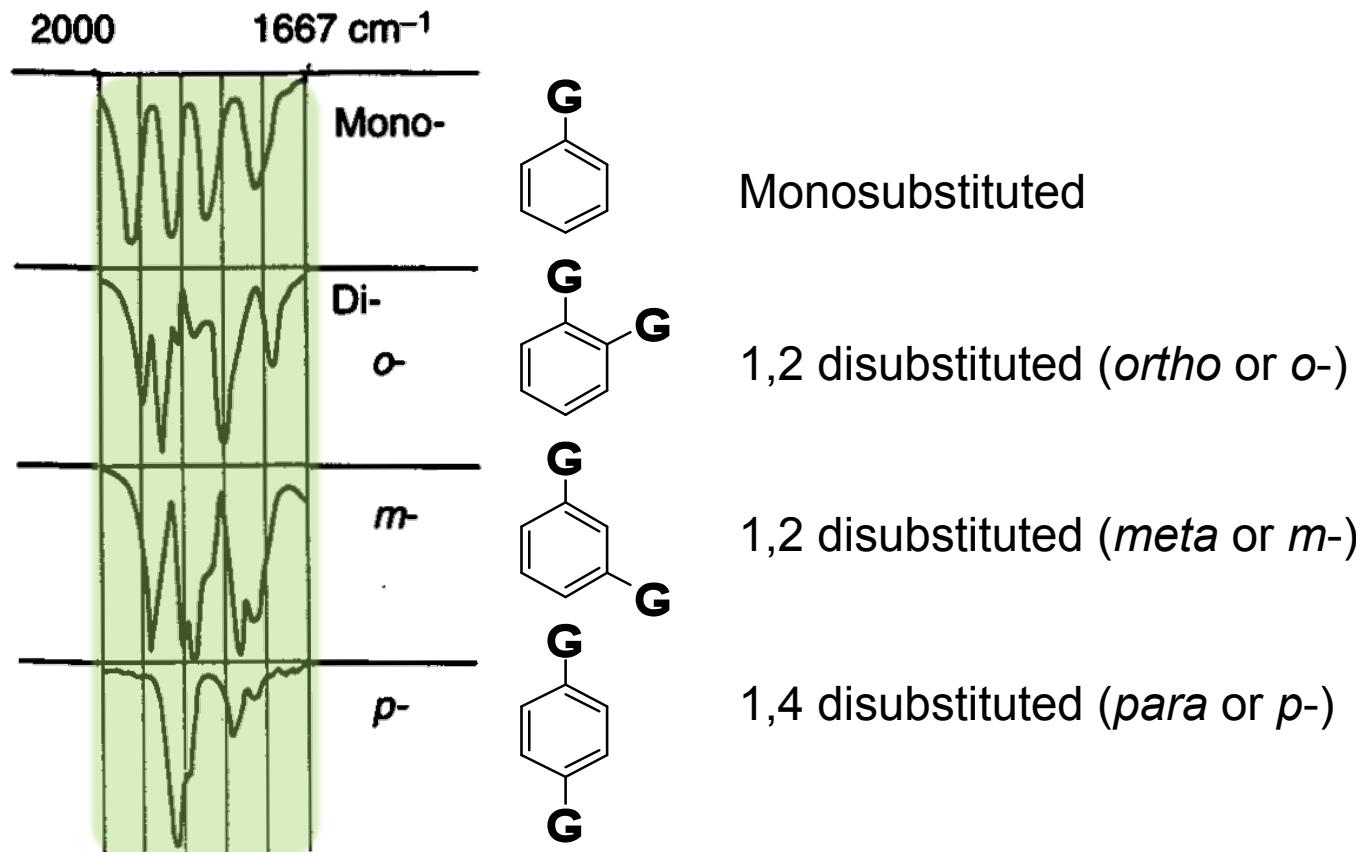
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

# IR SPECTROSCOPY of Arenes

- =C-H stretching            3100 -3000 cm<sup>-1</sup>
- C=C                        1600 and 1500 cm<sup>-1</sup>
- =C-H bending
  - Monosubstituted 770 – 730 and 710 – 690 cm<sup>-1</sup>
  - *o*-substituted      770-735 cm<sup>-1</sup>
  - *m*-substituted      900 -860, 810 – 750 & 725-680 cm<sup>-1</sup>
  - *p*-substituted        840 – 810 cm<sup>-1</sup>
  - 1,2,4-substituted 900 – 860 and 840 – 780 cm<sup>-1</sup>
  - 1,2,3-substituted 780 – 740 and 710 – 680 cm<sup>-1</sup>
  - 1,3,5-substituted 910 -830 and 700 – 675 cm<sup>-1</sup>

## Aromatics

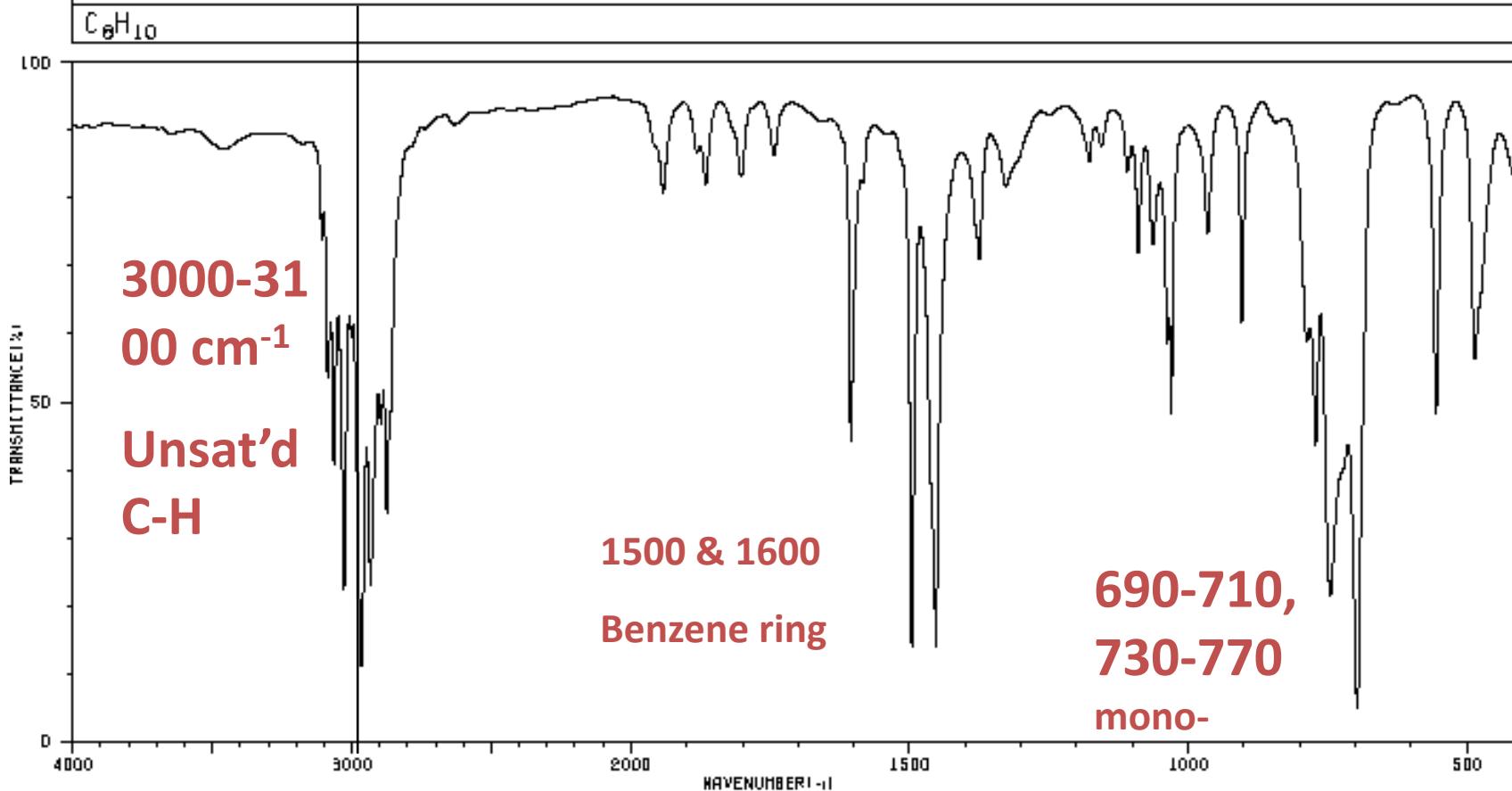
- If the region between 1667-2000 cm<sup>-1</sup> (w) is free of interference (C=O stretching frequency is in this region) a weak grouping of peaks is observed for aromatic systems
- Analysis of this region, called the *overtone of bending* region, can lead to a determination of the substitution pattern on the aromatic ring



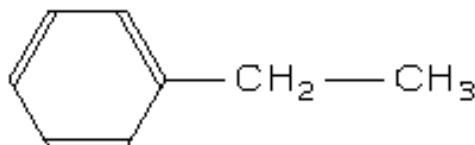
HIT-NO=1402 SCORE= ( ) SDBS-NO=1332 IR-NIDA-05258 : LIQUID FILM

ETHYLBENZENE

## ethylbenzene



3458	84	2933	21	1802	79	1178	81	904	66
3108	70	2896	44	1744	84	1110	81	788	57
3087	52	2875	32	1806	42	1090	70	772	42
3066	39	1966	84	1496	13	1064	70	746	20
3028	21	1942	77	1453	13	1037	57	697	4
3003	57	1881	84	1376	88	1030	46	556	46
2967	10	1866	78	1329	79	966	72	486	63

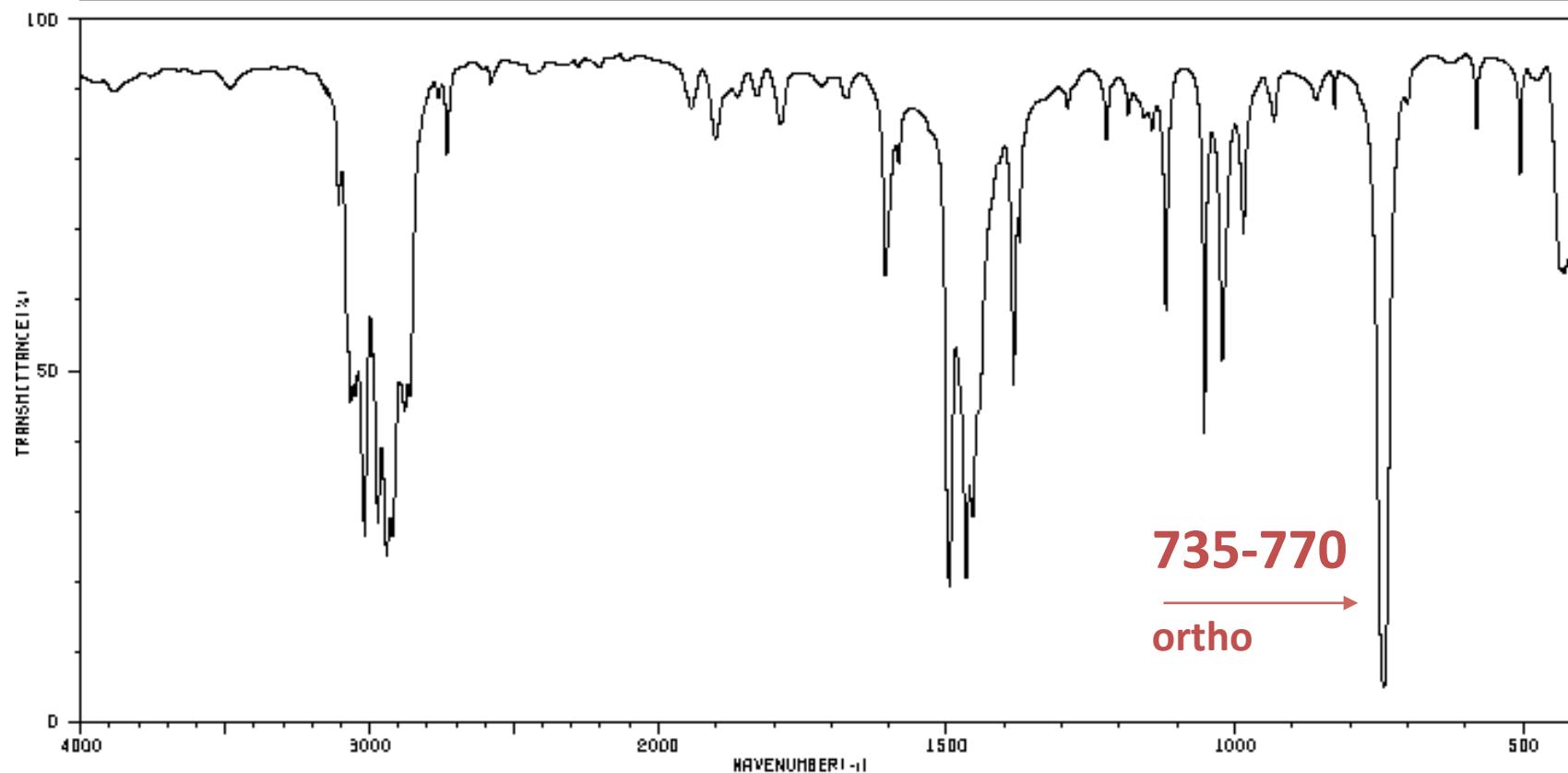


HIT-NO=1272 SCORE= ( ) SDBS-NO=1028 IR-NIDA-21942 : LIQUID FILM

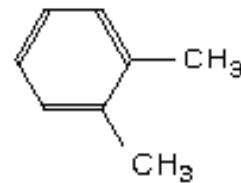
O-XYLENE

***o-xylene***

C<sub>8</sub>H<sub>10</sub>



3108	70	2878	42	1683	77	1223	79	986	66
3066	43	2860	44	1495	18	1186	84	932	81
3050	44	2732	77	1467	20	1157	81	742	4
3018	26	1942	84	1456	27	1146	81	682	81
2971	26	1901	79	1384	46	1120	57	506	74
2940	22	1787	81	1374	86	1053	39	436	52
2921	26	1606	60	1291	84	1022	40	431	62



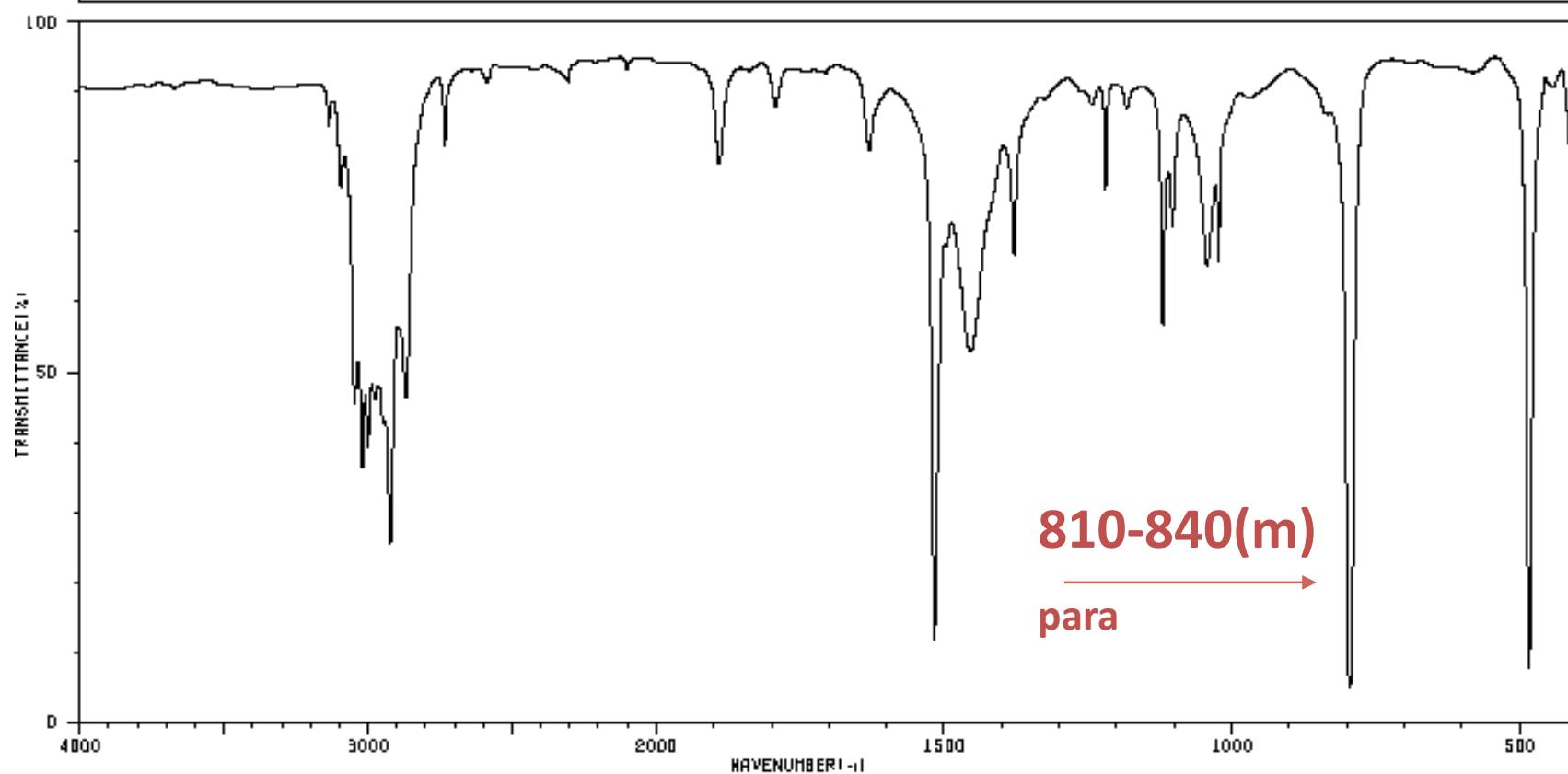
HIT-NO=1238

SCORE= ( )

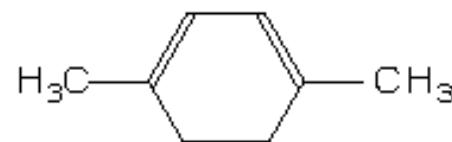
SDBS-NO=899

IR-NIDA-63598 : LIQUID FILM

P-XYLENE

***p-xylene***C<sub>8</sub>H<sub>10</sub>

3136	81	2923	24	1454	60	1043	62
3095	74	2868	44	1378	64	1023	64
3047	43	2733	79	1243	84	795	4
3020	36	1890	77	1220	72	484	7
3000	37	1793	84	1183	84		
2976	44	1630	79	1120	55		
2946	41	1516	11	1103	68		

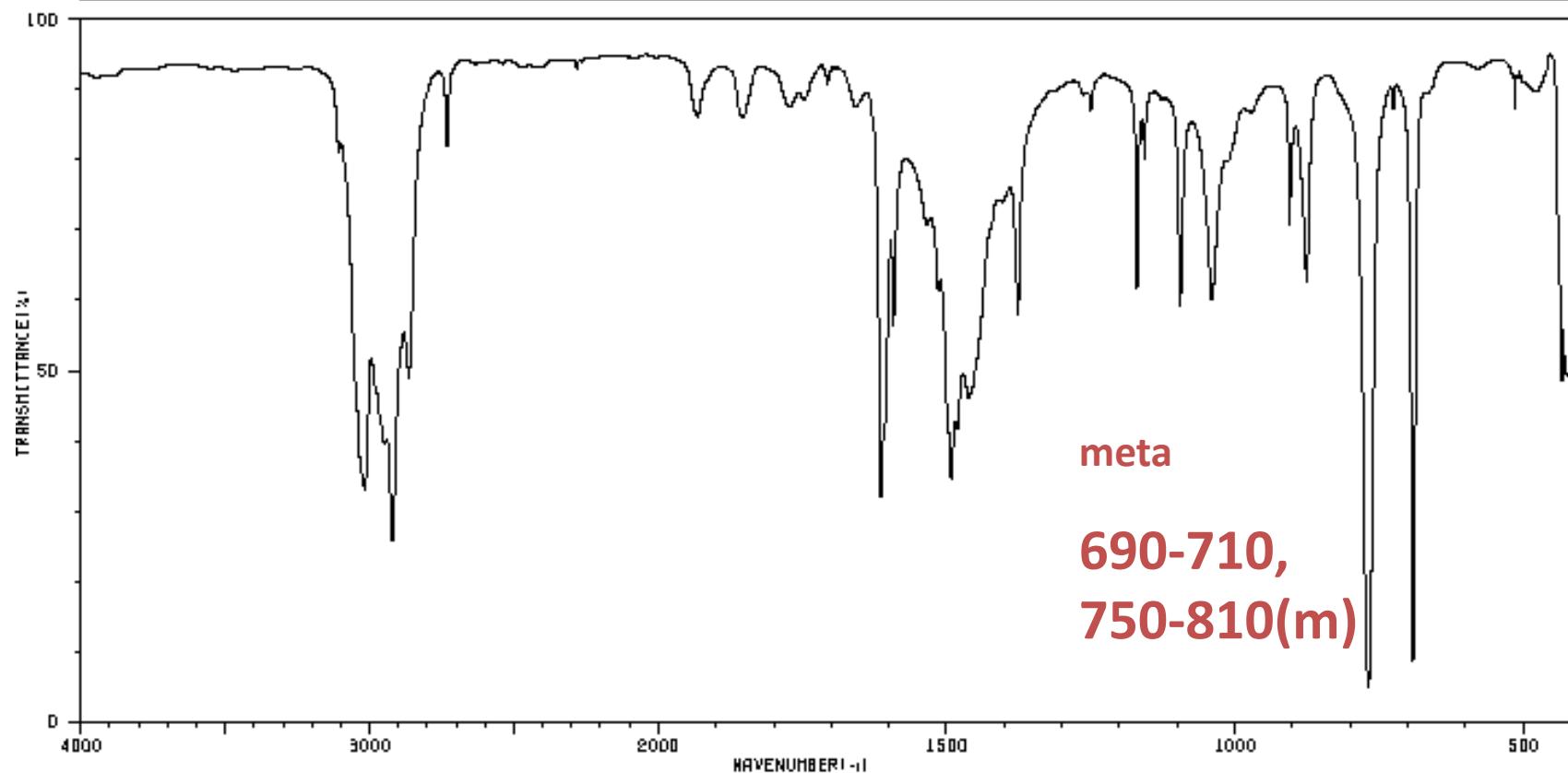


HIT-NO=1275 SCORE= ( ) SDBS-NO=1032 IR-NIDA-63601 : LIQUID FILM

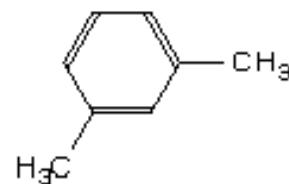
M-XYLENE

***m-xylene***

C<sub>8</sub>H<sub>10</sub>



3106	79	1864	84	1492	33	1170	68	726	84
3016	32	1772	84	1482	39	1157	77	691	8
2948	37	1754	84	1462	44	1095	57	515	64
2921	24	1668	84	1376	66	1040	67	483	86
2864	47	1614	31	1263	86	905	68	478	86
2752	79	1592	59	1256	86	876	60	434	46
1932	84	1616	68	1260	84	769	4		

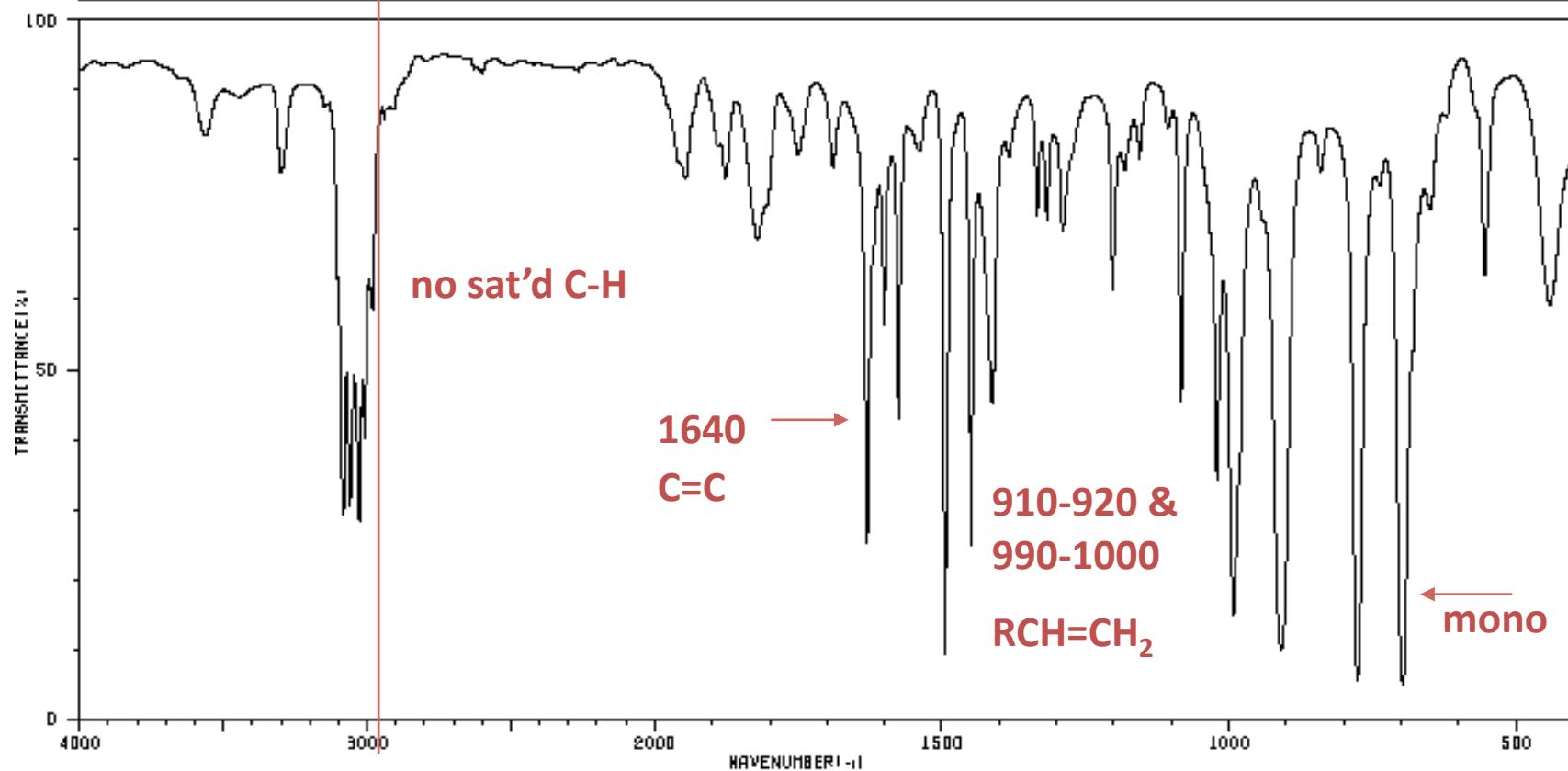


HIT-NO=2170 SCORE= ( ) SDBS-NO=3044 IR-NIDA-10290 : LIQUID FILM

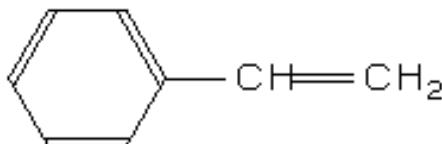
STYRENE

## styrene

C<sub>8</sub>H<sub>8</sub>



3299	74	1946	74	1495	9	1202	68	841	74
3082	28	1876	74	1449	23	1182	74	777	5
3060	29	1821	65	1412	43	1156	77	738	72
3027	27	1689	77	1383	77	1083	43	698	4
3009	38	1630	24	1334	70	1021	33	650	70
2980	57	1601	59	1317	88	992	14	555	60
1956	77	1576	41	1290	66	909	9	442	67

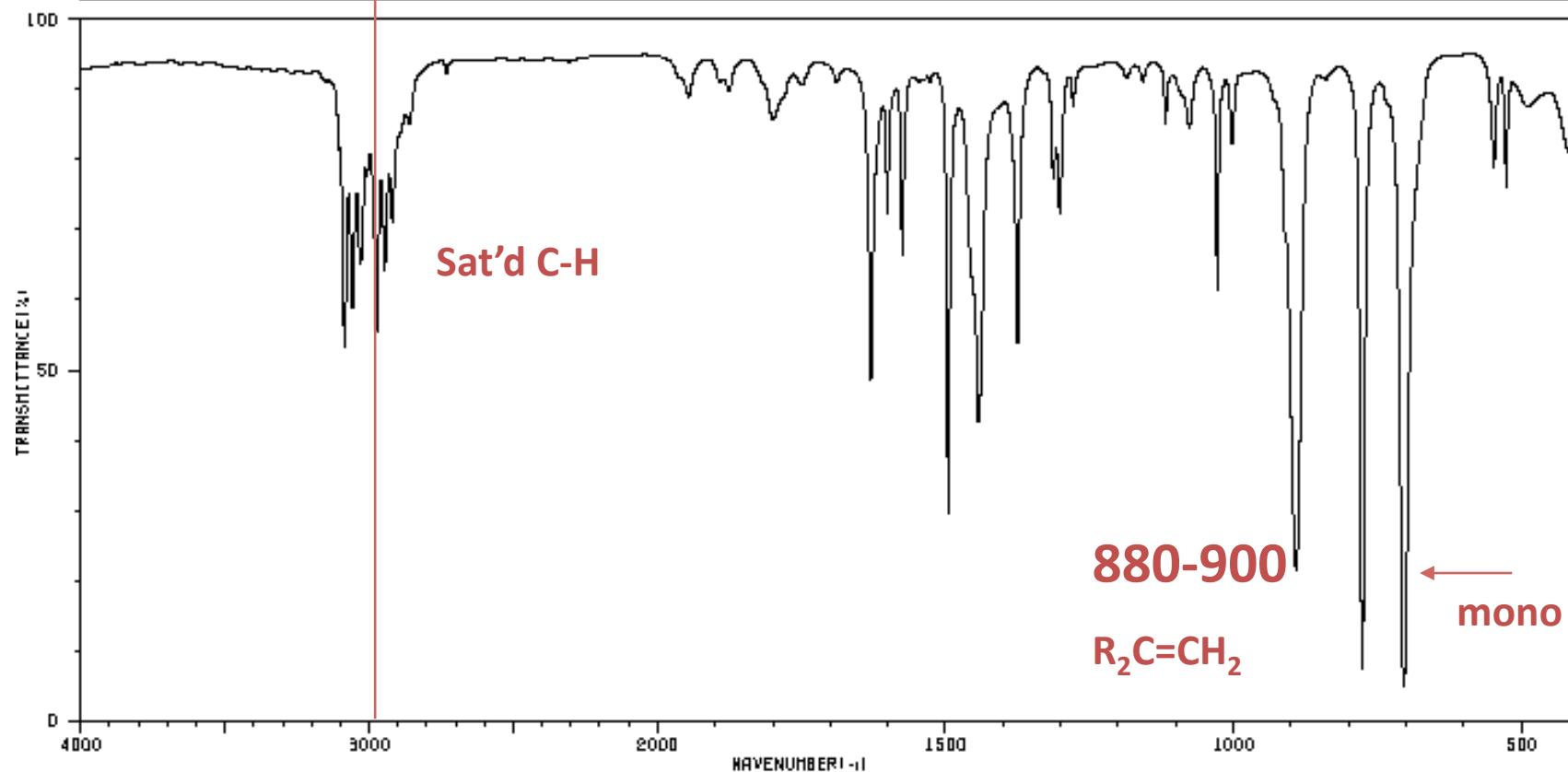


HIT-NO=1854 SCORE= ( ) SDBS-NO=2368 IR-NIDA-00385 : LIQUID FILM

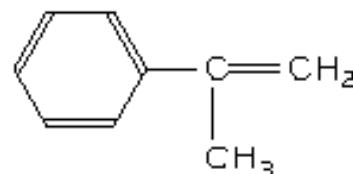
ISOPROPENYLBENZENE

## 2-phenylpropene

C<sub>9</sub>H<sub>10</sub>



3086	60	2861	81	1496	28	1077	81	627	72
3058	57	1946	86	1443	41	1028	58	488	84
3033	82	1878	86	1375	52	1003	79		
3008	74	1800	81	1313	74	892	20		
2974	53	1630	46	1302	70	777	7		
2946	82	1601	70	1279	84	704	4		
2920	68	1676	64	1118	81	648	77		



# IR SPECTROSCOPY of Alcohols, and Phenols

- Free O-H, sharp at  $3650 - 3600 \text{ cm}^{-1}$
- H-bonded O-H, broad at  $3650 - 3300 \text{ cm}^{-1}$
- C-O-H bending, broad and weak  $1400 - 1220 \text{ cm}^{-1}$
- C-O stretching at  $1260 - 1000 \text{ cm}^{-1}$

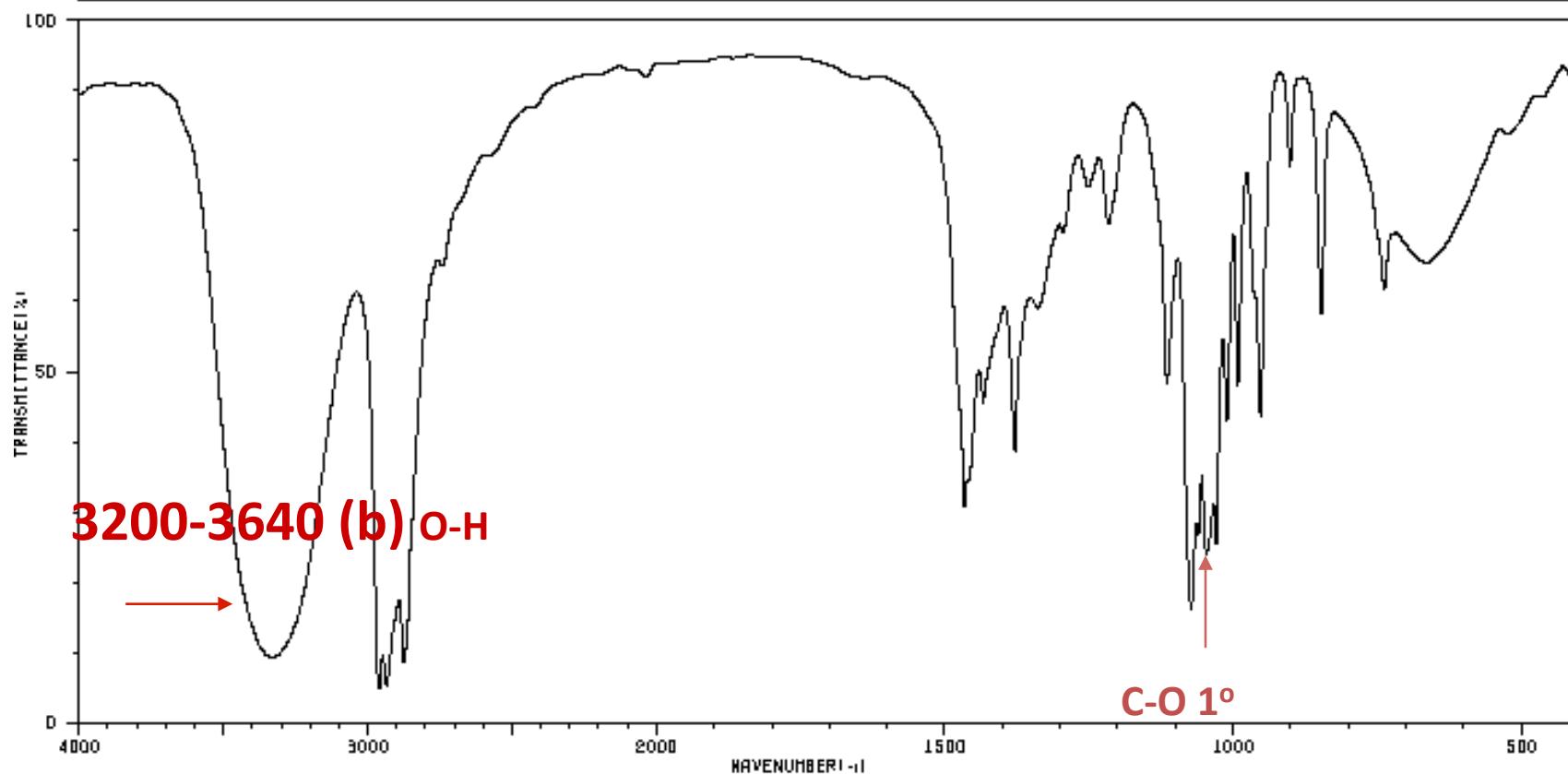
<b>Compound</b>	<b>O-H stretch</b>	<b>C-O stretch</b>
Phenol	$3610 \text{ cm}^{-1}$	$1220 \text{ cm}^{-1}$
$3^\circ$ Alcohol	$3620 \text{ cm}^{-1}$	$1150 \text{ cm}^{-1}$
$2^\circ$ Alcohol	$3630 \text{ cm}^{-1}$	$1100 \text{ cm}^{-1}$
$1^\circ$ Alcohol	$3640 \text{ cm}^{-1}$	$1050 \text{ cm}^{-1}$

HIT-NO=1418 SCORE= ( ) SDBS-NO=1374 IR-NIDA-05408 : LIQUID FILM

1-BUTANOL

## 1-butanol

C<sub>4</sub>H<sub>10</sub>O



3333	9	1434	49	1073	16	901	77
3323	9	1379	37	1060	26	847	57
2960	4	1338	57	1047	23	738	58
2934	6	1296	68	1029	24	670	62
2875	8	1252	74	1011	42	665	62
1466	30	1217	68	992	46		
1461	33	1116	46	963	42		

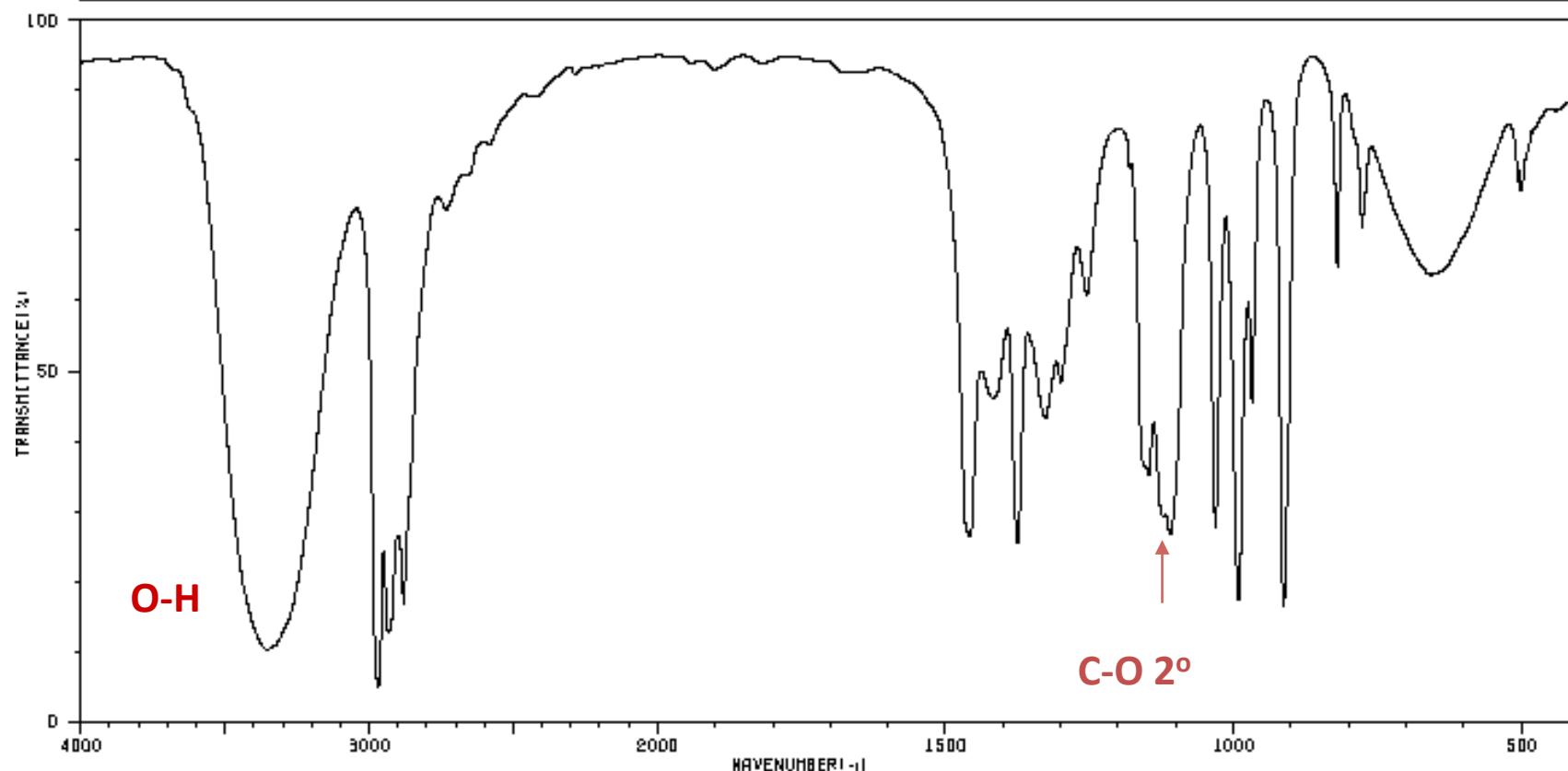


HIT-NO=1035 SCORE= ( ) SDBS-NO=507 IR-NIDA-04700 : LIQUID FILM

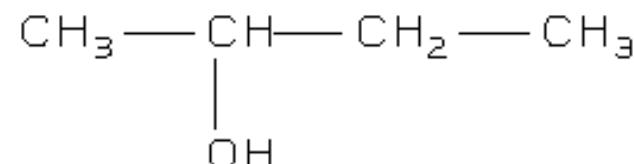
2-BUTANOL

## 2-butanol

C<sub>4</sub>H<sub>10</sub>O



3353	10	1376	24	1110	26	666	60
2968	4	1327	42	1031	26	651	60
2932	12	1300	46	991	16	501	72
2880	16	1266	68	968	43		
2734	70	1154	35	913	15		
1457	25	1148	34	820	82		
1416	44	1122	28	777	68		

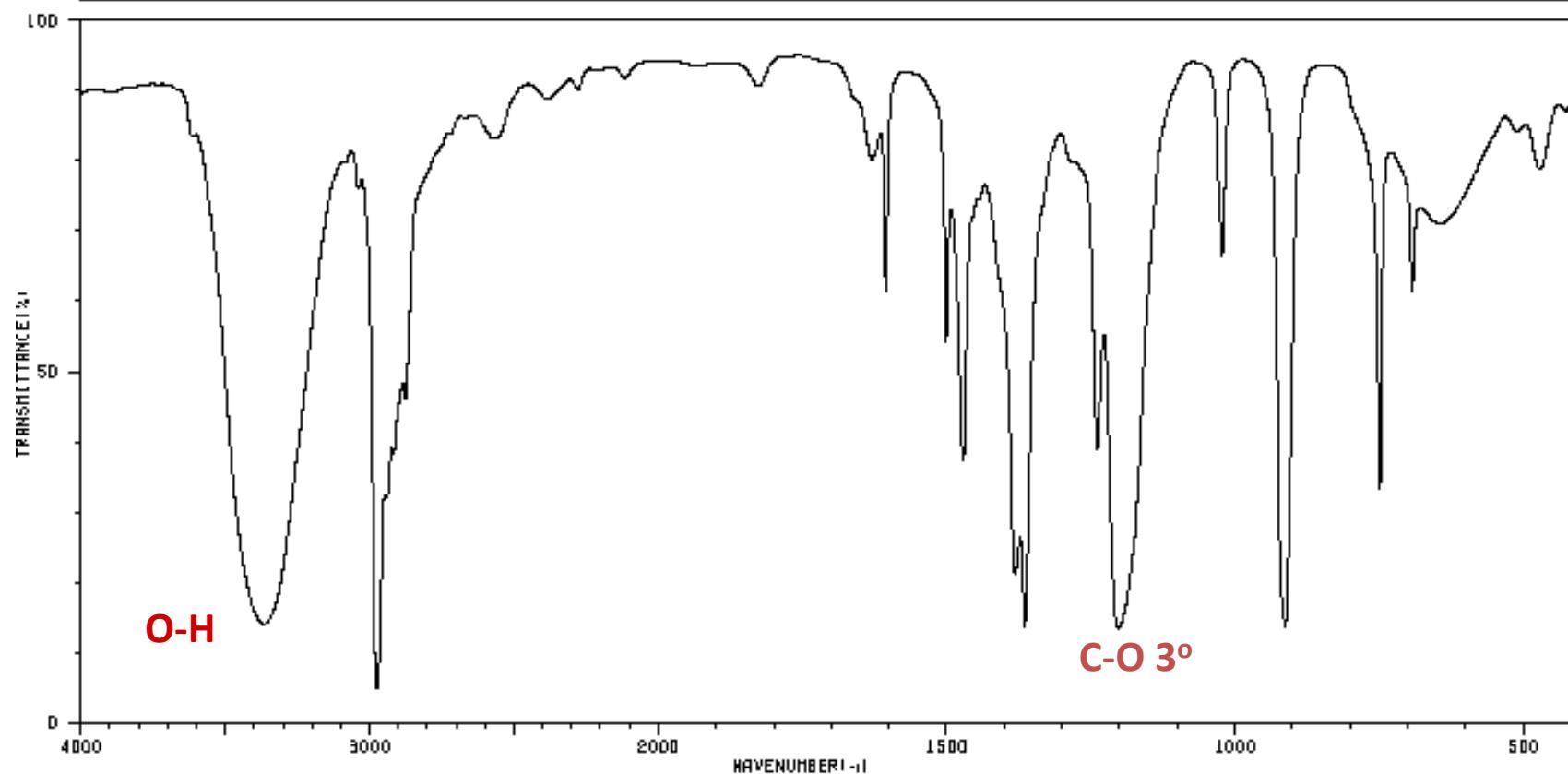


HIT-NO=1034 SCORE= ( ) SDBS-NO=506 IR-NIDA-05409 : LIQUID FILM

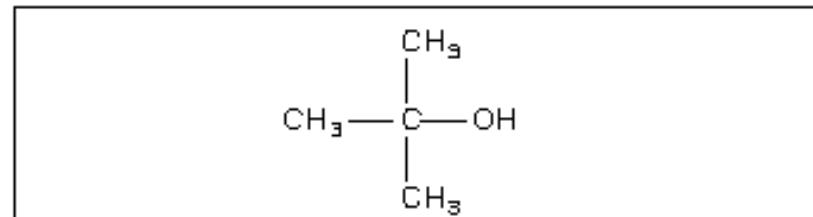
2-METHYL-2-PROPANOL

***tert*-butyl alcohol**

C<sub>4</sub>H<sub>10</sub>O



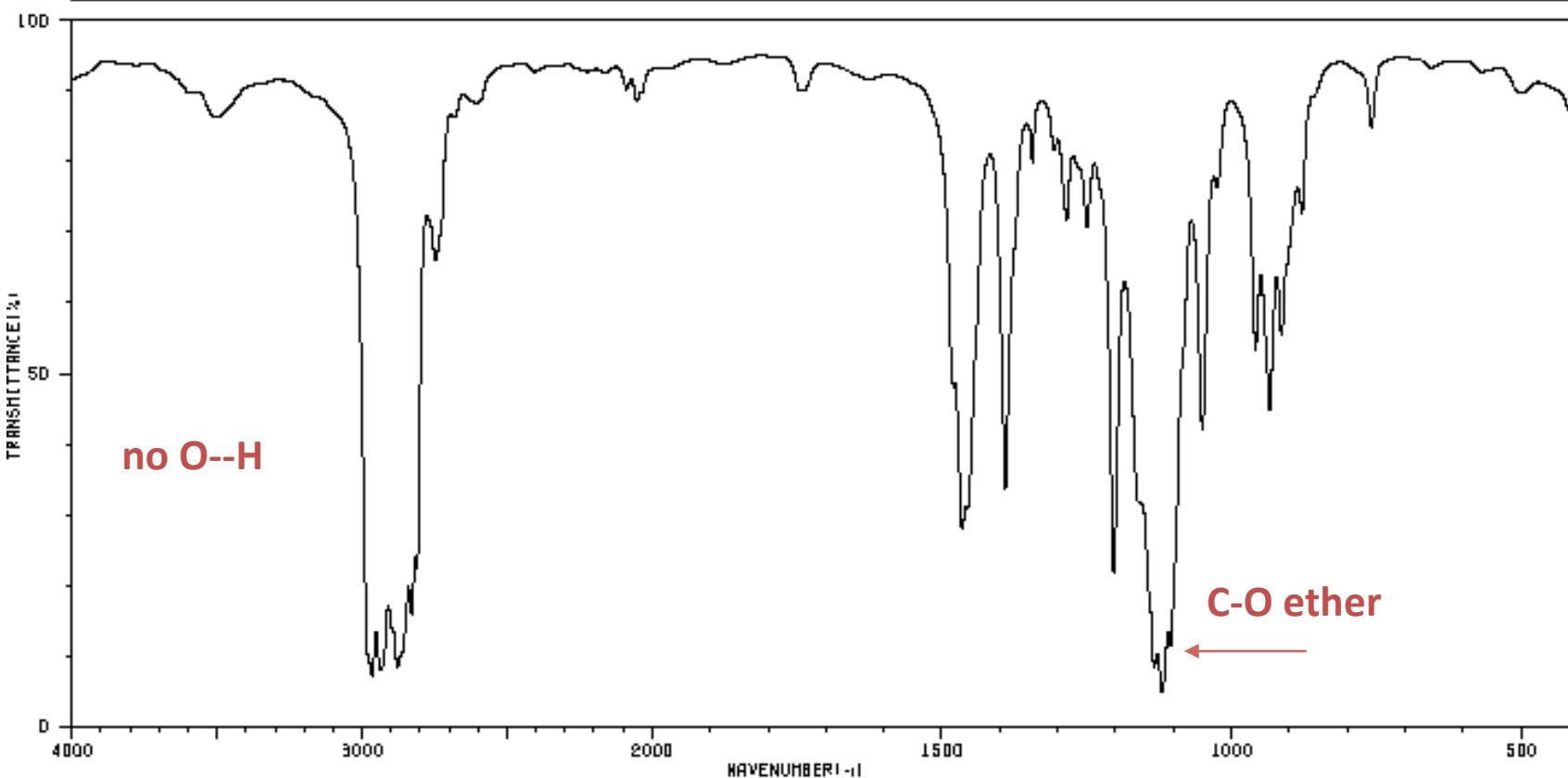
3366	13	1630	77	1202	12	611	81
3038	72	1606	58	1022	64	471	77
2974	4	1501	52	913	13		
2940	31	1471	36	749	32		
2875	44	1381	20	693	58		
2564	79	1365	19	646	88		
2386	86	1239	37	643	68		



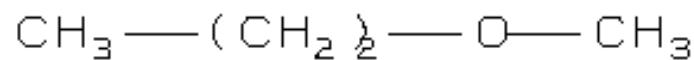
# IR SPECTROSCOPY of Ethers

- C-O                            $1300 - 1000 \text{ cm}^{-1}$
- Phenyl alkyl ethers        $1250$  and  $1040 \text{ cm}^{-1}$
- Aliphatic ethers               $1120 \text{ cm}^{-1}$

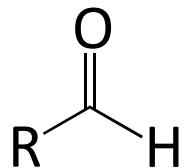
HIT-NO=2077 SCORE= ( ) SDBS-NO=2841 IR-NIDA-03073 : LIQUID FILM  
 METHYL PROPYL ETHER  
**methyl *n*-propyl ether**  
 $C_4H_{10}O$



3600	84	2616	84	1344	77	1106	10	769	81
2965	7	2605	84	1307	79	1050	41	501	86
2935	7	2053	84	1285	86	1024	72		
2879	7	2038	86	1260	68	969	60		
2830	15	1465	26	1204	21	934	43		
2810	21	1458	29	1154	7	914	55		
2746	64	1391	32	1120	4	879	70		



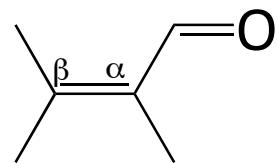
# IR SPECTRUM of Carbonyl Family, Aldehydes



C=O at 1740 - 1725 (s)  $\text{cm}^{-1}$

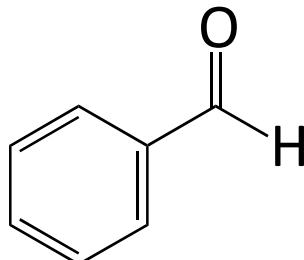
 C=O at 2860 - 2800  $\text{cm}^{-1}$   
2760 - 2700  $\text{cm}^{-1}$

both are weak bands about  
same intensities



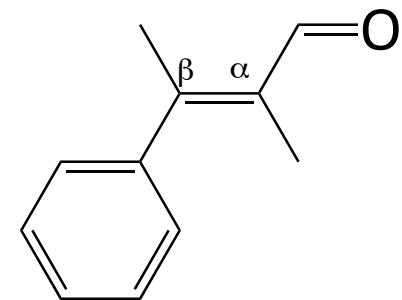
C=O at 1700 - 1680 (s)  $\text{cm}^{-1}$

C=C at 1640 - 1600  $\text{cm}^{-1}$



C=O at 1700 - 1660 (s)  $\text{cm}^{-1}$

C=C at 1600 and 1450  $\text{cm}^{-1}$

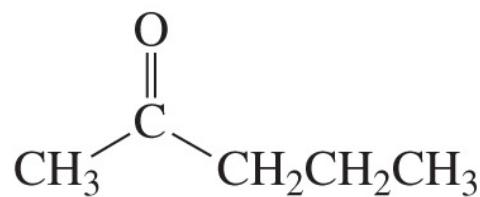


C=O at 1680 - 1640 (s)  $\text{cm}^{-1}$

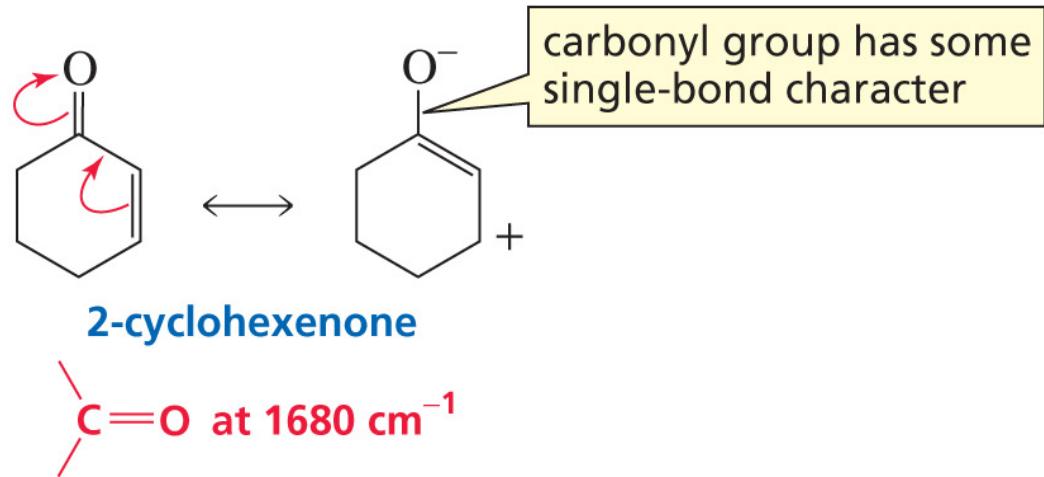
Highly conjugated system

# ELECTRON DELOCALIZATION (Resonance)

## Affects the Frequency of the Absorption

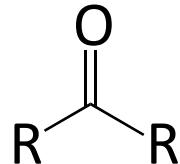


2-pentanone

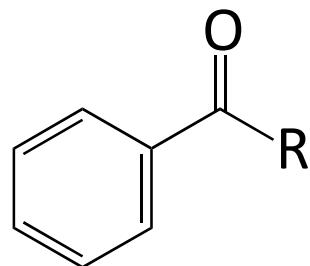


The more double bond character, the greater the frequency (wavenumber).

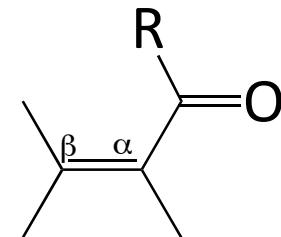
# IR SPECTRUM of Ketones



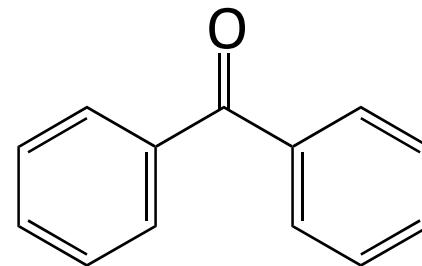
C=O at 1720 - 1708 (s)  $\text{cm}^{-1}$



C=O at 1700 - 1680 (s)  $\text{cm}^{-1}$   
C=C at 1600 and 1450  $\text{cm}^{-1}$



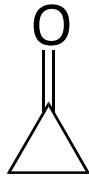
C=O at 1700 - 1675 (s)  $\text{cm}^{-1}$   
C=C at 1644 - 1617  $\text{cm}^{-1}$



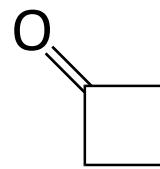
C=O at 1670 - 1600 (s)  $\text{cm}^{-1}$   
C=C at 1600 and 1450  $\text{cm}^{-1}$

# IR SPECTRUM of Cyclic Ketones

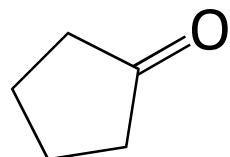
- Both acyclic and cyclic bending appears as a medium intensity  $1300 - 1100 \text{ cm}^{-1}$
- Cyclic ketones C=O frequency increases with decreasing ring size
- **Strain effects** – changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore, bond strength
- As bond angle decreases, carbon becomes more electronegative, as well as less  $\text{sp}^2$  hybridized (bond angle  $< 120^\circ$ )



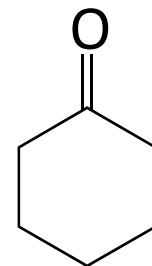
$1815 \text{ cm}^{-1}$



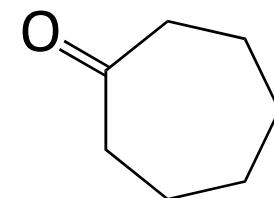
$1780 \text{ cm}^{-1}$



$1745 \text{ cm}^{-1}$

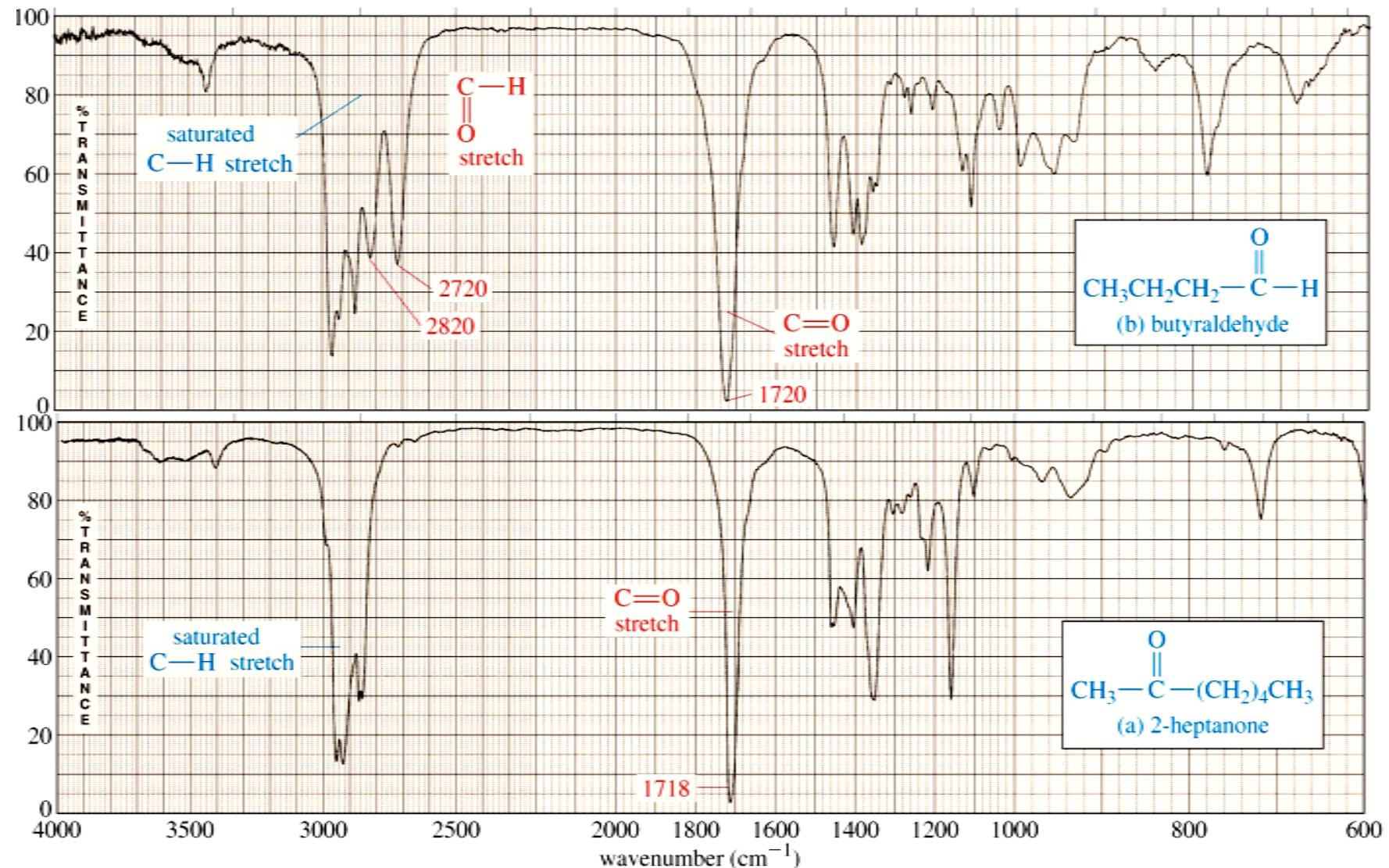


$1715 \text{ cm}^{-1}$



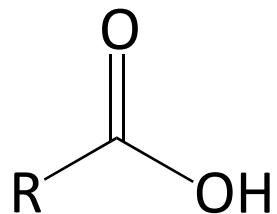
$1705 \text{ cm}^{-1}$

# IR SPECTRUM OF ALDEHYDES AND KETONES



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

# IR SPECTRUM of Carboxylic Acids

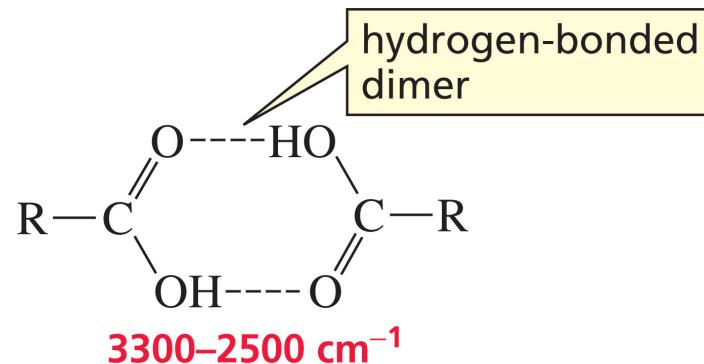


O-H at 3600 - 2400  $\text{cm}^{-1}$

C=O at 1730 - 1700 (s)  $\text{cm}^{-1}$

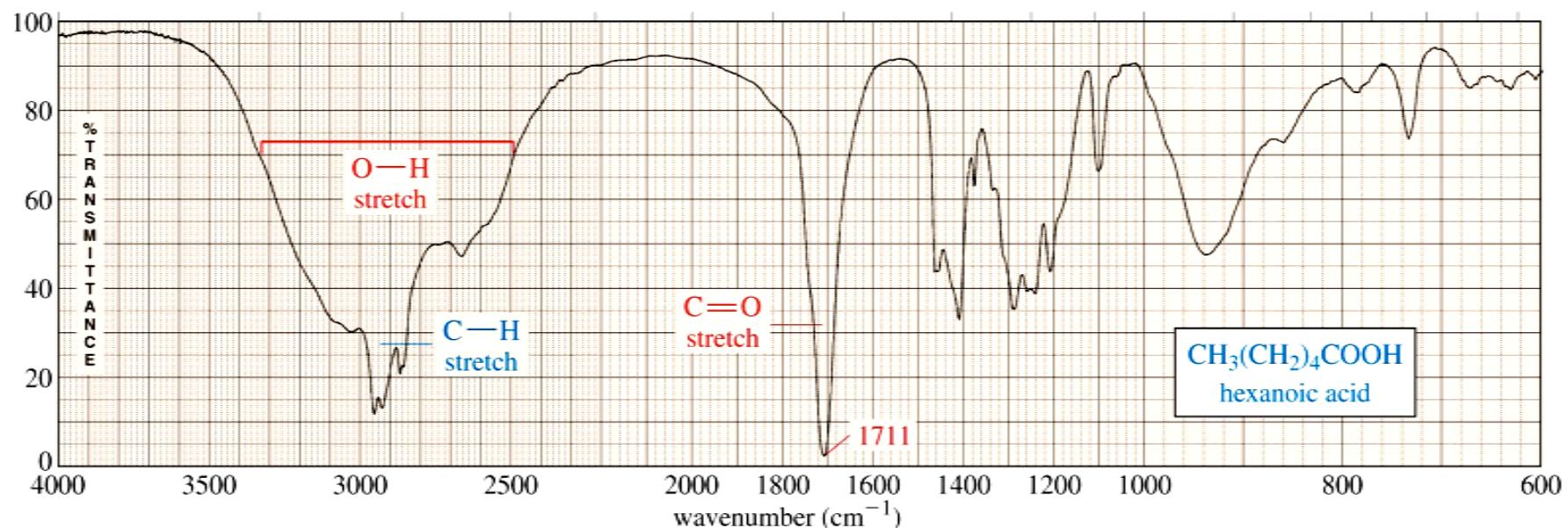
C-O at 1320 - 1210  $\text{cm}^{-1}$

- Conjugated carboxylic acids have lower frequency.
- Hydrogen bonded OH group stretch at lower frequency.



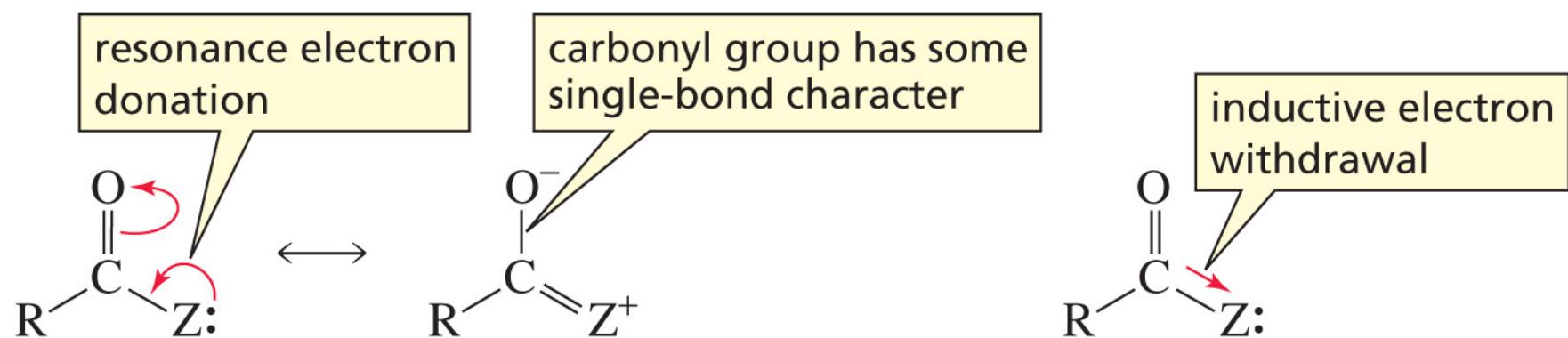
# IR SPECTRUM OF A CARBOXYLIC ACID

A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm<sup>-1</sup>** for the O-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm<sup>-1</sup>** corresponding to the C=O stretch.

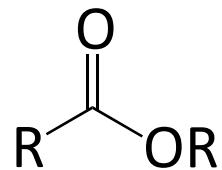


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

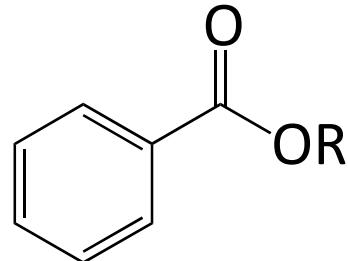
# RESONANCE ELECTRON DONATION DECREASES the FREQUENCY while INDUCTIVE ELECTRON WITHDRAWL INCREASES the FREQUENCY



# IR FREQUENCIES of Esters



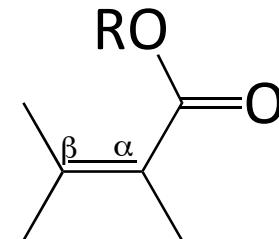
C=O at 1750 - 1735 (s)  $\text{cm}^{-1}$



C=O at 1740 - 1715 (s)  $\text{cm}^{-1}$

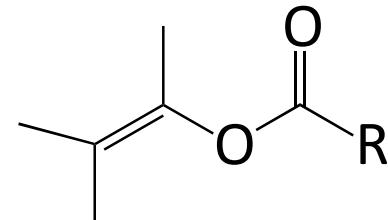
C=C at 1600 and 1450  $\text{cm}^{-1}$

C-O 2 bands, one stronger and broader than other, 1300-1000  $\text{cm}^{-1}$



C=O at 1740 - 1715 (s)  $\text{cm}^{-1}$

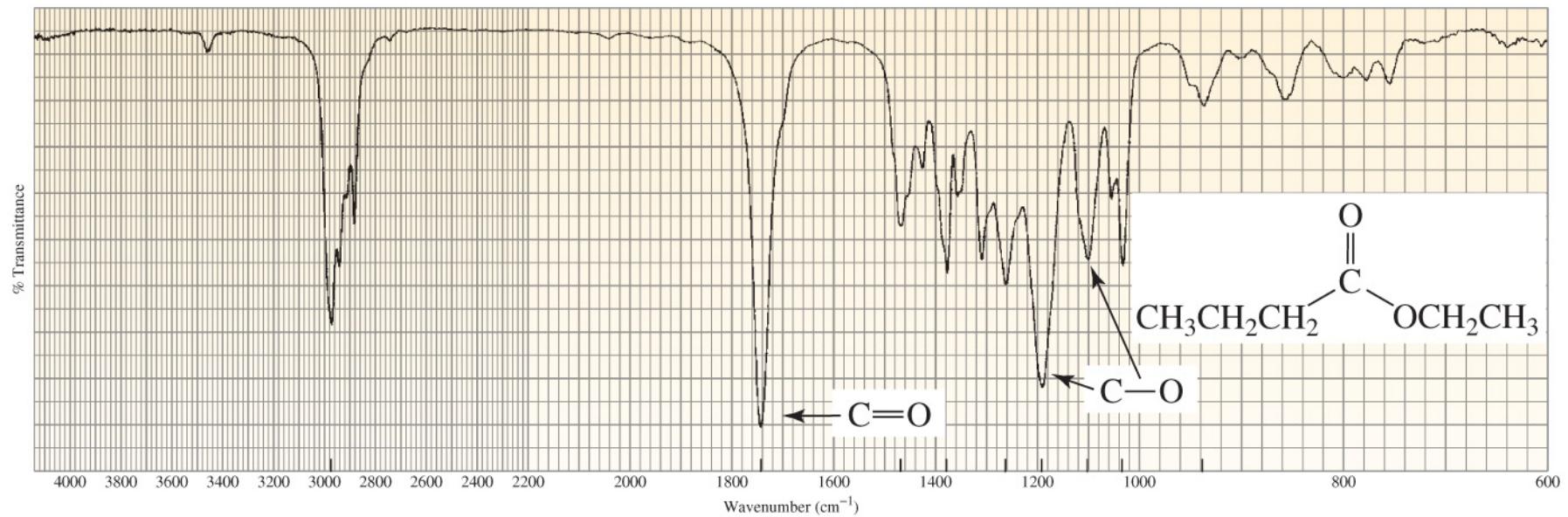
C=C at 1640 - 1625  $\text{cm}^{-1}$



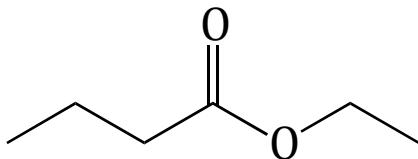
C=O at 1765 - 1762 (s)  $\text{cm}^{-1}$

C=C at 168 - 1640  $\text{cm}^{-1}$

# The IR Spectrum of an Ester

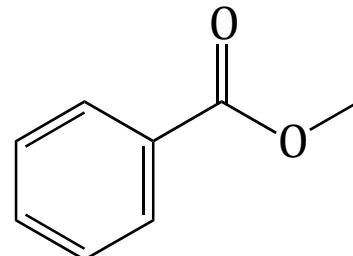


# ESTER IR FREQUENCIES



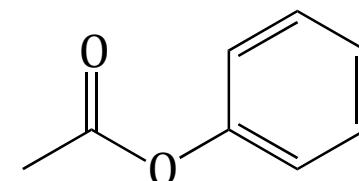
Ethyl butyrate

1738 cm<sup>-1</sup>



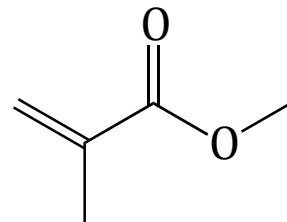
Methyl benzoate

1724 cm<sup>-1</sup>



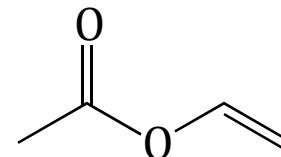
Phenyl acetate

1765 cm<sup>-1</sup>

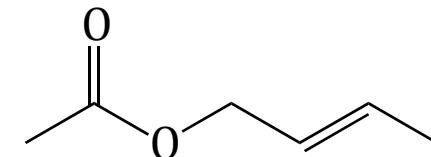


Methyl methacrylate

1725 cm<sup>-1</sup>

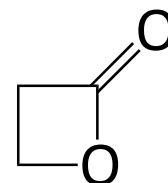


Vinyl acetate

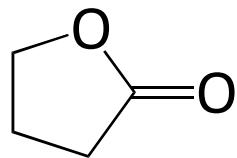


(E)-But-2-en-1-yl acetate

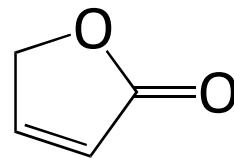
# IR FREQUENCIES OF Cyclic Esters (Lactones)



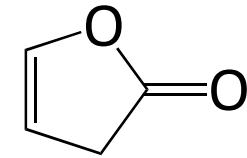
$1820 \text{ cm}^{-1}$



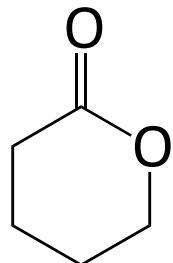
$1770 \text{ cm}^{-1}$



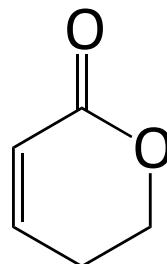
$1750 \text{ cm}^{-1}$



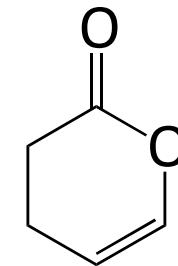
$1800 \text{ cm}^{-1}$



$1735 \text{ cm}^{-1}$

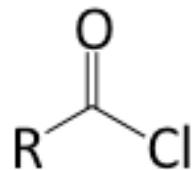


$1725 \text{ cm}^{-1}$



$1760 \text{ cm}^{-1}$

# IR FREQUENCIES of Acid Chlorides and Anhydrides

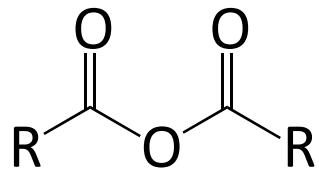


C=O at 1810 - 1775 cm<sup>-1</sup>

conjugated 1780 - 1760cm<sup>-1</sup>

C-Cl in the range of 730 -550 cm<sup>-1</sup>

## Anhydride and Cyclic Anhydride



C=O at 1830 - 1800 and 1775 - 1740 cm<sup>-1</sup>

variable intensities

C-O in the range of 1300 - 900 cm<sup>-1</sup>

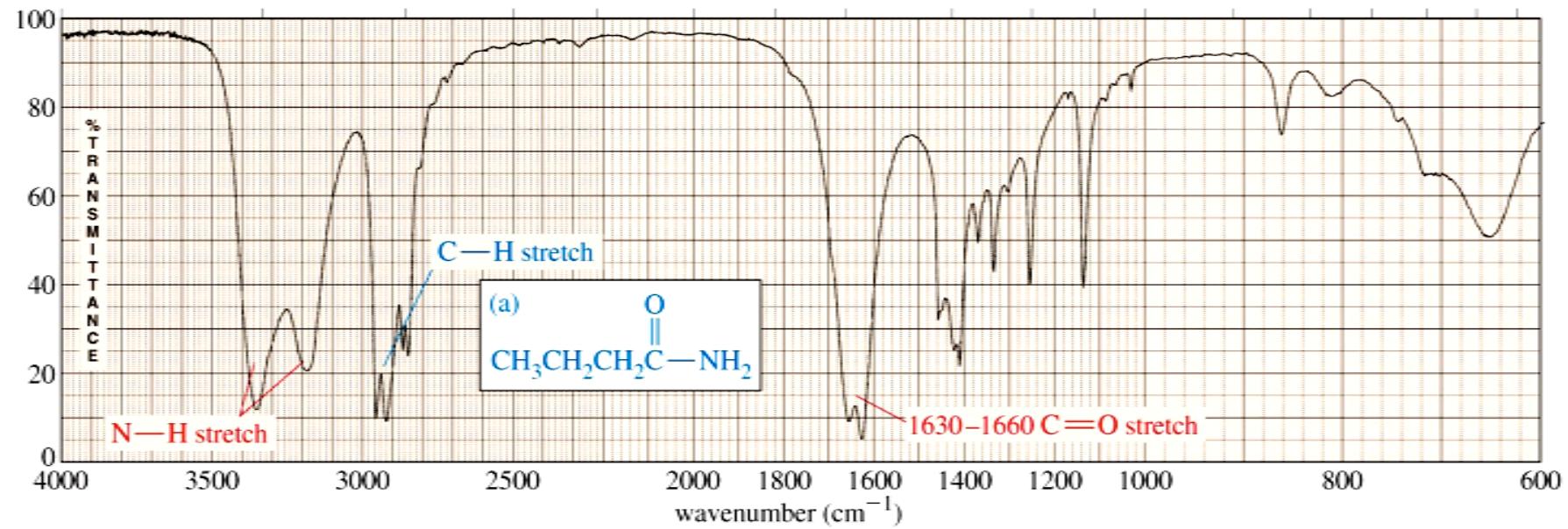
Conjugation moves the absorption to lower frequency

Ring strain (cyclic) moves the absorption to a higher frequency

# IR FREQUENCIES of Amides

- C=O       $1680 - 1630 \text{ cm}^{-1}$
  - N-H       $3350$  and  $3180 \text{ cm}^{-1}$  for  $1^\circ$  Amides
  - N-H       $3300 \text{ cm}^{-1}$  for  $2^\circ$  Amides
  - N-H       $1640 - 1550 \text{ cm}^{-1}$  for  $1^\circ$  and  $2^\circ$  Amides  
(bending vibrations)
- 

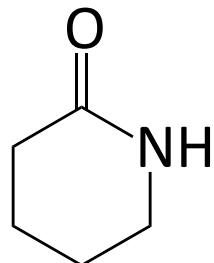
# IR SPECTRUM OF AMIDES



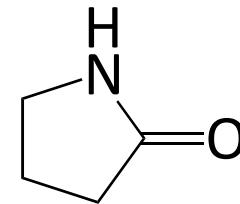
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

# IR FREQUENCIES of Cyclic Amides (Lactams)

Increase in C=O frequency for decreasing ring size



1660 cm<sup>-1</sup>

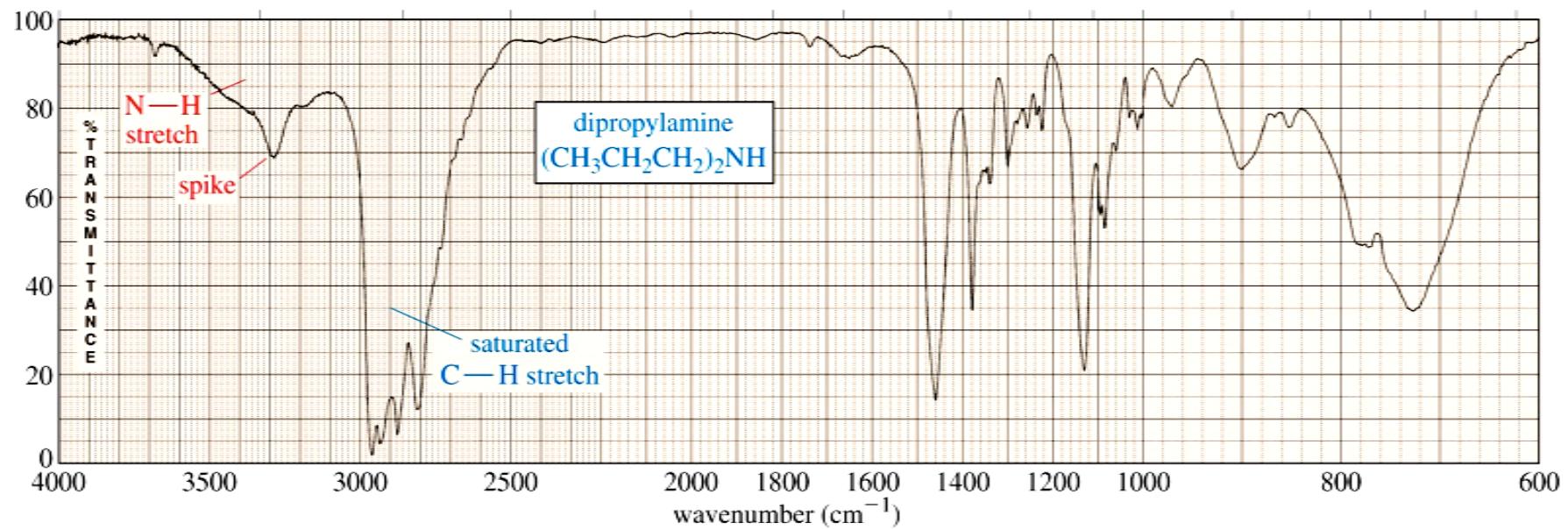


1705 cm<sup>-1</sup>

# IR FREQUENCIES of Amines

- Amines
- N-H       $3350$  and  $3180\text{ cm}^{-1}$  for  $1^\circ$  Amines  
 $1640 - 1560\text{ cm}^{-1}$  for bending vibration
- N-H       $3300\text{ cm}^{-1}$  for  $2^\circ$  Amines  
 $1500\text{ cm}^{-1}$  for bending vibrations  
N-H      oop bending  $800\text{ cm}^{-1}$   
C-N       $1350 - 1000\text{ cm}^{-1}$

# IR SPECTRA OF AMINES



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

# IR FREQUENCIES of Nitrogen Containing Compounds

## Nitriles

- Carbon-Nitrogen triple bond with medium intensity at  $2250\text{ cm}^{-1}$



- $\text{N}=\text{C}=\text{O}$  broad intense peak at  $2270\text{ cm}^{-1}$



- $\text{N}=\text{C}=\text{S}$  broad intense peak at  $2125\text{ cm}^{-1}$



- $\text{C}=\text{N}$  variable intensity at  $1690 - 1640\text{ cm}^{-1}$