



INFRARED SPECTROSCOPY (IR)

*Theory and Interpretation of IR
spectra*

ORGANIC STRUCTURE DETERMINATION

How do we know:

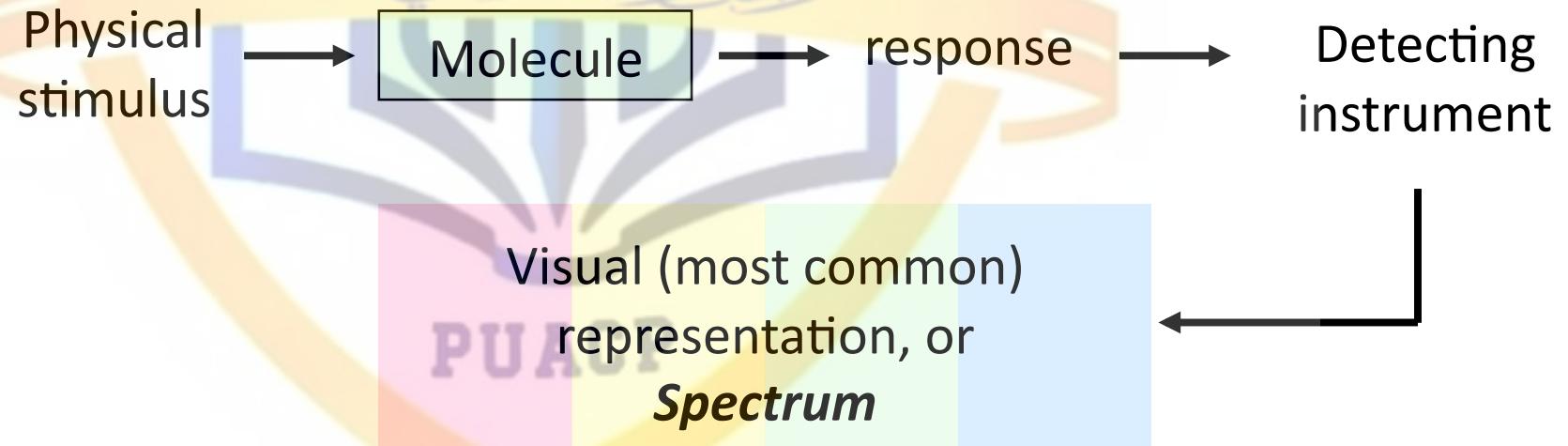
- How atoms are connected together?
- Which bonds are single, double, or triple?
- What functional groups exist in the molecule?
- If we have a specific stereoisomer?

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 π 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.”

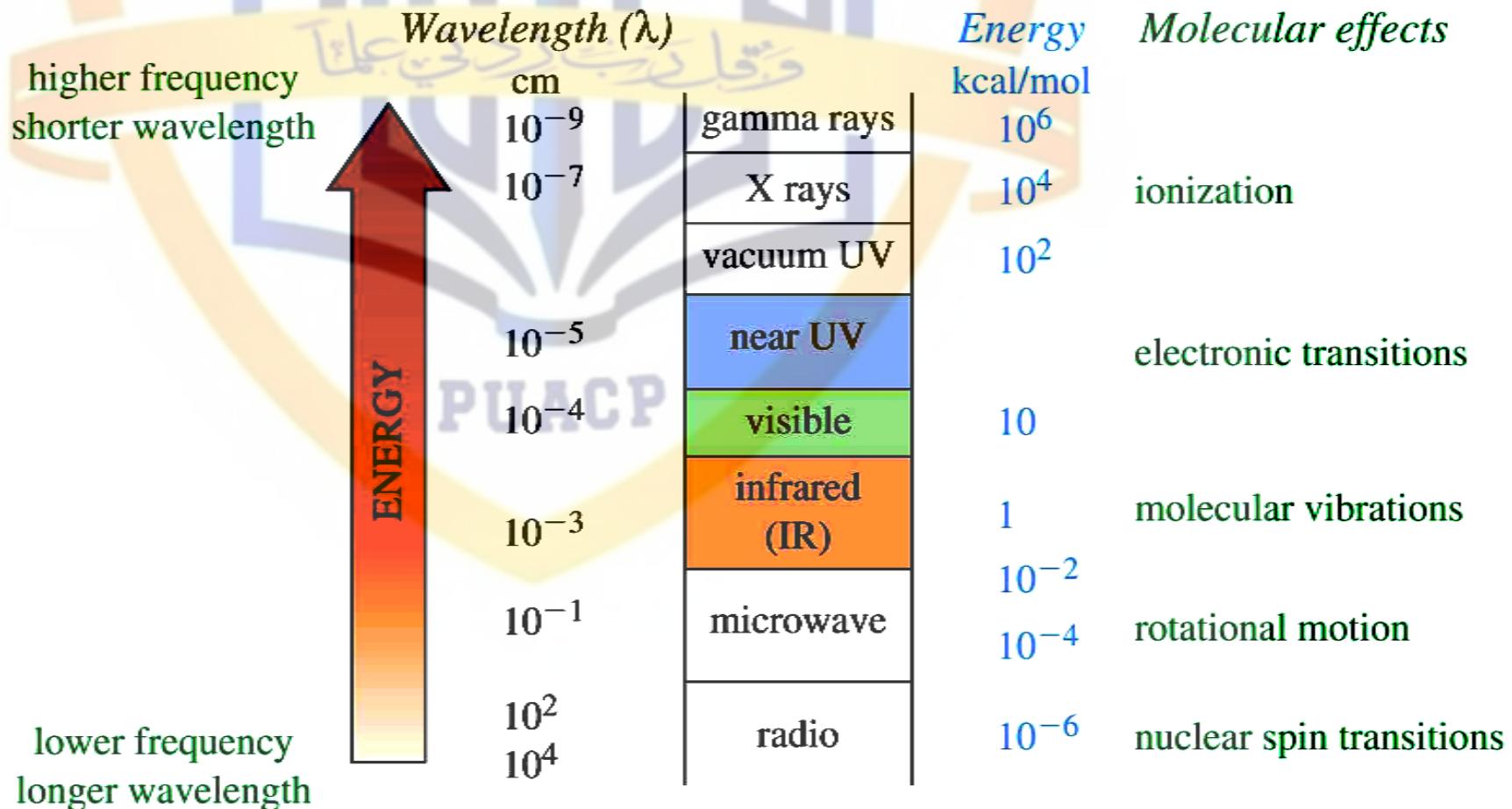
Other types of radiation such as alpha rays, which consist of helium nuclei, have a detectable mass component and therefore cannot be categorized as electromagnetic energy.

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 (μ)**
- **Wavelength (λ)**

$$E = h\mu$$

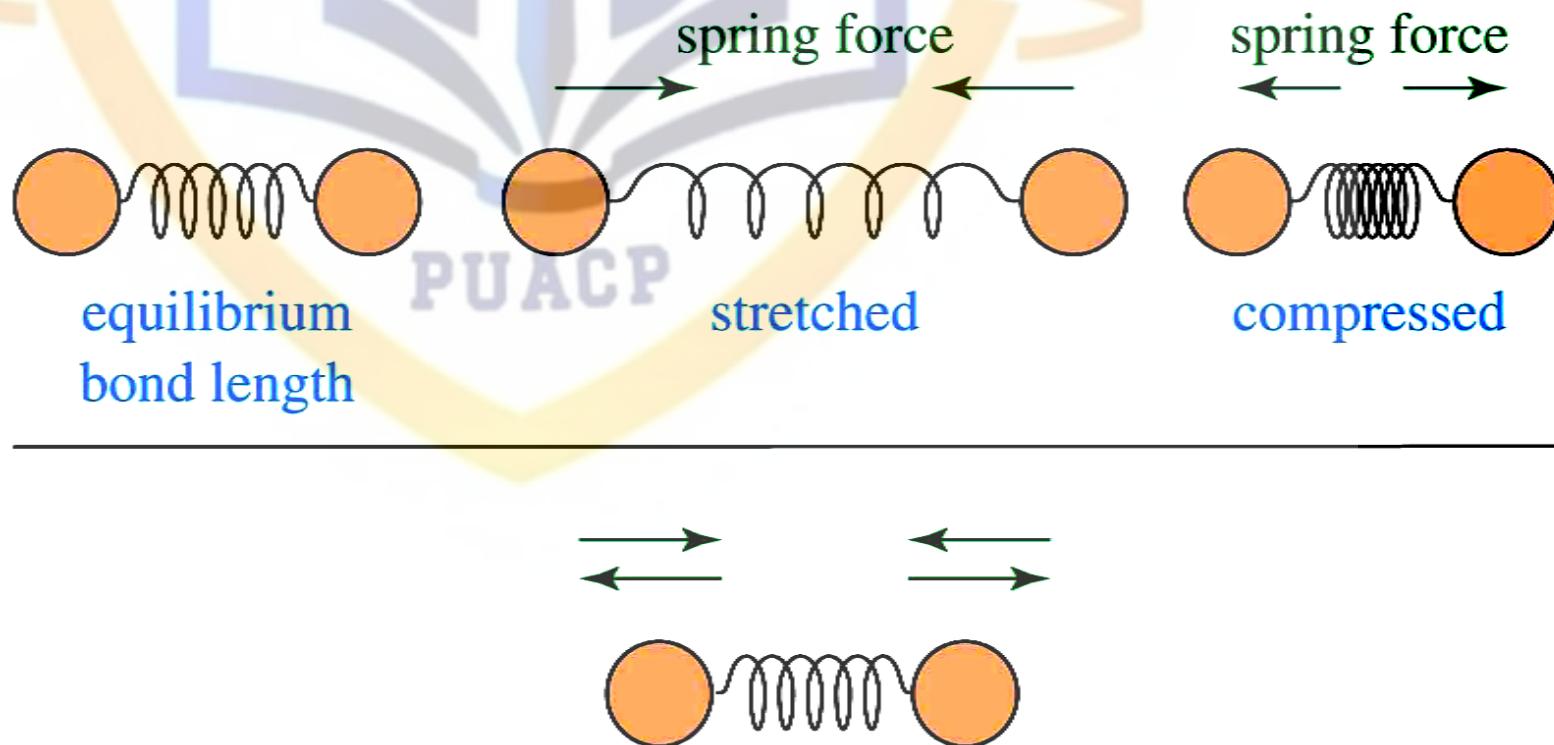
EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES



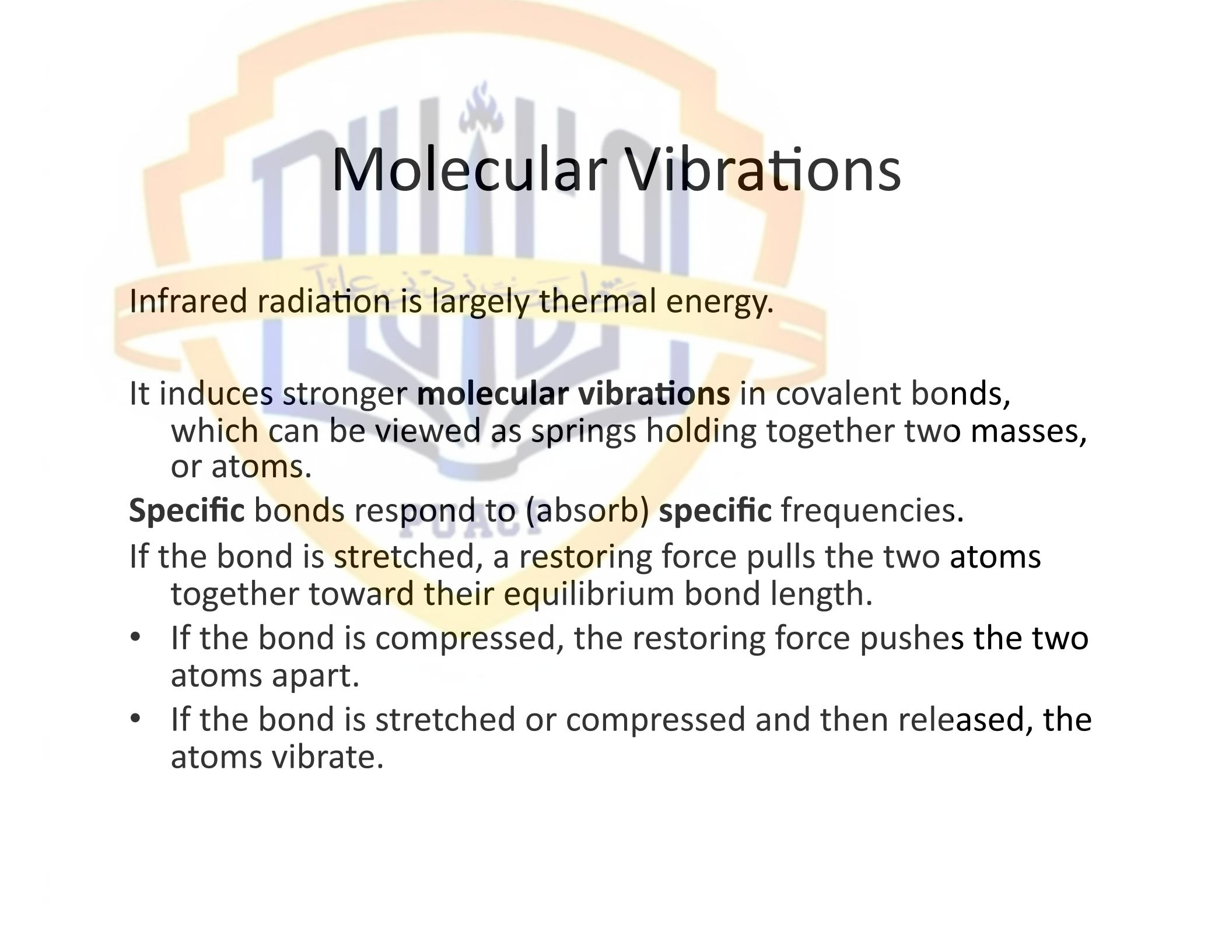
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

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.

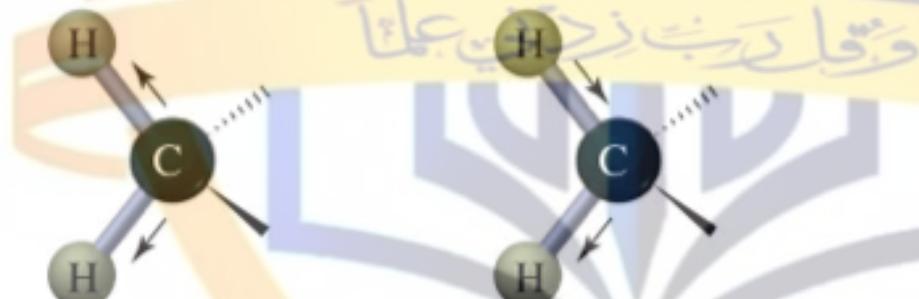
Specific bonds respond to (absorb) **specific** frequencies.

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

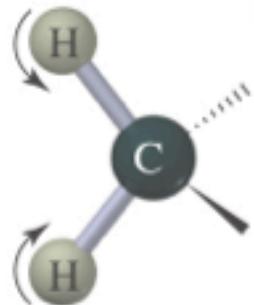
Stretching vibrations



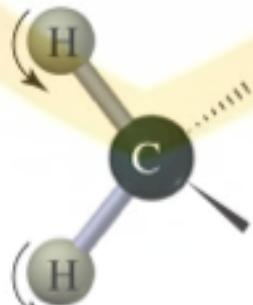
symmetric stretch

asymmetric stretch

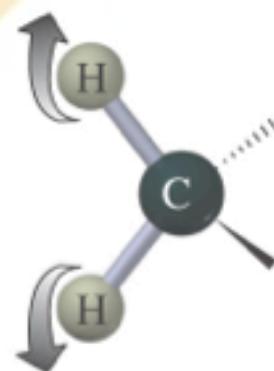
Bending vibrations



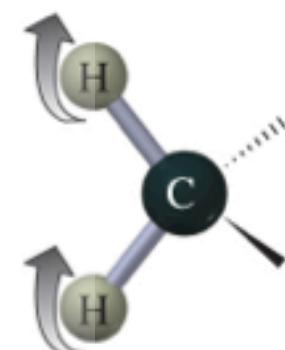
symmetric in-plane
bend (scissor)



asymmetric in-plane
bend (rock)



symmetric out-of-plane
bend (twist)

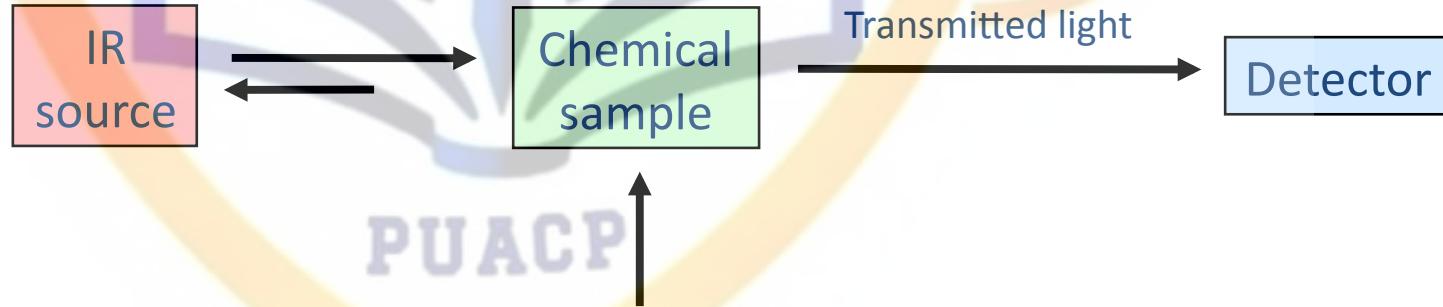


asymmetric out-of-plane
bend (wag)

PUACP

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.

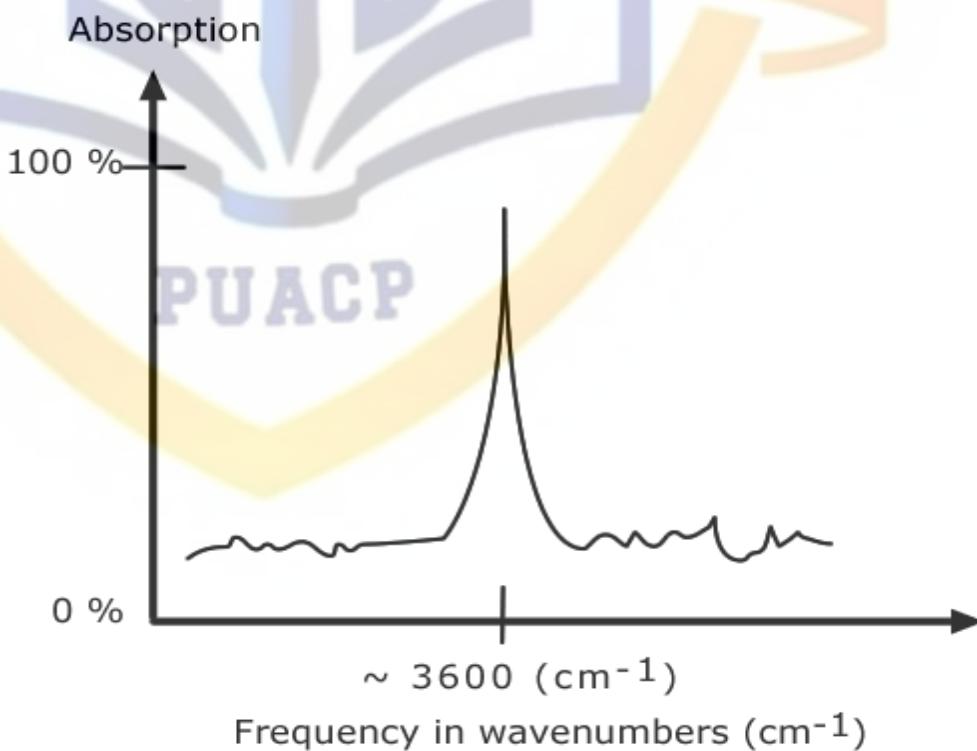


From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

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

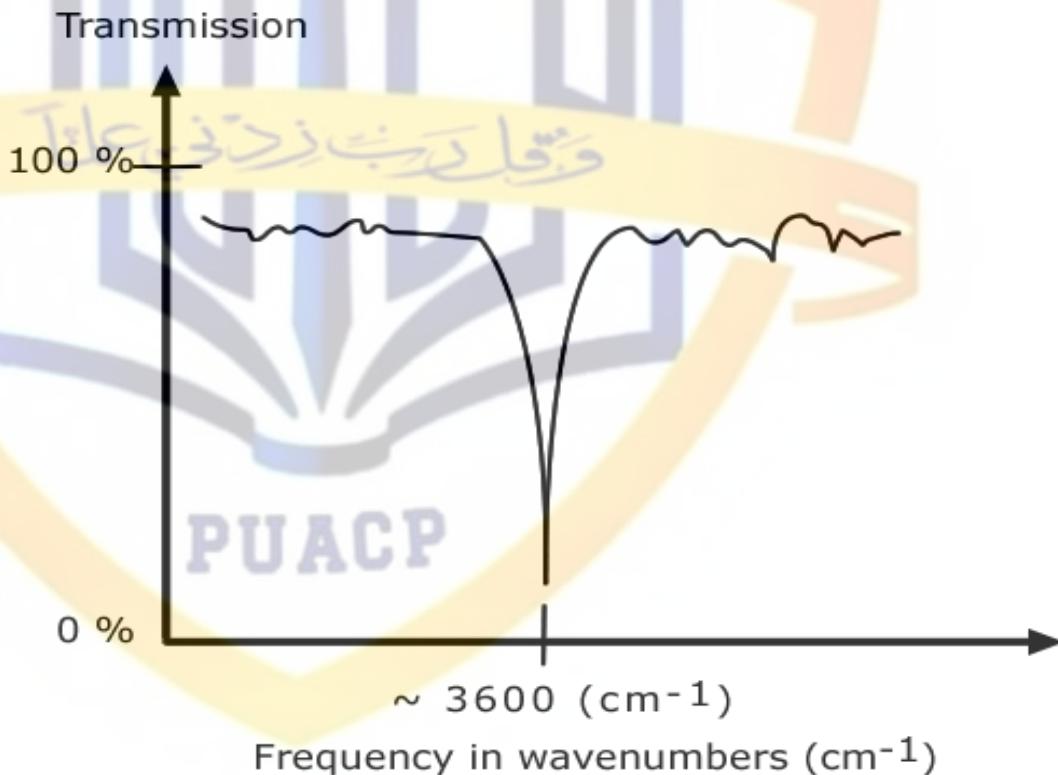
AN IR SPECTRUM IN ABSORPTION MODE

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



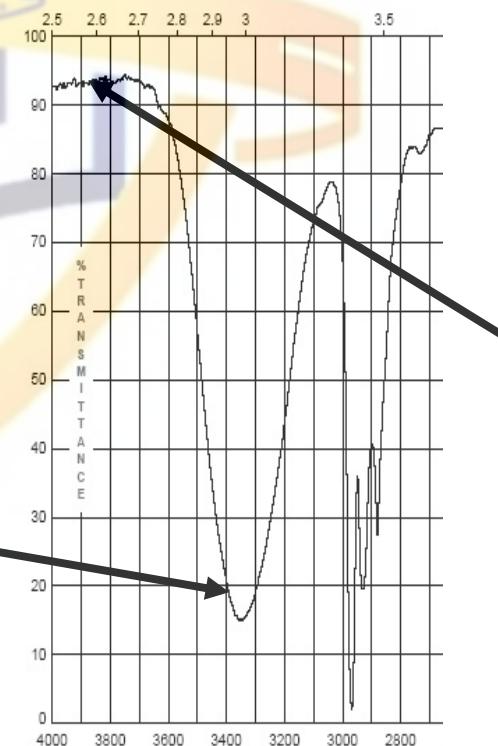
The graph above shows a spectrum in **transmission** mode.
This is the most commonly used representation and the one found in most chemistry and spectroscopy books. Therefore we will use this representation.

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

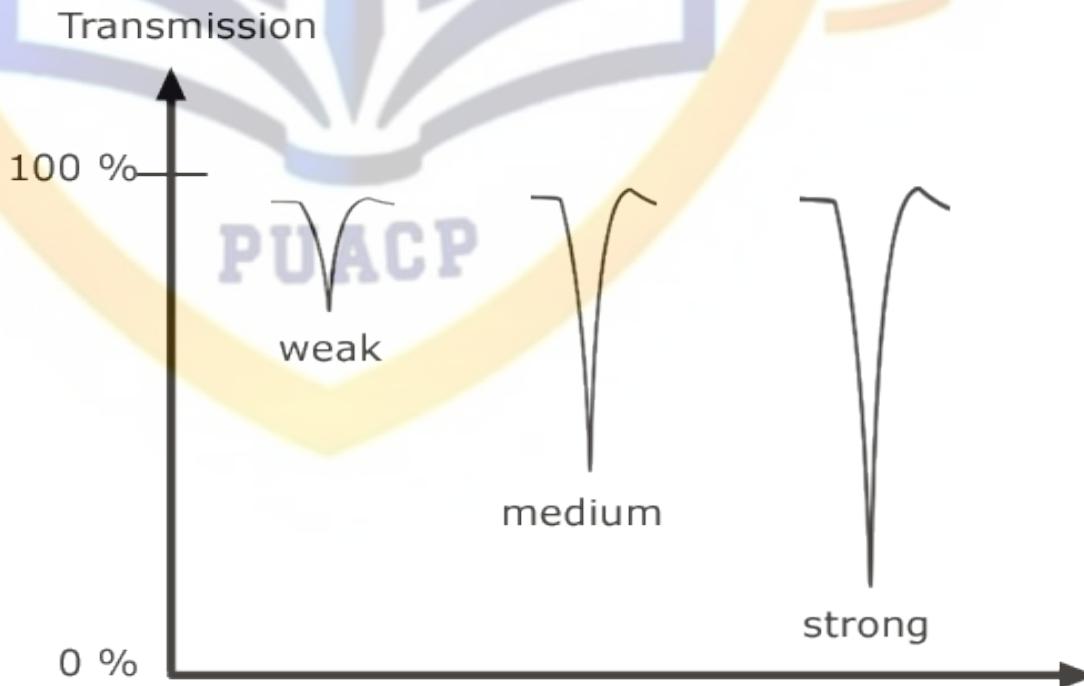
In regions where the EM field of an osc. bond interacts with IR light of the same ν – transmittance is low (light is absorbed)



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.



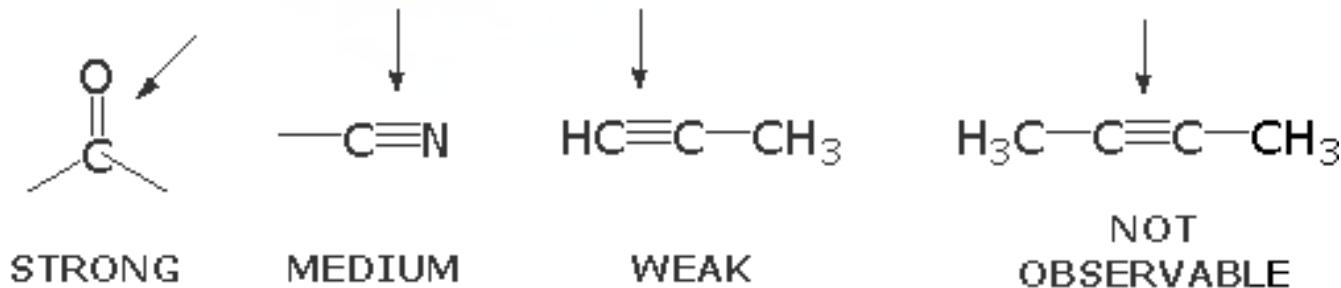
INFRARED ACTIVE BONDS

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:

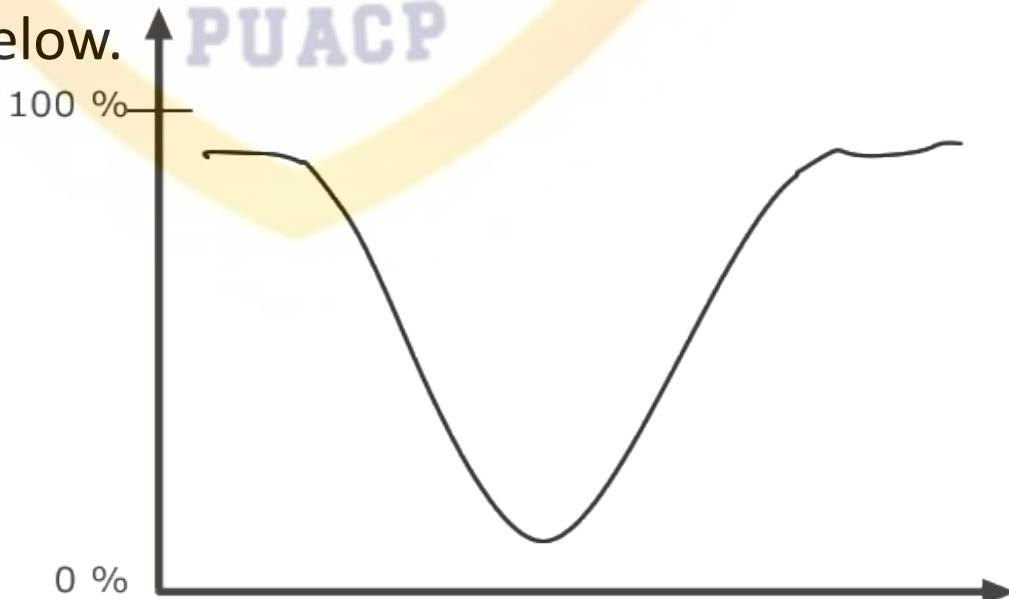
- Strongly polar bonds such as carbonyl groups ($\text{C}=\text{O}$) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.

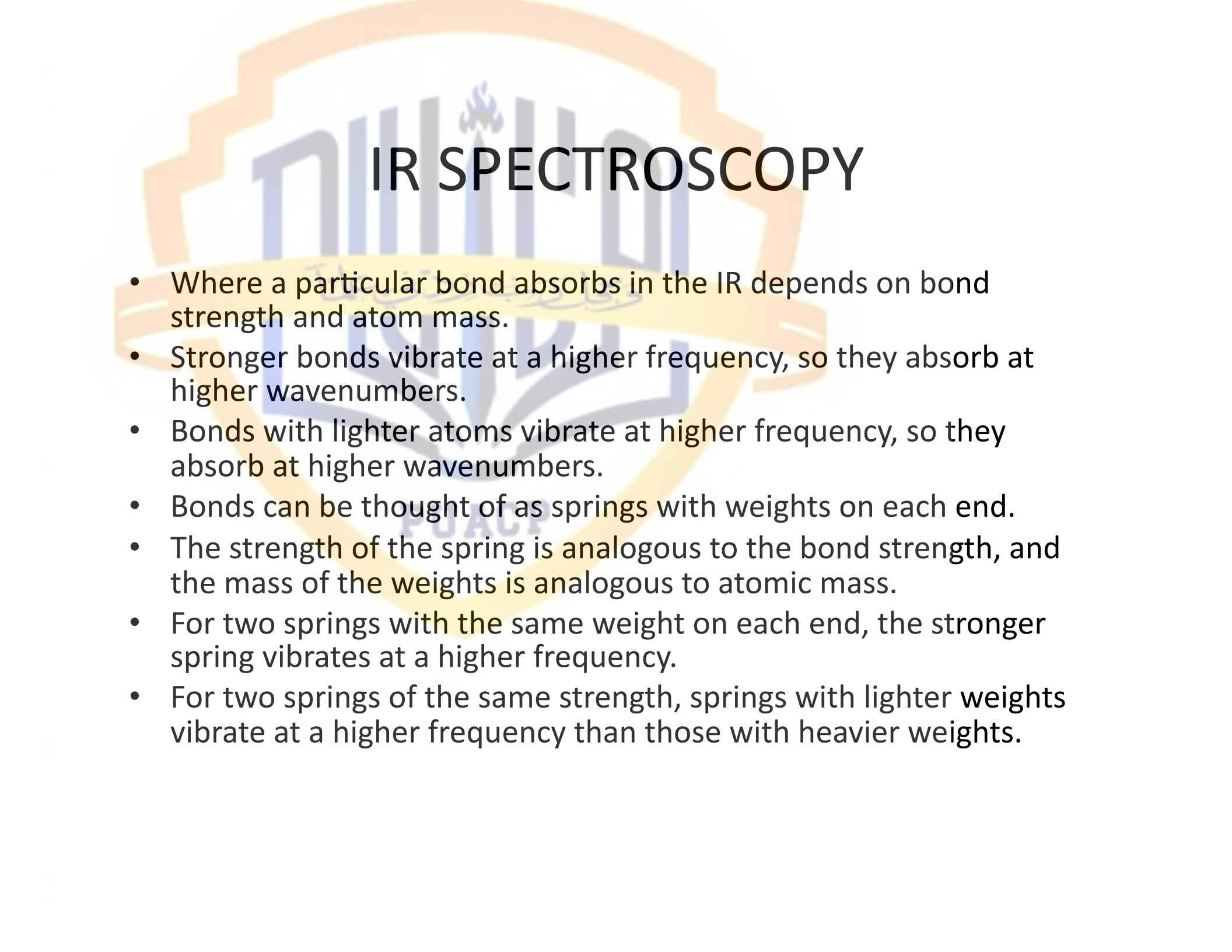


INFRARED BAND SHAPES

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:

The diagram shows the derivation of the formula for bond frequency. It starts with the text "Hooke's law" and the equation $\ddot{v} = k \sqrt{\frac{f}{m}}$. To the right of the equation, there is a box containing the text "stronger bond ---> higher frequency". Below the equation, another box contains the text "smaller mass ---> higher frequency". Arrows point from the text boxes to the corresponding terms in the equation (f and m). To the right of the equation, definitions are provided: f = force constant, m = mass, and k = constant.

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

stronger bond ---> higher frequency

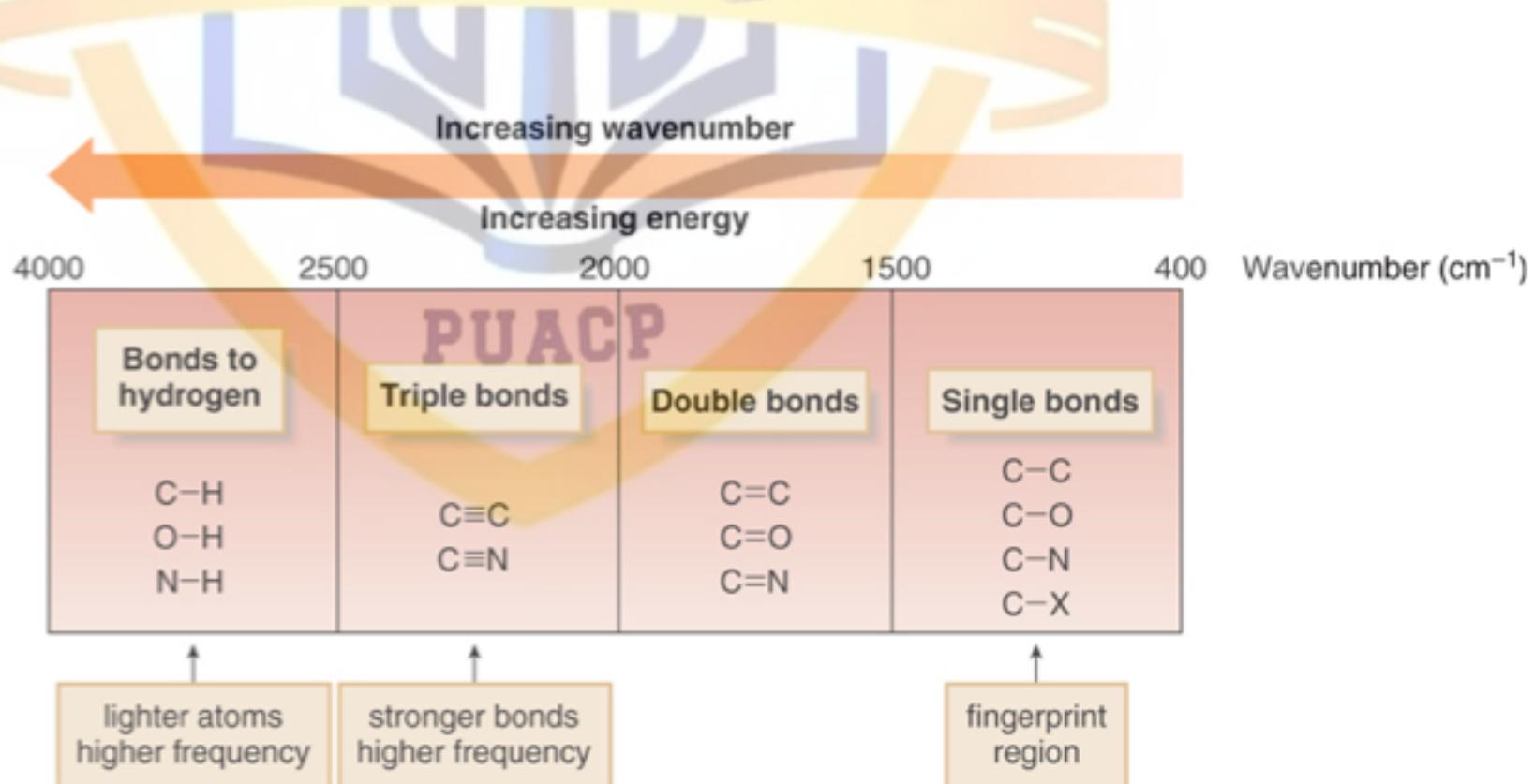
smaller mass ---> higher frequency

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 \ddot{v} of vibration.
- The mass (m) is the mass of atoms (or weights). The smaller the value of m , the higher the \ddot{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.

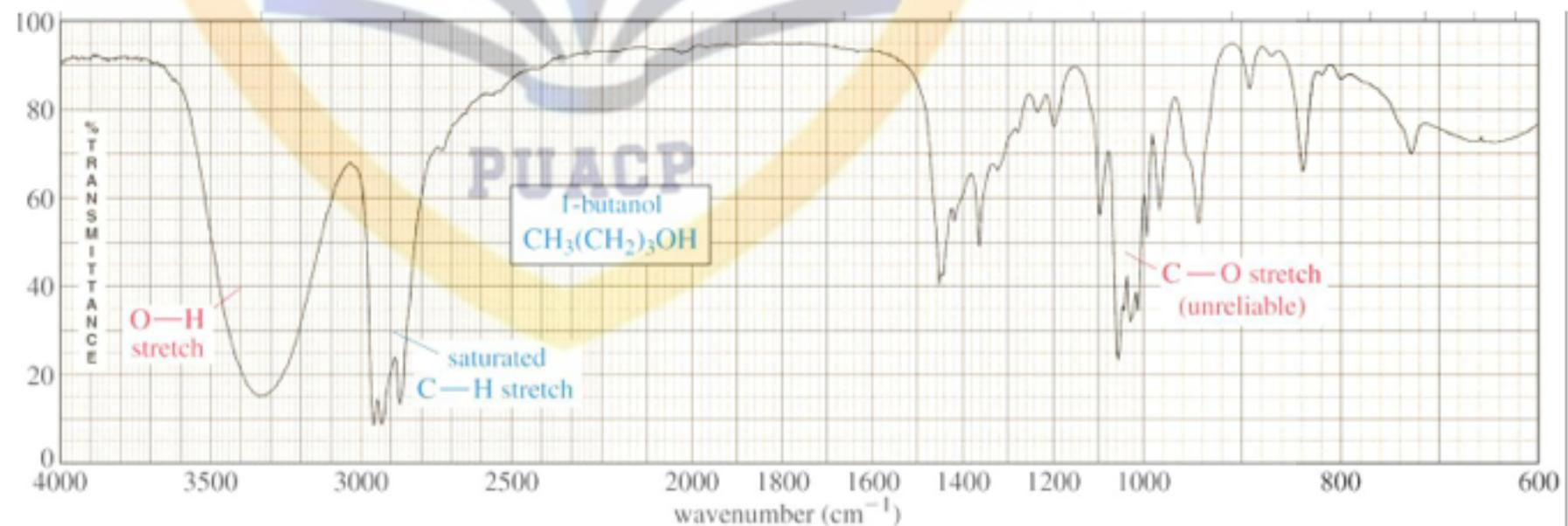


IR ABSORPTION RANGE

- The typical IR absorption range for covalent bonds is **600 - 4000 cm⁻¹**. 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⁻¹** 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⁻¹.

THE FINGERPRINT REGION

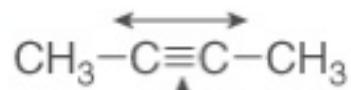
Functional Group Region Fingerprint Region



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⁻¹ (stretches), ~3000 cm⁻¹

C-C 1350-1470 cm⁻¹

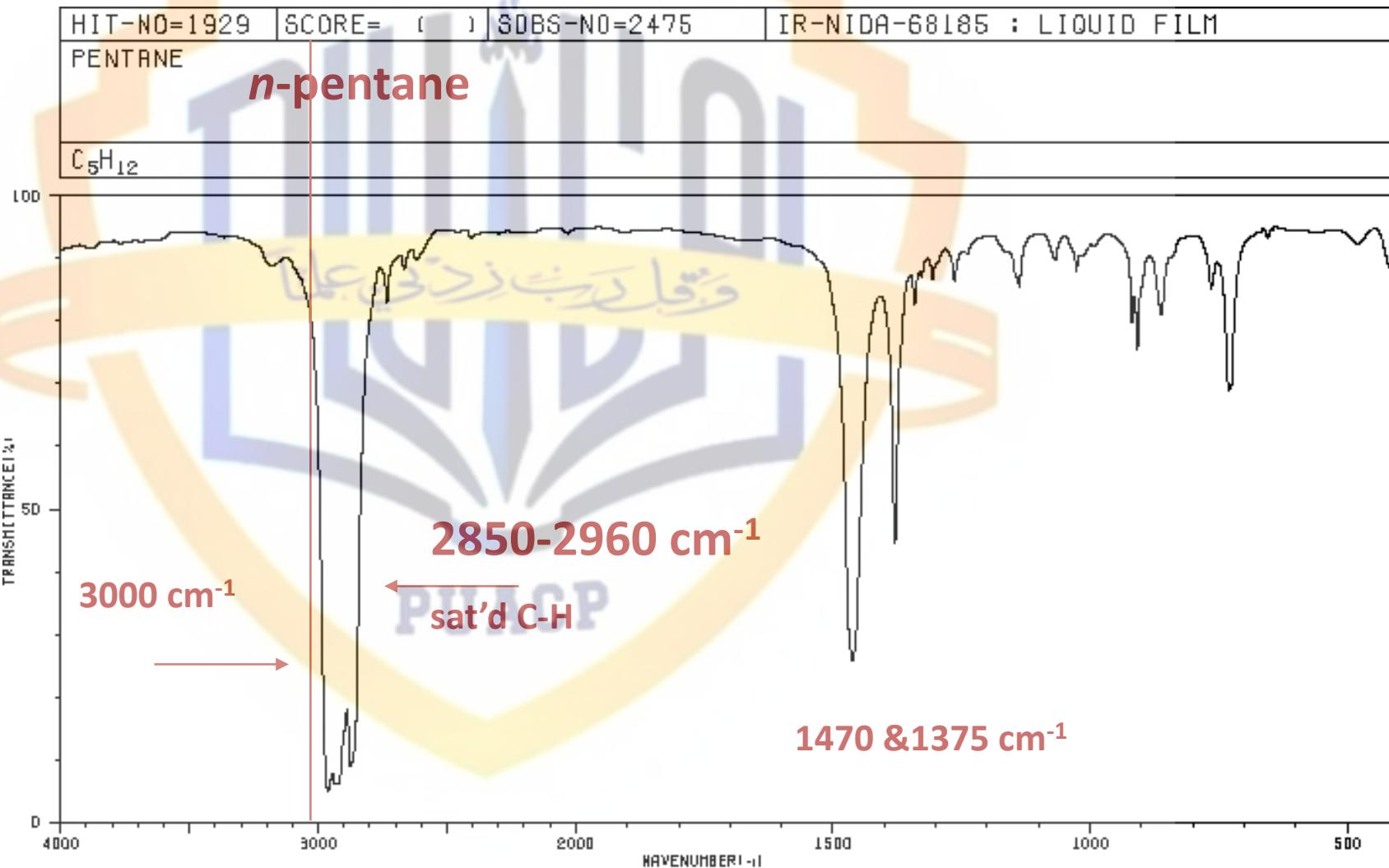
CH₂-CH₂ 1450-1470 cm⁻¹

CH₂-CH₃ 1360-1390 cm⁻¹

CH₃ 1450 cm⁻¹ (asymmetric) and
 1375 cm⁻¹ (symmetric)

(CH₃)₂CH 1380 and 1370 cm⁻¹

(CH₃)₃C 1395 (medium) and 1370 (strong) cm⁻¹



3182	86	2619	86	1138	81	732	66
3172	86	1462	24	1068	86		
2961	4	1380	45	1027	84		
2928	6	1342	79	919	77		
2875	8	1307	84	908	72		
2753	79	1264	84	862	79		
2666	84	1144	84	766	81		



HIT-NO=4225

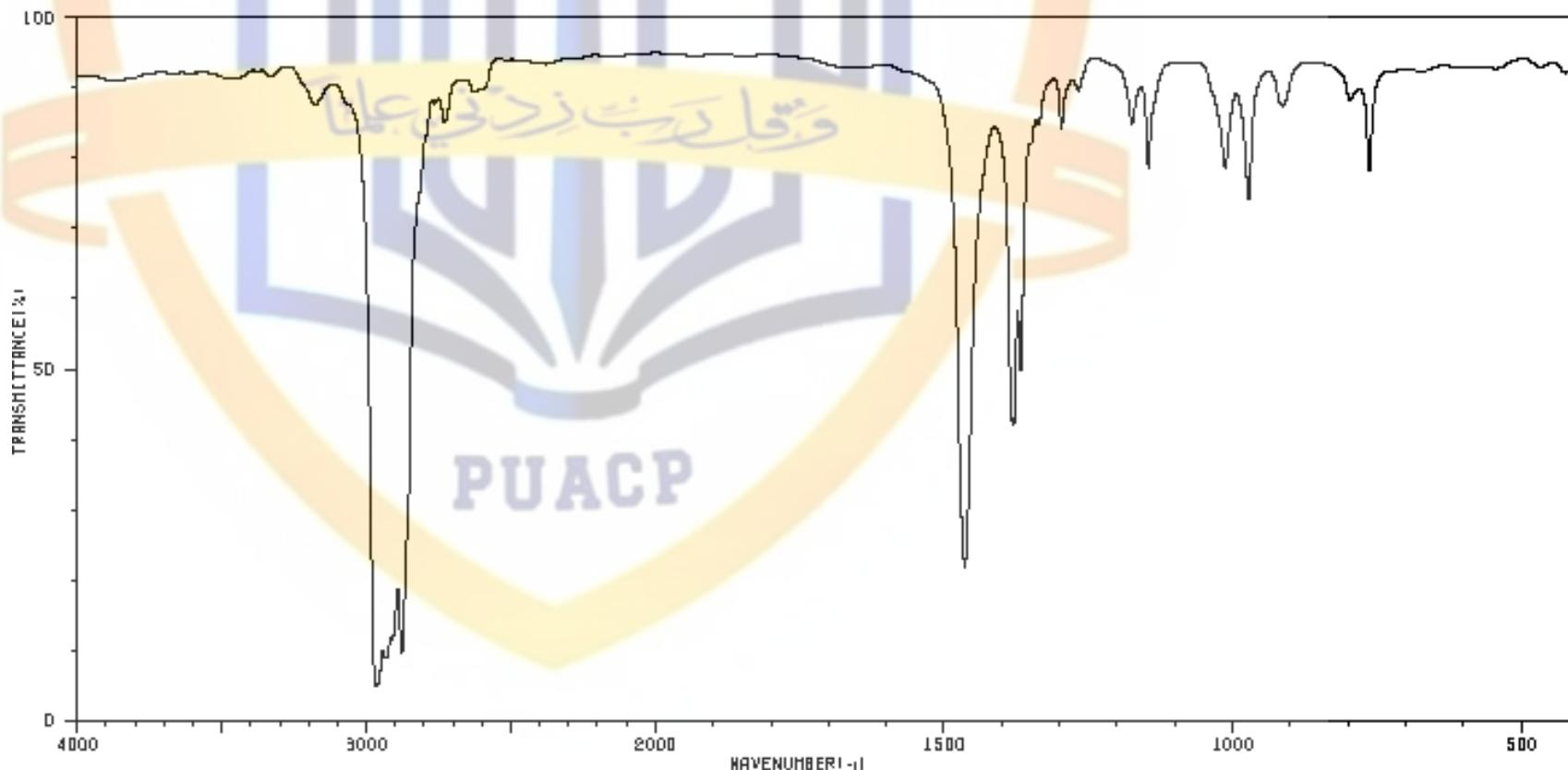
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SOBS-NO=10633

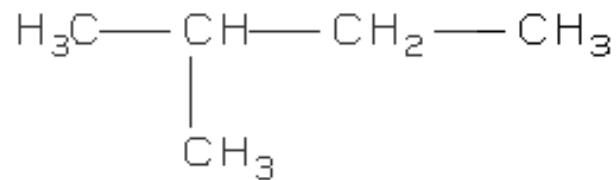
IR-NIDA-03327 : LIQUID FILM

ISOPENTANE

2-methylbutane (isopentane)

 C_5H_{12} 

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		

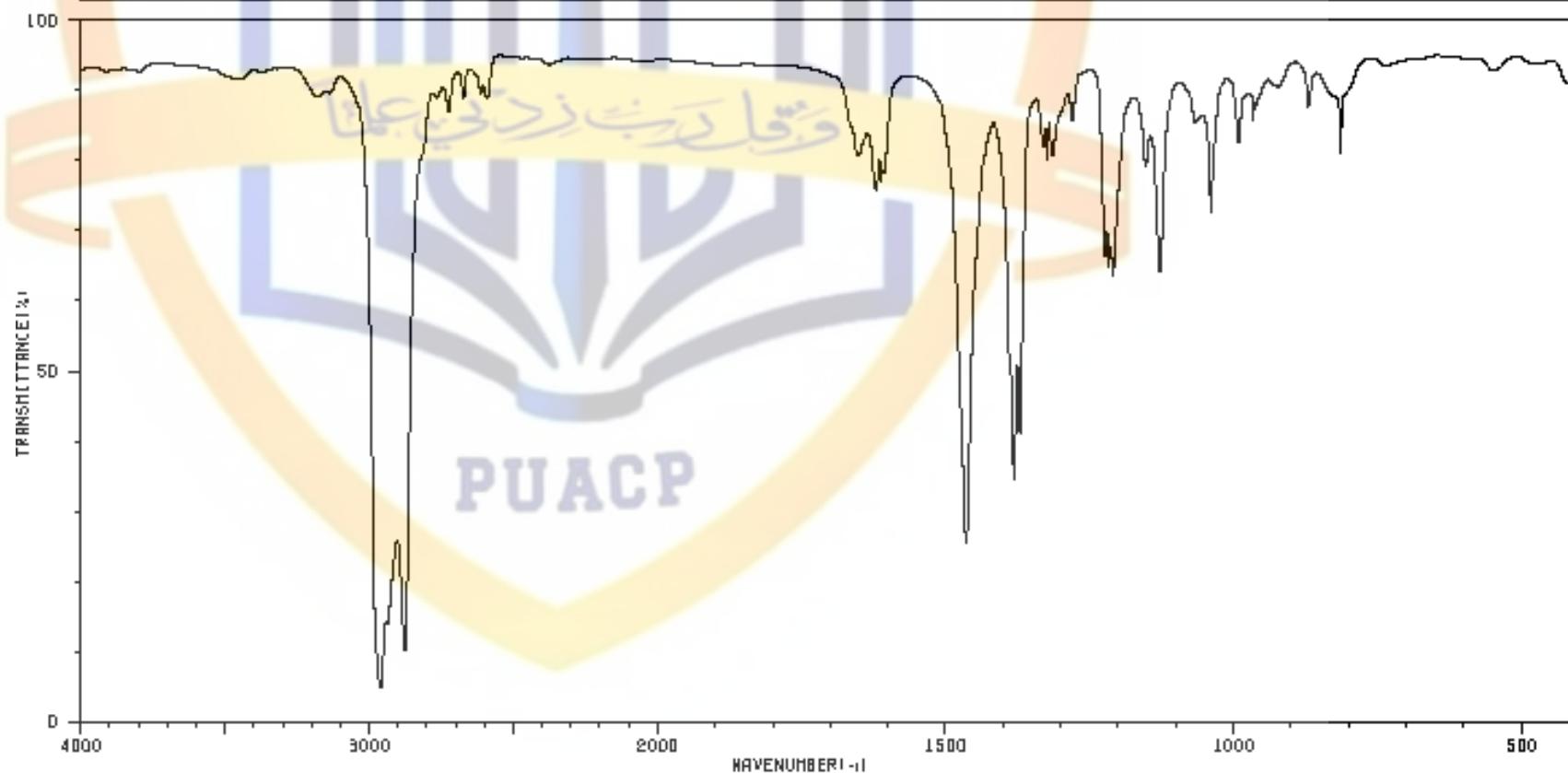


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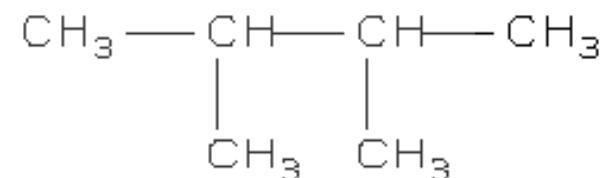
2,3-DIMETHYLBUTANE

2,3-dimethylbutane

C₆H₁₄



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		



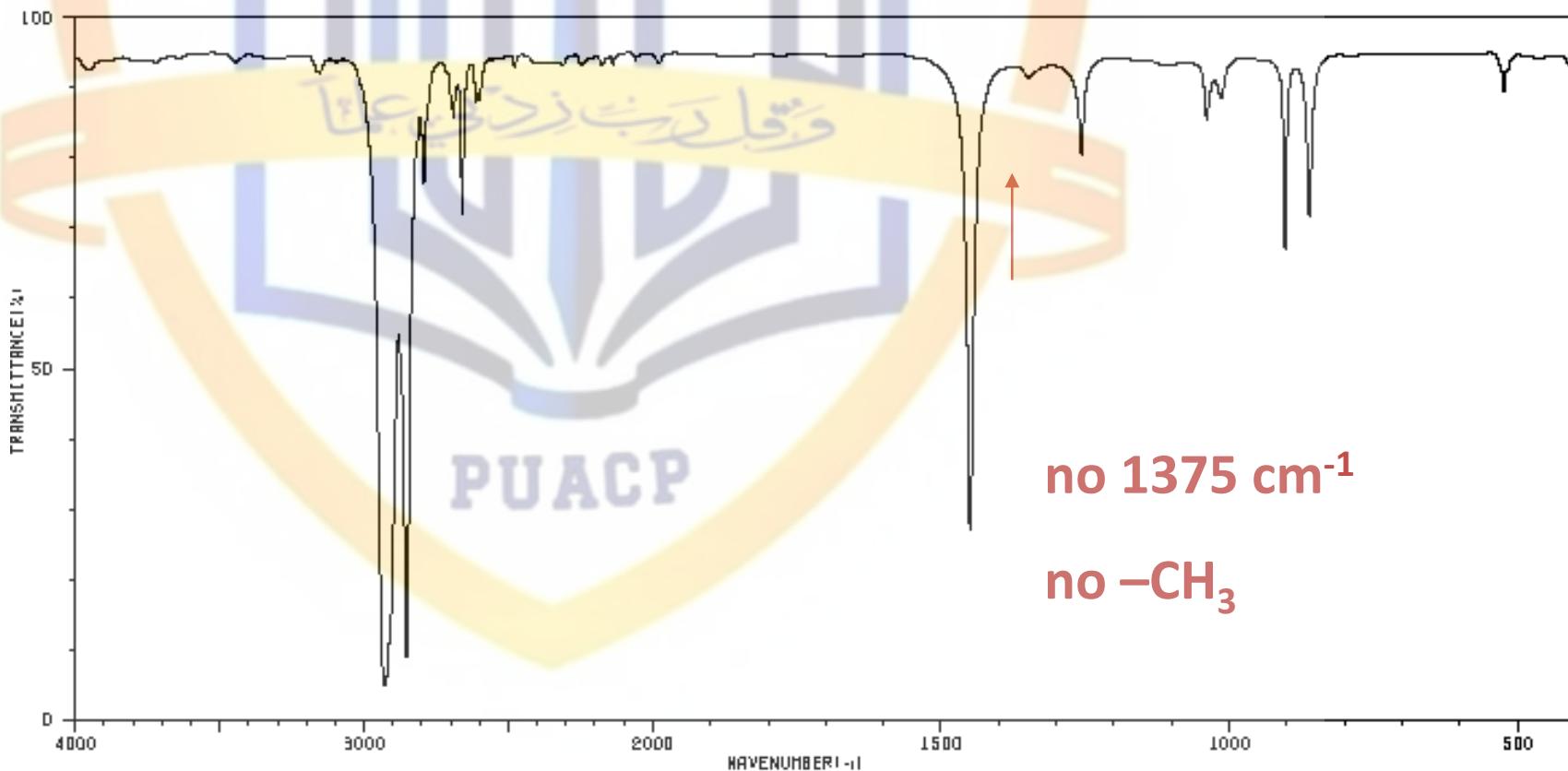
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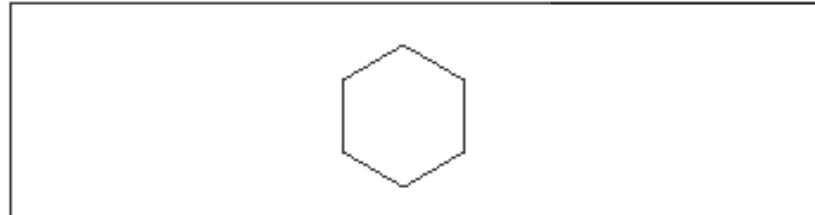
SOBS-NO=897

IR-NIDA-05221 : LIQUID FILM

CYCLOHEXANE

cyclohexaneC₆H₁₂

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⁻¹

=C-H (stretch)

3080 – 3020 cm⁻¹ (~3100 cm⁻¹)

=C-H (oop bending)

Monosubstituted

920 -910 (s) and
1000 – 990 (s) cm⁻¹

1,1-Disubstituted

880 – 900 (s) cm⁻¹

cis-Disubstituted

730 – 675 (s) cm⁻¹

trans-Disubstituted

975 – 965 (s) cm⁻¹

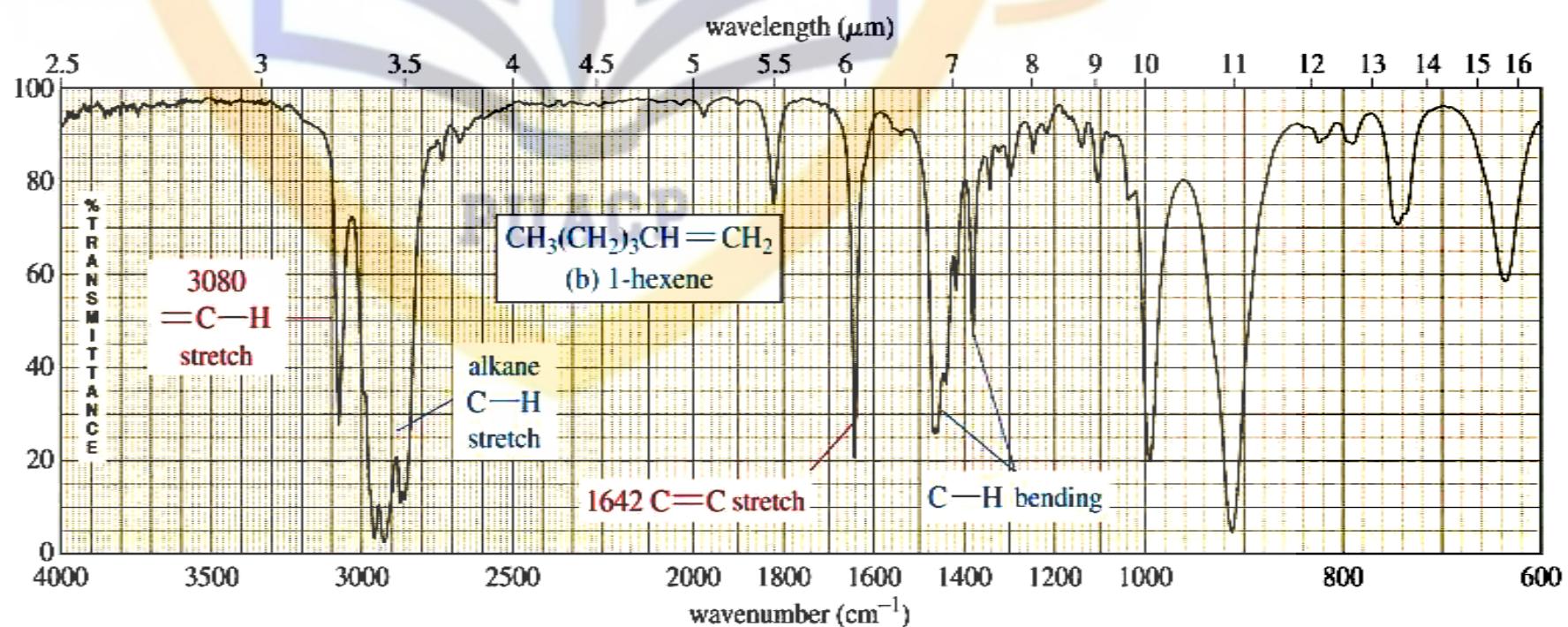
Trisubstituted

810 – 780 (m) cm⁻¹

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⁻¹**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm⁻¹** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm⁻¹ (see next slide)



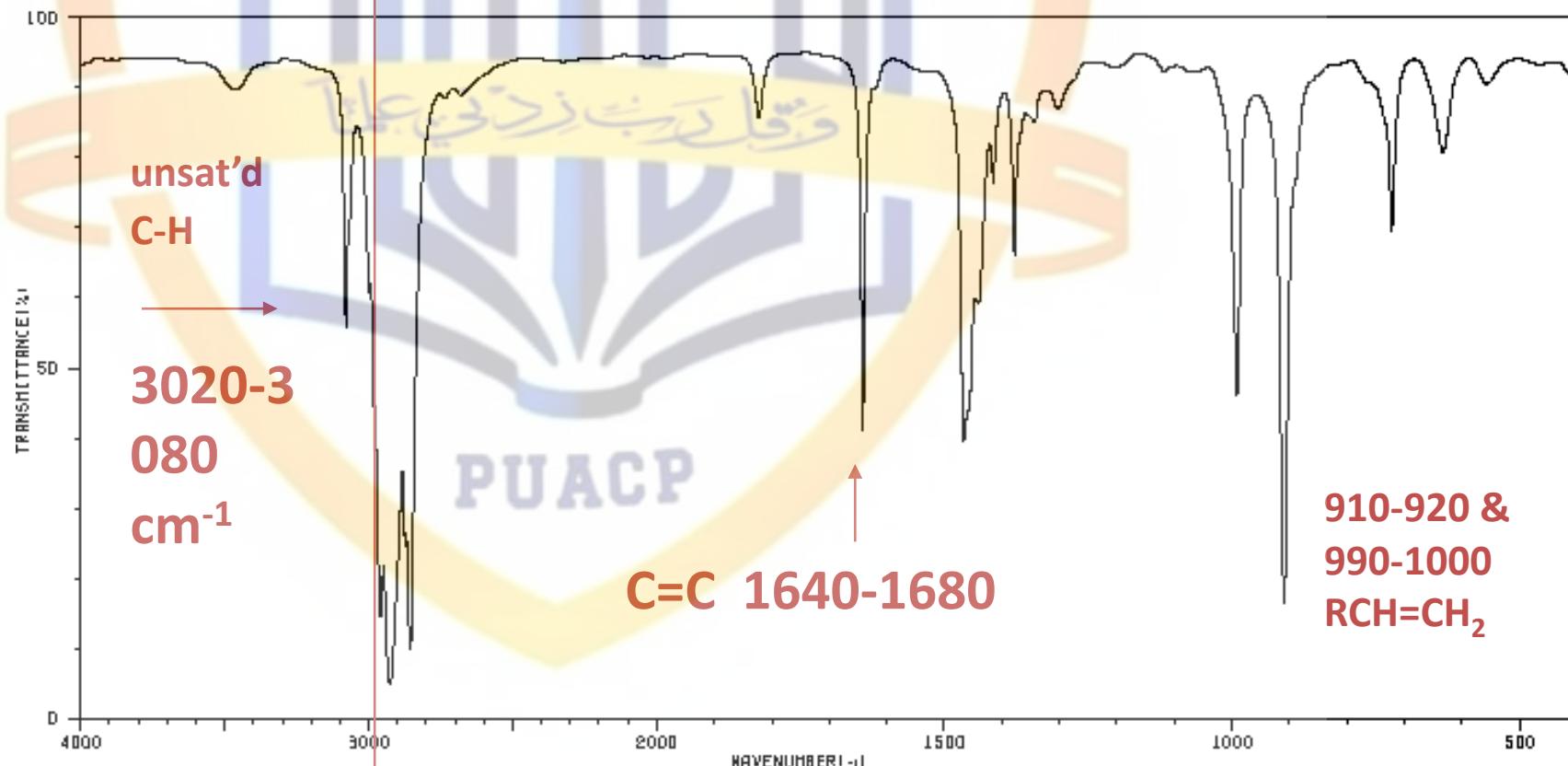
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

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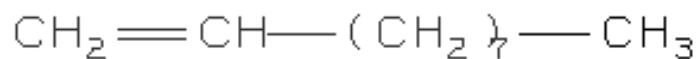
1-DECENE

1-decene

C₁₀H₂₀



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

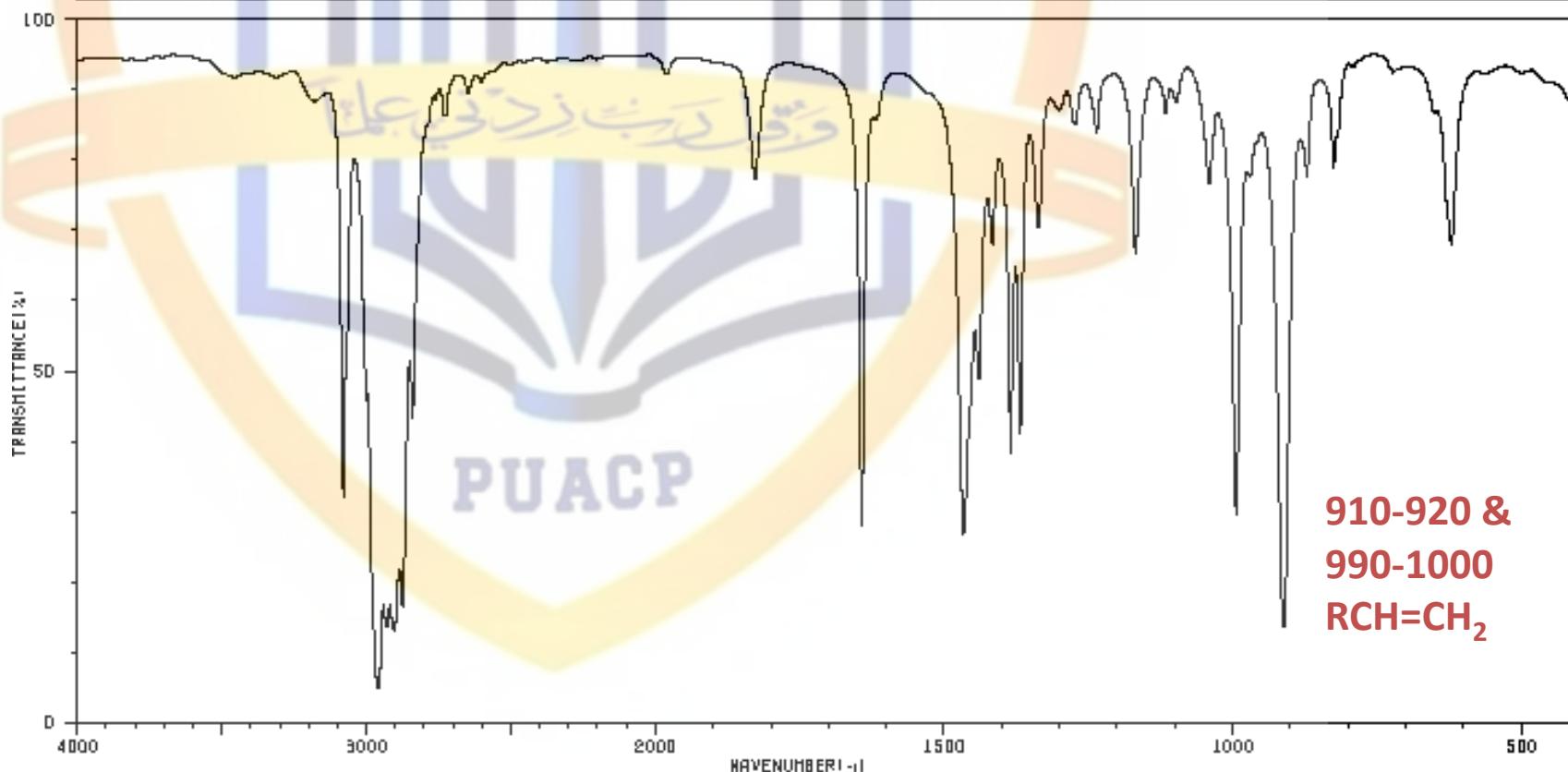


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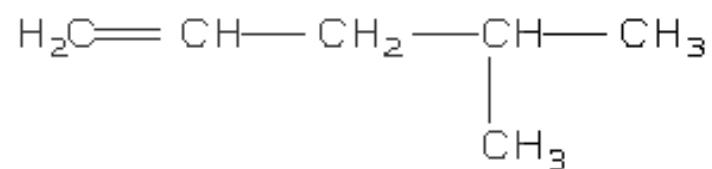
4-METHYL-1-PENTENE

4-methyl-1-pentene

C₆H₁₂



3178	84	2727	84	1385	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		

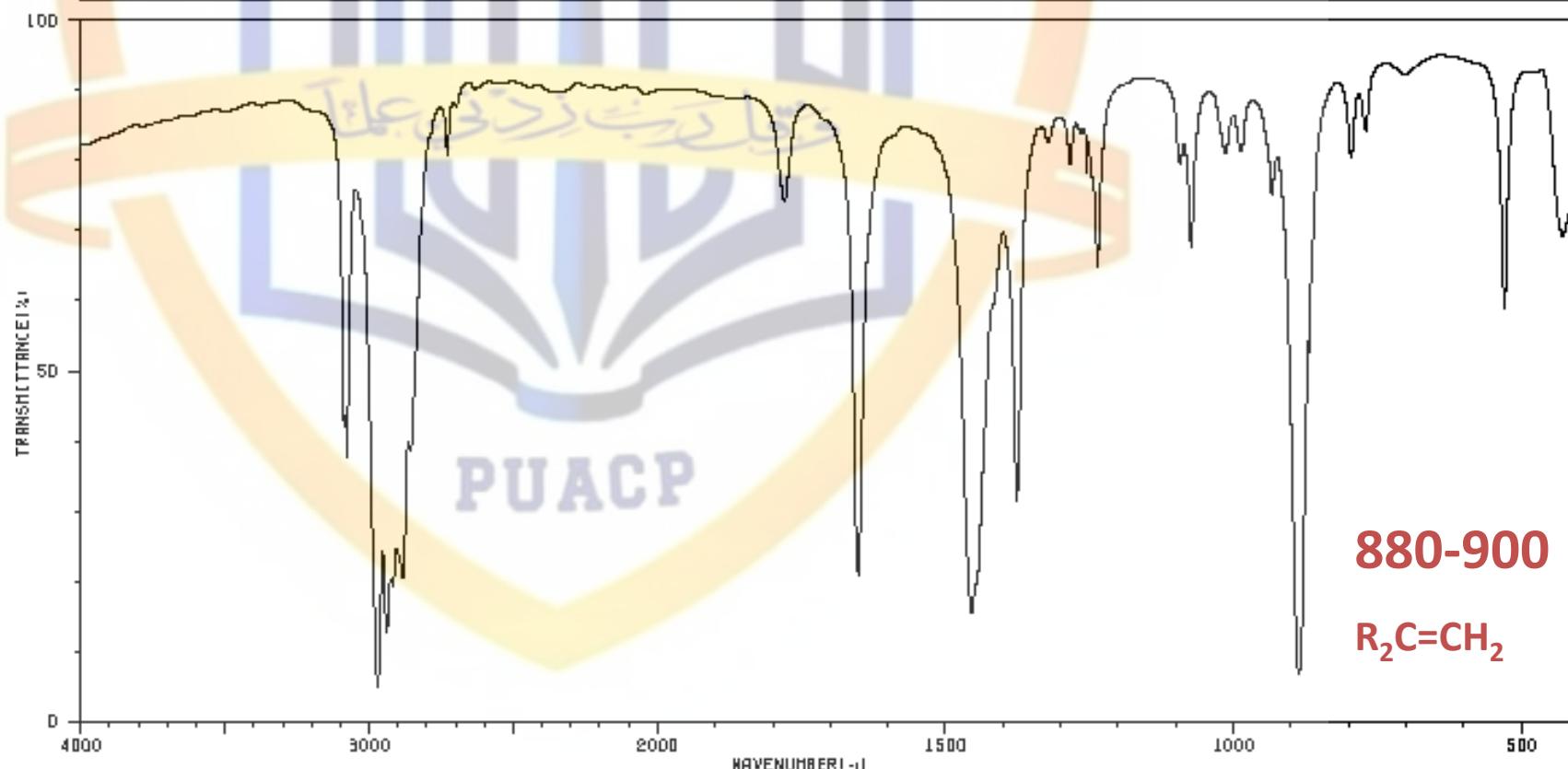


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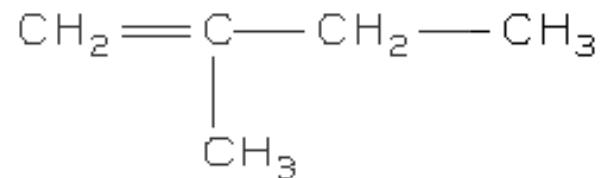
2-METHYL-1-BUTENE

2-methyl-1-butene

C₅H₁₀

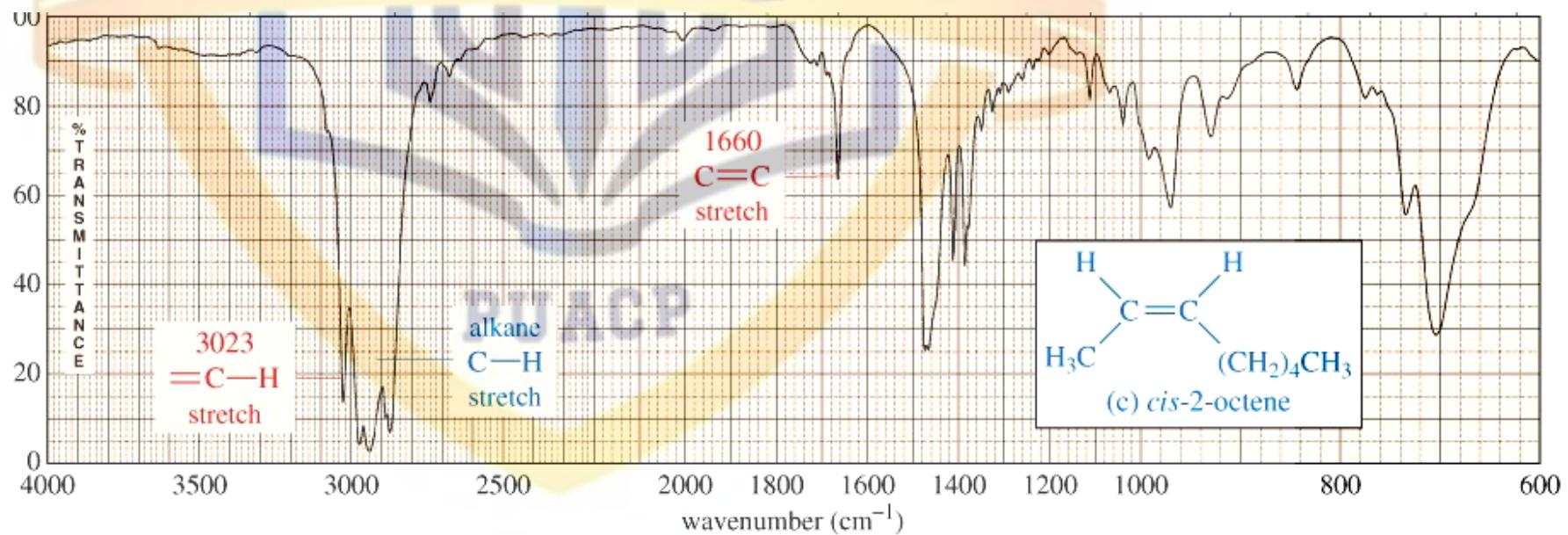


3087	41	2728	77	1266	74	887	6
3077	36	1780	72	1237	62	869	50
2970	4	1651	20	1093	77	796	77
2939	12	1466	14	1074	64	770	81
2919	18	1377	30	1014	79	530	57
2863	20	1322	79	987	79	429	66
2856	37	1284	77	933	72		



IR SPECTRUM OF ALKENES

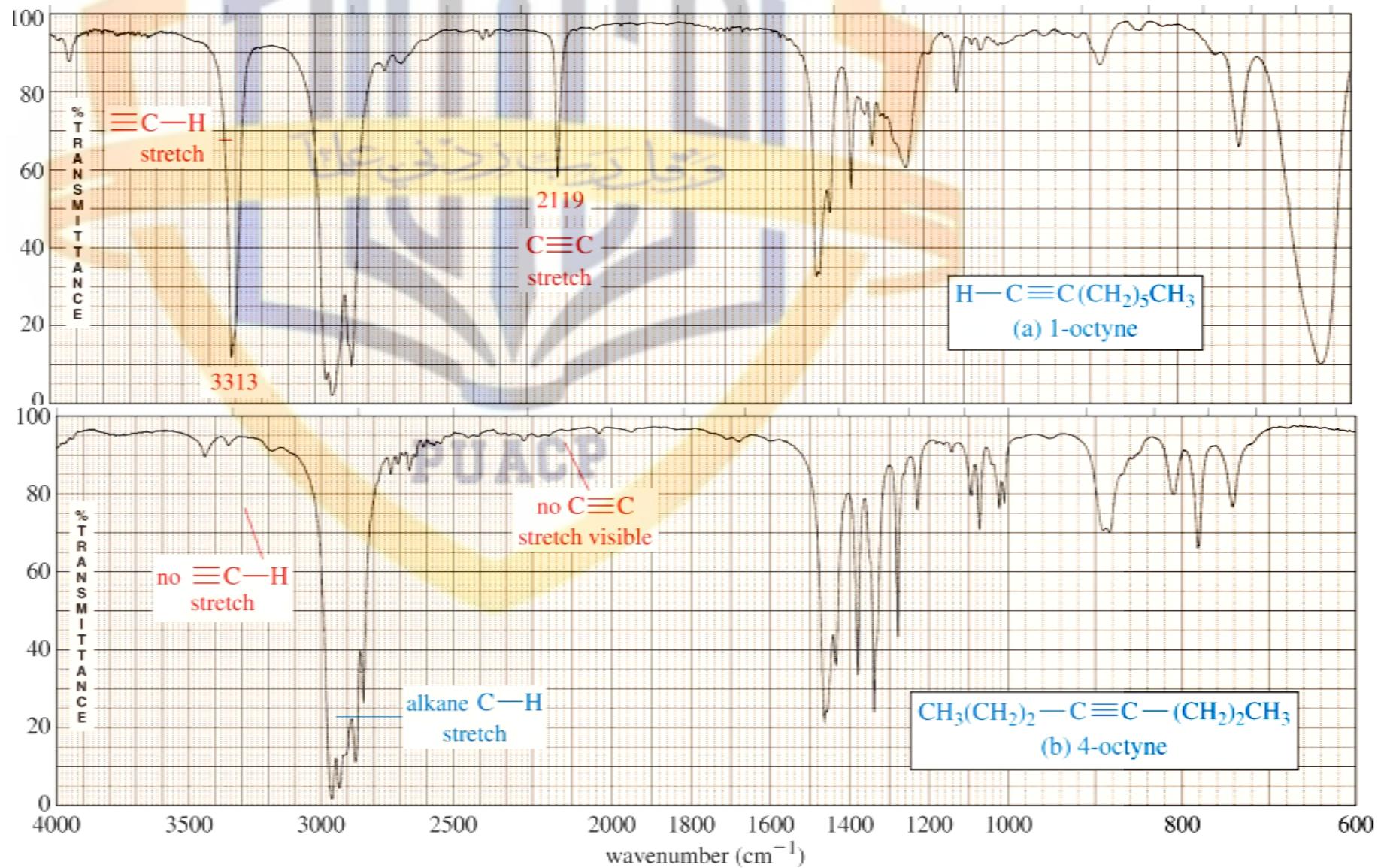
This spectrum shows that the band appearing around 3080 cm^{-1} can be obscured by the broader bands appearing around 3000 cm^{-1} .



IR SPECTROSCOPY of Alkynes

- Terminal C-H (sp) 3300 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

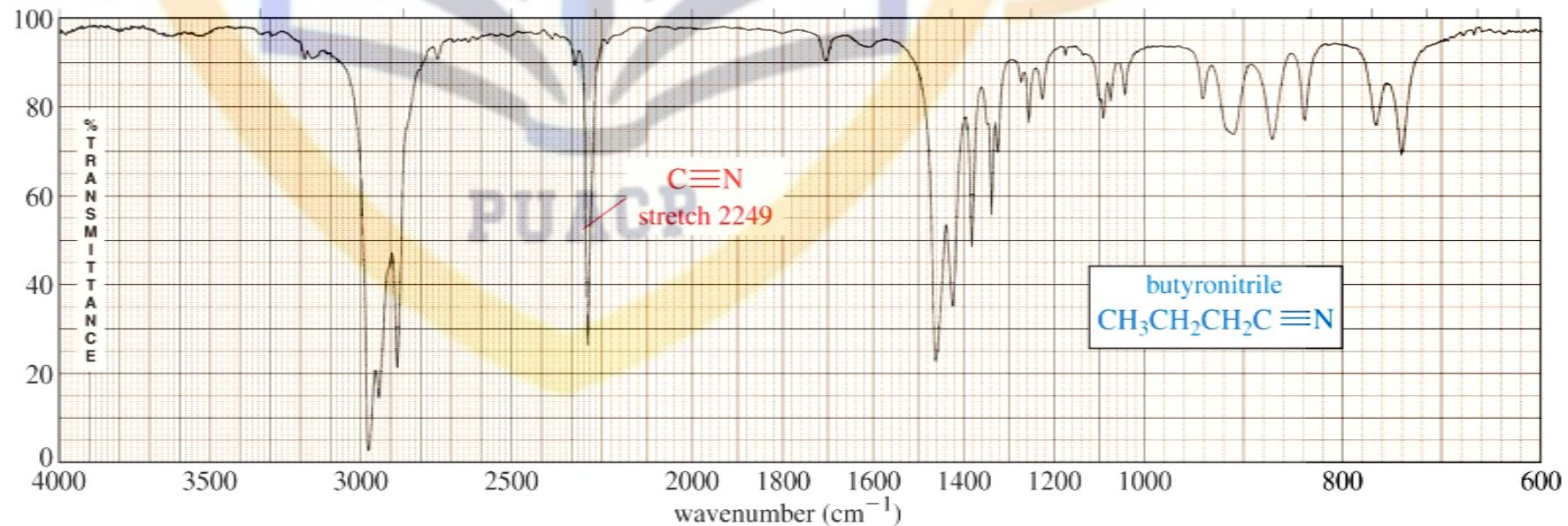
IR SPECTRUM OF ALKYNES



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⁻¹** 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.



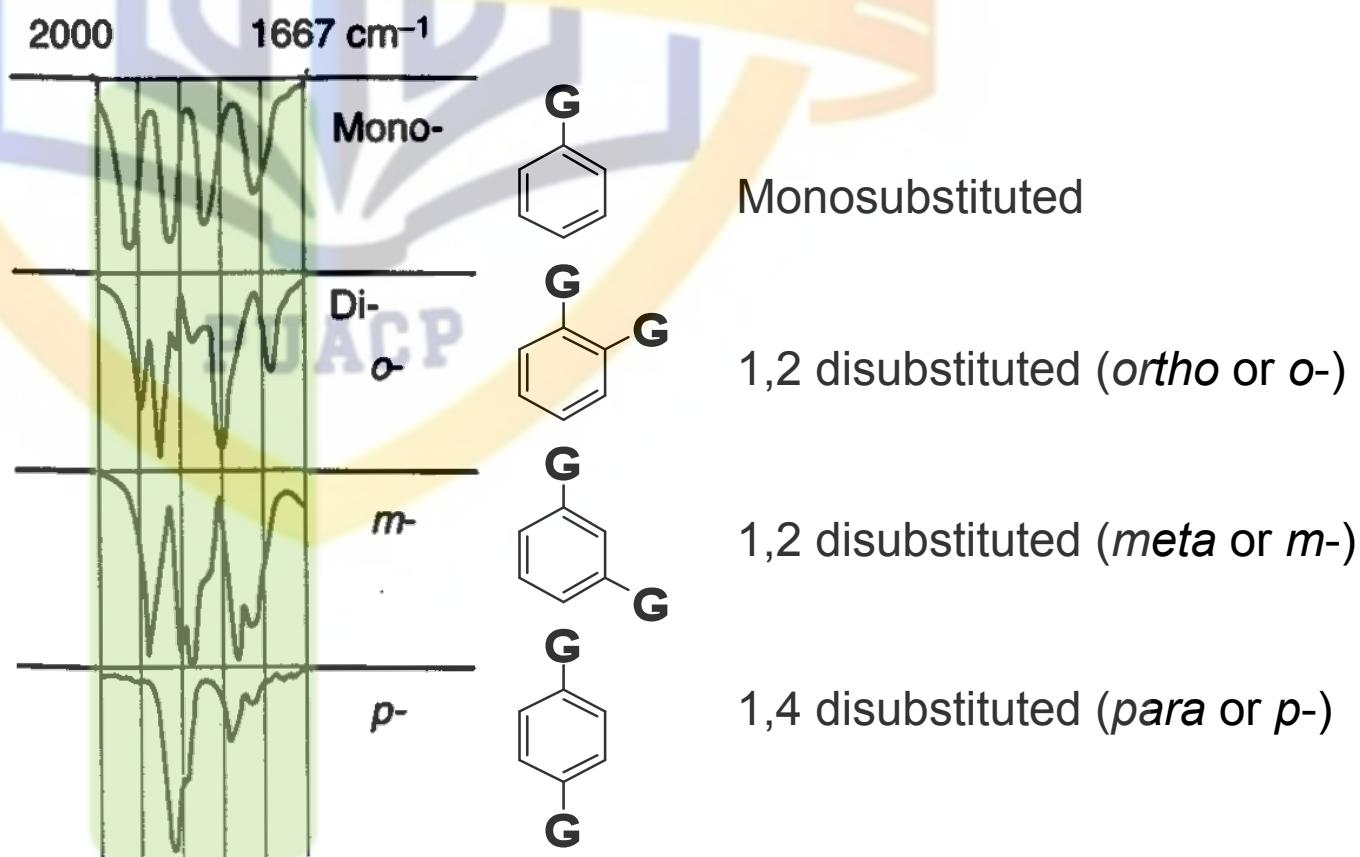
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR SPECTROSCOPY of Arenes

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

Aromatics

- If the region between 1667-2000 cm⁻¹ (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



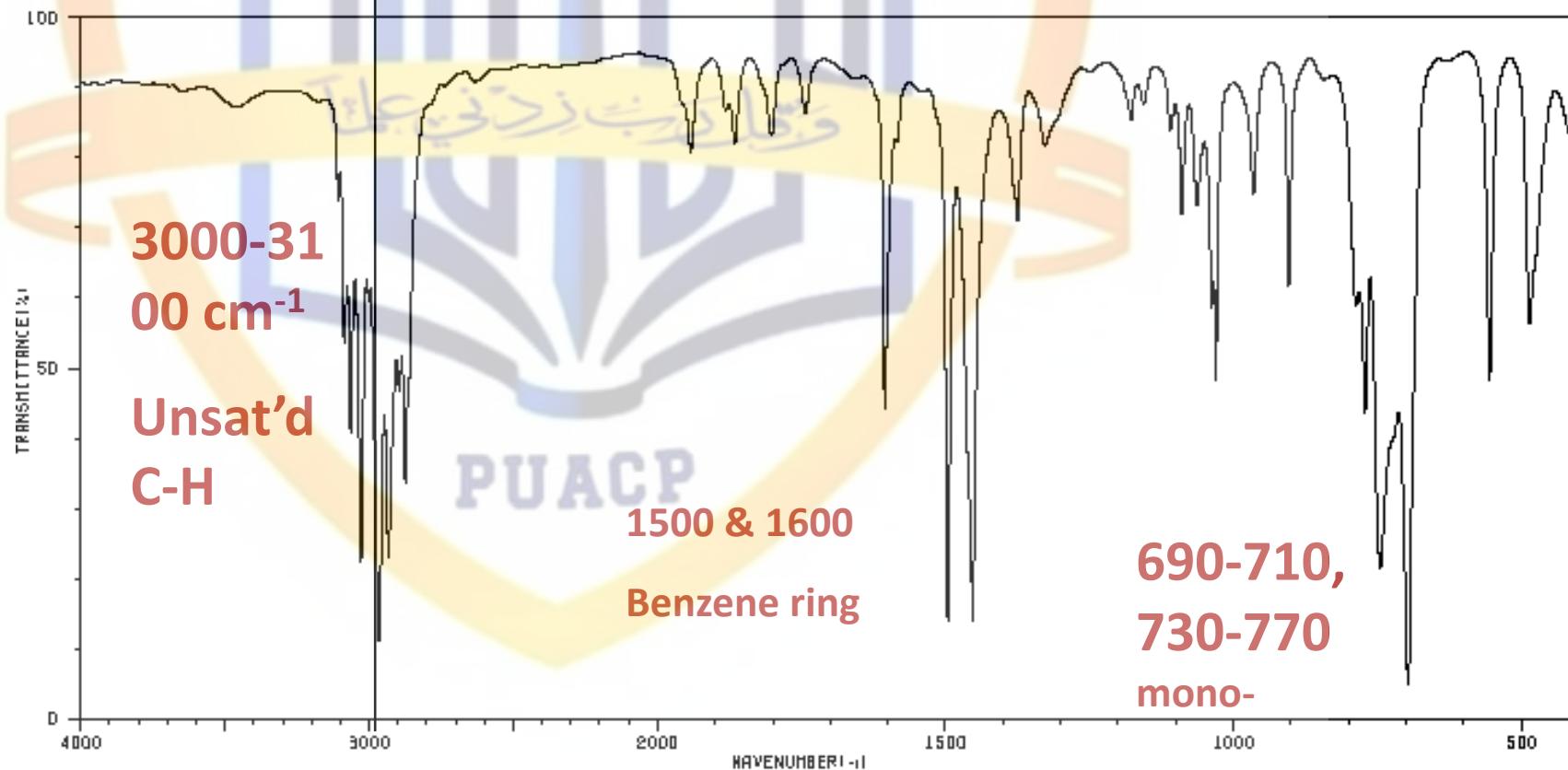
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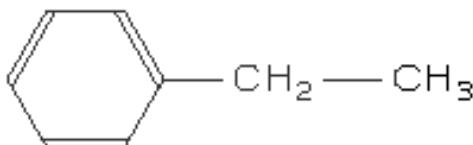
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IR-NIDA-05258 : LIQUID FILM

ETHYLBENZENE

ethylbenzene C_8H_{10} 

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

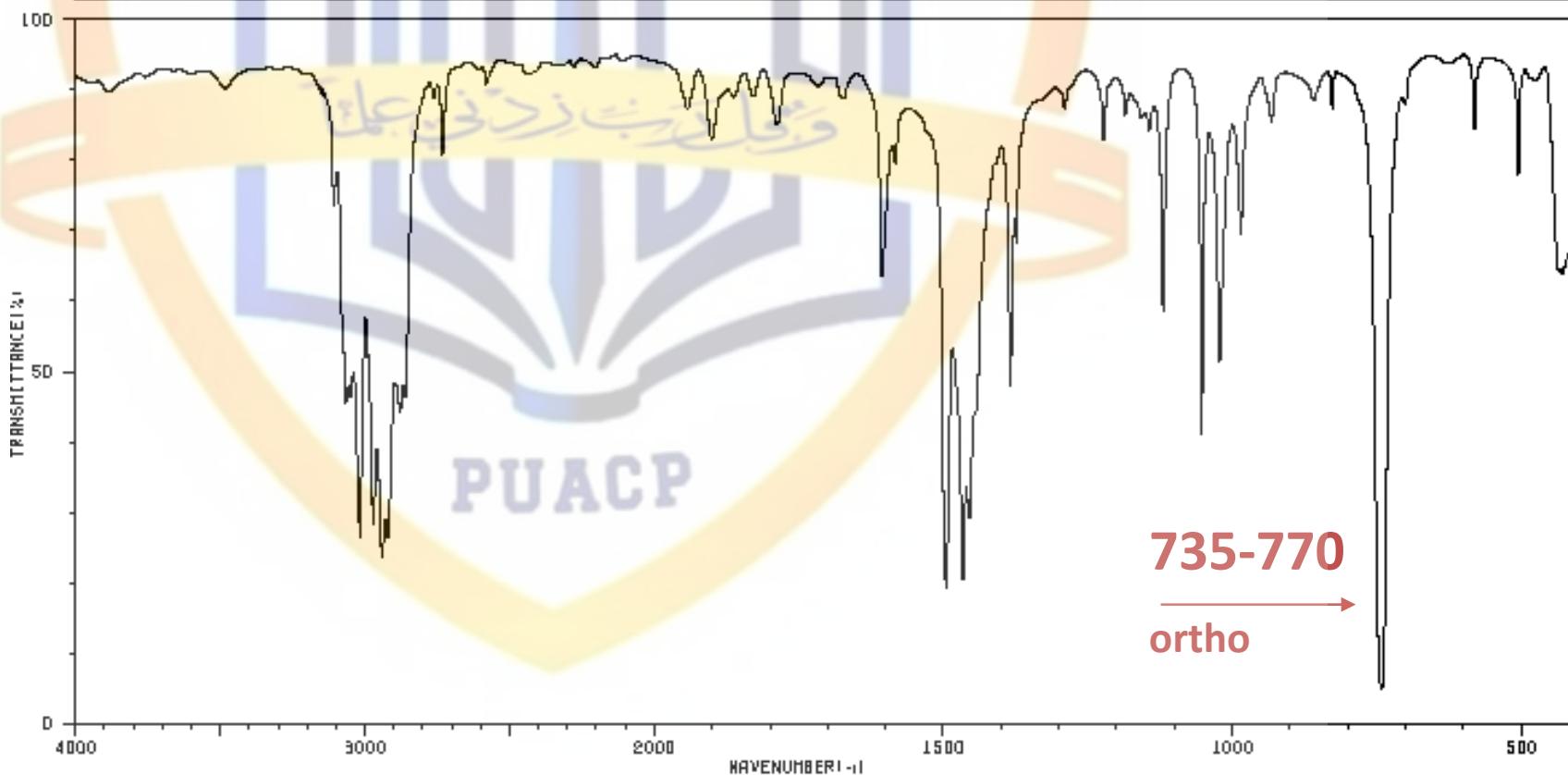


HIT-NO=1272 SCORE= () S0BS-NO=1028 IR-NIDA-21942 : LIQUID FILM

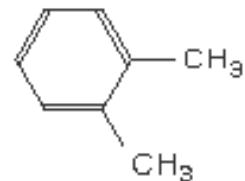
O-XYLENE

o-xylene

C₈H₁₀



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



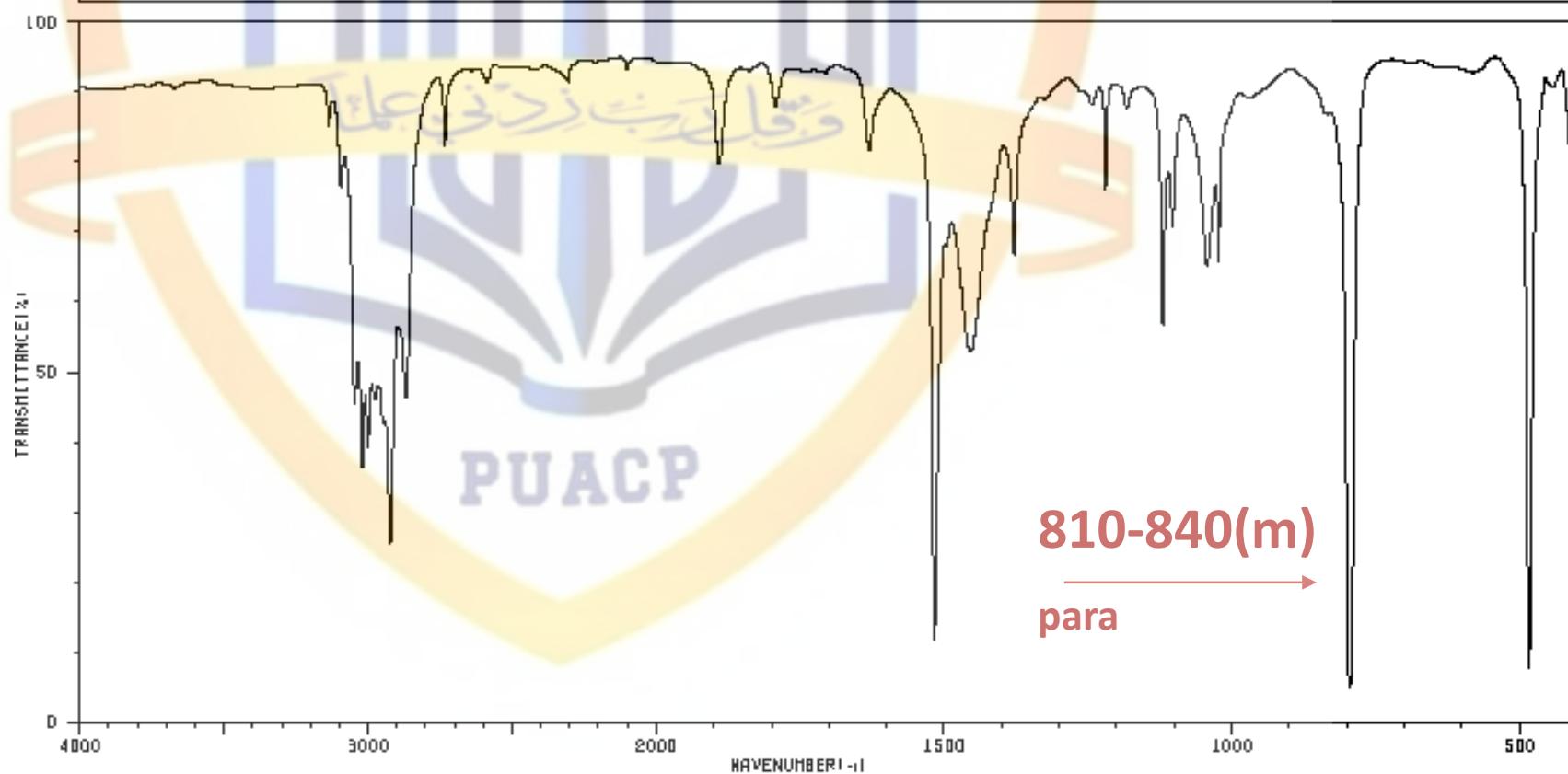
HIT-NO=1238

SCORE= ()

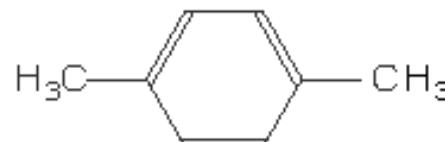
SDBS-NO=899

IR-NIDA-63598 : LIQUID FILM

P-XYLENE

p-xylene C_8H_{10} 

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		

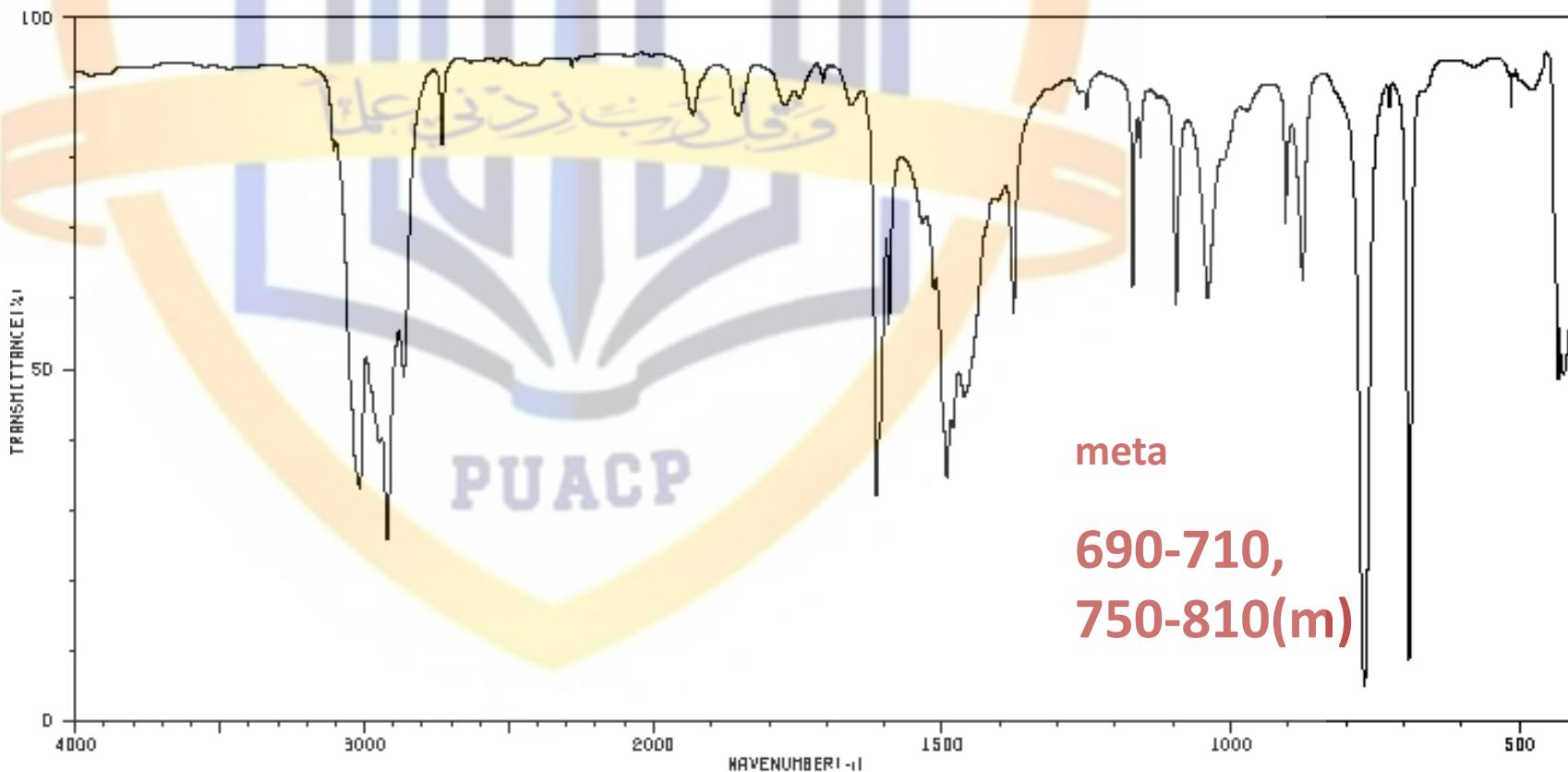


HIT-NO=1275 SCORE= () S0BS-NO=1032 IR-NIDA-63601 : LIQUID FILM

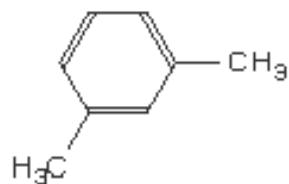
M-XYLENE

m-xylene

C₈H₁₀



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		

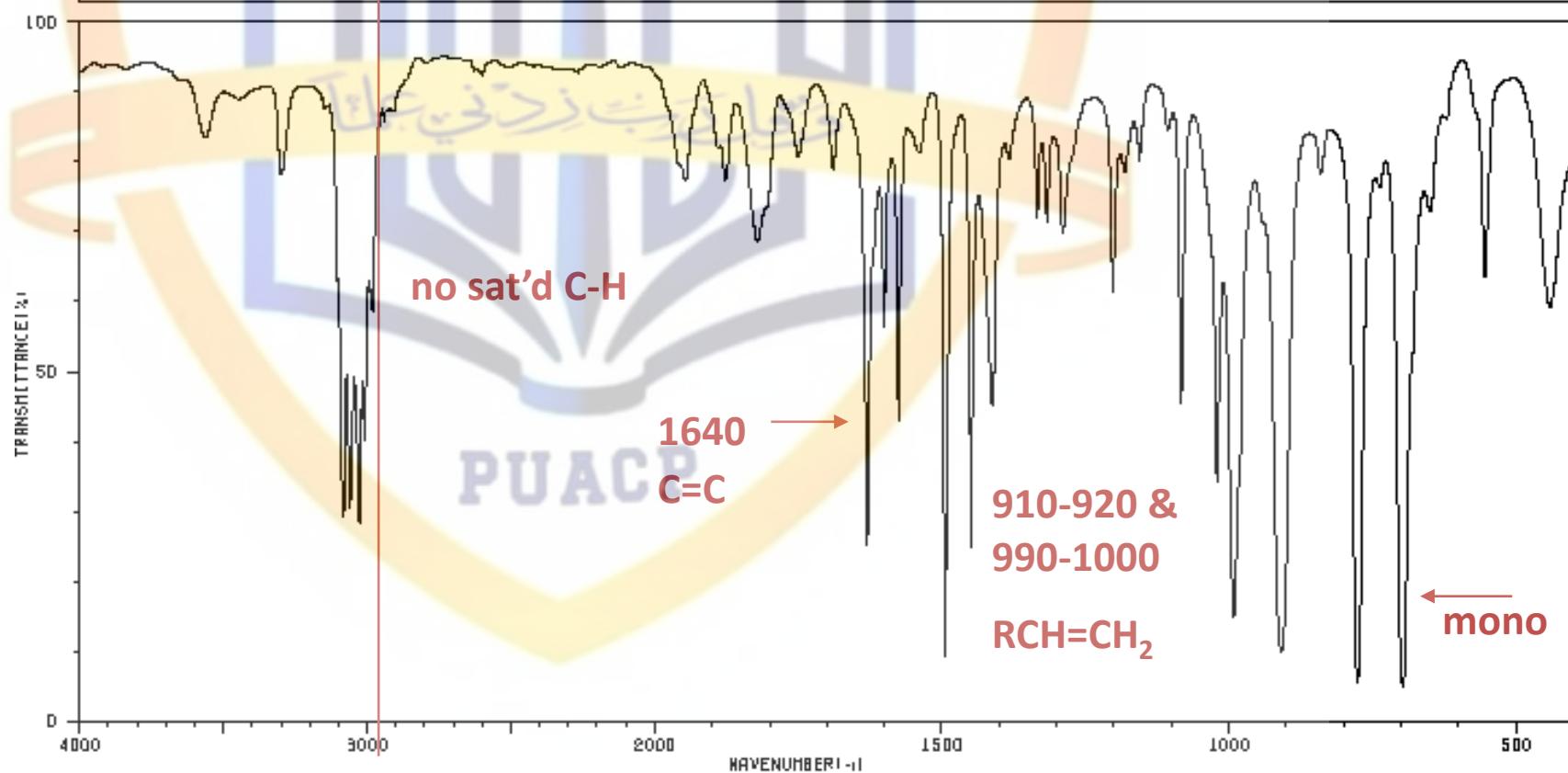


HIT-NO=2170 SCORE= () SDBS-NO=3044 IR-NIDA-10290 : LIQUID FILM

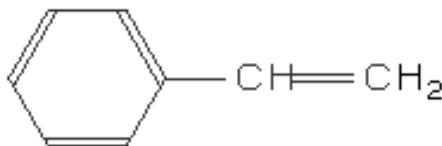
STYRENE

styrene

C₈H₈



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	8	442	67

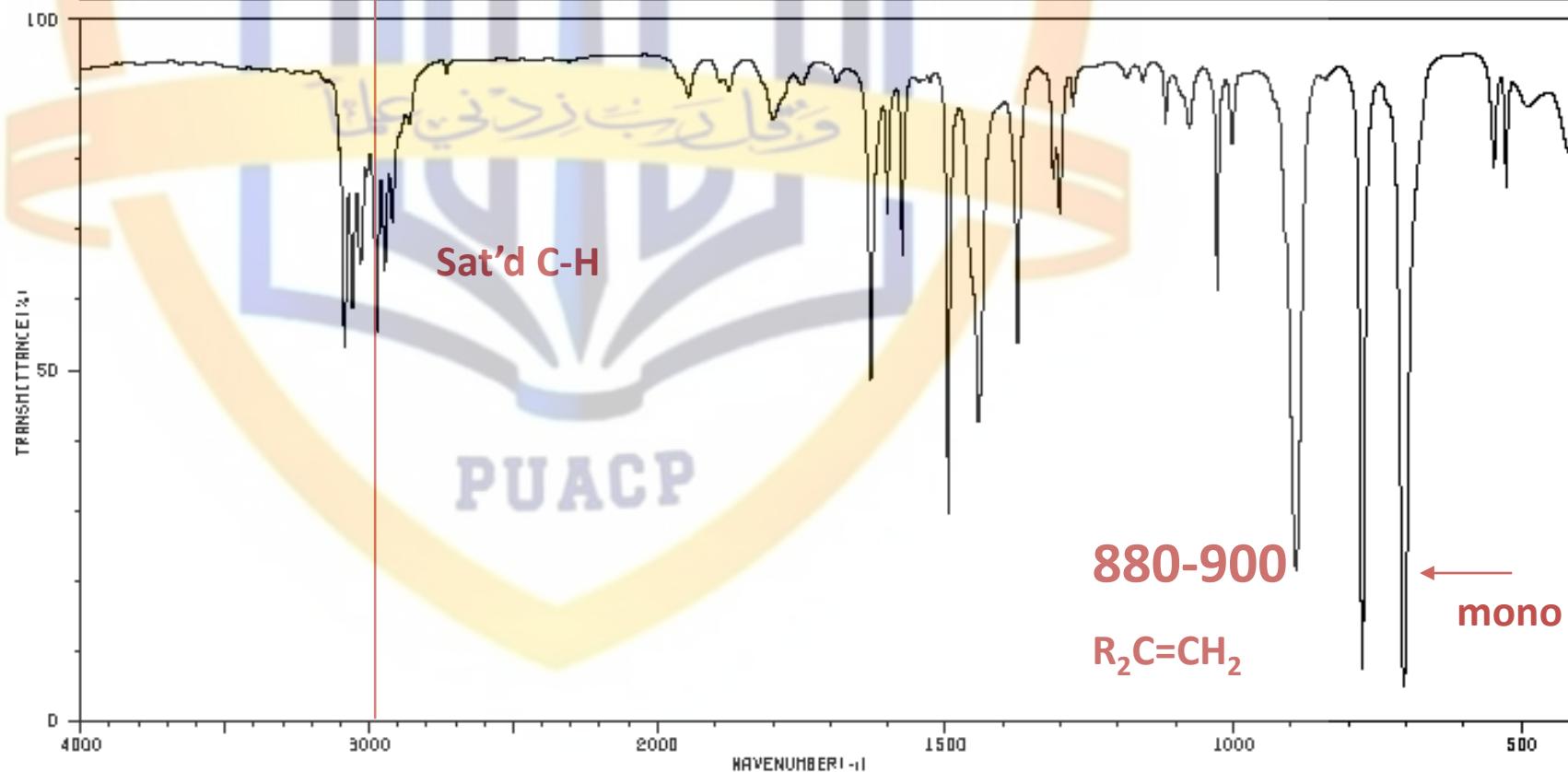


HIT-NO=1854 SCORE= () S0BS-NO=2368 IR-NIDA-00385 : LIQUID FILM

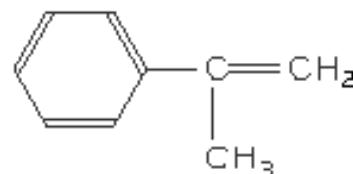
ISOPROPENYLBENZENE

2-phenylpropene

C₉H₁₀



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 $1260 - 1000 \text{ cm}^{-1}$

Compound	O-H stretch	C-O stretch
Phenol	3610 cm^{-1}	1220 cm^{-1}
3° Alcohol	3620 cm^{-1}	1150 cm^{-1}
2° Alcohol	3630 cm^{-1}	1100 cm^{-1}
1° Alcohol	3640 cm^{-1}	1050 cm^{-1}

HIT-NO=1418

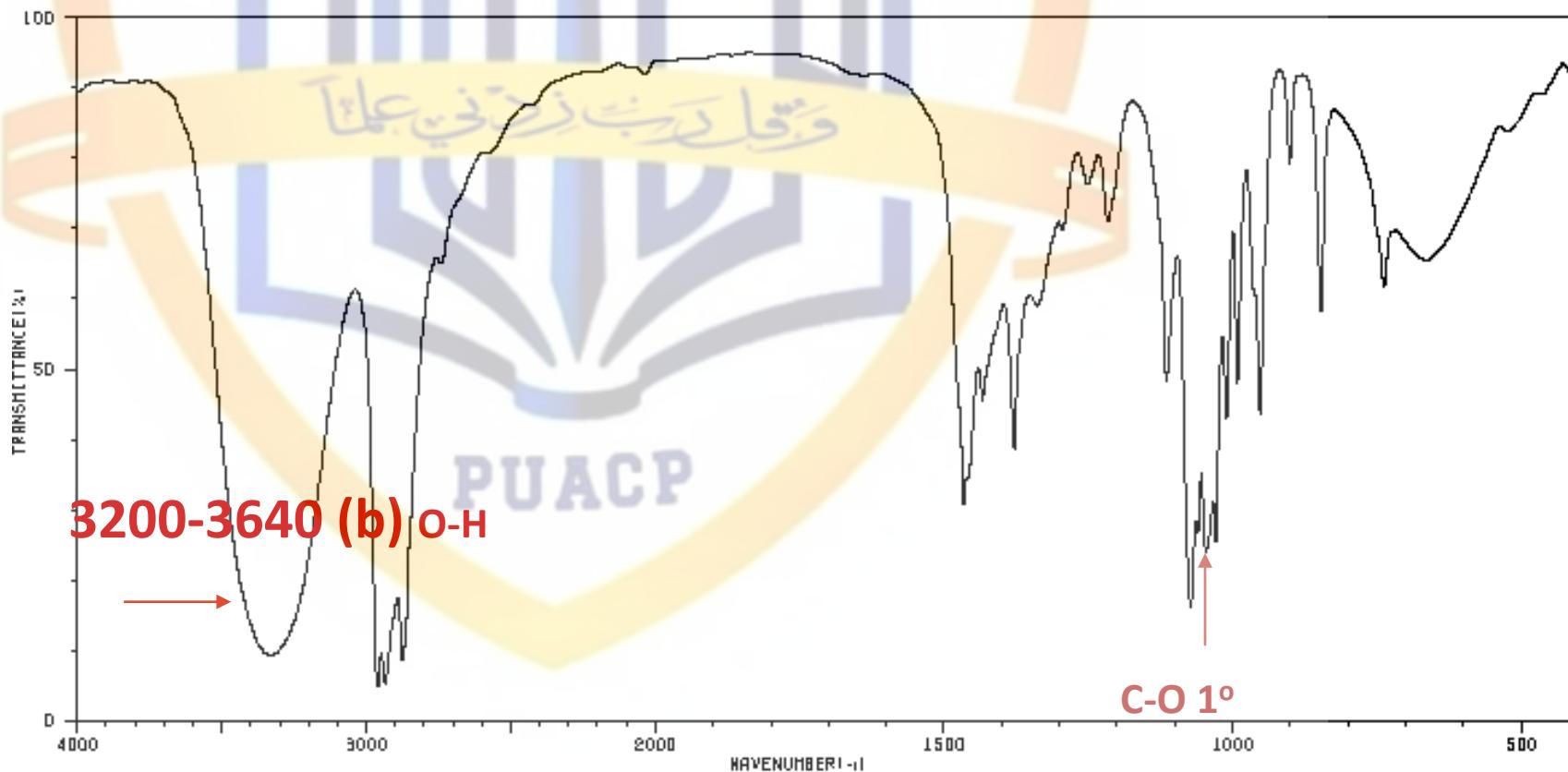
SCORE= ()

SOBS-NO=1374

IR-NIDA-05408 : LIQUID FILM

1-BUTANOL

1-butanol

 $C_4H_{10}O$ 

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		

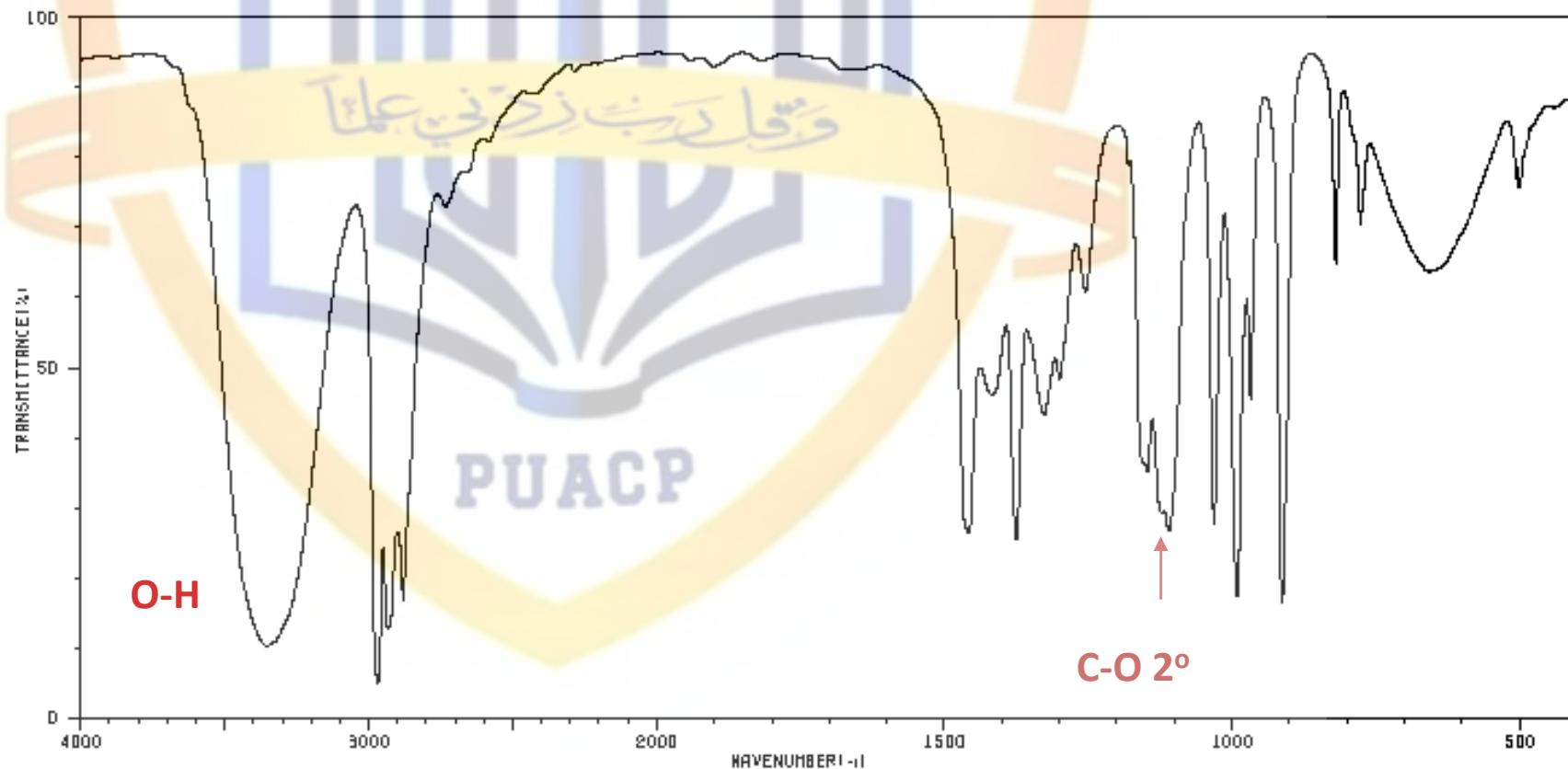


HIT-NO=1035 SCORE= () S0BS-NO=507 IR-NIDA-04700 : LIQUID FILM

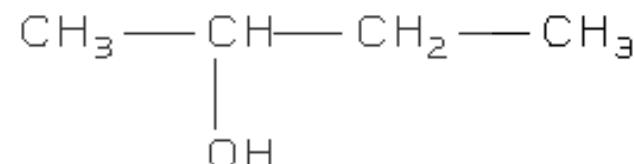
2-BUTANOL

2-butanol

C₄H₁₀O



3363	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		

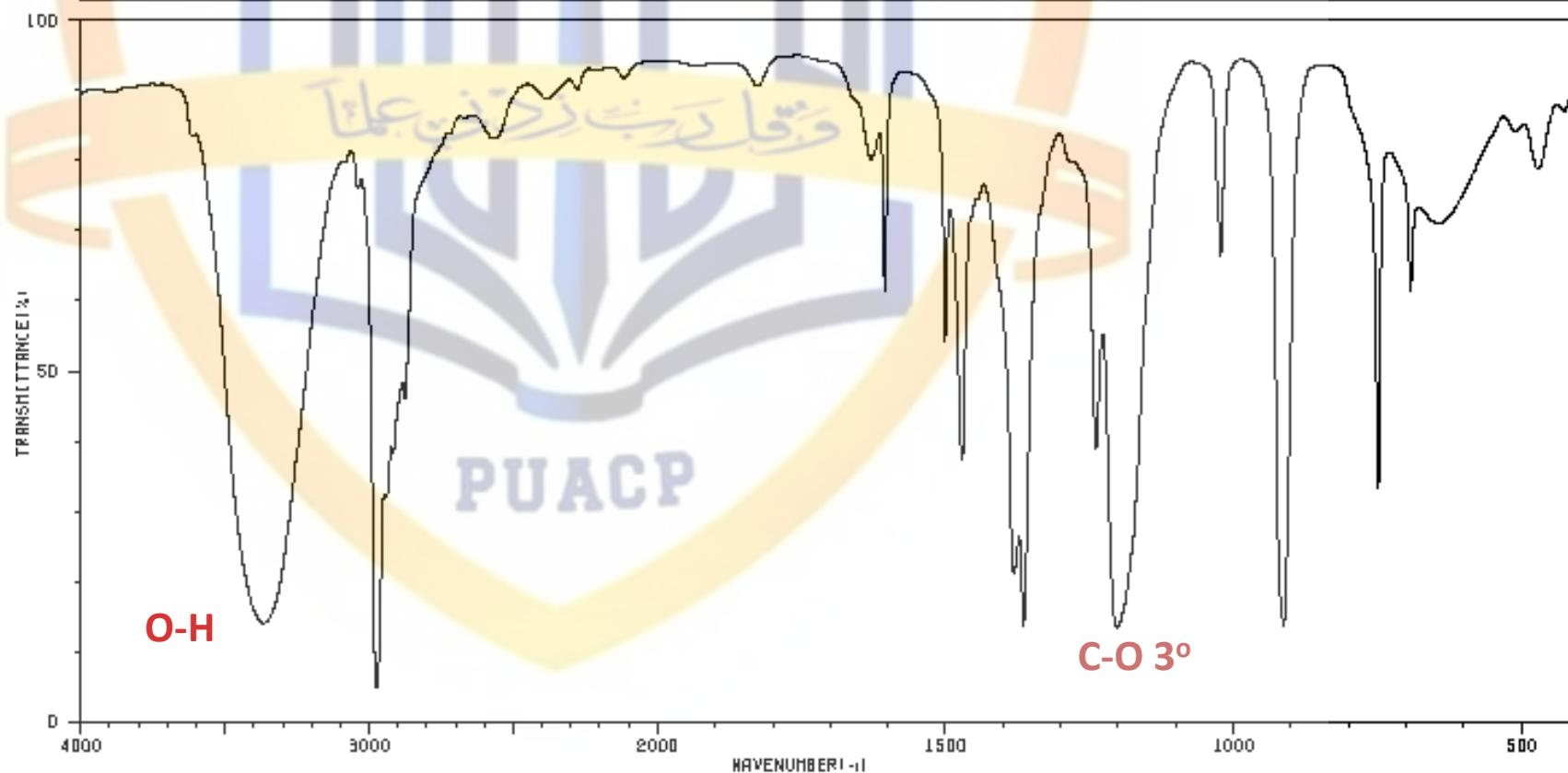


HIT-NO=1034 SCORE= () S0BS-NO=506 IR-NIDA-05409 : LIQUID FILM

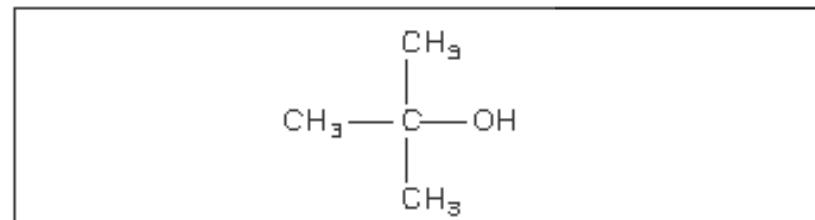
2-METHYL-2-PROPANOL

***tert*-butyl alcohol**

C₄H₁₀O



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		



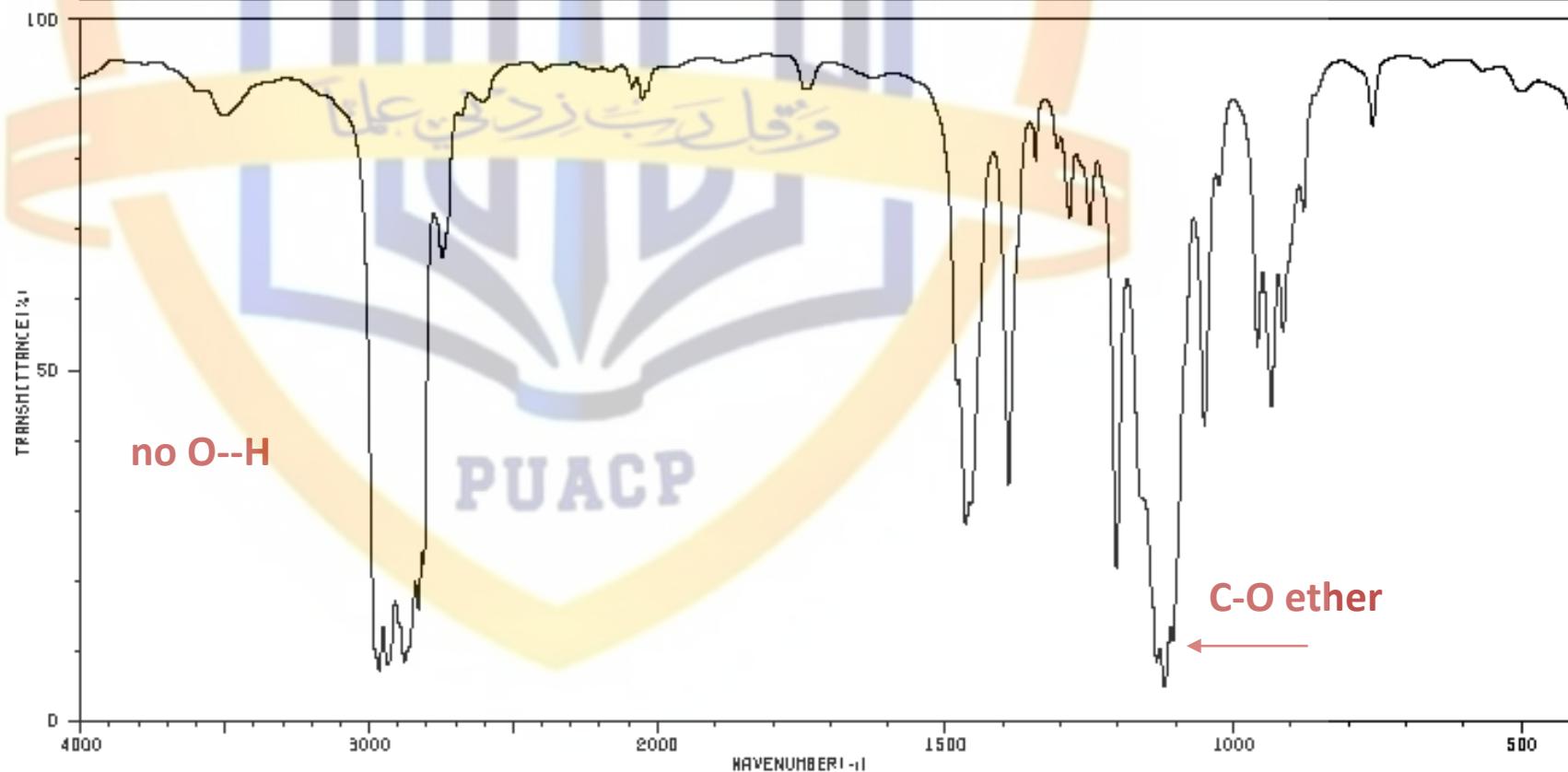
IR SPECTROSCOPY of Ethers

HIT-NO=2077 SCORE= () S0BS-NO=2841 IR-NIDA-03073 : LIQUID FILM

METHYL PROPYL ETHER

methyl *n*-propyl ether

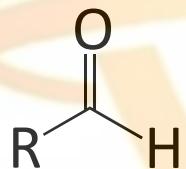
C₄H₁₀O



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		



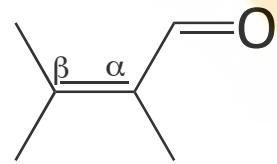
IR SPECTRUM of Carbonyl Family, Aldehydes



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

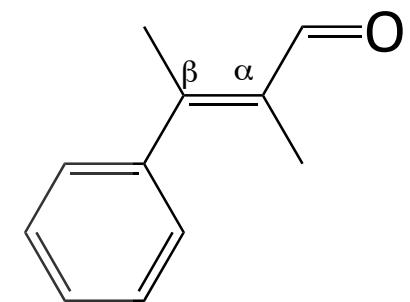
C=O at 2860 - 2800 cm^{-1}
2760 - 2700 cm^{-1}

both are weak bands about
same intensities



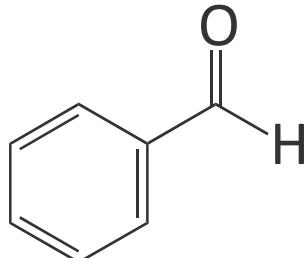
C=O at 1700 - 1680 (s) cm^{-1}

C=C at 1640 - 1600 cm^{-1}



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

Highly conjugated system

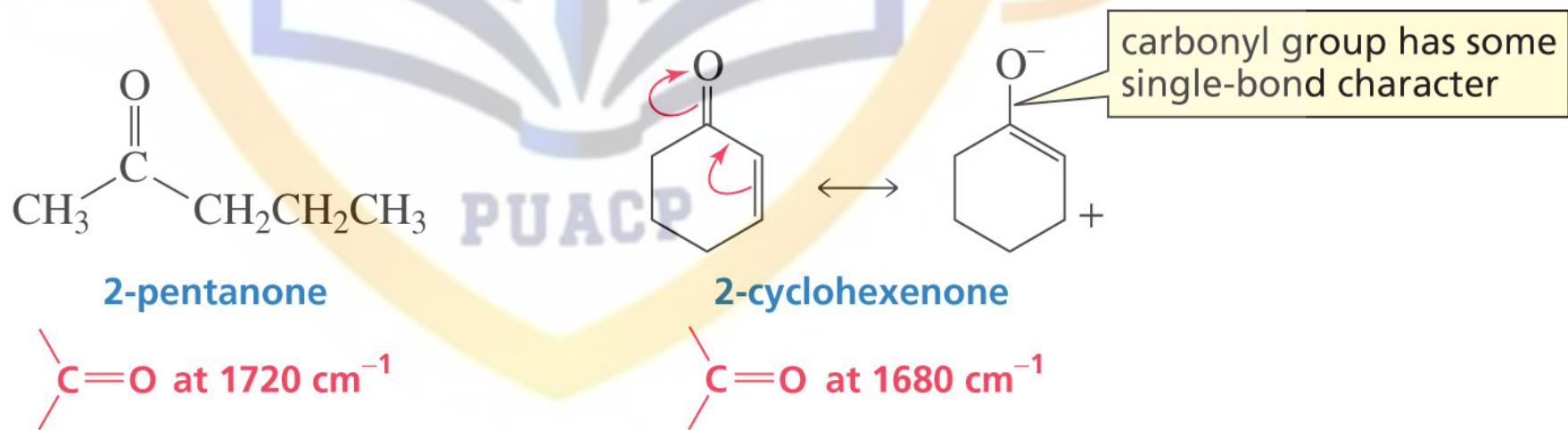


C=O at 1700 - 1660 (s) cm^{-1}

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

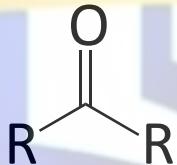
ELECTRON DELOCALIZATION (Resonance)

Affects the Frequency of the Absorption

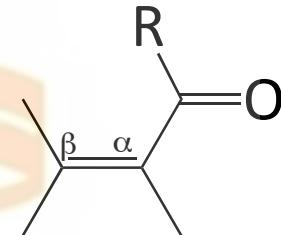


The more double bond character, the greater the frequency (wavenumber).

IR SPECTRUM of Ketones

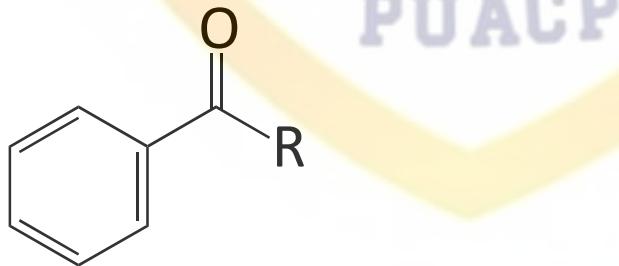


C=O at 1720 - 1708 (s) cm^{-1}



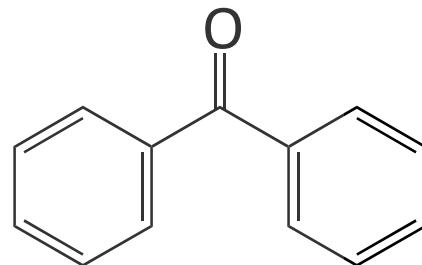
C=O at 1700 - 1675 (s) cm^{-1}

C=C at 1644 - 1617 cm^{-1}



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

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

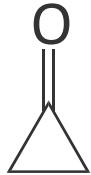


C=O at 1670 - 1600 (s) cm^{-1}

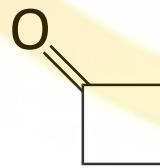
C=C at 1600 and 1450 cm^{-1}

IR SPECTRUM of Cyclic Ketones

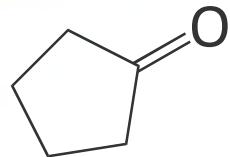
- Both acyclic and cyclic bending appears as a medium intensity $1300 - 1100 \text{ cm}^{-1}$
- Cyclic ketones C=O frequency increases with decreasing ring size
- **Strain effects** – changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore,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



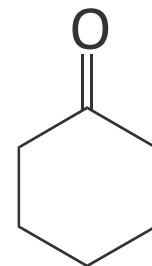
1815 cm^{-1}



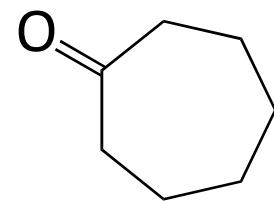
1780 cm^{-1}



1745 cm^{-1}

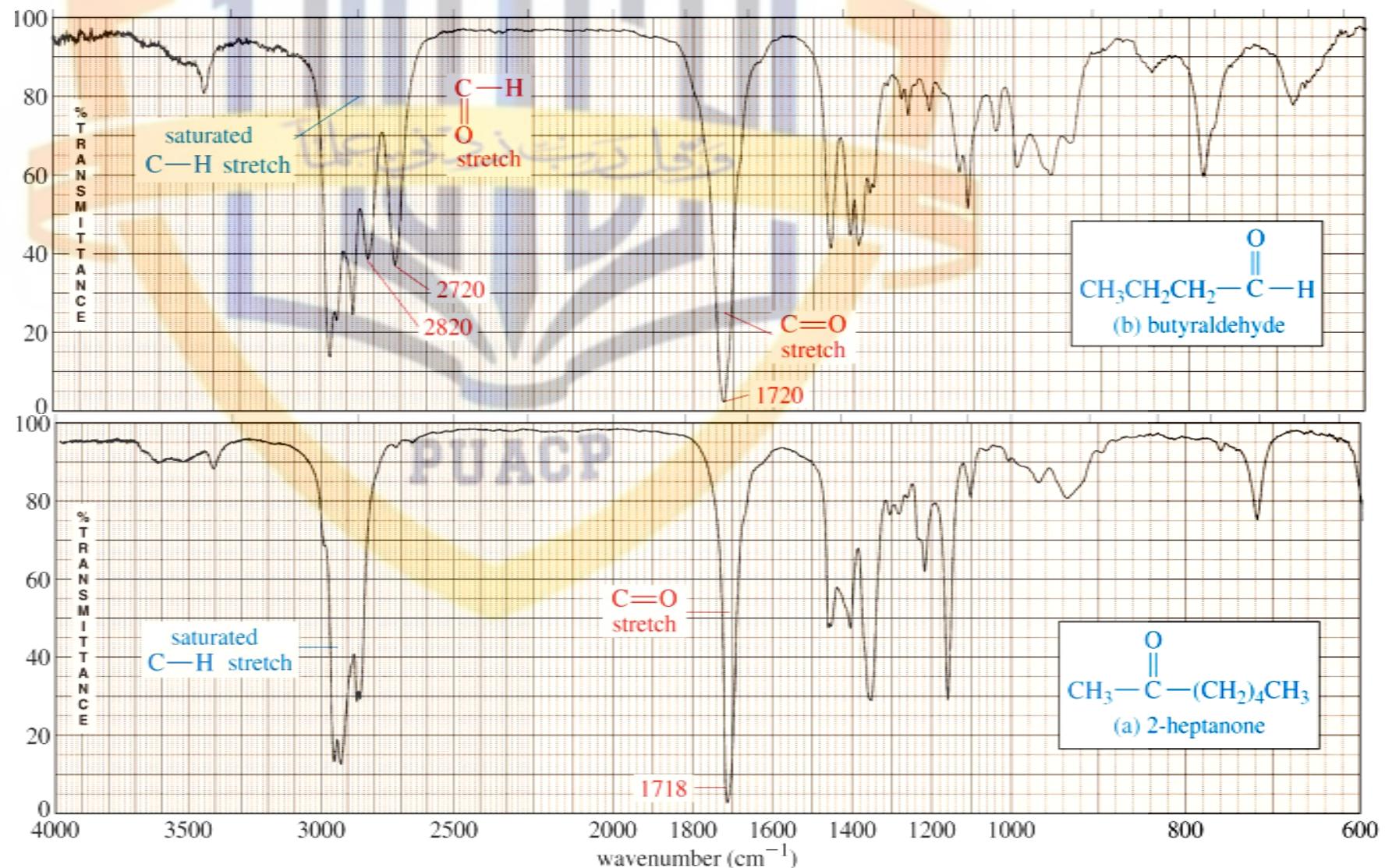


1715 cm^{-1}



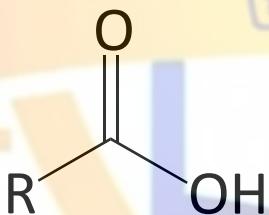
1705 cm^{-1}

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

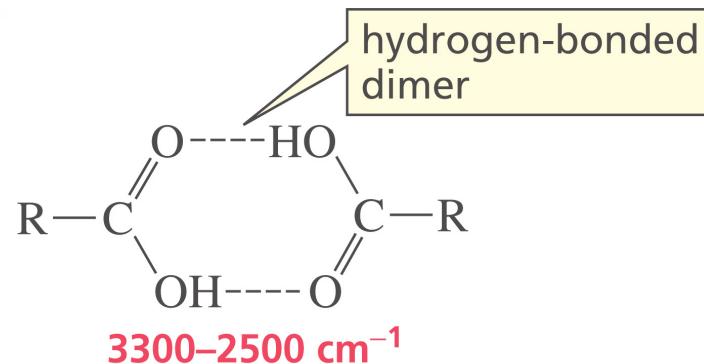


O-H at 3600 - 2400 cm^{-1}

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

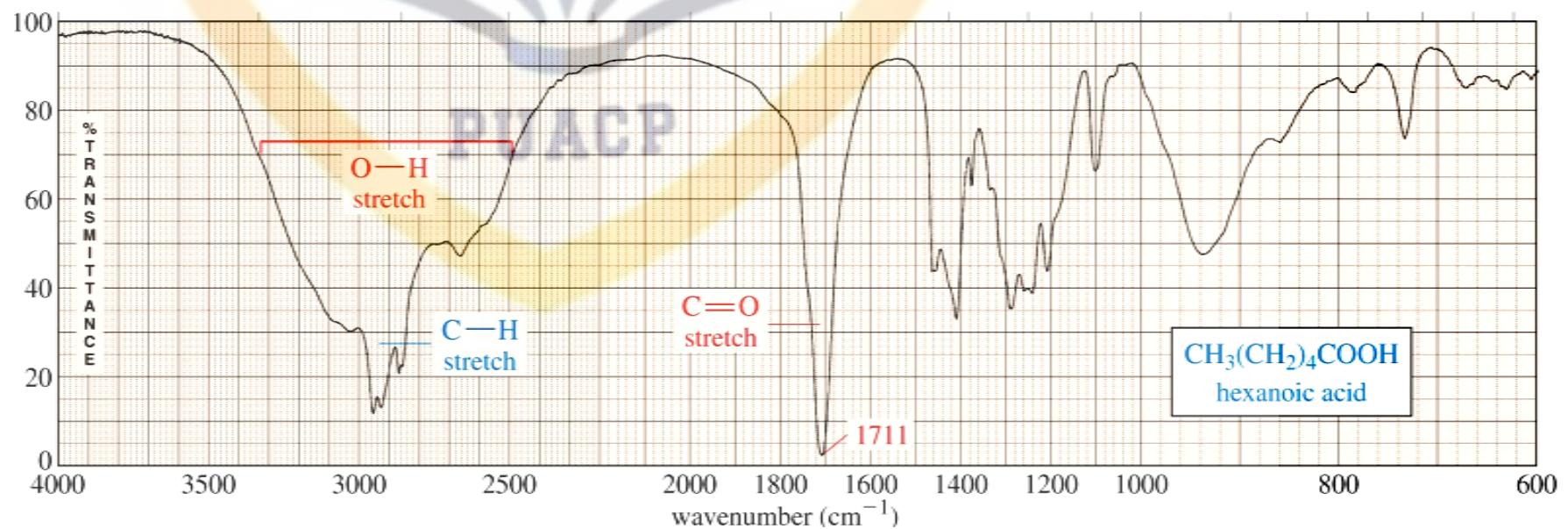
C-O at 1320 - 1210 cm^{-1}

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



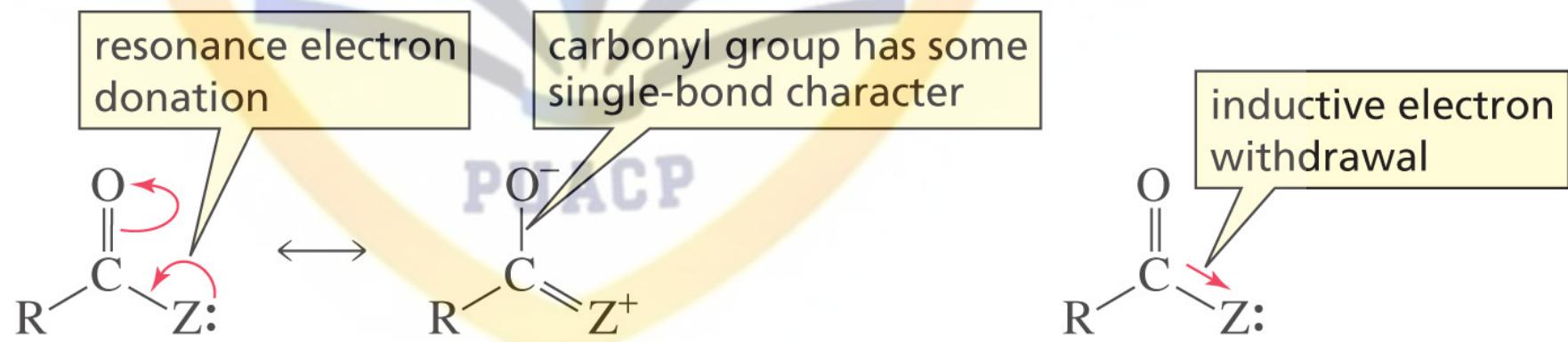
IR SPECTRUM OF A CARBOXYLIC ACID

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⁻¹** 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⁻¹** corresponding to the C=O stretch.

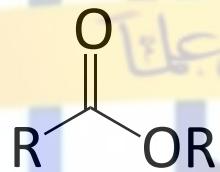


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

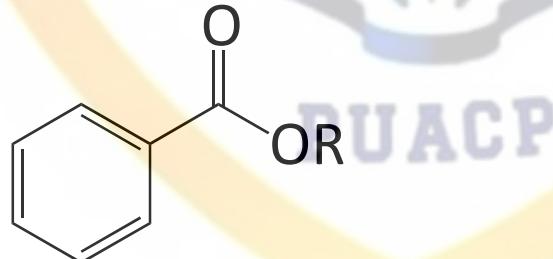
RESONANCE ELECTRON DONATION DECREASES the FREQUENCY while INDUCTIVE ELECTRON WITHDRAWL INCREASES the FREQUENCY



IR FREQUENCIES of Esters



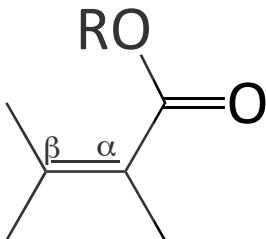
C=O at 1750 - 1735 (s) cm^{-1}



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

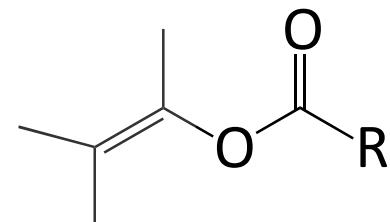
C=C at 1600 and 1450 cm^{-1}

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



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

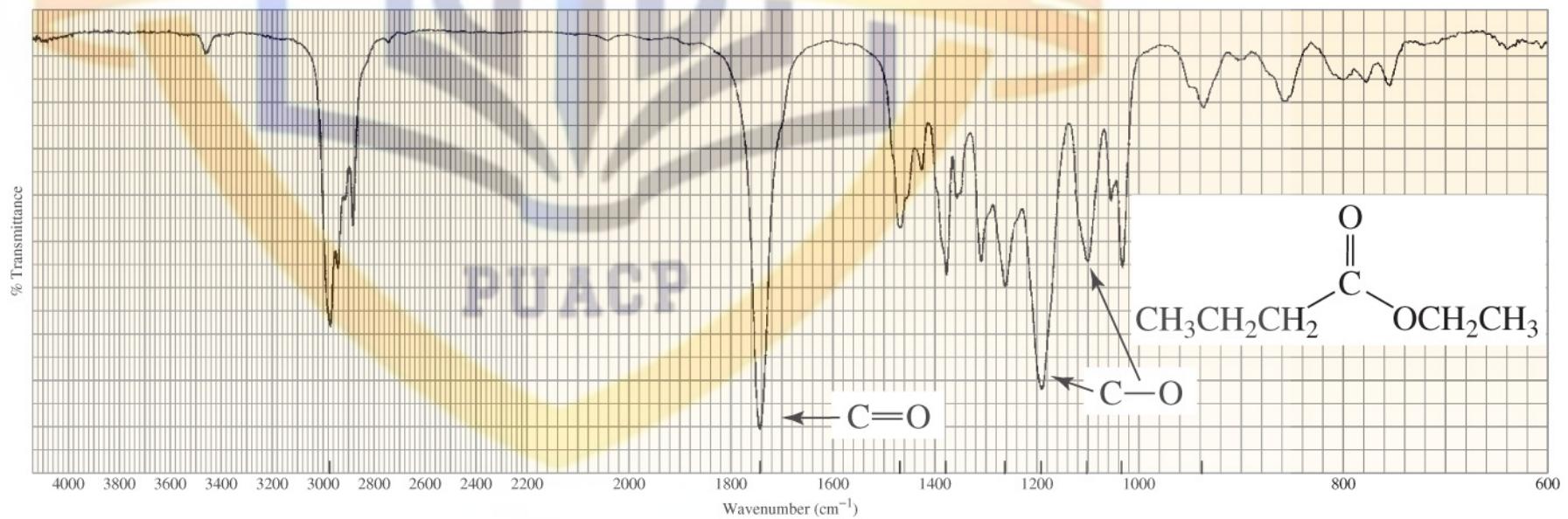
C=C at 1640 - 1625 cm^{-1}



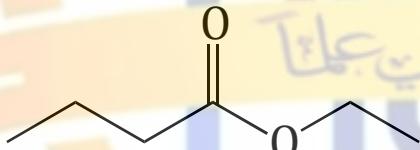
C=O at 1765 - 1762 (s) cm^{-1}

C=C at 168 - 1640 cm^{-1}

The IR Spectrum of an Ester

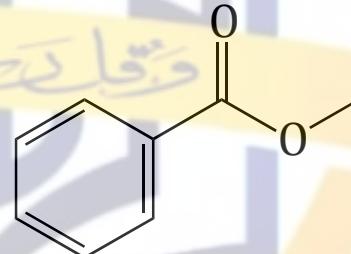


ESTER IR FREQUENCIES



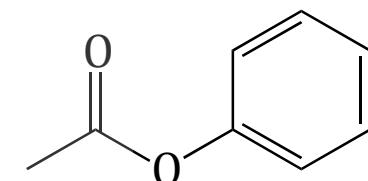
Ethyl butyrate

1738 cm^{-1}



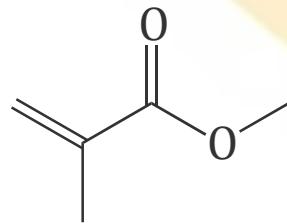
Methyl benzoate

1724 cm^{-1}



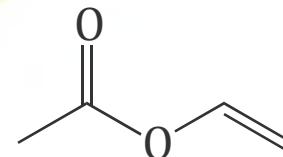
Phenyl acetate

1765 cm^{-1}

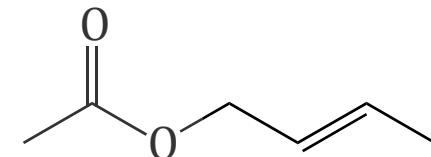


Methyl methacrylate

1725 cm^{-1}

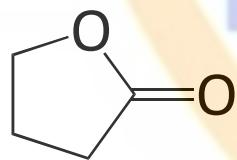


Vinyl acetate

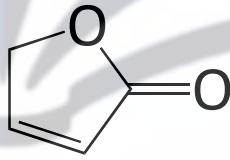


(E)-But-2-en-1-yl acetate

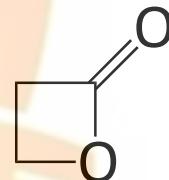
IR FREQUENCIES OF Cyclic Esters (Lactones)



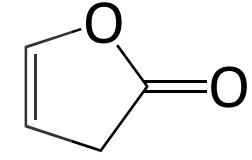
1770 cm⁻¹



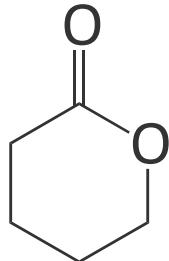
1750 cm⁻¹



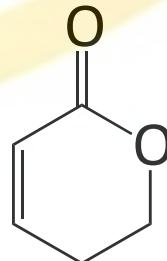
1820 cm⁻¹



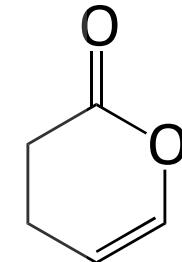
1800 cm⁻¹



1735 cm⁻¹

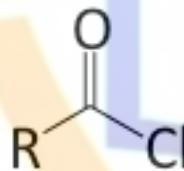


1725 cm⁻¹



1760 cm⁻¹

IR FREQUENCIES of Acid Chlorides and Anhydrides

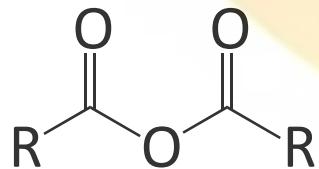


C=O at 1810 - 1775 cm^{-1}

conjugated 1780 - 1760 cm^{-1}

C-Cl in the range of 730 - 550 cm^{-1}

Anhydride and Cyclic Anhydride



C=O at 1830 - 1800 and 1775 - 1740 cm^{-1}

variable intensities

C-O in the range of 1300 - 900 cm^{-1}

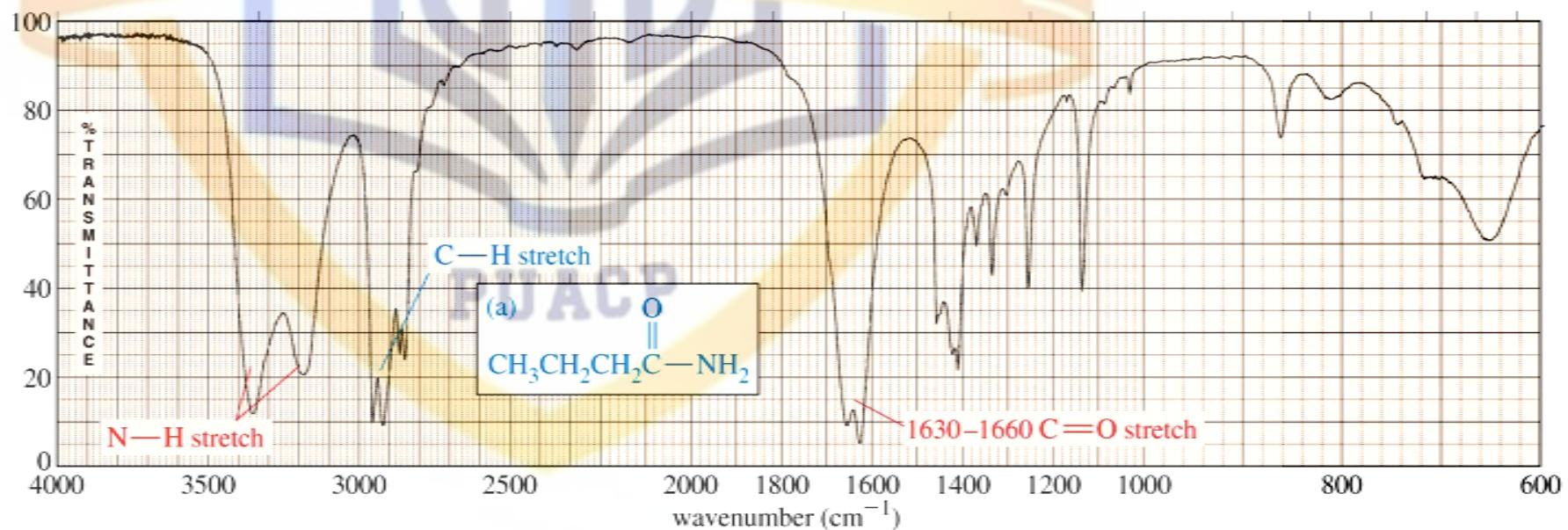
Conjugation moves the absorption to lower frequency

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 cm^{-1} for 1° Amides
 - N-H 3300 cm^{-1} for 2° Amides
 - N-H $1640 - 1550 \text{ cm}^{-1}$ for 1° and 2° Amides
(bending vibrations)
- 

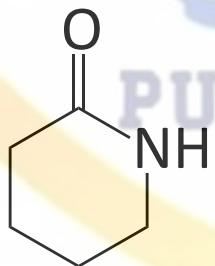
IR SPECTRUM OF AMIDES



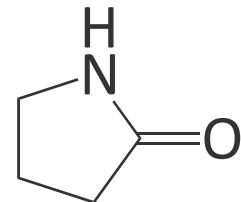
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR FREQUENCIES of Cyclic Amides (Lactams)

Increase in C=O frequency for decreasing ring size



1660 cm⁻¹

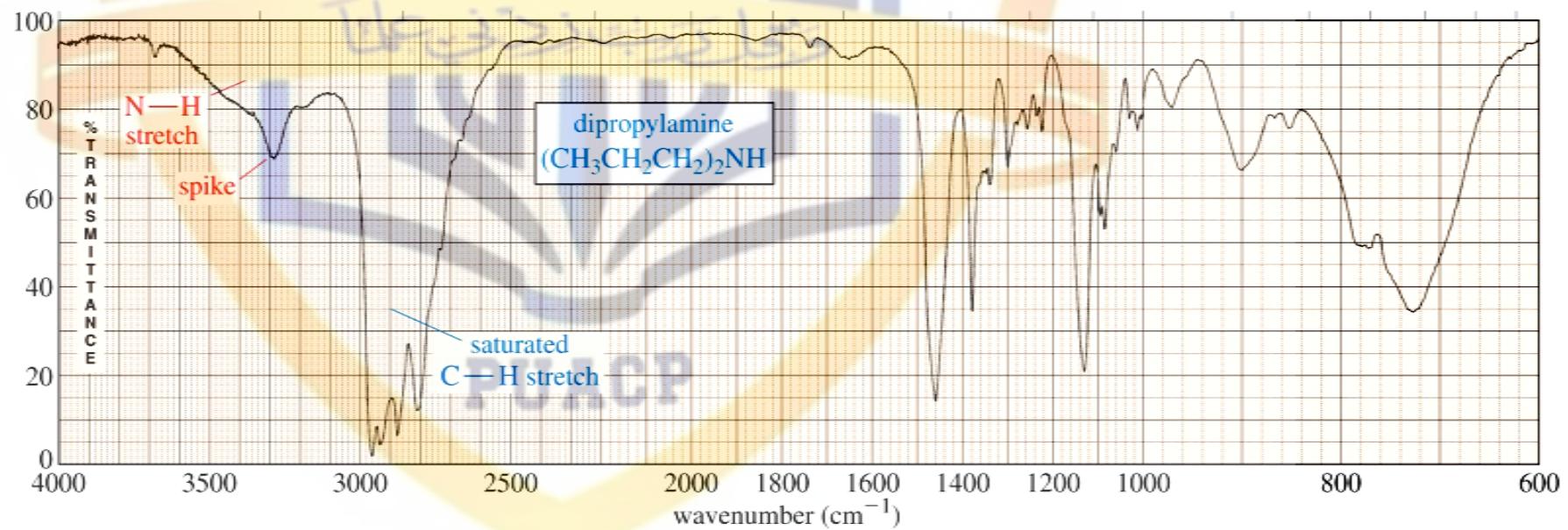


1705 cm⁻¹

IR FREQUENCIES of Amines

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



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



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



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